

PHOTOCHEMICAL REACTIONS
OF
CHLORO-QUINONES

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by

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TO MY MOTHER

ABSTRACT.

The first four chapters of this thesis are a comprehensive literature survey on the subject of

- a) the triplet state of aromatic carbonyl compounds,
- b) the visible and the ultraviolet spectroscopy of p-benzoquinone and its chlorine substituted derivatives,

and

- c) the abstraction of hydrogen from alcohols by free radicals.

Special attention is paid to the principles that are helpful in the understanding and interpretation of the experimental work recorded in this thesis, to setting up a correlation between the molecular orbitals of p-benzoquinone and chloranil, and presenting comprehensively the experimental evidence for the generally accepted principle that the photoreduction of aromatic carbonyl compounds proceeds via the triplet state.

In the experimental section the photochemical reduction of chloranil in 100 per cent isopropanol ($\lambda = 365$ nm and $T = 20^{\circ}\text{C}$) has been studied in detail and the products arising from the quinone as well as the main product from the substrate have been qualitatively and quantitatively analysed. Quantum efficiencies for formation of the various products have been measured both in aerobic and anaerobic solutions. Irradiation in an inert solvent was also carried out. By the use of sensitizers the nature of the photoreactive species of chloranil was investigated. These experiments also helped to establish the

approximate energy of the triplet state of chloranil which was found to agree well with theoretical predictions.

The results obtained in the study of the irradiation of chloranil led to an investigation of the photoreduction of trichloroquinone under identical conditions and the measurement of the quantum efficiency of the process. Trichloroquinone and trichlorohydroquinone were found to interact and preliminary experiments using mass spectrometry showed the system to be complex. A semiquantitative study of unirradiated as well as irradiated mixtures of trichloroquinone and trichlorohydroquinone has been made.

The experimental data recorded in the case of both quinones has been interpreted in terms of reaction mechanisms, and approximate values of some rate constants have been determined.

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CHAPTER 1

The Triplet State Of Aromatic Carbonyl Compounds

1.1. ELECTRONIC EXCITATION OF THE CARBONYL GROUP.

The properties of a molecule, and in particular its chemical reactivity, are determined principally by the electron distribution in it. Photochemical reactions take place because the electron distribution in the molecule has been substantially changed, relative to its ground-state distribution, in the process of excitation.

The electronic excitations of organic molecules which are of interest in relation to the photochemical reactions of the carbonyl group may be divided into two types on the basis of the molecular orbitals (MOs) from which electrons are excited.

(a) Excitation of an electron from the high-energy non-bonding orbital "n" to the lowest unoccupied antibonding molecular orbital " π^* " requires less energy than any other electronic transition. This transition, known as the $n \rightarrow \pi^*$ transition is responsible for the long wavelength, low intensity ultraviolet absorption of carbonyl compounds. The high-energy orbital "n" is essentially a "p" atomic orbital of oxygen which has an axis in the nodal plane of the " π " orbitals. The $n \rightarrow \pi^*$ transition is symmetry forbidden and this accounts for the low intensity of this absorption band.

(b) The promotion of an electron from a π -bonding orbital " π " to the lowest π -antibonding orbital " π^* " requires more energy than the $n \rightarrow \pi^*$ transition. At least one of the $\pi \rightarrow \pi^*$ transitions is allowed and appears as a high intensity absorption band at lower wavelengths.

A symmetry-forbidden $\pi \rightarrow \pi^*$ transition of lower intensity in relation to the $\pi \rightarrow \pi^*$ allowed transition is usually observed in

carbonyl compounds. The selection rule does not hold rigorously because the purity of the symmetry of various states is modified by vibrational motions having different symmetries. The effect becomes pronounced when the molecule has allowed transitions to excited states having energies fairly close to the energy of the excited state involving a forbidden transition. In such a case the forbidden transition borrows intensity from the allowed one, ⁽¹⁾ owing to the mixing of the wave functions of the two states.

When a carbonyl group is conjugated with a C = C group, the highest π orbital in the ground state is raised and the lowest π orbital in the excited state is lowered relative to the respective π and π^* orbitals in the non-conjugated group. As a result both the $n \rightarrow \pi^*$ and the $\pi \rightarrow \pi^*$ absorption bands shift to longer wavelengths, the magnitude of the $\pi \rightarrow \pi^*$ shift being larger than that for the $n \rightarrow \pi^*$ transition.

1.2. THE TRIPLET STATE OF AROMATIC CARBONYL COMPOUNDS.

The $n\pi^*$ and $\pi\pi^*$ excited states of carbonyl compounds formed directly by the absorption of a photon of light are labelled "singlets", because the two electrons in singly occupied orbitals have antiparallel spins. Spin-orbit coupling, which can be described qualitatively as the interaction between the magnetic field of the nuclei in the molecule and the magnetic dipole of the spinning electron exerts a torque which makes it possible for the electrons to change their total spin and undergo a forbidden

transition resulting in a "triplet" state, with parallel spins.

The contour plots of charge density in the symmetric and antisymmetric orbital states of two electrons of wave function

$$\psi_{\pm} = \psi_n(x_1) \psi_k(x_2) \pm \psi_n(x_2) \psi_k(x_1)$$

in a one-dimensional box, - (x_1 and x_2 are the position coordinates and n and k the quantum numbers of the energy levels of electron 1 and electron 2 respectively,) - show that whereas in the symmetric ψ_{+} state the two particles tend to come closer together, in the antisymmetric ψ_{-} state they tend to avoid one another.⁽²⁾ Since the interaction between the two electrons is repulsive and becomes zero only when $|x_1 - x_2| = \infty$, the energy associated with ψ_{+} is larger than that associated with ψ_{-} .

Now, if the two spin systems of the two electrons are considered, we have four spin wave functions - one antisymmetric and three symmetric with respect to spin interchange, - interacting with ψ_{+} and ψ_{-} . Remembering that the Pauli exclusion principle,⁽³⁾ - which states that two or more identical particles with half-integer spin cannot exist in identical states, - requires that the total electronic wave function for such particles be antisymmetrized, we have ψ_{+} interacting with the antisymmetric spin function and ψ_{-} interacting with the remaining three symmetric spin functions, with the result that ψ_{+} becomes the orbital part of a singlet state and ψ_{-} the orbital part of a triplet state.

The electrostatic exchange integral for the two electrons is given by

$$K_{nk} = \iint \psi_n(x_1) \psi_k(x_1) \psi_n(x_2) \psi_k(x_2) \left[\frac{e^2}{|x_1 - x_2|} \right] dx_1 dx_2.$$

K_{nk} must be positive, since the self-repulsion of any charge density distribution must be positive.

If this line of argument is extended to excited molecules, it turns out that for a given excited configuration of electrons, the singlet is always at a higher level than the corresponding triplet. The energy separation is given by

$$E_S - E_T = 2 K_{nk}$$

The magnitude of K_{nk} , as is seen above, depends on the magnitude of the overlap integral $\int \psi_n(x_1) \psi_k(x_1) dx$. Because of the very poor overlap between n and π^* orbitals - n and π^* orbitals occupy different regions in space - the avoidance tendency of the electrons in the $n\pi^*$ triplet state is greater than that in the $\pi\pi^*$ triplet state, thus accounting for the significantly smaller singlet-triplet energy gap in the $n\pi^*$ state relative to the $\pi\pi^*$ state of the same molecule.

1.3. FORMATION OF TRIPLET STATE.

Direct formation of a triplet as a result of photon absorption is a very improbable process since both the orbit and spin of the electron would have to change simultaneously. The triplet state, therefore, except in the case of some molecules containing heavy atoms or dissolved in heavy-atom solvents, - heavy atoms enhance spin - orbit coupling, - is not attained directly on irradiation, but is

generally formed as a result of a radiationless transition from the excited singlet. (Intersystem Crossing).

The rate of intersystem crossing theoretically depends on a number of factors, the most obvious being the energy gap between the states involved in the process. (Singlet - Triplet Splitting). Other factors affecting the rate of intersystem crossing are spin-orbit coupling and the value of the vibrational overlap integral between the states. Lower and El-Sayed ⁽⁴⁾ have shown that in the absence of significant spin-orbit coupling the rate of intersystem crossing should be of the order of 10^7 s^{-1} , a value that fits in well with the known fluorescence lifetimes and triplet yields of several symmetric aromatic compounds. Asymmetry, heteroatoms and heavy atoms enhance spin-orbit coupling and increase the rate of intersystem crossing.

Since this present work is concerned with the photochemical reactions of chloroquinones, it is good to note that recent studies ⁽⁵⁾ have indicated that the intramolecular heavy-atom effect of halogen substituents in the ring arises from the inclusion of the "p" orbital of the halogen in the aromatic π system which causes an enhancement of the small spin-orbit coupling already present in the parent molecule, by mixing a carbon-halogen $\sigma \pi^*$ singlet with the $\pi\pi^*$ triplet, and by vibronically coupling the $\sigma\sigma^*$ and the $\pi\pi^*$ states.

1.4. QUANTUM YIELD OF TRIPLET STATE.

Absolute values for the quantum yield of phosphorescence in

Table 1.1.

Compound	Φ phosphorescence in frozen glasses	Φ ISC in benzene
Benzophenone	0.84	0.99
p-Methylbenzophenone		1.00
p-Bromobenzophenone		1.00
Acetophenone	0.74	0.99
p-Methylacetophenone	0.61	
p-Methoxyacetophenone	0.68	
9,10-Anthraquinone		0.88
Acetonaphtone		0.84

(For sources of information Cfr. ref. 129).

frozen glasses (Table 1.1) for a number of aromatic carbonyl compounds are rather high. Considering that the phosphorescent state is beyond doubt identical with the triplet state, considering also that radiationless deactivation competes with phosphorescence in depopulating the triplet state, the quantum yield of phosphorescence is only a minimum value for the intersystem crossover.

Direct measurements of the quantum yield for intersystem crossing for a few aromatic carbonyl compounds studied (Table 1.1) have substantiated the conclusion implied in the high values of the quantum yield of phosphorescence, viz. that intersystem crossing in such compounds is a highly efficient process. Since the values for quantum yield of triplets (Table 1.1) are close to unity, it is reasonable to assume that competing processes like fluorescence and chemical reaction of the singlet state in aromatic carbonyl compounds are insignificant. It has been estimated that the rate constant for intersystem crossing in the $n\pi^*$ states of aromatic carbonyl compounds is of the order of 10^{10} s^{-1} as against 10^7 s^{-1} for their aliphatic analogues. (6)

1.5. LIFETIME OF TRIPLET STATE.

The radiative lifetime of an excited state bears an inverse relation to the transition probability of absorption to that state. Excited states arising from forbidden transitions, therefore, have correspondingly longer lifetimes relative to those arising from allowed transitions.

The natural lifetime of a $n\pi^*$ singlet in aromatic carbonyl

compounds is of the order of 10^{-8} s, too short to account for their rates of hydrogen abstraction.⁽⁷⁾ Only a very rapid reaction having a rate constant greater than 10^8 s^{-1} would be able to compete with deactivation of the $\pi\pi^*$ singlet. The probability of a reaction taking place is equally small in the case of many $\pi\pi^*$ singlets, since their natural lifetimes for fluorescence are about $10^{-8} - 10^{-9}$ s.⁽⁷⁾

The natural lifetimes of $\pi\pi^*$ triplets of aromatic carbonyl compounds are of the order of 10^{-2} s or higher. Studies done by Herkstroeter and Hammond,⁽⁸⁾ Cohen and Sherman⁽⁹⁾ in solution, and by Pitts and co-workers⁽¹⁰⁾ in frozen glasses have shown that $\pi\pi^*$ triplets of phenyl ketones are nearly hundred times longer-lived than their corresponding $\pi\pi^*$ triplets.

The longer lifetimes bestowed on the triplet by the appreciably large energy gap involved in the $T^* \rightarrow S_0$ transition and the spin-forbidden nature of the same, largely contribute to making the excited triplet an almost exclusive intermediate in the photochemical reactions of aromatic carbonyl compounds. Experimental evidence in support of this claim will be presented in Chapter 3.

1.6. $\pi\pi^*$ and $\pi\pi^*$ REACTIVITY IN PHOTOREDUCTION.

Since electron distribution and energy of $\pi\pi^*$ states is different from the distribution and energy of the $\pi\pi^*$ states, differences in the reactivities of the two states are only to be expected. This question of $\pi\pi^*$ versus $\pi\pi^*$ reactivity has given rise to considerable speculation and various interpretations of

existing data. It must be noted that these interpretations lean too heavily on quantum yield measurements since accurate determinations of rate constants of the reactions involved are not always available. Another factor that makes a quantitative interpretation impossible at the moment is the lack of knowledge of the geometry of the excited state which in most cases differs from that of the ground state.

In the $\pi\pi^*$ state of aromatic carbonyl compounds the carbonyl oxygen is the most electrophilic atom in the system and accordingly behaves as a highly reactive centre in hydrogen abstraction. This localization of excitation on the heteroatom is more pronounced in the triplet than in the higher lying singlet.⁽¹¹⁾ The oxygen atom in the $\pi\pi^*$ state of such compounds has a higher electron density than in the ground state and will therefore be nucleophilic rather than electrophilic. The greater delocalization of electrons, in contrast to the $\pi\pi^*$ state, will make hydrogen abstraction more endothermic and hence much less efficient.

Labelling the lowest triplet of aromatic carbonyl compound as a $\pi\pi^*$ or a $\pi\pi^*$ state can be done experimentally on the basis of the following criteria:^(12a)

(a) The O-O band for the $S_0 \rightarrow T_{\pi\pi^*}$ transition is usually located within about 2000 cm^{-1} of the O-O band of the corresponding $S_0 \rightarrow S_{\pi\pi^*}$ transition. No fixed location with respect to the O-O band of the $S_0 \rightarrow S_{\pi\pi^*}$ transition is observed in the case of a $\pi\pi^*$ triplet.

(b) Addition of heavy-atom components to the solvent does not affect the $S_0 \rightarrow T_{\pi\pi^*}$ transition, but significantly intensifies the

$S_0 \rightarrow T_{\pi\pi}^*$ transition.

(c) The phosphorescence spectrum of a $\pi\pi^*$ state usually exhibits prominent C = O vibrational progression and the lifetime of the excited state is short, typically 10^{-3} s. The vibrational structure of a $\pi\pi^*$ state is very much different from that of a $n\pi^*$ state and the lifetime of the excited species is considerably longer, of the order of a second in some cases.

(d) More or less regular ($\sim 1800 \text{ cm}^{-1}$) spacing between vibronic bands is characteristic of the $n\pi^*$ triplet whereas the $\pi\pi^*$ triplet shows irregular spacing.

Tables 1.2 and 1.3 show that it is well nigh impossible to make a clear-cut distinction between $n\pi^*$ and $\pi\pi^*$ reactivity with respect to the photochemical reactions of aromatic carbonyl compounds. Some such compounds having their lowest triplet in the $\pi\pi^*$ state still exhibit appreciable reactivity with respect to hydrogen abstraction from alcohols, whereas others that are not photoreduced in alcohols, are easily reduced in the presence of a good hydrogen donor like tri-n-butylstannane (12b), showing that delocalization of electron density does not absolutely prohibit hydrogen abstraction.

A similar scale of reactivities has been observed in type II elimination of phenylketones. Type II elimination involves the abstraction of a γ -hydrogen from the alkyl chain by the excited carbonyl group and subsequent cleavage of the six-membered cyclic intermediate to give the enolic form of a ketone and an olefin.

Table 1.2

 $\lambda = 313 \text{ nm.}$

Compound	Φ Photoreduction (isopropanol solution)	Φ Photoelimination (benzene solution)	$E_T - 1$ cm^{-1}	Lowest Triplet
Acetophenone	0.68		25900	$n\pi^*$
p-Methyl acetophenone	0.66		25500	$\pi\pi^*$
3,4-Dimethyl "	0.12		25000	$\pi\pi^*$
p-Methoxy "	0.04		25000	$\pi\pi^*$
3,5-Dimethyl "	0.018		24900	$\pi\pi^*$
1-Acetonaphthone	0.00		19700	$\pi\pi^*$
2-Acetonaphthone	0.00		20750	$\pi\pi^*$
Valerophenone (VP)		0.35		$n\pi^* + \pi\pi^*$
p-Methyl VP		0.33		$n\pi^* + \pi\pi^*$
p-Methoxy VP		0.10		$\pi\pi^*$
$\text{PhCOCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$ (GMV)		0.25		$n\pi^* + \pi\pi^*$
p-Methoxy GMV		0.16		$\pi\pi^*$
Butyrophenone		0.42	26100	$n\pi^* + \pi\pi^*$
p-Chloro "		0.43	25300	$n\pi^* + \pi\pi^*$
p-Methyl "		0.39	25700	$n\pi^* + \pi\pi^*$
p-Methoxy "		0.10	25600	$\pi\pi^*$
p-Hydroxy "		0.00	22600	$\pi\pi^*$

(For sources of information cfr. ref. 130)

Table 1.3

 $\lambda = 365 \text{ nm}$

Compound	Φ Photoreduction (isopropanol)	Photocycloaddition to isobutylene % yield oxetane	E_T cm^{-1}	Lowest Triplet
Benzophenone	1	93%	24100	$n\pi^*$
4-Phenyl "	0.1		23800	$\pi\pi^*$
2-Phenyl "	No reaction	No reaction	~ 23800	$\pi\pi^* + n\pi^*$ (a)
3-Phenyl "	0.1	91%		$\pi\pi^*$
4-Hydroxy "	0.02			$\pi\pi^*$
Anthraquinone	1		22000	$n\pi^*$
1,8-Dihydroxy "	Little, if any			$\pi\pi^*$
1,5-Dihydroxy "	"			$\pi\pi^*$
1-Chloro "	Some reaction			$n\pi^* + \pi\pi^*$
p-Benzoquinone	0.8	> 90%	18550	$n\pi^*$
Toluquinone	0.9	> 90%	18950	$n\pi^*$
Thiobenzophenone	0.3 ^(b)	72%	14000	$n\pi^*$

(a) Spectrum has a maximum in the region expected for $n\pi^*$ emission.

(b) Value for Φ as measured in the present work.

(For sources of information cfr. ref. 130).

Triplet butyrophenone and valerophenone with $\pi\pi^*$ triplets undergo type II elimination with rate constants $8 \times 10^6 \text{ s}^{-1}$ and $1.4 \times 10^8 \text{ s}^{-1}$ respectively. p-Phenylbutyrophenone and α -valeronaphthone whose lowest triplets are known to be $\pi\pi^*$ do not undergo this reaction in a readily measurable yield ⁽¹³⁾, and p-hydroxy and p-amino substituted butyrophenones, also with $\pi\pi^*$ lowest triplets, do not undergo the elimination at all ⁽¹⁰⁾.

However, Wagner and Kemppainen ⁽¹⁴⁾ have recently warned that the correlation between quantum yield and reactivity in type II elimination is fortuitous since they found that substituents which were predicted to increase the reactivity in type II photoelimination actually reduce the over-all efficiency of the process, while others decrease triplet-state reactivity but increase quantum yields. Coulson and Yang ^(15a) have reported similar results for 2-hexanone indicating that such behaviour may be common to all triplet-state photoreactions which involve biradical intermediates.

1.7. MIXING OF $\pi\pi^*$ AND $\pi\pi^*$ STATES.

Considering that quinones in general have the same magnitude of singlet-triplet splitting, (Table 1.4) and have comparable quantum efficiencies for photoreduction in alcohols as the phenyl ketones, it is reasonable to assume that the behaviour of quinone triplets parallels that of the triplets of phenyl ketones as to reactivity and lifetimes. A brief review of the work done in the photochemical reactions of phenyl ketones is opportune also in view of the fact

Table 1.4.

Singlet-Triplet Splitting For $n\pi^*$ States.

		S_1	T_1	ΔE_{ST}
p-Benzoquinone	(heptane)	20900 cm^{-1}	18550 cm^{-1}	2350 cm^{-1}
	(vapour)	20030 (absorption)	18683 (emission)	1349
2,5-Dichloro p-benzoquinone	(vapour)	21301 (absorption)	19294 (emission)	2007
Toluquinone	(heptane)	21500	18950	2550
2-Methyl p-benzoquinone	(n hexane)	21050	18940	2110
p-Xyloquinone	(")	21300	19200	2100
9,10-Anthraquinone	(isopropanol)	24400	22000	2400
	(frozen glass)	22000	20000	2000
1,4-Napthoquinone	(vapour)	21945	18782	3163
Benzophenone	(frozen glass)	26000	24250	1750
Acetophenone	(frozen glass)	27750	25200	2550
p-Trifluoroacetophenone	(frozen glass)	28090	25900	2190

(For sources of information cfr. ref. 131)

that some of the principles used to interpret experimental data will be applied in the discussion of the results of the present work.

Wagner and Kemppainen ⁽¹⁴⁾ have reported that their values for $k_{\text{photoelimination}}$ of substituted valerophenones were too low for pure $n\pi^*$ states and too high for pure $\pi\pi^*$ states. This experimental observation taken in conjunction with the data supplied by Yang and co-workers ^(15b) and Kearns and Case ^(12a) which shows that $n\pi^*$ and $\pi\pi^*$ triplets in substituted ketones lie very close together, justifies the suggestion that the reactive intermediate in the photoelimination is of mixed $n\pi^*$ and $\pi\pi^*$ character.

The correlation between photochemical reactivity with respect to photoreduction in isopropanol and the nature of excited states of acetophenone and substituted acetophenones was investigated by Yang and co-workers. ^(15b) Empirical calculations by Murov ⁽¹⁶⁾ and experimental work by Lamola ⁽¹⁷⁾ established that acetophenone has a low-lying $n\pi^*$ triplet and a nearby $\pi\pi^*$ triplet. Kearns, ⁽¹⁸⁾ using the phosphorescence excitation method developed by himself, demonstrated that p-methoxy acetophenone has a low-lying $\pi\pi^*$ triplet state, and also detected a higher $n\pi^*$ triplet state. Yang and his team ^(15b) used the phosphorescence excitation method to show that p-methyl acetophenone and 3,5-dimethyl acetophenone also had a low-lying $\pi\pi^*$ triplet and a higher $n\pi^*$ triplet.

Although these last-mentioned substituted acetophenones have a low-lying $\pi\pi^*$ triplet, they still exhibit photoreactivity with

respect to photoreduction in isopropanol comparable to that of acetophenone, whereas polymethyl and methoxyacetophenones with low-lying $\pi\pi^*$ triplets exhibit decreased photoreactivity. They also found that whereas the triplet energies of all the substituted acetophenones mentioned are comparable and that the spacings between their $\pi\pi^*$ triplet and $n\pi^*$ triplet states do not vary substantially, there is a rough qualitative correlation between photoreactivity and radiative lifetime, viz the shorter the radiative lifetime, the higher the reactivity.

First-order perturbation theory enables the calculation of an approximate ratio of the $\pi\pi^*$ triplet state lifetime to the value for the $n\pi^*$ triplet state of acetophenone to be made. This calculated value was only half the observed value, a discrepancy that might have arisen due to the many assumptions made in the calculation of the theoretical value. However, the rough correlation between decrease of reactivity and increase of lifetime, the near constancy of the energy of the reacting state and the spacings between $n\pi^*$ and $\pi\pi^*$ triplets suggested that a factor in the electronic structure of the reacting state is responsible for change in reactivity with substitution.

Carrying the investigation further, they determined the rate constants for photoreduction and those for radiationless decays of p-trifluoromethylacetophenone, acetophenone, p-methylacetophenone and 3,4-dimethyl acetophenone in degassed solutions in benzene containing 2M isopropanol and a variable amount of cis 1, 3-pentadiene as the

quencher. Their data clearly indicated that acetophenone and p-trifluoromethyl acetophenone with low-lying $\pi\pi^*$ triplets are substantially more chemically reactive but have faster non-radiative decay processes whereas p-methyl acetophenone and 3, 4 dimethyl acetophenone with a low-lying $\pi\pi^*$ triplet are less chemically reactive but have slower non-radiative processes.

p-Trifluoromethylacetophenone gave a quantum yield of 0.72 (measured as the quantum yield of acetone formation in benzene containing 2M isopropanol) compared to a value of 0.35 for acetophenone under the same conditions. This higher quantum yield indicated that an electron-withdrawing group like $-\text{CF}_3$ reduces the coupling between the $\pi\pi^*$ triplet and the $\pi\pi^*$ states and enhances the photochemical reactivity of the $\pi\pi^*$ triplet state.

3, 4-Dimethylacetophenone with a low-lying $\pi\pi^*$ triplet has a relatively long radiative lifetime and is quite unreactive in photoreduction as well as photoelimination compared to acetophenone. p-Methyl acetophenone also with a low-lying $\pi\pi^*$ triplet has a shorter radiative lifetime compared to 3, 4-dimethylacetophenone but is as reactive, both in photoreduction as well as photoelimination, as acetophenone. These observations can only be rationalized by assuming that the $\pi\pi^*$ triplet mixes with $\pi\pi^*$ states. The $\pi\pi^*$ triplet state is spin-orbitally coupled with the $\pi\pi^*$ singlet state (19) and vibronically coupled with the $\pi\pi^*$ triplet state (17). Since $\pi\pi^*$ singlet energy levels do not vary substantially in methylated acetophenones, spin-orbit coupling between the $\pi\pi^*$ triplet state

and the $\pi\pi^*$ singlet state does not account for the substantial variation in their radiative lifetimes and chemical reactivities. The $\pi\pi^*$ triplet state of methylated acetophenones lies slightly above the low-lying $\pi\pi^*$ triplet state and hence the increased reactivity of these compounds which is accompanied by a shortening of their radiative lifetimes may be attributed to the vibronic coupling of the $\pi\pi^*$ triplet with the $\pi\pi^*$ triplet in addition to the spin-orbit coupling with the $\pi\pi^*$ singlet state.

Yang and co-workers obtained experimental confirmation to justify the above conclusions. The energy level of a $\pi\pi^*$ state shifts to the red when the medium is changed from a polar to a nonpolar one, while the energy level of a $\pi\pi^*$ triplet exhibits little solvent dependence. A change of medium from EPA (polar) to methylcyclohexane (nonpolar) will decrease the energy gap between the $\pi\pi^*$ triplet and both the $\pi\pi^*$ states of methylated acetophenones. This decrease in the energy gap will promote the mixing of the $\pi\pi^*$ triplet state with the $\pi\pi^*$ singlet and triplet manifolds and increase the $\pi\pi^*$ character of the $\pi\pi^*$ triplet. They observed, as expected from what has been said above, a decrease in the phosphorescence lifetimes of p-methyl, m-methyl, 3,5-dimethyl and 3,4,5-trimethyl acetophenone when the medium was changed from EPA to methylcyclohexane. A change of medium did not produce any significant change in the phosphorescence lifetimes of acetophenone and p-trifluoromethyl acetophenone.

Fig. 1.1 summarizes schematically the conclusions that experimental observations allow us to draw in relation to the energy levels of the

various states of aromatic carbonyl compounds and compares them with those of aliphatic carbonyl compounds.

We can now offer a plausible reason for efficient intersystem crossover in aromatic carbonyl compounds and for the very high rate constant of the process. In general, the proximity of the $\pi\pi^*$ and $\pi\pi^*$ levels of aromatic carbonyl compounds as compared to their aliphatic analogues, facilitates the mixing of $\pi\pi^*$ and $\pi\pi^*$ states. The small gap between the $\pi\pi^*$ and $\pi\pi^*$ triplet states, in particular, will ensure that aromatic carbonyl compounds do not have pure $\pi\pi^*$ states but rather a greater or smaller $\pi\pi^*$ character depending upon the magnitude of the energy gap between them. This mixing of the two triplet manifolds explains, at least partially, the efficient intersystem crossing in these compounds since theoretical calculations predict that intersystem crossing between dissimilar electronic states, e.g. $^1(\pi\pi^*) \rightarrow ^3(\pi\pi^*)$, is favoured relative to the same transition between similar states, e.g. $^1(\pi\pi^*) \rightarrow ^3(\pi\pi^*)$.⁽¹⁹⁾ Also, a $^1(\pi\pi^*) \rightarrow ^3(\pi\pi^*)$ transition has been calculated to be 10^3 times faster than a $^1(\pi\pi^*) \rightarrow ^3(\pi\pi^*)$ transition.⁽⁷⁾

1.8. IS A CHARGE-TRANSFER STATE A $\pi\pi^*$ TRIPLET?

Porter^(20a) correlated solvent shifts in absorption spectra of substituted benzophenones with their photoreactivity. In order to explain the rather intense long wavelength absorption of aromatic ketones having donor or acceptor substituents on the ring, he postulated a "charge transfer state" distinct from the $\pi\pi^*$ state,

and cited the effect of solvents on the reactivity of such molecules as proof for the validity of the distinction. From absorption and phosphorescence studies he was able to construct energy level diagrams which indicated that such molecules had a low-lying charge-transfer state in isopropanol, but a low-lying $\pi\pi^*$ state in cyclohexane, thus predicting that they would be photoreduced, contrary to chemical expectations, in the latter but not in the former solvent. He confirmed his predictions experimentally with p-amino and p-hydroxybenzophenone and explained their reactivity by assuming that the nonpolar medium destabilizes the charge-transfer state so that the lowest-lying state is $\pi\pi^*$.

Wagner and Hammond ⁽²¹⁾ however, do not see the necessity of postulating a charge-transfer state at all. The charge-transfer state, according to them, is in fact a $\pi\pi^*$ triplet in which electron density is strongly directed by hetero atoms. A comparative study of the spectra of benzene and phenyl ketones in general, leads to the conclusion that the shoulder around 280 nm in the absorption spectrum of phenyl ketones corresponds to the ${}^1B_{1u} \leftarrow {}^1A_g$ transition of benzene (around 200 nm) which is the conjugation or charge-transfer band. ⁽²²⁾ The lowest $\pi\pi^*$ triplet of benzene has ${}^3B_{1u}$ symmetry ⁽²³⁾ and thus correlates with the charge-transfer excited state. It is, therefore, probable that the lowest $\pi\pi^*$ triplet of all phenyl ketones is equivalent to a charge-transfer state, and electron donating substituents merely enhance the transfer of charge. ⁽²⁴⁾

Porter's observation ^(20a) that substitution and solvents greatly affect the 280 nm band relative to other bands in the spectrum lends support to this theory.

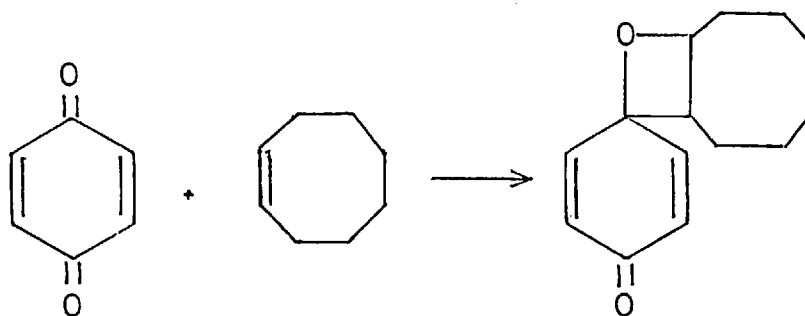
The reactivity of p-amino and p-hydroxybenzophenone in cyclohexane would be explained by suggesting that the nonpolar solvent destabilizes the $\pi\pi^*$ triplet state relative to the $n\pi^*$ triplet state by minimizing the charge-transfer contribution to the $\pi\pi^*$ triplet state.

It must be noted, however, that reports as to the reactivity of p-amino benzophenone in isopropanol are contradictory. Porter ^(20a) found p-amino benzophenone to be unreactive in isopropanol whereas Atkinson ⁽²⁵⁾ has reported that it does react. Similarly Porter and Suppan ⁽²⁰⁾ report that 4, 4' N, N-dimethylaminobenzophenone, which is known to be non-reactive in isopropanol solvent, is reactive in cyclohexane with a quantum yield of disappearance of 0.6, whereas Walling and Gibian ^(26a) have reported that this same compound is nonreactive in both isopropyl alcohol and cyclohexane. Several research workers ^(26b) have reported that the product of the photoreactions of such molecules in cyclohexane are not pinacols, indicating that the semipinacol radicals of these ketones interact differently with cyclohexyl radicals than do the semipinacol radicals of other ketones.

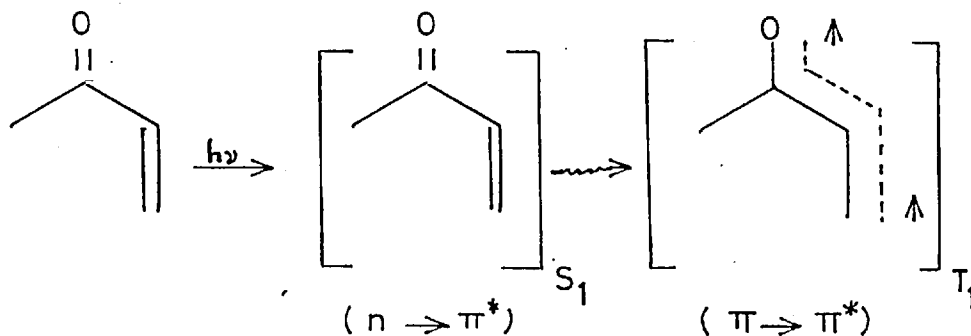
Pitts ⁽²⁷⁾ working with analogous substituted butyrophenones and Wagner and Kemppainen ⁽¹⁴⁾ working with analogous substituted valerophenones, have failed to observe any correlation between substituent effects with respect to photoreactivity and uv spectra.

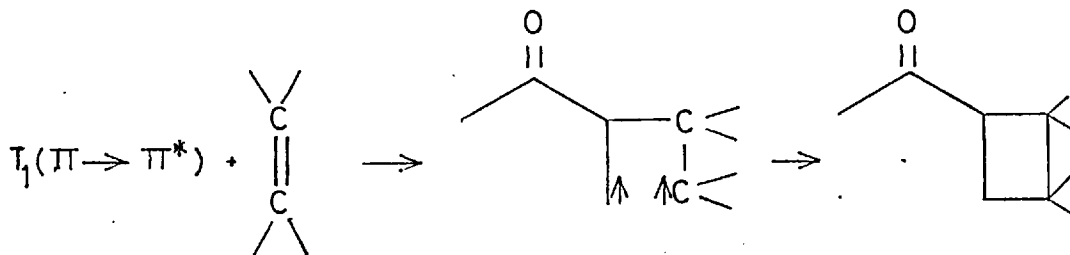
1.9. $n\pi^*$ and $\pi\pi^*$ STATES IN PHOTOCYCLOADDITION.

The general differences in the mode of photocycloaddition of carbonyl compounds to olefins also reflect the differences in the nature of their excited states. Aromatic carbonyl compounds whose lowest triplets have the $n\pi^*$ configuration with its electrophilic oxygen atom, undergo electrophilic addition to the olefin substrate. This probably occurs in such a way as to give rise to the classically most stable diradical intermediate which then cyclizes to give an oxetane:⁽²⁸⁾



In the case of aromatic carbonyl compounds whose lowest triplet states are more $\pi\pi^*$ in character than $n\pi^*$, the most electrophilic atom is one of the π carbon atoms of the ring and accordingly addition to the olefin involves the formation of a carbon-carbon bond between the π -carbon of the aromatic compound and the olefin.





The mixing of $n\pi^*$ and $\pi\pi^*$ states in substituted aromatic carbonyl compounds is best exemplified by the behaviour of p-benzoquinone and chloranil in photocycloaddition reactions with cyclo-octene. Parabenzoquinone yields only products which arise from addition of the olefin to the oxygen atom, whereas chloranil under certain conditions gives a mixture of products arising from the addition of the olefin to the oxygen atom as well as to the ring carbon atoms ⁽²⁹⁾.

In conclusion, it can safely be assumed that, in principle, the $n\pi^*$ states of aromatic carbonyl compounds possess some $\pi\pi^*$ character and vice versa. The triplet state of these compounds can be described as

$$T = a (n\pi^*) + b (\pi\pi^*)$$

where a and b are measures of the extent to which each configuration contributes to the actual state of the triplet. ⁽³⁰⁾ The magnitude of the contribution of a given state will depend on several factors, like the energetic separation (for which the contribution can be expected to vary inversely as the square of the energy difference) of the configurations involved, the conditions of the reaction, the nature of the second reactant and several other factors.

CHAPTER 2

The Visible And Ultraviolet Spectroscopy Of p-Benzoquinone And Its Chlorine-substituted Derivatives

2.1. THE ABSORPTION SPECTRUM OF p-BENZOQUINONE.

The absorption spectrum of p-benzoquinone in saturated hydrocarbons or alcohols normally shows a high intensity band with a maximum at about 245 nm, a medium intensity band with a maximum at about 290 nm and a low intensity band in the visible region with an ill-defined maximum at about 450 nm. The extinctions in the above regions are approximately 2×10^4 , 2.5×10^2 and $20 \text{ l mol}^{-1} \text{ cm}^{-1}$ respectively. (Cfr. Fig. 2.4).

The first band (I) is ascribed to an allowed $\pi \rightarrow \pi^*$ transition, the second (II) to a formally forbidden $\pi \rightarrow \pi^*$ transition and the third (III) to a $n \rightarrow \pi^*$ transition which is also forbidden by the selection rules. All three transitions ⁽³¹⁾ are polarized in the same direction and consequently the two forbidden transitions acquire their intensity by mixing with the allowed $\pi \rightarrow \pi^*$ transition.

The $n \rightarrow \pi^*$ band is of the greatest importance in the photochemical reactions of p-benzoquinone since the first triplet state can be derived from it by intersystem crossing. Because of the small spatial overlap between n and π^* orbitals, which makes, as was noted earlier, singlet-triplet splitting small, and because of the low intensity of this particular transition, intersystem crossing to the triplet from the singlet state can be expected to be an efficient process. ⁽³²⁾

2.2. THEORETICAL CALCULATIONS OF MOs OF p-BENZOQUINONE.

Theoretical calculations of the electronic levels of

p-benzoquinone were done by J.W. Sidman (33). He employed the self-consistent field (SFC) procedure to determine the best molecular orbitals, for the lowest configuration, which can be formed as linear combinations of the atomic orbitals (LCAO-MO). Electronic repulsion integrals and core parameters involved in the calculation were determined by semi-empirical methods developed by Moffitt, Pariser and Parr, and Pople. A discrete choice of parameters and integrals made possible a semi-quantitative evaluation of the π -electron ionization potentials, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transition energies of p-benzoquinone. Sidman also assessed the effect of configurational interaction (CI) upon the calculated transition energies for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

TABLE 2.1.

Nature of transition	Experimental cm^{-1}	Sidman only π electrons		Sado n and π electrons	
		without CI cm^{-1}	with CI cm^{-1}	without CI cm^{-1}	with CI cm^{-1}
$\pi_4 \rightarrow \pi_5$ (S)	41130	51600	50800	48430	39500
$\pi_4 \rightarrow \pi_5$ (T)		35490	29850	26960	
$\pi_3 \rightarrow \pi_5$ (S)	35490	47590	45980	43230	39550
$\pi_3 \rightarrow \pi_5$ (T)		41950	35490	39500	
$n \rightarrow \pi_5$ (S)	21770	39520	31450	26500	21700
$n \rightarrow \pi_5$ (T)	18400	37100	23400	24600	

An earlier work published by Anno,, Matubara and Sado (34) calculated the energy levels of p-benzoquinone by the Pariser and Parr semi-empirical MO method taking into account explicitly the nonbonding electrons localized at the heteroatoms as well as the π electrons, but neglecting CI. Since their results were wide off experimental observations they repeated the calculations making allowance for CI.

Table 2.1 presents a summary of theoretical data and compares it with experimental data available.

As can easily be seen, the transition energies for the $n\pi^*$ as well as $\pi\pi^*$ states, except for Sado's values for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ forbidden transitions calculated taking into account CI, are in poor agreement with experiment, the discrepancies being more pronounced in the $n \rightarrow \pi^*$ transitions. This seems to be an inherent defect of the MO theory which places excessive emphasis on ionic structures involving in this case a very large transfer of electronic charge away from the oxygen atom. The inclusion of CI in the calculation tends to overcome this defect but not always sufficiently enough to bring the values to agree with experimental observations. When n and π electrons are explicitly taken into account as in Sado's calculation and CI terms also included, theory seems to come closer to experiment.

Fig. 2.1 attempts to represent the energy levels of p-benzoquinone schematically. According to Sidman's calculations,

the lower-energy band II arises from a $\pi_3 \rightarrow \pi_5$ singlet transition and the higher-energy band I from a $\pi_4 \rightarrow \pi_5$ transition, though π_3 lies deeper than π_4 . This is entirely due to differences in electrostatic interaction, since the MO repulsion integral of the $\pi_4 \rightarrow \pi_5$ transition is found to be much larger than that for the $\pi_3 \rightarrow \pi_5$ orbital jump. Similarly, the fact that the forbidden $n \rightarrow \pi^*$ transition requires the least energy, notwithstanding the nearly equal energies of the n MO and the highest filled π_4 MO, is also accounted for by the values of the repulsion and exchange integrals. Calculations showed that whereas the coulomb repulsion integral $J_{n\pi}$ is approximately the same as the corresponding integral $J_{\pi\pi}$, the MO exchange integral $K_{n\pi_5}$ is very much smaller than either $K_{\pi_3\pi_5}$ or $K_{\pi_4\pi_5}$.

2.3. THEORETICAL CALCULATION OF THE MOs OF CHLORANIL.

Giacometti and co-workers followed the same LCAO MO, SCF semi-empirical method to evaluate the energy levels of chloranil.⁽³⁵⁾ Their values for transition energies without CI are in fair agreement with experimental values. They have placed the first two excited singlets, ie $\pi_4 \rightarrow \pi_5$ and $\pi_3 \rightarrow \pi_5$ at 36150 cm^{-1} and 24400 cm^{-1} which compare very well with the observed values of 35340 cm^{-1} in alcohol and 36115 cm^{-1} ⁽³⁶⁾ in the vapour phase for the $\pi_4 \rightarrow \pi_5$ singlet, and 27320 cm^{-1} in alcohol solution for the $\pi_3 \rightarrow \pi_5$ singlet ($\sim 26,000 \text{ cm}^{-1}$ in vapour).

The 27320 cm^{-1} band of chloranil cannot be assigned to a $n \rightarrow \pi_5$ transition because this band is not blue-shifted when the solvent is

changed from perfluoroheptane to alcohol.⁽³⁷⁾ Its assignment to a $\pi_3 \rightarrow \pi_5$ transition is therefore justified.

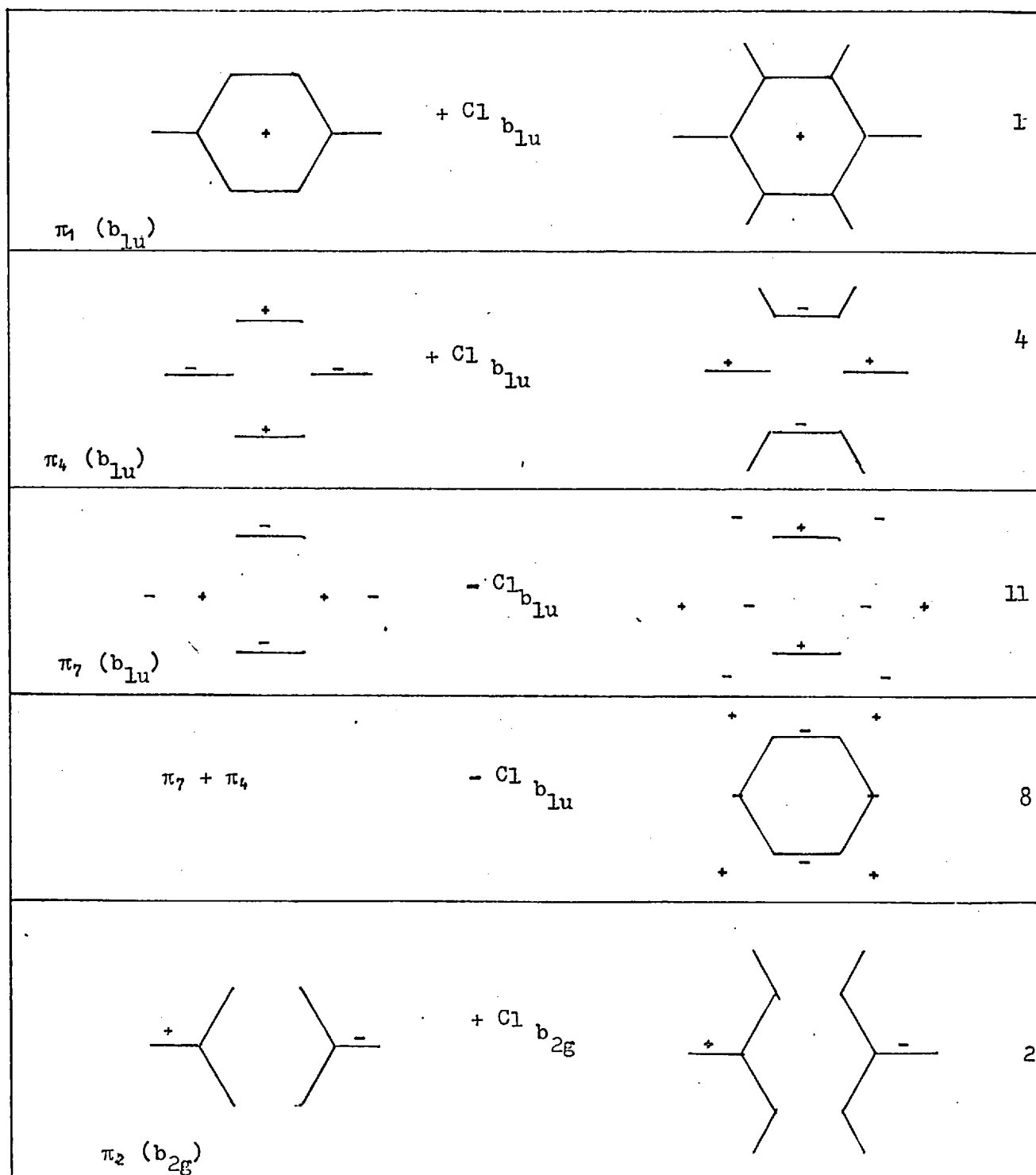
The electronic states of chloranil can be assumed to be derived from those of p-benzoquinone. The MOs of the parent molecule will interact with the AOs of chlorine to produce a new set of bonding and antibonding orbitals. The chlorine atoms will exert an inductive effect through the σ bond electron which will, given the electronegative nature of the chlorine atom, draw the electron density towards itself. This inductive perturbation will tend to disturb the overall electron distribution of the molecule, but the magnitude of such an effect is not at present predictable due to the lack of theoretical calculations in this field.

The mesomeric or conjugative perturbation resulting from the introduction of chlorine in the p-benzoquinone ring will be exerted by feeding the lone pairs of electrons on the chlorine atom into the π system of the ring. Experimental evidence for this assumption has come from the work of Baker⁽³⁸⁾ who explains the unexpected appearance of two extra peaks in the photo-electron spectra of compounds like chlorobenzene, in terms of the two chlorine lone pair orbitals interacting to different extents with the aromatic ring π electrons.

2.4. CORRELATION OF p-BENZOQUINONE AND CHLORANIL MOs.

From the coefficients of the self-consistent, non-equivalent MOs of p-benzoquinone given by Sidman⁽³³⁾ and similar coefficients for the MOs of chloranil given by Giacometti⁽³⁵⁾ and co-workers, it is possible

Fig. 2.2 Correlation of the MOs of p-benzoquinone and chloranil
(numbers on the right refer to the numerical order in
Table 2.2 on page 45)



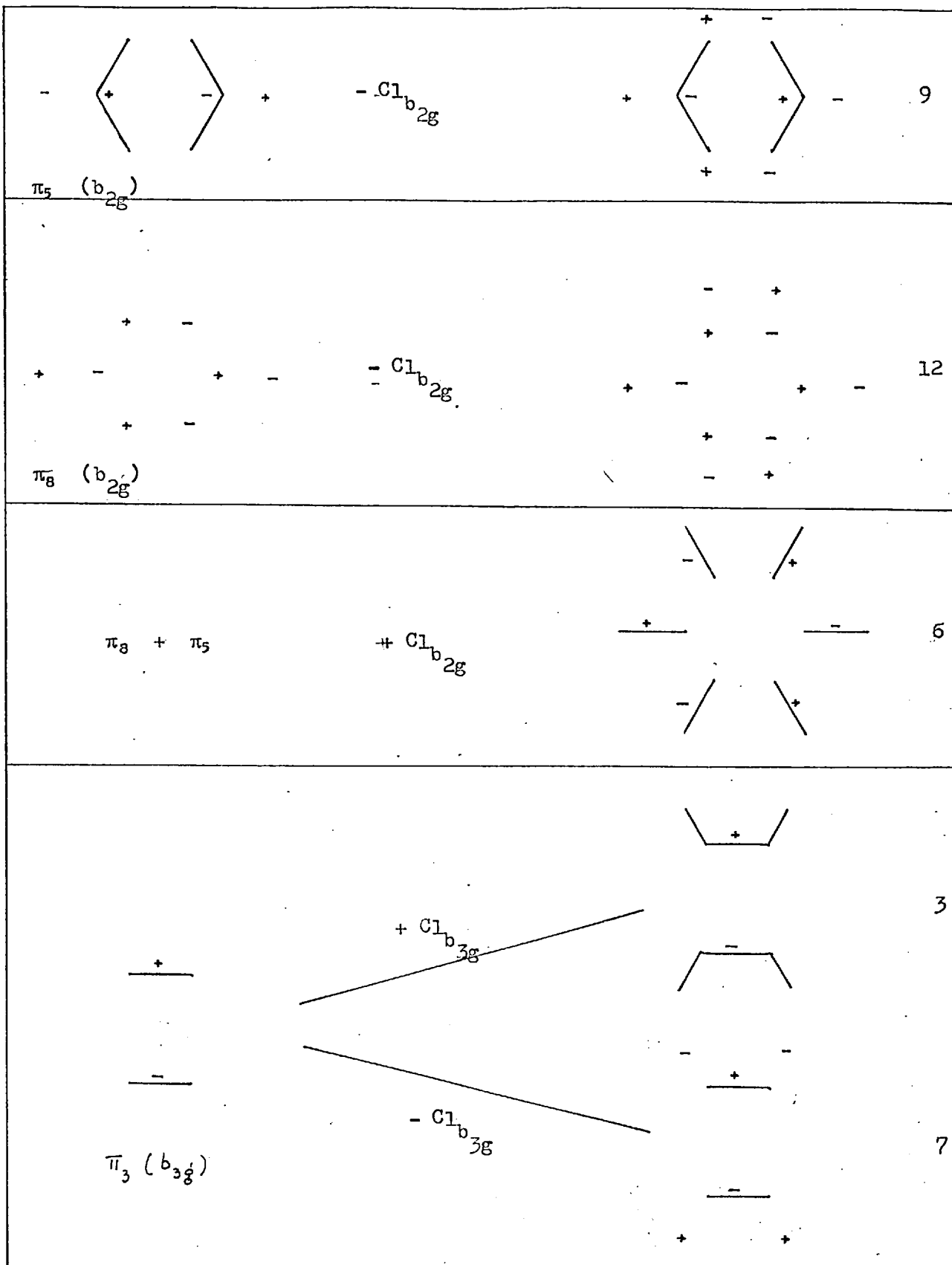


Figure 2.2 (Contd.)

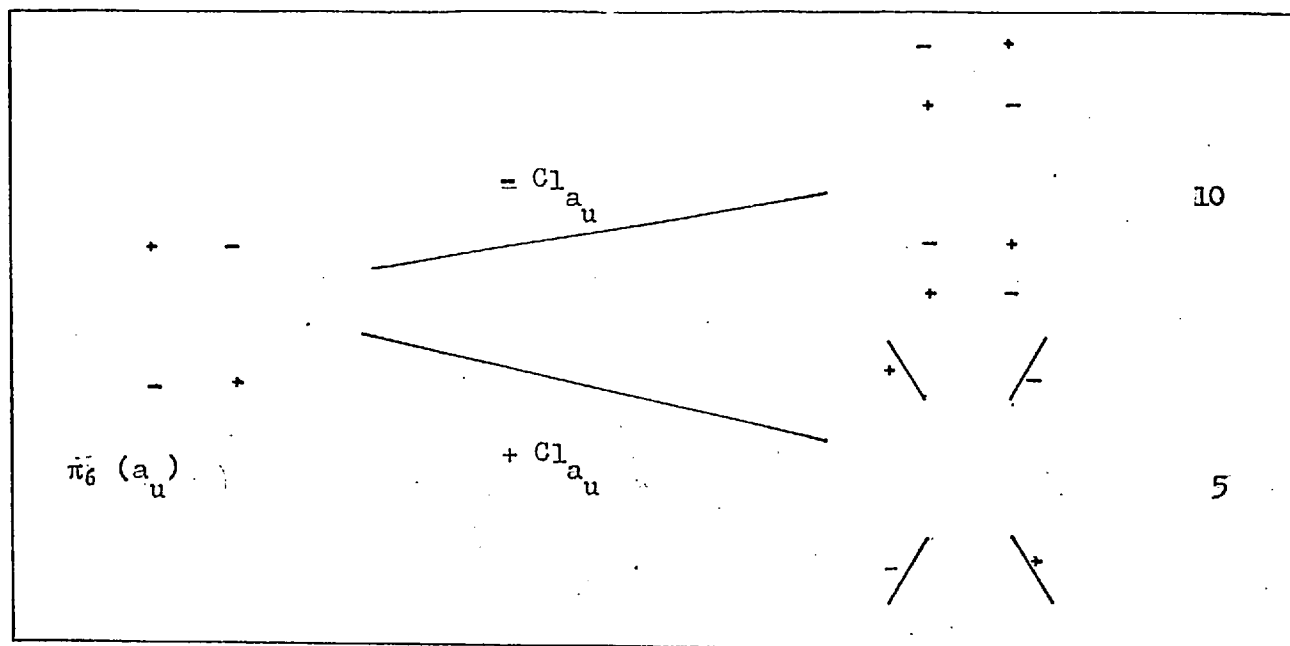


Figure 2.2 (contd.)

Table 2.2

p-benzoquinone			chloranil
(1) π_1 (b_{1u})	- 13.66 eV	- 17.137 eV	$\pi_1 + Cl_{blu}$
(2) π_2 (b_{2g})	- 12.45	- 15.731	$\pi_2 + Cl_{b2g}$
(3) π_3 (b_{3g})	- 11.11	- 15.116	$\pi_3 + Cl_{b3g}$
(4) π_4 (b_{1u})	- 9.95	- 14.210	$\pi_4 + Cl_{blu}$
(5) π_5 (b_{2g})	+ 0.26	- 14.107	$\pi_6 + Cl_{au}$
(6) π_6 (a_u)	+ 2.10	- 13.989	$\pi_8 + \pi_5 + Cl_{b2g}$
(7) π_7 (b_{1u})	+ 2.86	- 11.322	$\pi_3 - Cl_{b2g}$
(8) π_8 (b_{2g})	+ 4.44	- 11.279	$\pi_7 + \pi_4 - Cl_{blu}$
(9)		- 3.289	$\pi_5 - Cl_{b2g}$
(10)		- 0.408	$\pi_6 - Cl_{au}$
(11)		+ 1.174	$\pi_7 - Cl_{blu}$
(12)		+ 3.089	$\pi_8 - Cl_{b2g}$

to derive the bonding and antibonding MOs of chloranil starting with those of p-benzoquinone and mixing them with the AOs of chlorine having corresponding symmetries. This is done schematically in Fig. 2.2.

The various electronic levels of p-benzoquinone and chloranil are tabulated in the order of increasing energy in Table 2.2. The actual numerical values of the electronic energies for the two molecules cannot be compared because the authors used different sets of repulsion integrals and core parameters in their calculations. However, a comparison of the values given can help to build a semi-quantitative picture of the six bonding and six antibonding MOs of chloranil arrived at by interacting eight MOs of p-benzoquinone with the four AOs of corresponding symmetry supplied by each of the chlorine atoms.

It is seen at once that the higher energy MOs of p-benzoquinone hybridize to produce two of the orbitals of chloranil. π_6 and π_5 hybridize to accept a bonding contribution from the AOs of chlorine, whereas the nonbonding contribution of the same AOs is made to the pure π_8 and pure π_3 orbitals. π_7 and π_4 hybridize to accept a nonbonding contribution from chlorine whereas a bonding contribution is made by chlorine to π_4 and a nonbonding one to π_7 . One would reasonably expect that both the bonding and nonbonding contributions of the AOs of chlorine would be made to the same hybridized orbital. The reason for this lack of regularity is not clear.

The remarks made with regard to p-benzoquinone as to the reason why energetically $n \rightarrow \pi_5 < \pi_3 \rightarrow \pi_5 < \pi_4 \rightarrow \pi_5$, also apply to chloranil.

2.5. EFFECTS OF SUBSTITUTION ON THE ABSORPTION SPECTRUM OF p-BENZOQUINONE.

In general, of the two $\pi \rightarrow \pi^*$ transitions, band II appears to be most sensitive to substituent effects, both electronic and ring strain. For example, introduction of a methoxy group in the p-benzoquinone ring moves both $\pi \rightarrow \pi^*$ transitions towards longer wavelengths, but the shift for band II is eight times that for band I. Such substitution also tends to move the $n \rightarrow \pi^*$ band towards shorter wavelengths with the result that in many substituted quinones, the latter is partially or entirely hidden beneath the $\pi \rightarrow \pi^*$ absorption. (39)

The effect of chlorine substituents on the absorption spectrum of p-benzoquinone follows, as will be seen a little later, the same general rules.

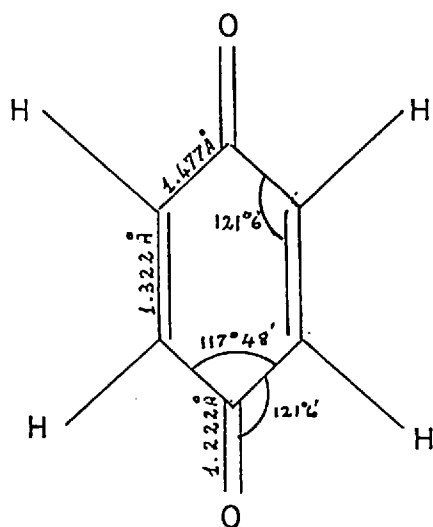
Schubert and Sweeney, (40) studying the absorption spectra of cyclic α - β unsaturated carbonyl compounds, enunciated a general rule to correlate and explain the effect of ring strain on the $\lambda_{\max}$ value for the $\pi \rightarrow \pi^*$ (Band II) transition. If a conjugated chromophore is strained in one part, then excitation to a dipolar type excited state will occur at a longer wavelength relative to the corresponding unstrained molecule if electron displacement in the excited state is away from the region of strain, and conversely absorption will occur at a shorter wavelength if displacement is towards that region.

The aromatic ring is strained when the angle α between a C = C bond is decreased.

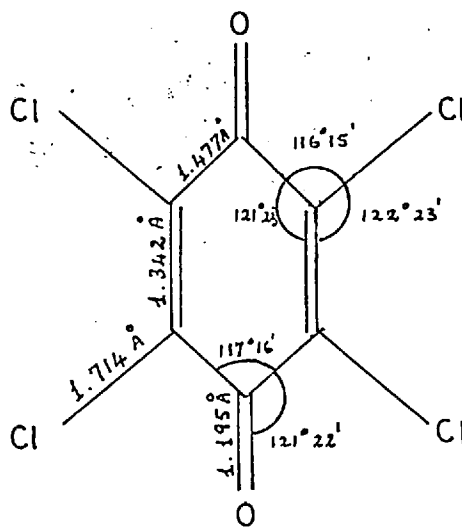
Figure 2.3



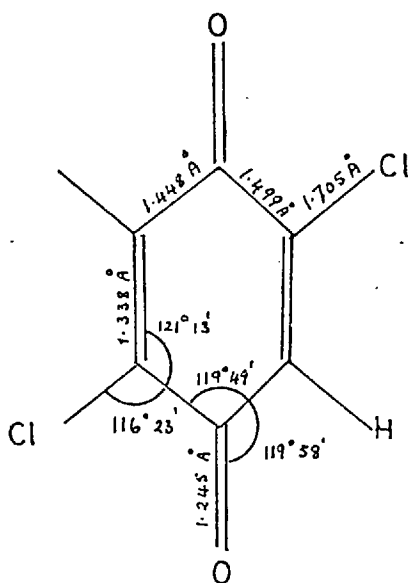
Bond lengths and bond angles



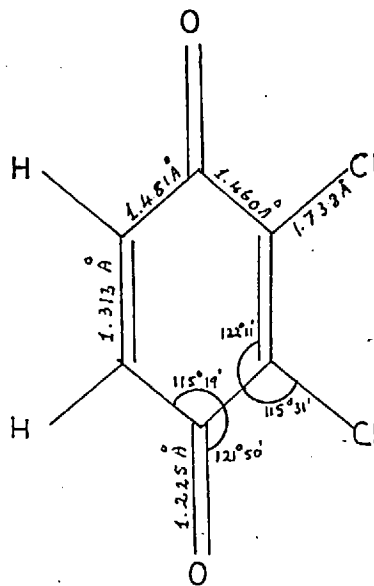
p-benzoquinone.



chloranil



2,5-dichloro p-benzoquinone



2,6-dichloro p-benzoquinone

Since electron displacement in the excited quinone molecule is undoubtedly towards the ring, the widening of the angle α , if Schubert and Sweeny's rule is assumed to be true in the converse, will be expected to cause a red shift of band II.

2.6. FREQUENCY SHIFTS IN THE ABSORPTION SPECTRA OF SUBSTITUTED p-BENZOQUINONES. (a) In solution

Stevenson,⁽⁴²⁾ following the methods Petruska applied to benzene, derived formulae for the changes of intensity and shifts in frequency of the $\pi \rightarrow \pi^*$ allowed and forbidden transitions of p-benzoquinone and its substituted derivatives as a function of type, number, and position of substitution in an attempt to interpret the experimental data. He regarded the transitions of substituted p-benzoquinones as derived from the transitions of p-benzoquinone itself. Thus, changes in the intensities and energies of the transitions are caused:

- a) by the inductive perturbation in which the substituent causes the states of p-benzoquinone to mix with each other;
- and b) by the conjugative perturbation in which the p-benzoquinone states mix with states which come about through the introduction of the extra π electrons and orbitals of the substituents.

Stevenson found that if "ortho effect" correction terms are introduced into the formulae, whenever two substituents are adjacent to each other, the formulae for the intensity of the $\pi \rightarrow \pi^*$ forbidden transition and for the frequency shifts of both transitions hold to

within $\pm 10\%$ for a number of substituted p-benzoquinones. Relevant experimental data taken from various sources is presented in Table 2.3 and 2.4. They allow us to draw the following conclusions:

a) Substituents in the p-benzoquinone ring, irrespective of their electron-releasing or electron-attracting nature, produce a red shift in the ${}^1A \rightarrow {}^1K$ ($\pi_3 \rightarrow \pi_5$ forbidden) transition as well as in the ${}^1A \rightarrow {}^1J$ ($\pi_4 \rightarrow \pi_5$ allowed) transition of the parent molecule.

b) Electron-releasing substituents, e.g. $-\text{CH}_3$, produce a smaller red shift than that caused by electron-attracting substituents e.g. $-\text{Cl}$. This is contrary to what is expected on theoretical grounds. The red shift is produced because of the resonance interaction between the π -electron system and the substituent, and one would expect that electron-releasing substituents which facilitate such interaction would produce a larger red shift than electron-attracting substituents which inhibit the interaction.⁽⁴⁵⁾

c) The red shift is more pronounced in the ${}^1A \rightarrow {}^1K$ transition. This is presumably due to the fact that the introduction of extra π electrons and orbitals of the substituents, in general, raises the energy of the higher-lying π bonding orbitals and lowers the energy of the lower-lying antibonding π^* orbitals, but this increase or decrease is significant only in the case of the highest-lying bonding orbitals and the lowest-lying unoccupied antibonding orbitals.

TABLE 2.3.

Frequency shifts of the $^1A \rightarrow ^1K$ transition ($\pi \rightarrow \pi^*$ forbidden) in substituted p-benzoquinones.

Substituent Position	Frequency shift cm^{-1} in				Substituent
	$\text{CHCl}_3^{(42)}$	$\text{nC}_6\text{H}_{14}^{(42)}$	$\text{C}_2\text{H}_5\text{OH}^{(43)}$	Vapour ⁽³⁶⁾	
2	2040	2410			- CH_3
2,3	4120	4720			
2,5	3070	3440			
2,6	3370	3660			
2,3,5	4380	5000			
2,3,5,6	5480	6020			
2	5780				- OCH_3
2,3	8660				
2,5	7690				
2,6	8190				
2,3,5	9870				
2,3,5,6	9720				
2	3080	2910	3740	3000	- Cl
2,3			6100	5500	
2,5	4670	5010	5240	3300	
2,6	5640	5010	6100	4400	
2,3,5	6570	6570	7310	6400	
2,3,5,6	8090	7970	7770	(~8000)	

TABLE 2.4.

Shifts in the ${}^1A \rightarrow {}^1J$ ($\pi \rightarrow \pi^*$ allowed) transition in
substituted p-benzoquinones.

Substituent Position	Frequency shift cm^{-1} in			Substituent
	CHCl_3 (42)	Vapour (36)	$\text{C}_2\text{H}_5\text{OH}$ (43)	
2	490			- CH_3
2,3	650			
2,5	1280			
2,6	1430			
2,3,5	1890			
2,3,5,6	2480			
2	1280			- OCH_3
2,3	1280			
2,5	5440			
2,6	5810			
2,3,5	6290			
2,3,5,6	7540			
2		1350	1630	- Cl
2,3		1340	1940	
2,5		2830	3630	
2,6		3360	3700	
2,3,5		3960	4590	
2,3,5,6		5210	5820	

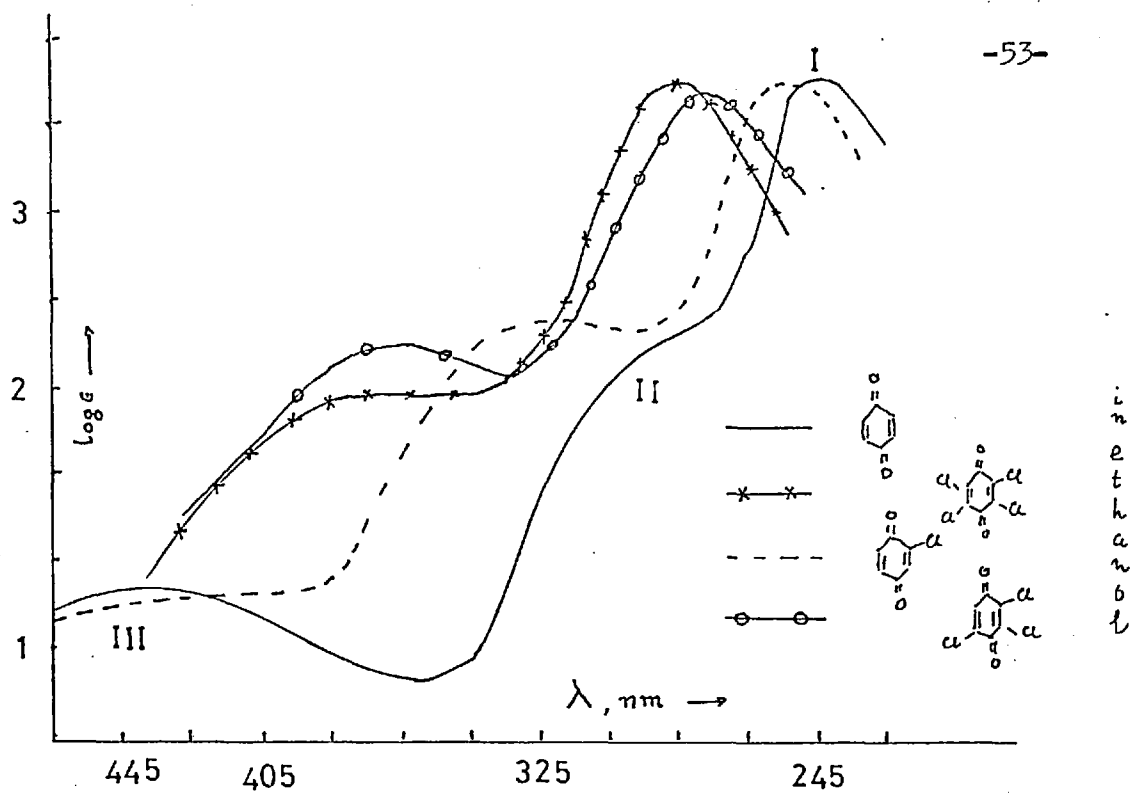


Fig. 2.4

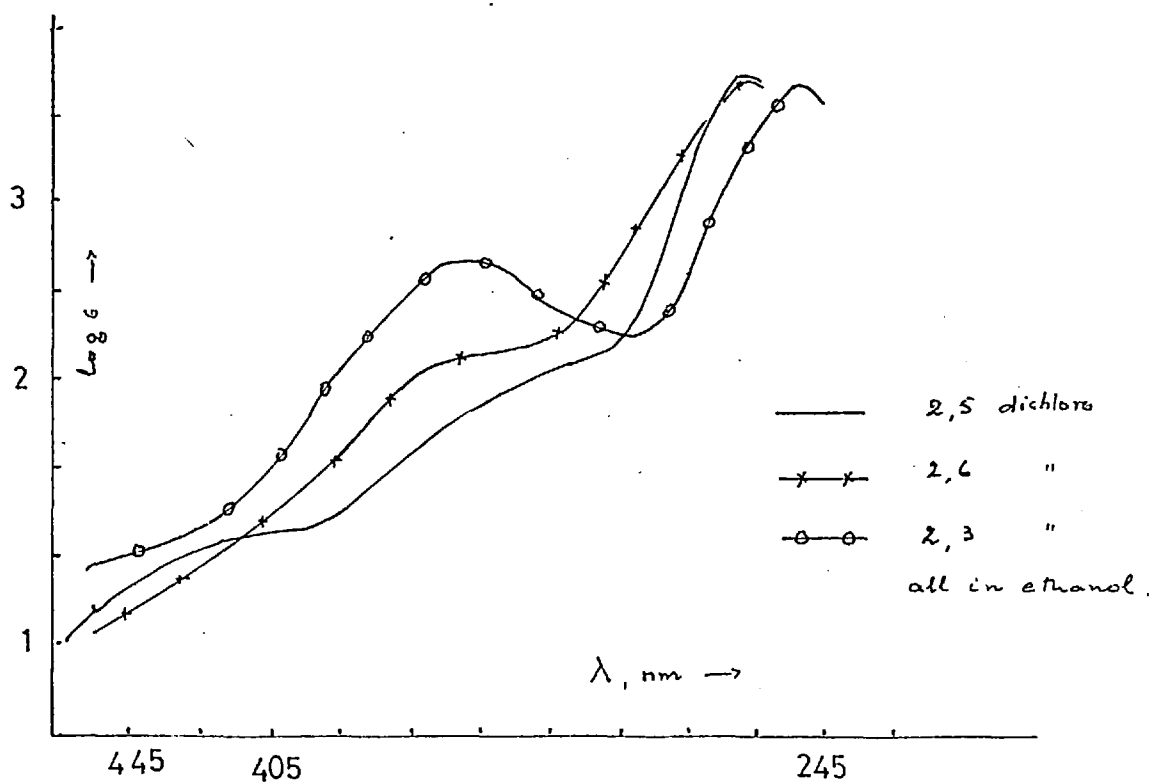


Fig. 2.5

The combined effect of the decrease in π_5^* and the increase in π_3 in the case of p-benzoquinone, it appears, is such that the closing of the energy gap between these two orbitals is more pronounced than the combined effect of the changes in the relative positions of π_4 and π_5 . With each successive introduction of a chlorine atom into the ring the $\pi_3 \rightarrow \pi_5^*$ energy gap is closed more significantly than the $\pi_4 \rightarrow \pi_5^*$ one, and hence the red shift is larger in the $^1A \rightarrow ^1K$ transition in relation to the $^1A \rightarrow ^1J$ transition.

Fig. 2.4 and Fig. 2.5, which give the absorption spectra of p-benzoquinone and its chloro-substituted derivatives in solution in alcohol show that the $n \rightarrow \pi^*$ band of p-benzoquinone is blue shifted in monochloro and 2,5-dichloro p-benzoquinone. In other chlorine-substituted derivatives, the $n \rightarrow \pi^*$ band is not seen, because the blue shift is presumably large enough to submerge this band under the $\pi \rightarrow \pi^*$ forbidden transition band.

Table 2.5 gathers the details, available from various sources, relative to this transition.

Again, we notice, substitution in the ring produces a blue-shift in the $n \rightarrow \pi^*$ band irrespective of the nature of the substituent. Theoretically, only electron-releasing substituents raise the energy of the excited state owing to the accumulation of electronic charge in a localized region. (45)

TABLE 2.5.

$n \rightarrow \pi^*$ Transition in substituted p-benzoquinones
 λ_{max} in nanometres.

Compound	Solvent		
	$n\text{C}_6\text{H}_{14}$ (44)	CHCl_3 (44)	$\text{C}_2\text{H}_5\text{OH}$ (43)
p-benzoquinone	434	437	435
	457	451	
	479		
2-methyl p-benzoquinone	434	436	
	455	435	
	475		
2,3-dimethyl "	433		
2,5- " "	437	434	
2,6 " "	424		
2,3,5-trimethyl "	435	434	
2,3,5,6-tetramethyl "	432	435	
2-ethyl "	434	437	
	453	472	
2-chloro "		~415	~420
2,5-dichloro "			~415

b) In the Vapour Phase

Trommsdorff and Kahane - Paillouls ⁽³⁶⁾ carried out a rigorous examination of the vapour-phase absorption spectra of p-benzoquinone and its chloroderivatives in the ultraviolet region. With an improved cell and detection equipment they obtained electronic spectra of the above compounds with a degree of resolution higher than that obtained by Singh ⁽⁴⁶⁾ and Sado ⁽⁴⁷⁾.

In its ground-state the p-benzoquinone molecule, as was mentioned earlier, is planar. It has a D_{2h} symmetry which it preserves in the excited state. All its derivatives with the exception of chloranil which, as is expected, has the same symmetry as p-benzoquinone, have a symmetry lower than that of the parent molecule. Fig. 2.6 shows the correlation between the species of the various symmetry groups to which the above mentioned compounds belong. Those which are underlined indicate the state an excited molecule is most likely to assume and correspond to allowed electronic transitions from the ground state.

The ${}^1A \rightarrow {}^1K$ transition is forbidden in p-benzoquinone because the excited state is a B_{1g} state. Fig. 2.6 shows that it is also forbidden in 2,5-dichloro and chloranil. It becomes allowed in mono, 2,3-dichloro and trichloro p-benzoquinone because of the interaction with the ${}^1A_g \rightarrow {}^1B_{2u}$ (${}^1A \rightarrow {}^1J$) transition which is formally allowed.

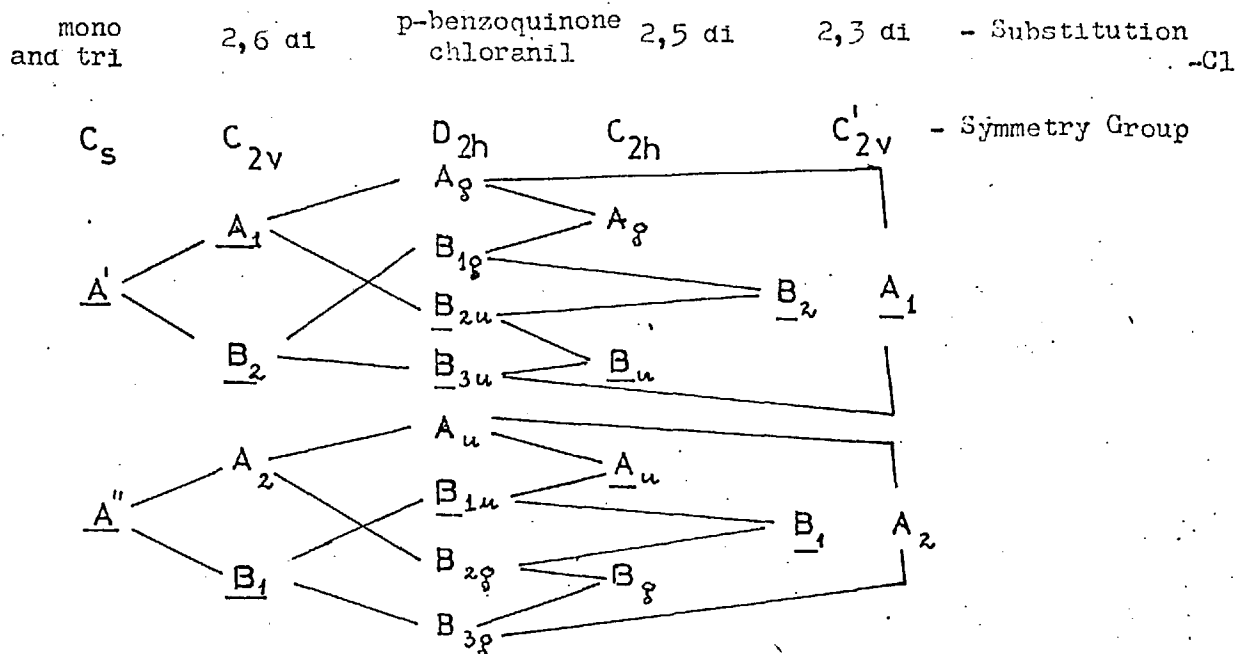


Figure 2.6.

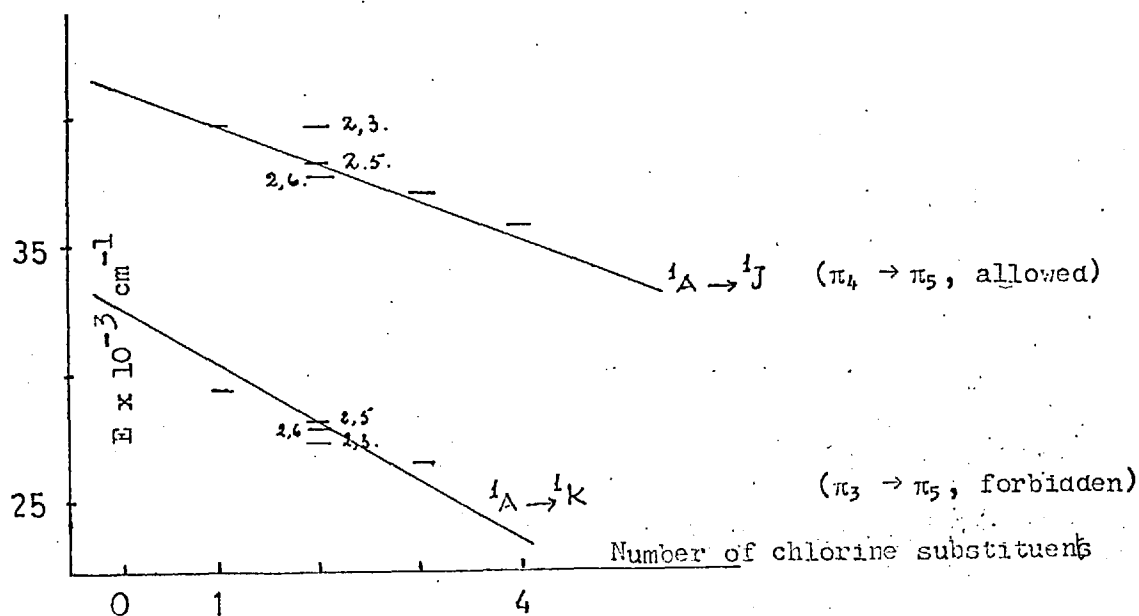


Figure 2.7.

Fig. 2.7 shows the positions of the electronic transitions ${}^1A \rightarrow {}^1J$ and ${}^1A \rightarrow {}^1K$ as given by Trommsdorff and Kahane-Paillous.⁽³⁶⁾

The red shift is roughly proportional to the number of chlorine atoms in the ring but the red shift in the forbidden ${}^1A \rightarrow {}^1K$ transition seems to be more pronounced in relation to the shift of the ${}^1A \rightarrow {}^1J$ allowed transition with increase in the number of chlorine atoms.

The spectrum of chloranil obtained by the above authors was not sufficiently well resolved to determine the position of the ${}^1A \rightarrow {}^1K$ transition. However, if one assumes that the position of this band varies linearly with the number of substituents in the ring, the electronic transition for chloranil should take place at about $22,000\text{ cm}^{-1}$ and the maximum absorption should occur at about $26,000\text{ cm}^{-1}$. These values are in brackets in Table 2.6 which summarizes the data given by the authors mentioned above.

It is opportune to note that the fact that the ${}^1A \rightarrow {}^1K$ transition which is forbidden in p-benzoquinone becomes allowed in mono, 2,3-dichloro and trichloro p-benzoquinone for reasons already mentioned, is reflected in the absorption spectrum of these compounds. The intensity of the ${}^1A \rightarrow {}^1K$ transition in the above mentioned compounds is certainly larger than in others, where, by reasons of symmetry, this transition still remains forbidden, as is seen by the higher extinction coefficients in that region (Cfr. Fig. 2.4 and 2.5 and Table 2.7).

TABLE 2.6.

Compound	$^1A \rightarrow ^1J$	$^1A \rightarrow ^1K$	
	O-O Band cm^{-1}	(1) cm^{-1}	(2) cm^{-1}
p-Benzoquinone	41330	32800	35600
Monochloro	39975	29500	32600
2,3-Dichloro	39990	27600	30100
2,5- "	38495	28200	32300
2,6- "	37970	28000	31200
Trichloro	37370	26600	29200
Tetrachloro	36115	(23500)	(26500)

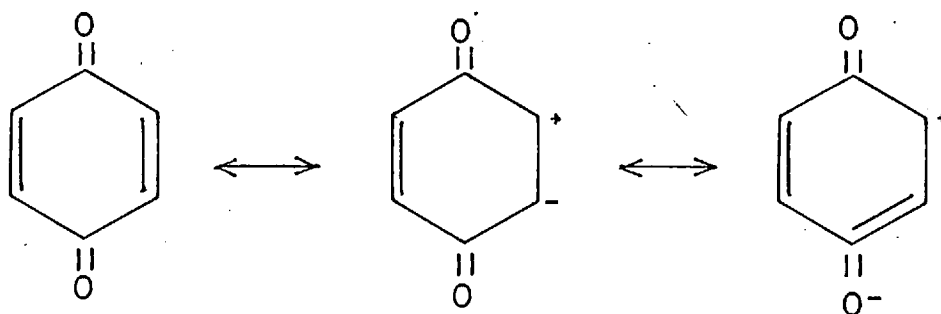
(1) = Position of the electronic transition - evaluated.

(2) = Maximum absorption - observed.

TABLE 2.7.

Compound (in ethanol)	$\log \epsilon_{\max}$ for $l_A \rightarrow l_K$	$\log \epsilon_{\max}$ for $l_A \rightarrow l_J$
p-Benzoquinone	~2.60	4.28
Monochloro p-benzoquinone	2.88	4.23
2,3-Dichloro "	3.15	4.14
2,5- " "	~2.5	4.22
2,6- " "	~2.65	4.17
Trichloro "	2.72	4.17
Tetrachloro "	2.48	4.20

It must also be observed here that theoretical considerations predict a higher intensity for the ${}^1A \rightarrow {}^1J$ transition in mono and 2,5-dichloro p-benzoquinone, since substitution by chlorine at these positions will enhance resonance between the following p-benzoquinone structures (41).



A study of the bond angles of 2,5-dichloro p-benzoquinone given in Fig. 2.3 shows that the ring angles in this compound are nearly 120° , the theoretical value for sp^2 hybridization. π electron delocalization and consequently conjugation of the quinonoid structure will be facilitated.

Both these predictions are borne out by experiment. Table 2.7 shows that mono and 2,5-dichloro p-benzoquinone have almost equal extinctions for the ${}^1A \rightarrow {}^1J$ transition and that these are higher than those of the remaining chlorine-substituted derivatives for the same transition.

2.7. THE p-BENZOQUINONE TRIPLET FROM ITS EMISSION SPECTRUM, AND EFFECTS OF SUBSTITUTION.

Jayswal and Singh^(48a), who studied the vapour-phase emission spectrum of p-benzoquinone sensitized by benzene vapour excited by transformer discharge, found that their measurements of the various bands agreed precisely with measurements published by Hollas⁽⁴⁹⁾ on the vapour phase absorption spectrum of p-benzoquinone. Both the absorption and the emission spectrum have a prominent 0-0 band at 18683 cm^{-1} and the assignments made to other bands present in the spectra show that only the totally symmetric modes of vibration are involved. This can only be the case if similar transitions are involved in the absorption and emission spectrum viz ${}^3A_u \xrightleftharpoons[\text{emiss}]{\text{abs}} {}^1A_g$, and if the excited states preserve their ground state symmetries.

Combining data given by Kanda⁽⁵⁰⁾ with theirs, they calculated the lifetime τ_0 of the p-benzoquinone triplet to be $2.1 \times 10^{-2}\text{ s}$.

Table 2.8 groups the 0-0 bands of the emission spectra in the vapour phase sensitized by benzene and in the absorption spectra in n-heptane of 2,5 and 2,6-dichloro p-benzoquinone. It can be inferred that the 0-0 emissions of these two chloroderivatives which can be seen to be in the same visible region as p-benzoquinone and show red shifts in their corresponding 0-0 absorption bands in heptane, just as p-benzoquinone does, involve a ${}^3A_u \rightarrow {}^1A_g$ transition in the vapour phase, that the excited states preserve

their ground state symmetries and that their triplets have a lifetime of the order of 10^{-2} s.

Theoretically, heavy atom perturbation should affect the $S_0 \rightarrow T_{\pi\pi^*}$ transition (ie ${}^3A_u \leftarrow {}^1A_g$) only very slightly but should enhance the $S_0 \rightarrow T_{\pi\pi^*}$ transition (ie ${}^3B_{1g} \leftarrow A_g$) quite considerably (51). Since no new band was observed in the absorption spectra of 2,6-dihalogeno p-benzoquinones as a result of external heavy atom perturbation effect, Cilento (52) and co-workers concluded that these compounds have a $\pi\pi^*$ triplet as their lowest triplet, thus confirming at least one of Jayswal and Singh's conclusions.

TABLE 2.8.

Triplet-Singlet Transitions in p-Quinones.

	Position of O-O band in emission, vapour state (48b)	Absorption peak in n-heptane (48c)
p-benzoquinone	18,688 cm^{-1}	18,553 cm^{-1}
2,5-dichloro	19,290 cm^{-1}	19,230 cm^{-1}
2,6-dichloro	18,545 cm^{-1}	18,350 cm^{-1}

CHAPTER 3

Photochemical Reactions Via The Triplet
State Of Aromatic Carbonyl Compounds -
Experimental Evidence.

3.1. REACTIONS VIA THE TRIPLET STATE OF AROMATIC CARBONYL COMPOUNDS.

In Chapter 1, it was stated that certain features of the triplet state make it an almost exclusive intermediate in the photochemical reactions of aromatic carbonyl compounds. Experimental evidence in support of this claim is presented in the following pages.

Experiments done with p-benzoquinone in cyclo-octene have shown that the same photoadduct and similar quantum yields are obtained when the initial excitation was either to the $\pi\pi^*$ or $n\pi^*$ excited state, suggesting that these two different excited states produce a common species which is responsible for the photoadduct. Considering the principles that were elucidated in Chapter 1 regarding the triplet state of aromatic carbonyl compounds, the only possible common species that could arise from the $\pi\pi^*$ and $n\pi^*$ excited states is the $n\pi^*$ triplet.

The transition from the singlet to the triplet when the initial excitation is to the $n\pi^*$ state is readily envisaged by intersystem crossing. The transition from the $\pi\pi^*$ singlet to the $n\pi^*$ triplet may either take place directly, since such a transition, as was pointed out earlier, is theoretically favoured ⁽⁷⁾, or may take place via the $n\pi^*$ singlet. In this latter case, according to Brand and Gordwin's ⁽⁵³⁾ treatment of orbital symmetries and electronic levels in p-benzoquinone, an allowed intramolecular transition $B_{3g} \leftarrow B_{3u}$

will be involved, a transition that should be accompanied by infra-red emission.

Though the evidence cited above is in itself not conclusive, the fact that saturation with oxygen reduces the formation of the photoadduct to about 30% of that obtained in anaerobic solutions, seems to indicate that the hypothesis of a triplet intermediate is reasonable in principle, since oxygen is known to be efficient in triplet quenching.

Schulte-Frohlinde and Sontag ⁽⁵⁴⁾ have shown that p-benzoquinone is reduced in isopropanol with unit efficiency when the quinone is selectively excited to either the $\pi\pi^*$ or the $n\pi^*$ state, again suggesting that crossing may occur to give a common state responsible for the reaction. The most obvious common candidate also here is the $n\pi^*$ triplet. Similar results were obtained by Atkinson and D1 ⁽⁶⁰⁾ for the irradiation of p-benzoquinone and ethanol in carbon tetrachloride at 436 nm ($n \rightarrow \pi^*$) and 365 nm ($\pi \rightarrow \pi^*$).

Another example reported in the literature is that of 1,4-naphthaquinone which yields the same dimer with the same quantum efficiency when it is selectively excited either to the $n\pi^*$ or the $\pi\pi^*$ state in benzene solutions. The reaction has been interpreted as arising from the interaction of the $n\pi^*$ triplet with ground-state naphthaquinone. ⁽⁵⁵⁾ Irradiated in isopropanol solutions, 1,4-naphthaquinone is reduced with the same quantum efficiency with either $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ selective excitation. ⁽⁵⁵⁾

Kemp and Porter ⁽⁶³⁾ using laser flash photolysis ($\lambda = 347$ nm) obtained the absorption spectrum of excited chloranil in outgassed ethanol and assigned the maximum observed at 500 nm to the chloranil triplet and the maximum at 420 nm to the semiquinone radical since the species producing the 500 nm band absorption decayed with first-order kinetics and the one responsible for the 420 nm band with second-order kinetics. They also found that the 420 nm species grew as the 520 nm species decayed. The 520 nm species was inefficiently quenched by oxygen and more efficiently by anthracene, and though the growth of the 420 nm species was not observed in the presence of these quenchers, the initial absorption at 420 nm was still there. Reference will be made to these observations later in the discussion on the results of the present work, but it must be remarked here that the absorption at 500 nm corresponds to excitation of the first excited triplet to the second excited triplet state.

Tickle and Wilkinson ⁽⁶⁵⁾ studied the quantum yield of the photo-reduction of anthraquinone as a function of anthraquinone concentration, the rate of absorption and the wavelength of excitation. The work of Bolland and Cooper ⁽⁶⁶⁾ had shown that inert aromatic hydrocarbons with lower triplet levels than anthraquinone ($E_T = 62$ kcal mole⁻¹) inhibited the photoreduction, while those with higher triplet levels had no effect. Tickle and Wilkinson ⁽⁶⁵⁾ tried to resolve

this discrepancy. They found that the quantum yield of photoreduction of anthraquinone in alcoholic solution varies with concentration of the quinone and the intensity of light absorption, but not with the wavelength of excitation. At low anthraquinone concentrations and with high rates of absorption of light, the quantum yield of photoreduction approaches a lower limit of 0.5, whilst at high concentrations and low intensities the upper limit is 1.0. These limits in conjunction with the lack of wavelength dependence suggest that the lowest triplet state is the only reactive species in the photoreduction of this quinone.

The suggestion that 9, 10-anthraquinone reacts via its triplet state is corroborated by the work of Dearman and Chand (68) who irradiated a range of 9, 10-anthraquinone derivatives in EPA glass, and obtained an e.s.r. signal due to the semiquinone only for those compounds which showed phosphorescence, a characteristic of the triplet state. Those that did not phosphoresce and at the same time failed to give an e.s.r. spectrum under the same conditions as the others, however, gave semiquinone radical ions by the usual chemical reduction in basic methanol. Table 3.1 summarizes some of their results.

If the appearance of an e.s.r. signal on irradiation of quinones in alcoholic substrates, may be taken, on the strength of Dearman and Chand's evidence, to be indicative of abstraction of

Table 3.1. Correlation of emission with photochemical activity of substituted anthraquinones.

Derivative	O-O phosphorescence band (+ 100 cm ⁻¹)	O-O fluorescence band (+ 100 cm ⁻¹)	ϕ for quinol formation in absence of O ₂	No. of resolved lines and width of esr spectrum
Anthraquinone	21900	-	0.9	13 line; 6.0 G
2-CH ₃	21800	-	≈ 1	31 line; 7.6 G
2-SO ₃ Na	21700	-	1	25 line; 4.9 G
2,6-di SO ₃ Na	21800	-	1	20 line; 3.7 G
1-Cl	21900	-	≈ 1	13 line; 6.5 G
1,5-di Cl	21500	-	≈ 1	16 line; 5.8 G
2, Cl	21700	-	≈ 1	22 line; 6.2 G
1,8-di Cl	21600	-	≈ 1	9 line; 5.1 G
1-NH ₂	-	18200	≈ 0.1	None
1,4-di OH	-	18800	≈ 0.1	None
1,5-di OH	-	17400	≈ 0.1	None

hydrogen by the quinone triplet, then it may be worthwhile to note that White and Tollin (62) showed that on ultraviolet irradiation, p-benzoquinone and chloranil give in pure ethanol the expected typical five-line and single-line semiquinone e.s.r. spectrum respectively.

Bridge and Porter (61a) in a flash-photolysis study of the photoreduction of duroquinone in liquid paraffin arrived at the conclusion that the first excited singlet state was the reactive state in the photoreduction. Later, Porter (61b) suggested that the reaction of duroquinone with the solvent via the singlet state should probably be reinterpreted as an intramolecular reaction. Recent work, however, in which triplet energy transfer to inert acceptors was shown to inhibit photoreduction of duroquinone has established the triplet state as the reactive species in isopropanol. (61c)

Backstrom and Steneryr (69) studied the effect of nitric oxide, a paramagnetic gas, on the photoreduction of benzophenone by isopropanol. They explained the retarding effect that nitric oxide had on the reaction by assuming a metastable biradical state of benzophenone as an intermediate in the photoreduction, and identified this biradical state with the triplet state of benzophenone.

Hammond and Moore (70) irradiated solutions of benzophenone and benzhydrol in benzene with ultraviolet light and found the ratio $K_{\text{deactivation}} / K_{\text{reaction}}$ to be 0.050. Considering that K_{reaction}

has an upper limit of $10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ for a diffusion controlled reaction, the upper limit for K_d is $5 \times 10^7 \text{ s}^{-1}$. The fluorescence rates common for singlets are normally of the order of 10^8 s^{-1} .

Since benzophenone has no fluorescence, the authors concluded that the actual rate of non-radiative quenching of the lowest singlet state must be at least 10^{10} s^{-1} and that therefore there must necessarily be some longer-lived excited state involved in the competition between deactivation and reaction. This longer-lived excited state can only be the triplet.

Porter and Wilkinson (71) conclusively proved that the excited state of benzophenone taking part in the photochemical reaction is the triplet state. They observed the transient absorption upon flashing benzophenone in benzene with various concentrations of added naphthalene in a soda-glass reaction vessel which filtered out almost all the light in the region of naphthalene absorption. With increase in naphthalene concentration the absorption due to the ketyl radical decreased and the absorption of triplet naphthalene increased as a result of energy transfer from benzophenone. Complex formation between benzophenone and naphthalene was ruled out because the spectral intensities and positions of mixed solutions were identical with those of separate solutions. Quenching of the first excited singlet state of benzophenone by naphthalene is not possible because the first excited state of naphthalene lies above that of benzophenone.

The interaction between an excited singlet donor molecule and a ground-state singlet acceptor molecule to give a ground-state singlet donor molecule and an excited triplet acceptor molecule is spin forbidden and hence bound to be inefficient and unimportant in comparison with the allowed



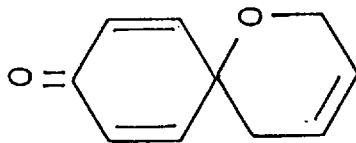
The inevitable conclusion that benzophenone reacts exclusively via the triplet state was further demonstrated by the observation that pinacolization is quenched in the presence of naphthalene, and naphthalene had been shown by Terenin and Ermolaev⁽⁷²⁾ to be efficient in quenching the phosphorescence of benzophenone in frozen glass.

A number of research teams⁽⁷³⁾ have since reported that well-known triplet quenchers such as azulene, cis-piperylene, 1-methylene-4,4-diphenyl-2-cyclohexene, ferric dipivaloylmethane and ferric acetylacetonate inhibit to a greater or lesser extent the photoreduction of benzophenone.

Irradiation of carbonyl compounds in the presence of dienes usually leads either to isomerization⁽⁵⁶⁾ and, in concentrated solutions, to dimerization⁽⁵⁷⁾ but no photocyclo-addition products, or to photocyclo-addition products alone, depending on whether the triplet energy of the carbonyl compound is above or below that of the diene triplet (≈ 60 kcal/mole). Whereas there is still doubt

as to whether, in all cases, isomerization involves the singlet or the triplet state ⁽⁵⁸⁾, dimerization is known to take place via the triplet. ⁽⁵⁹⁾ These reactions can only be rationalized by assuming a triplet - triplet energy transfer from the carbonyl compound to the diene when the triplet energy of the former is above that of the latter.

p-benzoquinone ($E_T = 53 \text{ kcal mole}^{-1}$) reacts with 1,3-dienes on irradiation, to give spiro-pyrans of the type ⁽⁶⁰⁾



Considering that the diene has added on to the quinone via the oxygen atom, it is reasonable to assume that p-benzoquinone gives on irradiation the $n\pi^*$ triplet whose electrophilic oxygen atom would account for photocycloaddition as well as hydrogen abstraction reactions.

The irradiation of benzaldehyde in cyclohexene solutions gives rise to products arising from both photocycloaddition as well as photoreduction reactions. ⁽⁶⁴⁾ If the two reactions were to result from different excited species, naphthalene with a triplet energy of $61 \text{ kcal mole}^{-1}$ would be expected to quench the triplet but not the

singlet and thus change the ratio of the products. The rate of product formation was slowed down, on addition of naphthalene, but the ratio of products was unaltered, proving that photoreduction and photocycloaddition involve the same triplet state.

Ferric dipivaloylmethane, an efficient quencher of benzophenone photoreduction,⁽⁷³⁾ was shown by Yang and co-workers⁽⁷⁴⁾ to inhibit the photocycloaddition of benzophenone to 2-methyl - 2-butene, proving the same point.

The claim, therefore, that the triplet state of aromatic carbonyl compounds is almost exclusively responsible for their photochemical reactions is fairly well substantiated by experimental evidence.

CHAPTER 4

Hydrogen Abstraction By Free Radicals And Excited Quinones

4.1. THE PHOTOREDUCTION OF QUINONES.

The abstraction of hydrogen from alcoholic substrates by photoexcited quinones has been studied in the presence and absence of oxygen. Quantum efficiencies that ranged from 0.5 to 1 under varying conditions were observed in most cases, and using steady-state approximations, it was found possible to work out reaction mechanisms consistent with experimental data. The general picture that emerges from these studies is summarized in the following paragraphs.

a) Anaerobic Solutions.

The mechanism of the photoreduction of quinones by alcoholic substrates in the absence of oxygen, is generally accepted to be:

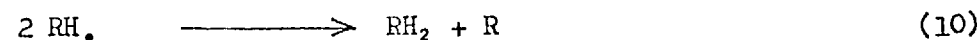
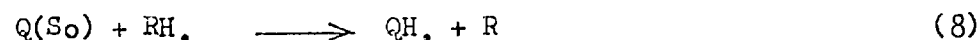
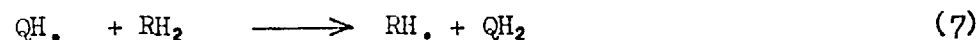
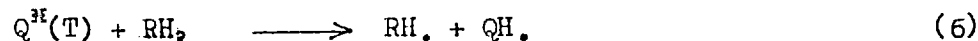
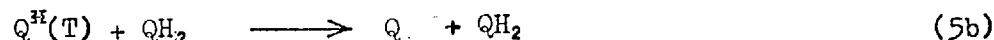
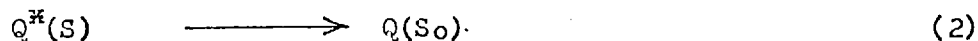


Fig. 4.1. shows the quinone and alcohol cycle schematically.

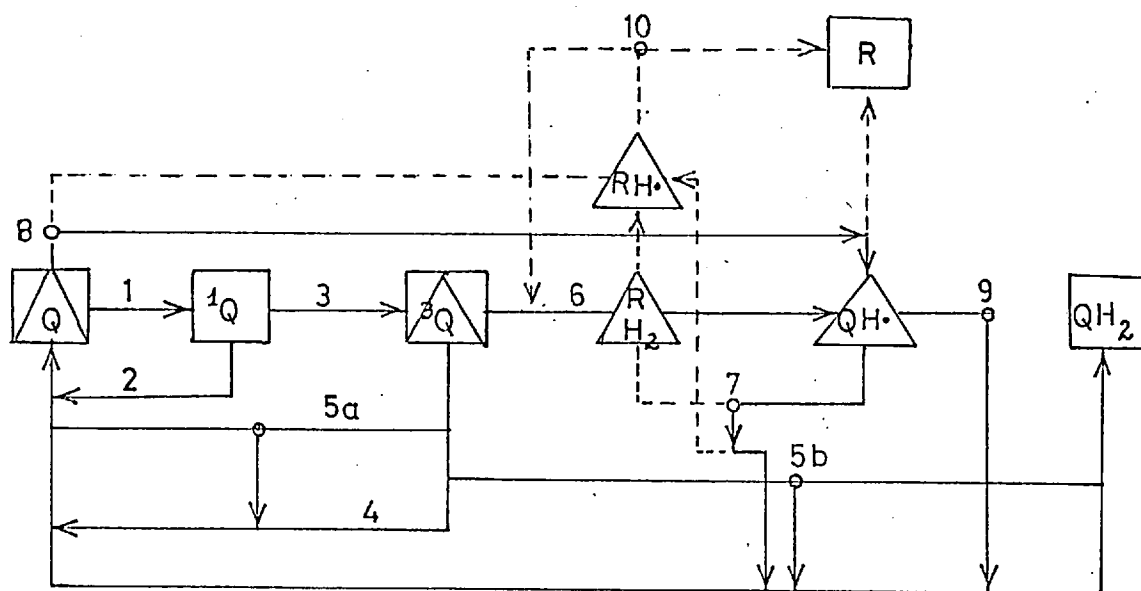


Figure 4.1.

The reaction cycle of Q (bold lines) and RH_2 (broken lines). Reaction numbers are shown along connecting lines. Reagents taking part in bimolecular reactions are enclosed in triangular boxes.  denotes reagent taking part in mono as well as bimolecular reactions.

Reaction (2) includes both the radiative and the non-radiative transitions of the quinone singlet. Since most quinones phosphoresce rather than fluoresce, and since their quantum yield of intersystem crossing is very nearly unity, reaction (2) is usually neglected. The self-quenching reaction (5) has been shown to be operative in the case of phenanthraquinone ⁽⁷⁵⁾, but not necessarily with other quinones ⁽⁷⁶⁾. Reaction (7) in conjunction with reaction (9) makes the quantum efficiency for loss of quinone dependent on light intensity and alcohol concentration. Reaction (8) makes the quantum efficiency dependent on quinone concentration and light intensity.

Since the normal upper limit for the photoreduction of quinones in alcoholic substrates has experimentally been found to be unity, reactions (7) and (8) cannot be taken to occur together in any given system. If they did, chain reactions would be initiated by the free radicals produced, leading to quantum yields much higher than unity. However, Walker ⁽⁷⁵⁾ has reported a quantum efficiency of 4 for loss of quinone in his work with low-intensity irradiation of phenanthraquinone in solutions in benzene containing high concentrations of alcohol, and has included reaction (7) and (8) in the mechanism.

Whether reaction (7) predominates over reaction (9) or vice versa is determined by the concentration of the alcohol in the system and on the nature of the semiquinone radical formed. Durosemiquinone, for instance, disproportionates even in 100 per cent isopropanol. ⁽¹⁰⁰⁾

Working with solutions of p-benzoquinone in benzene containing isopropanol, Scrutton ⁽⁷⁷⁾ found that decrease in alcohol concentration reduced the quantum efficiency below the limiting value of unity set by his proposed mechanism of photoreduction, and interpreted the result as being caused by the increasing influence of reaction (9) relative to reaction (7) with decrease in alcohol concentration.

Reaction (5b) is known to occur in the photoreduction of chloranil ⁽⁷⁷⁾ and duroquinone ⁽¹⁰⁰⁾. In the case of duroquinone it has been proved that inhibition by the hydroquinone results from the chemical reaction

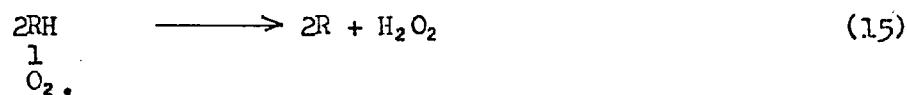


A quantity of durohydroquinone calculated to totally inhibit the permanent photoreduction of duroquinone was added to the solution of the quinone in isopropanol and the mixture was flash-photolysed. The yield of durosemiquinone was twice that observed when duroquinone alone is flashed under identical conditions.

b) Aerobic Solutions

In the presence of oxygen, the semiquinone radical is oxidized, regenerating the quinone. The reaction steps usually are:

Reactions (1) to (6), same as before.



and other disproportionation reactions of the peroxy radical which depend on whether the substrate is a primary or a secondary alcohol. Schematically, the cycle can be represented as in Fig. 4.2, starting with semiquinone radicals.

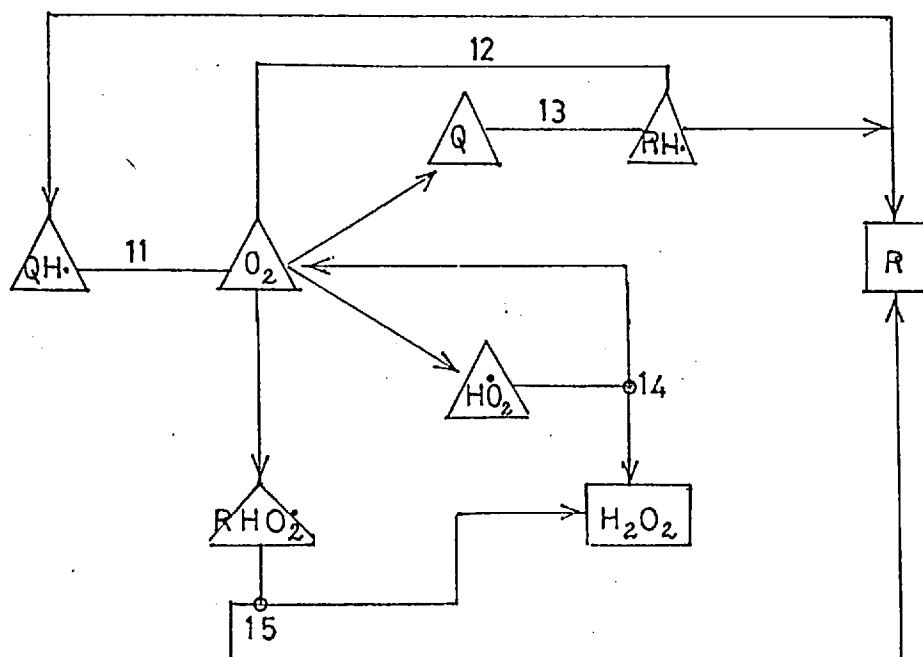


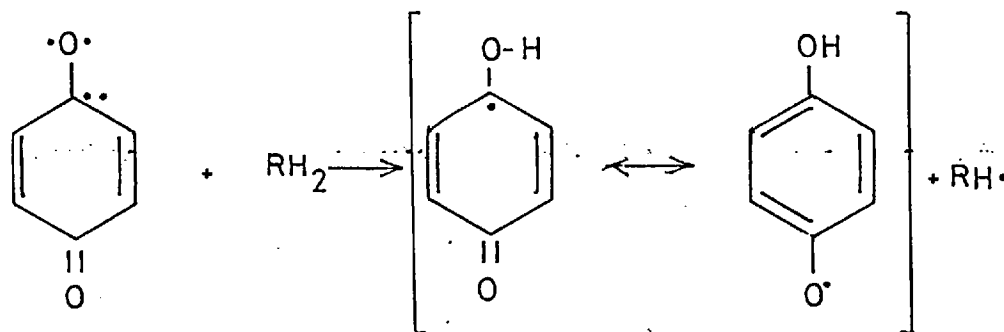
Figure 4.2.

4.2. THE EXCITED STATE INVOLVED IN HYDROGEN ABSTRACTION.

Kinetic considerations indicate that the photoreactive species in typical hydrogen abstraction is the first excited triplet. Singlet excited states usually decay to the ground state within about 10^{-8} s. Hydrogen abstraction, which typically has an activation energy of 7 kcal mol^{-1} is not expected to compete with these fast physical de-excitation processes. Triplets, however, have lifetimes of the order of 10^{-3} s or higher and hydrogen abstraction may be fast enough to compete with phosphorescence or intersystem crossing. This conclusion is amply supported by experimental observations which have succeeded in establishing that hydrogen abstraction does indeed take place via the triplet state. (cfr. Chapter 3)

It has been shown in Chapter 2, that in principle, the excited states of aryl ketones possess varying amounts of $\pi\pi^*$ and $n\pi^*$ character. Typical hydrogen abstraction, however, seems to be characteristic of the $n\pi^*$ state, since the electron distribution in this state is just what is needed for a reaction of this kind. The removal of the "n" electron from oxygen leaves this atom more electrophilic than in the ground state and the almost insignificant overlap of the "n" orbital with the other molecular orbitals results in a highly localized and essentially isolated site of photochemical activity, making the excited molecule react not unlike an electrophilic

alkoxy radical. Schematically, in valence bond terms



4.3. THE FATE OF FREE RADICALS FORMED.

The two radicals formed as a result of hydrogen abstraction from the substrate undergo ground-state reactions leading to products which are the quinol and an aldehyde or ketone.

The semiquinone radical ($\text{QH}\cdot$), in the absence of oxygen, seems to have, ordinarily, only disproportionation as the major pathway for the formation of quinol.⁽⁷⁸⁾ The substrate radicals may disproportionate, dimerize or be dehydrogenated or be scavenged by the ground-state quinone.⁽⁷⁹⁾

Dimerization, so available data suggests, is favoured for unbranched radicals, but disproportionation becomes more important as the radical becomes more branched.⁽⁸⁰⁾ In general, radicals with longer numbers of β -hydrogens have been found to give larger k_d/k_c ratios, where k_d is the rate constant for disproportionation

and k_c that for combination (dimerization). If it is assumed for sake of argument, that all the radicals listed in Table 4.1 have the same value for k_c , then the ratios of k_d/k_c can be taken to represent the relative rates of disproportionation of the radicals concerned. If this assumption is correct, the conclusion that is at once obvious is that there is much more disproportionation in branched radicals than can be accounted for by the number of β -hydrogens alone: e.g. the t-butyl radical has nine β -hydrogens and the ethyl radical has only three giving us the statistical ratio $(k_d/k_c)_{t\text{-but}} / (k_d/k_c)_{\text{ethyl}} = 3$, whereas in actual fact the observed value is 46.

The only plausible explanation of the anomaly seems to lie in the fact that the activation energy for recombination increases as the radical becomes more complex. $\text{CH}_3\cdot$ has a zero activation energy for recombination, whereas $\text{CH}_3\text{CH}_2\cdot$ needs 2 kcal mol^{-1} (81). The values of k_c may, therefore, very well decrease with complexity of the radical.

Table 4.1. Disproportionation / Combination Ratios.

Radicals	Temp °C.	k_d/k_c .
$\text{CH}_3\cdot \quad \text{C}_2\text{H}_5\cdot$	100	0.04
$2\text{CH}_3\text{CH}_2\cdot$	100	0.1
$2\text{CH}_3\text{CH}_2\text{CH}_2\cdot$	100	0.1
$2[(\text{CH}_3)_2\text{CH}\cdot]$	100	0.5
$2[(\text{CH}_3)_3\text{C}\cdot]$	100	4.6

There seem to be no well-established examples of direct combination of semiquinone and substrate radicals. Bruce and Knowles (83) irradiated benzene solutions of monosubstituted parabenzoquinones carrying side-chains from which hydrogen atoms could be abstracted intramolecularly to give diradicals for which diffusional separation of moieties carrying the unpaired electrons is impossible and from which, therefore, cyclization products could be expected to be formed. Their evidence showed that p-benzoquinones with olefinic side-chains gave bicyclic phenolic compounds whereas those with oxygenated side-chains usually gave the corresponding acyl quinols. By analogy, their work strongly supports the view that in light-induced intermolecular reactions between para-quinones and alcohols, more often than not, the substrate radical is scavenged by the ground-state quinone to give a hemiacetal or hemiketal which, because of the ease with which they are hydrolyzed, have not been isolated.

This scavenging process should, theoretically, be of the greatest importance for quinones of high oxidation potential. Thus p-benzoquinone ($E_{25}^{\circ} = 0.71$) would be expected to scavenge 2-hydroxyprop-2-yl radicals more readily than 9,10 anthraquinone ($E_{25}^{\circ} = 0.25$). However, the mechanism proposed by Atkinson and D1 (79) for the reduction of the former with isopropanol does not

include such a step, whereas that proposed by Tickle and Wilkinson ⁽⁶⁵⁾ for the reduction of the latter does so.

4.4. THE DIFFERENCE BETWEEN PHOTOCHEMICAL AND THERMAL HYDROGEN ABSTRACTION.

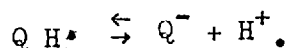
Some earlier workers ⁽⁸⁴⁾ did try to establish a correlation between the redox potential of a quinone and its quantum efficiency of reduction, since a correlation was in fact observed with respect to reactivity in thermal hydrogen abstraction. ⁽⁸⁵⁾ The potential is a measure of the free energy gain in converting the quinone into the quinol and hence a correlation with reactivity is to be expected independently of the reaction mechanism, though the precise relation will depend on the extent to which the additional resonance stabilization of the quinol is effective in the transition state as well as on a variety of other factors.

It seems pointless, however, to relate redox potentials to quantum efficiencies of reduction, since the latter quantity is not a measure of the reactivity of the excited molecule. When relative rates for hydrogen abstraction in photochemical reactions are considered in place of quantum efficiencies, no correlation between redox potentials and the relative rates is observed. ⁽⁸⁶⁾

This lack of correlation is perhaps indicative of the essential difference in the mode of hydrogen abstraction in photochemical

reactions as compared to that in thermal processes. Quinones act as electron acceptors in electrochemical and thermal hydrogen transfers. That this is indeed the case can be seen without considering redox potentials, from the fact that the reactivity is increased by electron-attracting substituents (e.g. -Cl) and decreased by electron donating substituents (e.g. -Me). From this viewpoint, the correlation with redox potentials is due to the circumstance that electron-attracting substituents decrease and electron-donating substituents increase the stability of the quinone relative to the quinol, because the double-bonded oxygen atoms in the former are electron-demanding, $C = C - C = O \quad \overset{+}{C} - C - C = \overset{-}{O}$, while the single-bonded oxygen atoms in the latter have a mesomeric effect, $C = C - \overset{-}{O}H \quad \overset{-}{C} - C = \overset{+}{O}H$, of the opposite sign.

In photochemical reactions, on the contrary, the primary oxidative act is a direct transfer of a hydrogen atom from the substrate to the excited quinone and not a slow electron transfer followed by a rapid proton expulsion from the substrate. (76) and (83) ESR studies (87) with duroquinone and 9,10-anthraquinone in simple alcohols indicate that the neutral semiquinone radical ($QH^{\bullet}$) is formed when the alcohol is pure, but that the semiquinone anion radical $Q^{\bullet-}$ results when the corresponding alkali metal alkoxide is present. The anion radical is believed to arise by ionization of the neutral radical.



4.5. GENERAL FEATURES OF HYDROGEN ABSTRACTION.

The abstraction of hydrogen from alcoholic substrates involves a transition state in which the quinone-hydrogen bond (Q - H) is partly formed and the R - H bond is ruptured. The strength of these partial bonds is to some extent influenced by the thermodynamic strengths of the Q - H and R - H bond themselves. The rate of the process of abstraction is indirectly dependent on these parameters.

a) Influence of the strength of the R - H bond.

In every hydrogen abstraction initiated by free radicals, - and here it must be recalled that excited quinone molecules in particular in the $m\pi^*$ states behave like free radicals, - the rates of abstraction from aliphatic substrates increase in the order primary < secondary < tertiary, an order that is independent of the nature of the radical initiating the abstraction.⁽⁸⁸⁾ It is easily seen that the order of reactivity is the reverse of the order of C - H bond strengths in primary, secondary and tertiary alcohols. Experimental data, however, indicates that factors other than the strength of the bond being broken are also involved since a certain measure of selectivity has been observed when the same radical is treated with various substrates.⁽⁸¹⁾

The order of hydrogen atom reactivity is also observed in the series, toluene < ethylbenzene < isopropylbenzene, and in the series toluene < diphenylmethane < triphenylmethane.⁽⁸⁹⁾

The increase in reactivity of the photoexcited quinone towards the hydrogen atom of alcohols, with increasing alkylation of the alcohol has been related by Wells (76) to the change in probability of energy transfer from the excited quinone to the α C - H bond brought about by the change in the inductive effect of the alkyl group on this same bond. Steric effects do not seem to play an important role despite considerable increase in length of chain and degree of branching.

The inductive electron repelling effect of alkyl groups and the resonance stabilization of the free radical resulting after hydrogen transfer would explain why the α C - H bond in alcohols is the weakest of all C - H bonds. The inductive effect will, in this case, result in a higher electron density in the α C - H bond or bonds and facilitate the removal of hydrogen with its electron by the electrophilic oxygen of the excited quinone. The mesomeric effect involving the electrons in the hydroxylic oxygen leads to structures such as $R_2\bar{C} \overset{+}{O}H$ contributing to the transition state, and results in a lowering of the α C - H bond energy relative to other C - H bonds. The specificity of attack on α C - H bonds by excited quinones indicates that the electron attracting inductive effect of the hydroxyl group which would tend to increase the α C - H bond energy for homolytic fission is outweighed by the mesomeric effect of the oxygen atom.

As no thermal energy was found to be required for hydrogen transfer in photochemical processes he studied, Wells (76) argued that the reduction in bond energy with increasing alkylation could only be assumed to facilitate the transfer of electronic energy from the quinone to vibrational energy needed to rupture the C - H bond. This could happen either because the number of effective collisions is increased due to the increase in the distance of approach over which energy can be transferred, or because the probability of energy transfer is increased for collisions with the appropriate orientation.

If change in the distance of approach is involved, then the rate of hydrogen abstraction will vary linearly with the sum of the collisional radii of the reactants. Consequently, additional CH_3 - groups on the α carbon atom can be expected to increase the reactivity linearly. If, on the other hand, it is the change in the probability of energy transfer that is involved, then the transition-state relationship for the rate constant

$$k = \frac{kT}{h} e^{-\Delta G^\ddagger / RT} \quad (\Delta G^\ddagger = \text{free energy of activation})$$

indicates that the reactivity should increase by a constant factor, since $\Delta G^\ddagger$ is expected to increase linearly with additional CH_3 - groups on the α carbon atom. Wells demonstrated experimentally that reactivity does indeed increase by a constant factor not only with increasing alkylation of the α carbon atom but also with the mere

addition of $-\text{CH}_2 -$ groups to a parent alcohol.

Wells also found that a Hammett type relationship given below is valid in the reactions he studied:

$$\log \left(\frac{k_1}{k_{\text{EtOH}}} \right)_H = \rho^H \sigma^H + E$$

where $\left(\frac{k}{k_{\text{EtOH}}} \right)_H$ is the relative rate with reference to ethyl alcohol divided by the number of α C - H bonds; ρ^H , as in the Hammett equation, is a constant indicating the tendency of a reaction to be subject to polar effects; σ^H is another constant measuring the tendency of a group to repel or attract electrons; and E represents resonance effects. Since E is constant for monohydroxylic compounds, the above relationship is a quantitative confirmation that increase in reactivity with increasing alkylation in the alcohols is caused by the inductive electron repelling effect of the alkyl groups on the α C - H bond.

b) Influence of the strength of the Q - H bond.

The influence of the strength of the bond being formed on the rate of hydrogen abstraction has proved more difficult to assess. Table 4.2 shows that though the bonds being formed are nearly of equal strength in the cases listed, the energy of activation differs significantly. This is presumably because the transition state may cause bond reorganization or even a change in the geometry of the

molecule, and such changes would require more or less energy.

Table 4.2.

Radical (X.)	Substrate		
	CH_4 E_a kcal mole ⁻¹	C_2H_6 E_a kcal mole ⁻¹	D (H - X) kcal mole ⁻¹
H•	---	9	103
CH ₃ •	14.0	11.2	102
CF ₃ •	10.3	7.5	103

Available data suggests that methyl, t-butoxy and phenyl radicals have similar reactivities⁽⁹⁰⁾. Walling and Gibian⁽⁹¹⁾ have shown that the benzophenone triplet and the t-butoxy radical abstract hydrogen atoms at similar rates since they both form bonds to hydrogen of similar bond energies (102 and 104 kcal mole⁻¹ respectively). By analogy, the principles that govern hydrogen abstraction by alkyl and alkoxy radicals may be said to apply to the same process initiated by excited quinone molecules which, because of their electron distribution on excitation, behave very much like free alkoxy radicals (Cfr. Tables 4.3 and 4.4)

Table 4.3. Relative Reactivities Of Hydrogen Donors Towards Various Radicals. (reference - reactivity in toluene).

Hydrogen donor	Methyl 65°C.	Phenyl 60°C	t-butoxy 40°C
Cyclohexane	---	1.00	1.5
Toluene	(1)	(1)	(1)
Ethylbenzene	4.1	4.6	3.2

Table 4.4. Relative Rates Of Hydrogen Abstraction By Benzophenone Triplet And t-Butoxy Radicals.

Hydrogen Donor	Relative Rates	
	$\phi_2\dot{C} - O\cdot$	t-Buto $\cdot$
Toluene	1	1
Mesitylene	5.5	4.1
m-Xylene	3.0	2.3
p-chlorotoluene	0.97	0.71
Cyclohexane	2.1	6.0

The polar effect and the solvent effect are two other factors which affect the rates of hydrogen abstraction by free radicals, but

the latter is so much smaller in radical reactions than in ionic reactions. Whereas in ionic reactions the effect of the solvent on the reaction is a function of the dielectric constant of the solvent, in free radical reactions, the effect is a function of the ability of the solvent to complex with the radical species.

CHAPTER 5

The Photoreduction Of Benzophenone In
Isopropanol - Brief Survey Of Recent Work

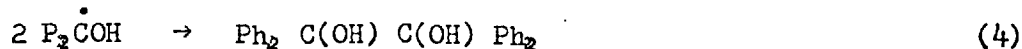
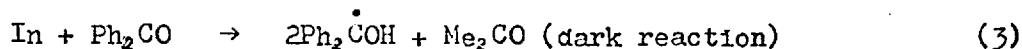
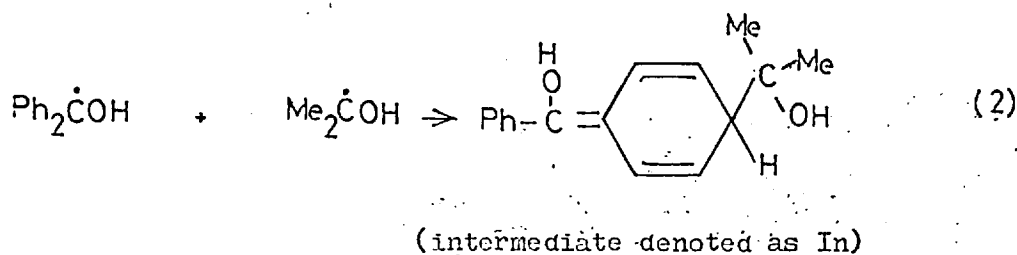
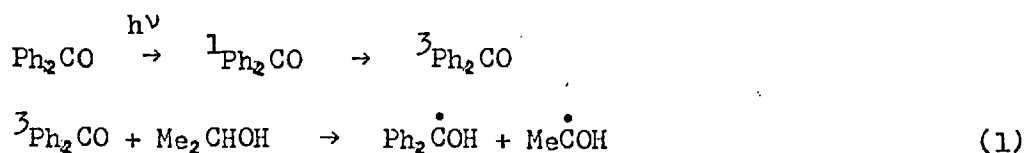
5.1. THE PHOTOREDUCTION OF BENZOPHENONE BY ISOPROPANOL.

Since the photochemical reactions of benzophenone resemble closely those of the quinones, it is opportune to consider briefly the photolysis of benzophenone in the light of the most recent experimental work done in this field, especially using isopropanol as the substrate.

The photoreduction of benzophenone in isopropanol has been extensively investigated by a number of authors.⁽⁹²⁾ The reaction is characterized by its high chemical yield of products, benzpinacol and acetone, as well as by its high quantum efficiency of reduction which approaches 2 under ordinary conditions. The photoreduction is both light intensity and concentration dependent.

Unlike the photoreduction of benzophenone in benzene in the presence of benzhydrol, the quantum yield in 100% isopropanol varies erratically, the measured value depending on initial benzophenone concentration, duration of irradiation and the interval allowed before air is admitted into the system.

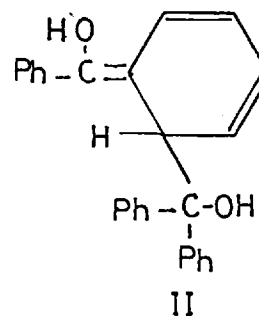
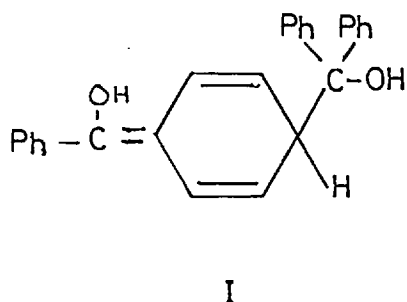
Filipescu and Minn⁽⁹³⁾ obtained the absorption spectrum of the intermediate by actinometry, low-temperature phosphorescence in a rigid matrix and many-component absorption spectroscopy. They proposed a mechanism which explains the erratic yield and is consistent with experimental data.



Erratic results can now be explained as depending on the length of irradiation and the differing concentration of Ph_2CO , both of which affect the $\text{Ph}_2\text{CO} \rightarrow$ Intermediate conversion. Again, if the dark reaction, which goes on for hours, is not completed before air is admitted, the quantum yield will depend on the extent to which the dark reaction has taken place. When the $\text{Ph}_2\text{CO} \rightarrow$ Intermediate conversion is over 50%, the reaction mixture will, when the dark reaction has been given enough time to go to completion, still contain the intermediate, which will react with oxygen on admission of air into the reaction vessel. Hence the quantum yield of Ph_2CO disappearance will range from 1 to 2 and will be closer to 2 if the $\text{Ph}_2\text{CO} \rightarrow$ Intermediate conversion is less than 50% and the dark reaction

has been allowed to go to completion.

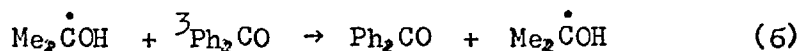
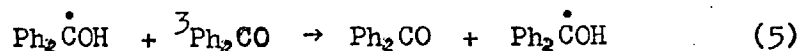
The earlier suggestion made by Schenck and co-workers (94) that the intermediate is a simple adduct of two $\text{Ph}_2\dot{\text{C}}\text{OH}$ radicals having structure I or II



does not fit in with the observation that well before the intermediate is completely consumed, the dark reaction stops indefinitely whenever more than half the initial PH_2CO is converted to the intermediate during the irradiation.

The light-intensity dependence of the reaction has been studied by Yang and Murov. (95) They suggest as a possible explanation of the variation of quantum yield with intensity, that the ketyl radical and the 2 - hydroxy - 2 - propyl radical (both being paramagnetic species) act as quenchers depending upon the conditions of the experiment.

In addition to the reactions already described previously, we have



Benzpinacol cannot act as the quencher, because the quantum yield of photoreduction is found to be linear with time at constant light intensity.

Using the steady-state expression, they deduced

$$\frac{2 - \phi}{\phi^{3/2}} = a I^{1/2} + b I \phi^{1/2}$$

where $a = k_5/k_1 (2k_4)^{1/2}$, $b = k_6/2k_1 k_3$

I = light intensity and ϕ = quantum yield.

If it is assumed that at low light intensity the second term is insignificantly small, the physical picture that emerges is that under such conditions the quenching is mainly due to ketyl radicals. A plot of $\frac{2 - \phi}{\phi^{3/2}}$ vs $a I^{1/2}$ should then give a straight line, and indeed they found it to be so.

At high light intensity, the second term becomes significant and the line slopes upwards.

These conclusions seem to be corroborated by the fact, that whereas O-deuteration of 2-propanol has no significant effect on the

quantum yield of photoreduction at low light intensity ⁽⁸¹⁾ the effect is measurable, as Yang and Murov ⁽⁹⁵⁾ observed, at high light intensity. Presumably, O-deuteration slows down reaction (2) and increases the concentration of 2-hydroxy - 2-propyl radicals and thus renders quenching more efficient.

Beckett and Porter ⁽⁹⁶⁾, using flash photolysis techniques investigated the reactivity of the benzophenone triplet with respect to hydrogen abstraction from a variety of substrates, and found that the triplet fails to abstract hydrogen from substrates with high R - H bond energies ($> 100 \text{ kcal mol}^{-1}$) and that it decays radiationlessly to the ground-state. They determined the rate constant for the primary abstraction from 100 per cent isopropanol and reported it to be $1.28 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$. A number of other research teams ⁽⁹⁷⁾ have reported values for the same process which are substantially in agreement with that of Beckett and Porter.

Walling and Gibian ⁽⁹¹⁾ studied the competitive consumption of different hydrocarbons by the benzophenone triplet and built a reactivity scale which they found was similar to that observed with t-butoxyradicals (Cfr. Table 4.4). Combination of their data with data supplied by Bell and Linschitz ⁽⁹⁷⁾, and Hammond, Baker and More ⁽⁹⁸⁾ leads to a value of $1 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ for the rate constant of primary abstraction from isopropanol in dilute benzene solutions.

This discrepancy between the rate constants for the same process, probably reflects a solvent effect similar to that observed in the case of alkoxy radicals.⁽⁹⁹⁾

CHAPTER 6

Experimental Work And Results

INTRODUCTION

Scrutton (77) investigated the photoreduction of chloranil in 100 per cent isopropanol at 365 nm and 25°C. He reported the initial quantum efficiency for formation of hydroquinone to be nearly 0.5, observed that the hydroquinone inhibited the photoreduction, detected a small quantity of a side-product which he did not identify, and assumed the product of oxidation of the substrate to be acetone.

Bruce and co-workers (83) irradiated solutions of chloranil in acetaldehyde with visible light and detected the presence of hydrogen chloride and trichloroacetylquinol in the irradiated solution, in addition to tetrachloroquinol and paraldehyde. It was, therefore, thought probable that a trichloro product would be formed in the irradiation of chloranil in isopropanol at 365 nm.

The present work aimed at a qualitative and quantitative study of all the products of irradiation of chloranil in isopropanol, an investigation of the nature of the photoreactive species, an assessment of the rate constant of hydrogen abstraction by excited chloranil, and the verification that acetone is indeed the product of oxidation of isopropanol as well as its quantitative estimation. A method for the estimation of low concentrations of chloride ions in the presence of isopropanol was developed in the course of this work.

The study of the photoreduction of trichloroquinone in isopropanol was undertaken because trichlorohydroquinone was found in irradiated solutions of chloranil. A method to prepare trichloroquinone by chlorinating a dichloroquinone with sulphuryl chloride was developed.

6.1. CHEMICALS.

6.1.1. QUINONES.

Chloranil. The GPR grade of chloranil supplied by Hopkin and Williams was purified by three crystallizations from toluene and the dried crystals were then subjected to vacuum sublimation.

All the quinones and hydroquinones used in the present work were tested for purity by mass spectrometry and by comparison of their melting points determined during the course of the present work with those given in the literature. (Cfr. Table 6.1a)

The purity of chloranil was also tested by n.m.r. spectroscopy which confirmed that the sample was very nearly 100 per cent pure.

Trichloroquinone. Two different methods were used to prepare this compound. The one described first was developed in the course of the present work.

(1) 0.01 mole of 2,6-dichloroquinone (Eastman Kodak) was dissolved in a minimum of analar carbon tetrachloride. 0.05 g of anhydrous aluminium chloride was added and the mixture heated gently on a steam bath for about 30 minutes. The chlorinating agent was sulphuryl chloride containing 1 gram-equivalent of active chlorine.⁽¹⁰¹⁾ The required amount plus a 15 per cent excess (0.78 g) of the chlorinating agent was diluted with an equal volume of carbon tetrachloride and added dropwise to the dissolved quinone through a dropping funnel

over a period of 20 - 30 minutes. When addition of the chlorinating agent was over, the reaction mixture was refluxed gently for about 12 hours, at the end of which it was poured over crushed ice to hydrolyze the aluminium chloride. Enough 1N sodium hydroxide was added to dissolve the aluminium hydroxide and the layers were then separated. Carbon tetrachloride was removed by evaporation under vacuum and the residue washed with 1N sodium hydroxide several times and then with distilled water.

Several crystallizations from alcohol failed to yield pure trichloroquinone, because, as later work showed, this quinone reacts to some extent with alcohols on heating to form the hydroquinone. Vacuum sublimation at 50 - 55°C gave the pure compound.

The yield of the impure quinone was over 60 per cent.

(2) A suspension of 2,5-dichlorobenzoquinone (1g) in glacial acetic acid (10 ml) was cooled in ice-water and saturated with dry hydrochloric acid for 15 minutes. The quinone dissolved, forming an orange-red solution. The colour subsequently faded and colourless crystals of trichlorohydroquinone separated. These were collected and crystallized from benzene. (102)

The hydroquinone was dissolved in acetone and added to an excess of Jones' reagent. (103) The yellow precipitate was filtered, washed with water, dried and purified by vacuum sublimation at 50 - 55°C. (Cfr. Table 6.1a)

Trichlorohydroxyquinone. Chloranil (G.P.R.) was dissolved in ice-cold 2M sodium hydroxide to give a pale yellow solution. Keeping the mixture cold, a slight excess of hydrochloric acid was carefully added. The residue was collected and recrystallized twice from a 1:1 mixture of benzene and heptane.⁽¹⁰⁴⁾ (Cfr. Table 6.1a)

6.1.2. HYDROQUINONES.

Tetrachlorohydroquinone was prepared by passing sulphur dioxide through a solution containing chloranil in ethyl alcohol. The solution was evaporated to dryness, the product recrystallized from toluene twice, and the resulting slightly grey needles dried under vacuum. (Cfr Table 6.1a)

Trichlorohydroquinone:- The product obtained in the first stage of the preparation of trichloroquinone was impure trichlorohydroquinone. This was crystallized three times from benzene and subjected to vacuum sublimation at 40°C. (Cfr. Table 6.1a)

Trichlorohydroxyhydroquinone:- The corresponding quinone prepared as described earlier was dissolved in alcohol and sulphur dioxide was passed till the colour of the solution faded. The alcohol was distilled off under vacuum and the residue crystallized three times from alcohol. (Cfr. Table 6.1a)

6.1.3. THIOBENZOPHENONE (Benzothiophenone)

This ketone was prepared by the method devised by Gofton and

Table 6.1a Comparison Of Melting Points.

Compound	m.p. - °C	
	Literature ⁽¹⁰⁵⁾	This Work
Chloranil	290	291 (Sealed Tube)
Tetrachlorohydroquinone	232	231
Trichloroquinone	168	167-168
Trichlorohydroquinone	138	138
Trichlorohydroxyquinone	198	198
Trichlorohydroxyhydroquinone	160	160-161
Benzothiophenone	53-54	53-54

Braude.⁽¹⁰⁶⁾ 0.07 mole of benzophenone was dissolved in 65 ml of ethanol and cooled in an ice-salt freezing mixture. Hydrogen sulphide and hydrogen chloride were simultaneously passed into the stirred solution for three hours. After this period the flow of hydrochloric acid was stopped and hydrogen sulphide alone was passed for a further 20 hours, with continued ice cooling. The solid thiobenzophenone was filtered from the solution in an atmosphere of carbon dioxide, immediately dried under high vacuum and recrystallized twice from about 10 ml of petroleum ether (b.p 40 - 60°C), giving long violet needles. (Cfr. Table 6.1a). Thiobenzophenone crystals were stored in vacuum, since exposure to air leads to decomposition.

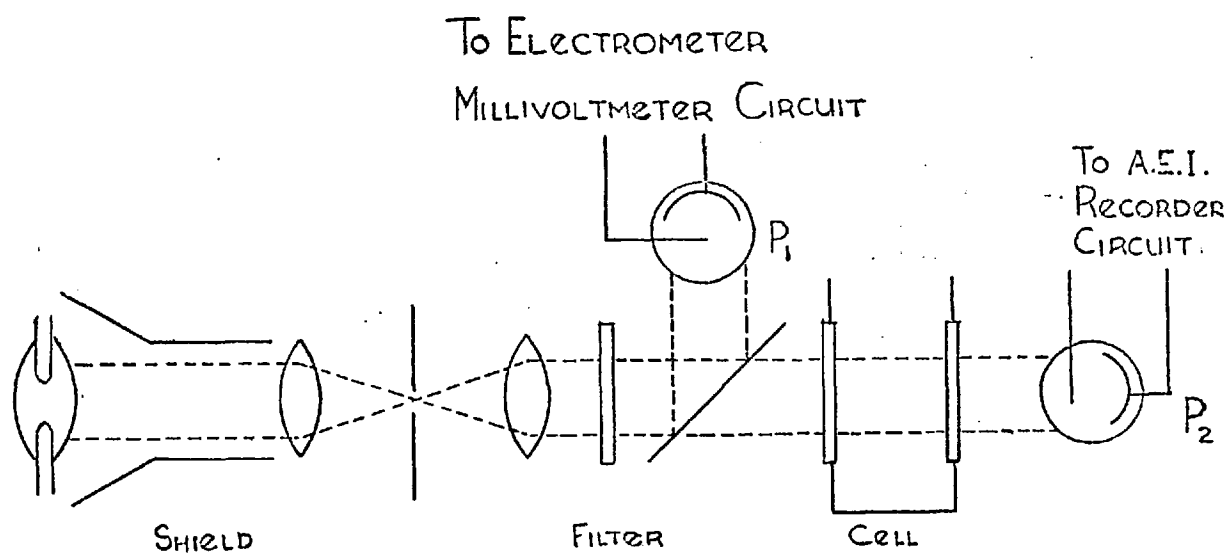
6.1.4. OTHER CHEMICALS.

Isopropanol (Analar, Hopkin and Williams), and anthracene were used without further purification. It was found advisable to check the ultraviolet absorption spectrum of each batch of isopropanol.

6.2. APPARATUS.

6.2.1. The Optical Bench.

A 250 watt high pressure mercury lamp (Me/D Mazda box type) was connected according to the circuit shown in Fig. 6.1 to the 240 volt AC mains. This lamp, which gives a steady intensity light beam after about 45 minutes of switching it on, was shielded from draughts with a



THE OPTICAL BENCH

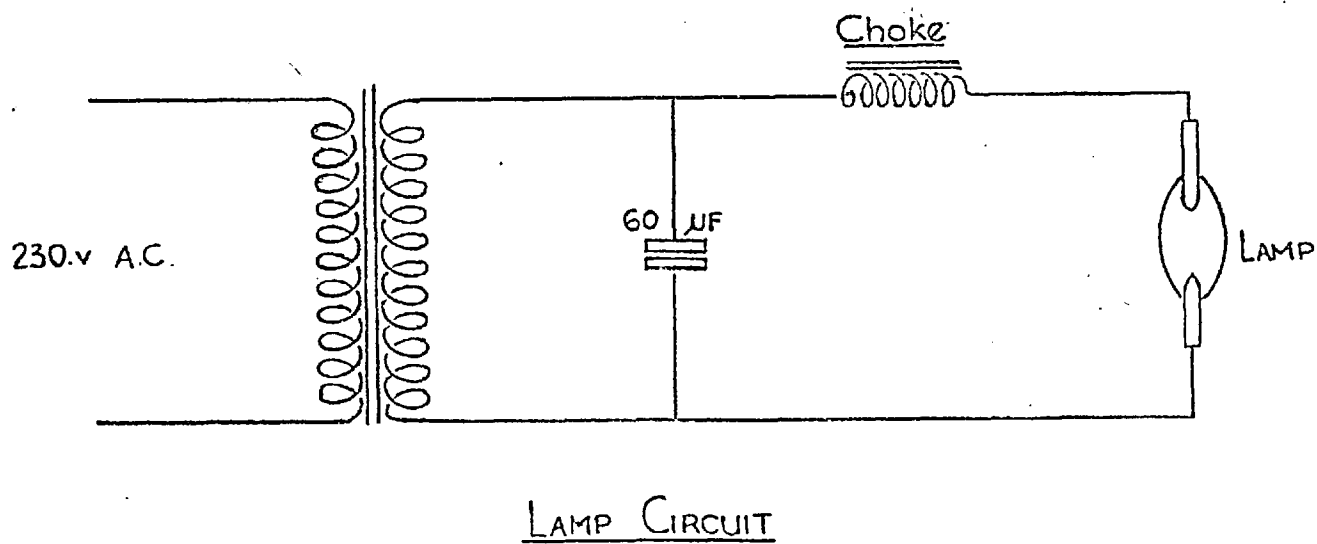


FIG. 6.1

metal shield to which was attached a cylindrical metal tube about 5 cm in diameter and 10 cm in length. The beam was focussed by a lens on to a small hole (2 mm diameter) in a metal plate thus giving a point source of light from the central portion of the arc, a portion which is relatively free from fluctuations. Another lens placed at a distance from the hole equal to its own focal length, gave a parallel beam of light.

The 365 nm line was isolated by using a combination of a Chance OX1 filter and two pyrex glasses. This combination transmits 61 per cent at 365 nm, less than 0.2 per cent at 313 nm and less than 2 per cent at 405 nm. When two Chance OX1 filters were used, the beam was virtually monochromatic, but the percentage transmission at 365 nm was reduced to 27 per cent. With two Chance filters, the extinction coefficient at 365 nm measured on the optical bench agreed within less than 1 per cent with that measured on a spectrophotometer. With just one Chance filter an error that varied between 4 - 6 per cent, according to the concentration of the solution, had to be allowed for in the extinction coefficients used in calculations involving measurements done on the optical bench.

The 437 nm line was isolated using an Ilford 806 filter.

Before entering the cell containing the solution to be irradiated the beam was split by a glass plate at 45° to the path of the beam

so that a fraction of it is reflected to a photocell placed perpendicular to the optical bench.

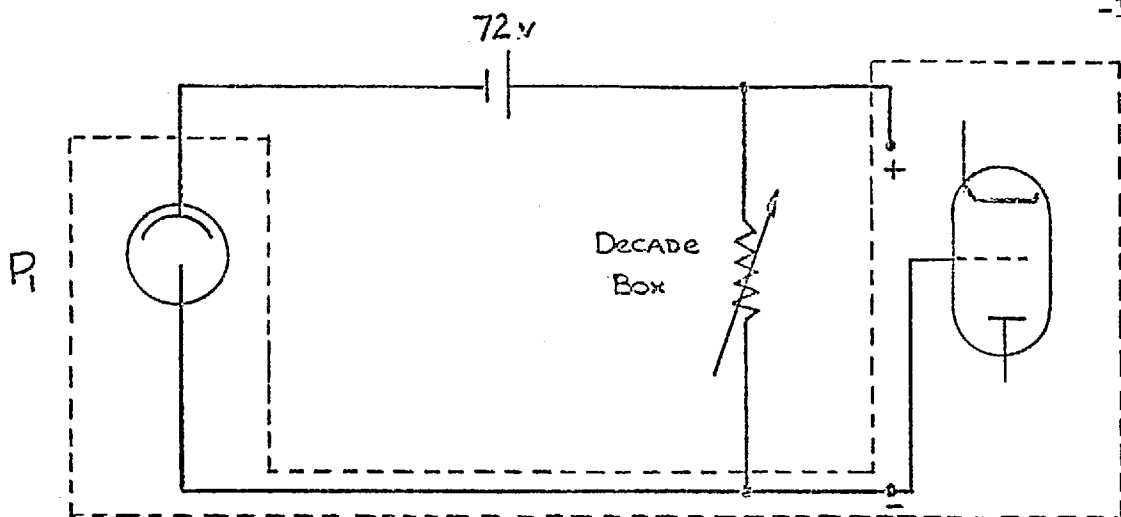
This arrangement is necessary to continuously monitor the intensity of the beam throughout each run, irrespective of the absorption of light by the solution, since this absorption keeps on changing as irradiation proceeds.

Both the photocells were Cintel QVA 39. The photocell P_1 was connected to a dry cell operating at 72 V, a $100\text{ k}\Omega$ resistance, and a decade box ($10^4 - 10^6\text{ k}\Omega$) across which was connected a Cambridge pH indicator used as an electrometer-millivoltmeter. The photocell P_2 which monitors the beam after it has passed through the solution in the cell was connected to a dry cell operating at 72 V, a $100\text{ k}\Omega$ resistance, a universal shunt and a AEI recorder (5 mV sensitivity) provided with an external zeroing circuit.

Circuit diagrams are shown in Fig. 6.2.

6.2.2. The Thermostat Tank.

The thermostated cell-holder was made of brass lined on the outside with sindanyo. The walls of the tank were hollow so that water at a prefixed temperature could be circulated with the aid of a Churchill thermocirculator. The inside of the tank was shaped so as to have the glass surface of the reaction cell touching the brass lining.



CAMBRIDGE 'pH' INDICATOR USED
AS ELECTROMETER MILLIVOLTMETER

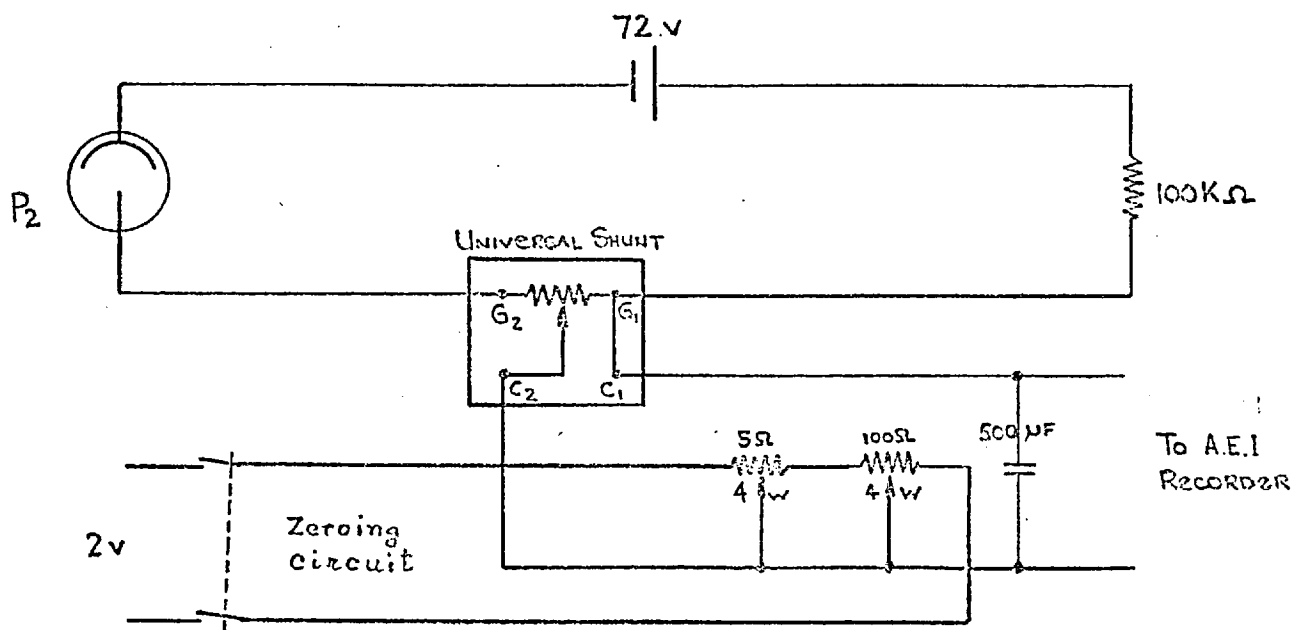


FIG. 6-2 ELECTROMETER AND RECORDER CIRCUITS

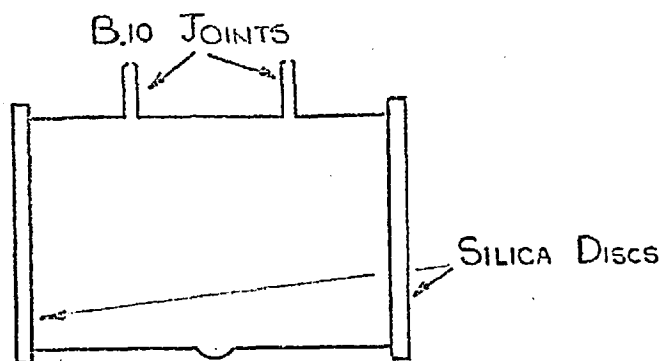
The top and bottom halves of the tank were linked by means of a flexible piece of nylon tubing so that the top half could be lifted up to gain access to the reaction cell without disturbing the flow of water in the system. A thermometer was inserted into the body of the tank.

To prevent the entry of stray light, a large box, painted with optical black paint and with holes in the appropriate places, enclosed the tank and the two photocells.

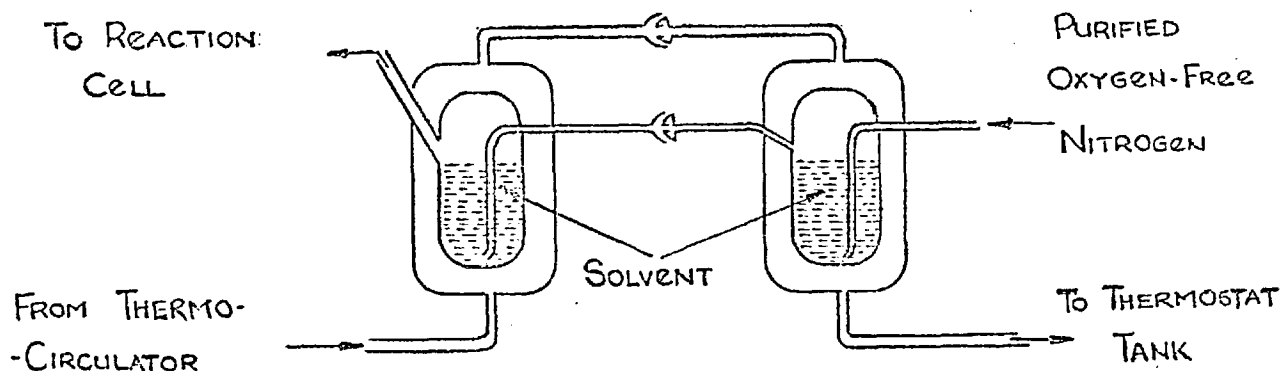
6.2.3. The Reaction Cell.

The reaction cell design was based on that used by Atkinson and Di (107). As shown in Fig. 6.3a, the cell is a cylinder (5.2 cm in length and 3.5 cm in diameter) with two flanged ends where silica windows are sealed with araldite. The vessel was provided with two side tubes carrying standard B10 joints. A retractable gas bubbling tube was fixed to one of the joints and the other is provided with a special arrangement shown in Fig. 6.3c which enabled a sample of the solution to be withdrawn with a microsyringe without admitting air to the system. The retractable gas bubbling tube provides a means of deoxygenating the solution with nitrogen and then retracting it without admitting air into the cell.

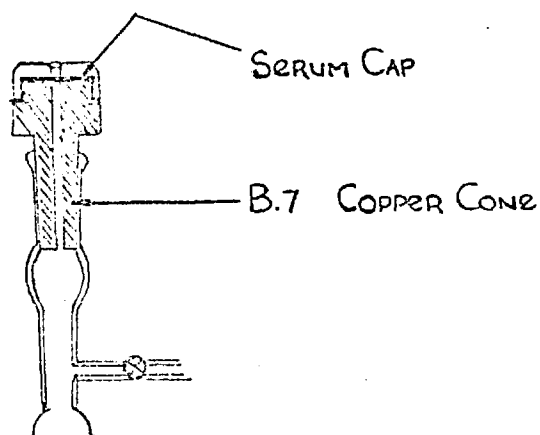
A depression in the centre of the cylindrical cell enabled a glass covered piece of metal to act as a stirrer under the action of a rotating magnet.



a.



b.



c.

FIG. 6-3

6.3. EXPERIMENTAL PROCEDURE.

6.3.1. Degassing with Oxygen-free Nitrogen.

Traces of oxygen present in 'oxygen-free' nitrogen were removed by passing the gas through two wash bottles containing Fieser's solution (16 gms sodium hydrosulphite, 15 gms sodium hydroxide and 0.8 gm sodium anthraquinone - 2-sulphonate in 100 ml of water). The gas was purified from traces of hydrogen sulphide by passing it through 5% sodium hydroxide solution, 5% lead acetate solution, and distilled water, and dried by passing it through a column of silica gel.

Before allowing the gas into the reaction cell, it was saturated with isopropanol by passing it through two specially designed saturators (Cfr. Fig. 6.3b) kept at the required temperature by the same thermocirculator used to thermostat the tank containing the reaction cell.

6.3.2. Method of Irradiation.

25 ml of the solution was pipetted into the reaction cell and a stream of oxygen-free nitrogen purified as described previously and saturated with isopropanol, (or any other solvent used to make the solution,) was passed through the solution for about 45 minutes using the retractable bubbling tube. After the degassing the tube was retracted, the flow of gas stopped and the system closed relative to air.

Prior to the irradiation, the recorder was zeroed without any input signal from photocell P_2 and the following measurements then recorded:

D_o = recorder reading without the reaction cell in the path of the beam

D_m = recorder reading with the reaction cell containing solvent.

Simultaneously with D_o and D_m , the reading D_r corresponding to photocell P_1 was read from the pH meter. Any change in the value of D_r indicated a fluctuation in the intensity of the incident beam and enabled appropriate corrections to be made so as to obtain the values of D_o and D_m for the same intensity of the incident beam.

To start the reaction, the shutter of the window of the thermostat tank was removed and the magnetic stirrer and a stop-clock were switched on. The reading, D_r on the pH meter was taken at zero time and then at regular intervals. The change in intensity of the transmitted beam was continuously recorded using the AEI recorder.

6.4. METHODS OF QUANTITATIVE ANALYSIS OF INDIVIDUAL PRODUCTS OF IRRADIATION.

6.4.1. Estimation Of Acetone.

Acetone, the product of the oxidation of isopropanol whose presence in the irradiated solution was detected by a method described later, was analysed by G.L.C. using a Pye Model 24 F.I. Chromatograph.

The 18" stainless steel, 1/4" diameter column was packed with Carbowax 20M on chromosorp P. 2 μ l of the irradiated solution were injected and the chromatograph run at 70°C. The flow rate of nitrogen carrier gas was adjusted to 30 ml per minute. The retention times of acetone and isopropanol in this column were 8 minutes and 18 minutes respectively. For the acetone peak an attenuation of 20 was used and for the isopropanol peak an attenuation of 200×10^3 .

The column was calibrated using standard solutions of acetone in isopropanol. Analar isopropanol was found to contain 6.5×10^{-4} mol l⁻¹ of acetone. For purposes of calibration, the acetone concentration range of interest in the present work was 6.5×10^{-4} to 17×10^{-4} mol l⁻¹. Areas of both acetone and alcohol peaks were measured by triangulation and with a planimeter. The average of the readings obtained by the two different methods was used in the relevant calculations.

Fig. 6.4 gives the calibration graph taking into account a correction for the amount of acetone initially present in the alcohol. The acetone / alcohol peak area ratio was plotted against concentration.

To obtain the correct value for the formation of acetone as a result of irradiation, samples of solution withdrawn from the reaction vessel by a microsyringe were chromatographed before and after irradiation. A serum cap inserted in the position shown in Fig. 6.3c enabled this withdrawal to be done without admitting air to the system.

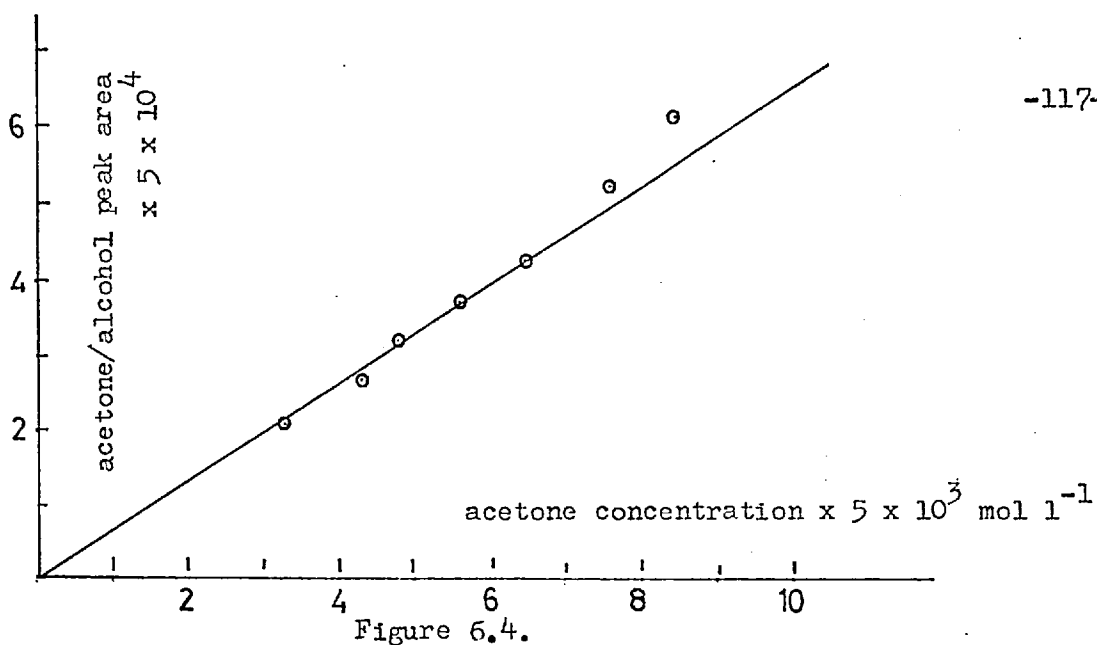


Figure 6.4.

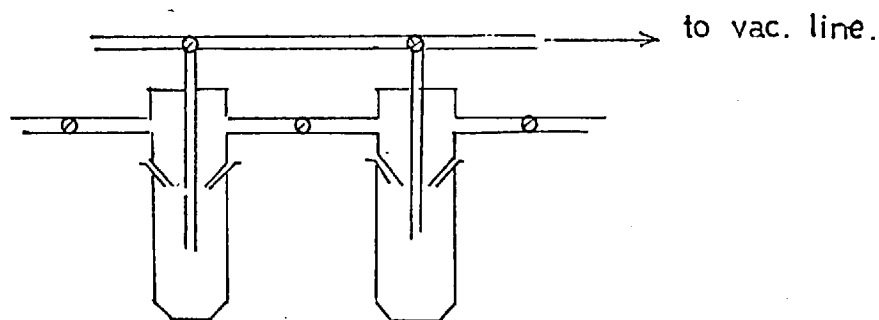


Figure 6.5.

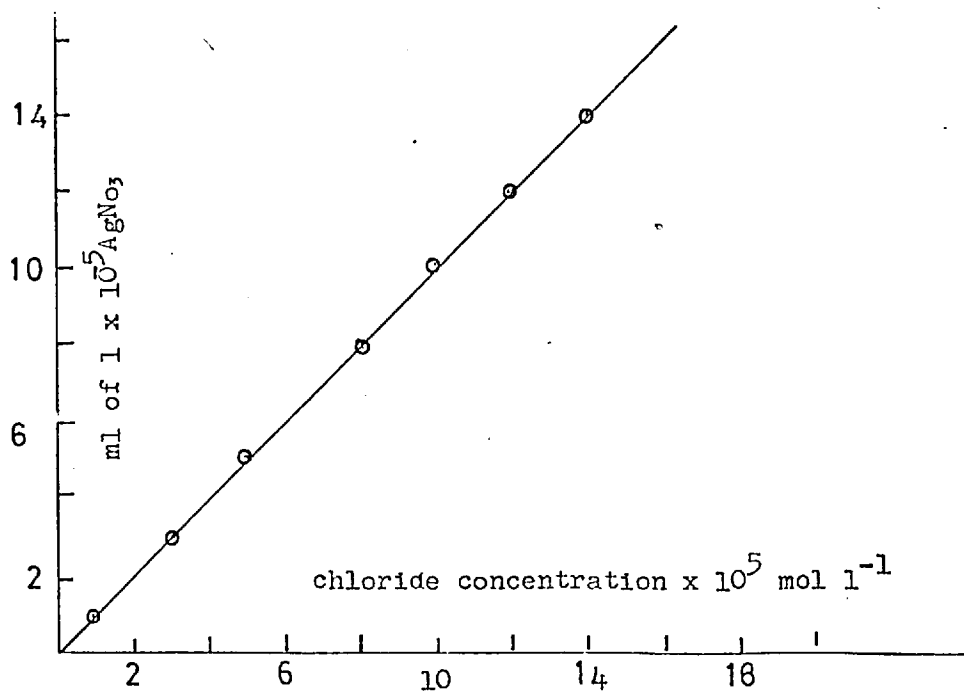


Figure 6.6.

6.4.2. Estimation of Chloride.

a) Distillation Of The Solvent.

The presence of hydroquinone in the irradiated mixture makes it impossible to titrate the mixture directly against silver nitrate, and hence the solvent plus the dissolved hydrogen chloride had to be distilled before the estimation of chloride ions.

This was done on a specially designed vacuum frame shown in Fig. 6.5, which enables the vacuum pump to suck not directly from the trap containing the solution but through a second trap which is kept at liquid nitrogen temperature so that the solvent vapour is efficiently condensed therein.

Before the distillation was allowed to proceed, the trap containing the irradiated solution is immersed in liquid nitrogen and, when the mixture has frozen, connected to the vacuum line through the second trap, also cooled in liquid nitrogen, for about 5 minutes to expel air. The vacuum line was disconnected, the liquid nitrogen removed and the irradiated mixture allowed to thaw. This process of freezing, sucking out air and thawing was repeated three times and then the distillation of the solvent into the second trap was allowed to take place.

The second trap was not left continuously connected to the vacuum pump, but the stopcock opened occasionally to the vacuum line after ascertaining that the level of liquid nitrogen in the Dewar

flask surrounding the trap was high enough, so that there was no possibility of losing any solvent vapour because of inefficient cooling of the trap.

To speed up the distillation, the trap containing the irradiated solution was immersed in water at about 5°C above room temperature.

In the first two runs an attempt was made to avoid the difficulties arising from titrations in a non-aqueous solvent by reacting the hydrogen chloride with alkali. A known weight of potassium hydroxide was placed in the second trap and the solvent was redistilled into a third trap. The residue obtained in the second trap contained potassium chloride and unreacted potassium hydroxide. It was dissolved in a known volume of water and neutralized with small known volumes of 1N nitric acid until the resultant solution was slightly acidic. Known volumes of this aqueous extract were titrated against silver nitrate as will be described a little later.

It was however found that the concentration of chloride estimated in this way was lower than the concentration of trichloro-hydroxyquinone, one of the products formed which entails the loss of a chlorine atom.

To check the efficiency of the method the process was repeated with isopropanol containing a known amount of hydrogen chloride. The results showed that not all the chloride ions were trapped by the

potassium hydroxide.

A suitable method of estimating chloride in the presence of isopropanol had therefore to be developed.

b) Methods Of Estimation.

In preliminary work using aqueous extracts of chloride trapped by alkali as described in section (a), a method developed by Bishop and Daneswhar (108) which, it is claimed, can estimate an initial chloride concentration of $5 \times 10^{-6} \text{ mol l}^{-1}$ was tried unsuccessfully. This method titrates chloride ions in approximately 80 per cent acetone medium bipotentiometrically against silver nitrate at silver electrodes between which flows a heavily stabilized current of density less than $1 \mu\text{A/cm}^2$. The electrodes, of 22-gauge silver wire, are sealed into blue glass, cut and polished so that the only metal exposed to the solution is the circular cross-sectional area of the wire. Lack of adequate equipment for stabilization of current and the difficulty in obtaining the specified electrodes led to very unsatisfactory results.

An attempt was then made to estimate the chloride - ion content of the aqueous extract of chloride referred to above using standard polarographic techniques, but again the results were unsatisfactory, probably because of the low concentration of chloride ions.

The method described below involving a potentiometric titration, was developed in the course of this work.

Earlier experiments were done with aqueous solutions of hydrogen chloride of known concentrations. These were titrated in 80 per cent acetone medium as will be described below. When the results were seen to be satisfactory, the same technique was successfully applied to the estimation of chloride ions in the presence of isopropanol.

Very satisfactory results, with less than 1.5 per cent error, were obtained with initial concentrations of chloride ions as low as $1 \times 10^{-6} \text{ mol l}^{-1}$. Chloride ion concentrations in irradiated solutions used in the present work were greater than $10^{-6} \text{ mol l}^{-1}$.

1 ml of the distillate obtained as in section (a), (or 1 ml of an aqueous solution of hydrogen chloride), was added to 1 ml of water and 7 ml of acetone so that the resultant solution was approximately 80 per cent acetone. The titration of this solution against $1 \times 10^{-5} \text{ mol l}^{-1}$ silver nitrate was carried out with a microburette, graduated in 0.01 ml, dipping in the solution to be titrated, and having a silver wire electrode fused in the tip below the stopcock. The second electrode was a silver wire fused into a glass tube. Mercury was used to provide good contact with an external lead. The electrodes were connected to a very sensitive pH meter used as a voltmeter. During the titration a magnetic stirrer was used to ensure efficient mixing and, consequently, a steady potential.

The calibration graph is shown in Fig. 6.6. The end point of a titration was determined by the standard differential method (109) in which change of e.m.f. per unit volume of titrant is plotted against burette readings. The volume of titrant corresponding to the maximum gives the end point.

6.4.3. Optical Density Measurements.

Manual measurements of absorbance were done on a Unicam SP 500.

Recorded spectra were obtained with the help of a Beckman DB spectrophotometer and during the later stages of this work with a Perkin Elmer 402.

6.5. METHODS OF QUALITATIVE ANALYSIS OF INDIVIDUAL PRODUCTS OF IRRADIATION.

6.5.1. Detection Of Irradiated Products.

About 200 ml of a saturated solution of chloranil in isopropanol was degassed with oxygen-free nitrogen and irradiated for six days or more at 365 nm. The visible and ultraviolet spectrum of the solution was determined both before and after irradiation as shown in Fig. 6.7. The alcohol was distilled off under reduced pressure. The spectrum (visible and ultraviolet) of a portion of the residue dissolved in isopropanol showed that no changes had taken place during work up.

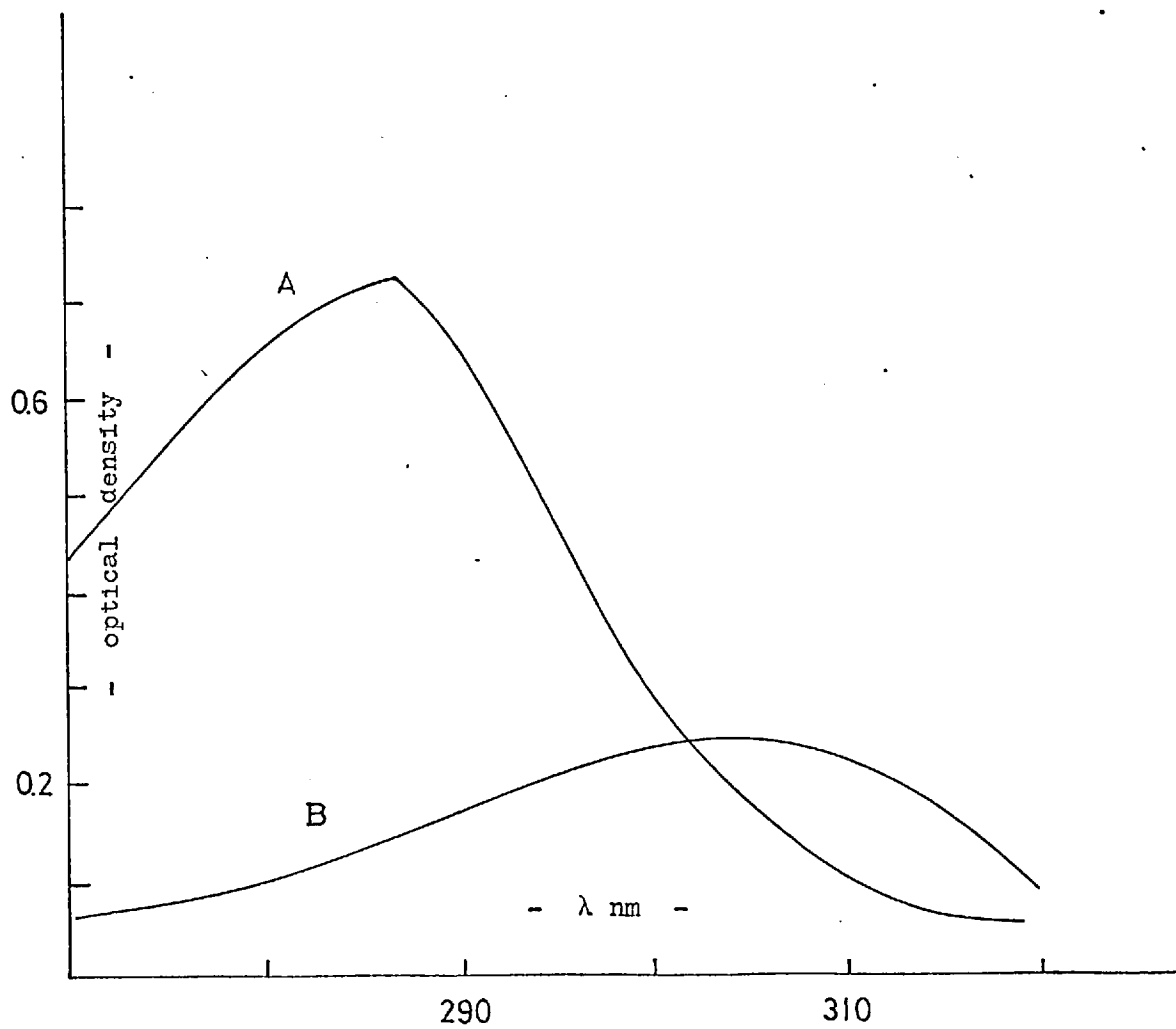
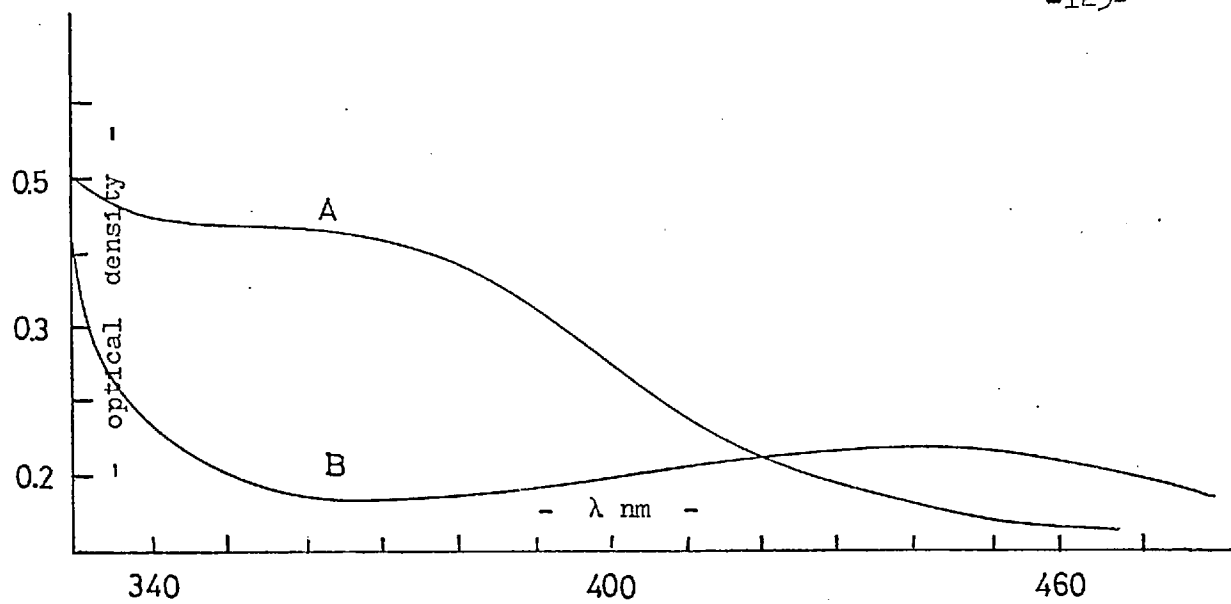


Figure 6.7

The distillate turned turbid on addition of silver nitrate solution indicating the presence of chloride ions.

The residue was sublimed at atmospheric pressure at about 50 - 60°C. The sublimate was orange yellow in colour and was found to give a strong purple colouration with water. A search in the literature suggested that trichlorohydroxyquinone was responsible for such a behaviour ⁽¹¹⁰⁾. The spectrum of the water solution of the sublimate gave peaks at 296 nm and 535 nm in agreement with data published by Hancock and co-workers ⁽¹⁰⁴⁾. The solution of the sublimate in isopropanol gave absorption maxima at 296 nm and 450 nm, again in agreement with published data ⁽¹⁰⁴⁾ and with experimental observations recorded in the course of work done in this laboratory with pure trichlorohydroxyquinone in isopropanol. Subsequently, Bredoux ⁽¹¹¹⁾ reported the identification of trichlorohydroxyquinone as one of the products of irradiation of chloranil in ethanol.

The residue left after sublimation was dissolved in isopropanol and the ultraviolet spectrum of the solution determined. A broad absorption peak situated between 300 nm and 310 nm showed that the residue contained more than one substance. Repeated treatment of the residue with small amounts of toluene and subsequent cooling of the filtrate in ice, gave colourless crystals. A solution of these crystals in isopropanol gave an ultraviolet spectrum with a

maximum at 303 corresponding to trichlorohydroquinone (112). The mass spectrum of the crystals had the parent peak at 212 and an expected three chlorine pattern, thus confirming that the isolated product was indeed trichlorohydroquinone.

The residue left after extraction with toluene, when dissolved in isopropanol gave an absorption peak at 308 nm, which is characteristic of tetrachlorohydroquinone.

6.5.2. Separation Of Products By TLC.

The residue left after distilling off the solvent under reduced pressure was separated into its components by thin layer chromatography using a standard method described by Elvidge and Sammes. (113) The chromatoplates were made of glass (5 x 20 cm) coated with silica. The developer consisted of a 4:1 mixture of methanol and acetone. Three spots were obtained, which when extracted with isopropanol gave absorption peaks at 295 nm, 273 nm and 288 nm, corresponding to trichlorohydroxyquinone, trichloroquinone and chloranil respectively. Since the presence of quinones only did not agree with observations recorded previously, it was decided to change the developer. A 5:1 mixture of ethyl acetate and methanol separated the residue into four regions. The absorption maxima of the extracts in isopropanol were found to be situated at 288 nm, 295 nm, 303 nm and 310 nm, characteristic of chloranil, trichlorohydroxyquinone, trichlorohydroquinone and tetrachlorohydroquinone, thus suggesting

that the hydroquinones were oxidized in the methanol-acetone developer (104) and (112).

The following symbols will, henceforward, be employed for the various quinones and hydroquinones used in the course of this work.

Chloranil	Q I
Tetrachlorohydroquinone	QH ₂ I
Trichloroquinone	Q II
Trichlorohydroquinone	QH ₂ II
Trichlorohydroxyquinone	Q III
Trichlorohydroxyhydroquinone	QH ₂ III

6.5.3. Oxidation Product Of Isopropanol.

Samples of the bulk-irradiated solution were chromatographed and the position of the peaks studied relative to the time of injection of the sample. The column used was packed with methyl silicone gum (SE 30), the flow rate was kept at 40 ml per minute and the temperature at 50°C. The separation between the various peaks was not satisfactory and variations of either flow rate of temperature or both did not improve it.

Porapak, type R, which according to the manufacturers (Water Associates Ltd.) is especially suited to the separation of ketones,

was the next choice for column packing. The separation between the various peaks was more satisfactory than in the case of SE 30 but the alcohol peak tailed very badly. Again adjustments of flow rate and temperature produced no improvement in the quality of the analysis.

Very efficient separation was obtained with Carbowax 20M on chromosorp P. The experimental technique has already been described.

a) Acetone.

When the chromatogram of the bulk-irradiated sample was compared with that of analar isopropanol used as solvent, the relative positions of the various peaks present in both were found to be the same, but one obvious difference was that the size of one of the peaks, whose area was very small in relation to the main alcohol peak and which appeared only at high sensitivity in the chromatogram of the solvent, was so significantly increased that it appeared at lower sensitivity in the irradiated sample.

Isopropanol can give acetone and/or pinacol as its oxidation product. To identify the product in the reaction under study, a small amount of acetone was added to the solvent and the sample was chromatographed. The relative position of the peak which showed an increase in size on addition of acetone, was exactly the same as that of the one which showed a significant increase after irradiation.

Considering that isopropanol itself contains about 5×10^{-2} per cent of acetone, the above-mentioned observations were taken as evidence that acetone is probably the major product of the oxidation of isopropanol in the photochemical reaction of chloranil with isopropanol.

To confirm this conclusion, small amounts of pinacol were added to the solvent before injecting the sample into the column. A new peak appeared in the chromatogram. Addition of pinacol to the irradiated sample also produced a new peak, the relative position of which was the same as in the previous chromatogram, thus verifying that no pinacol is formed as a result of irradiation.

b) Hydrocarbons.

It must be noted here that samples of solutions of chloranil irradiated in bulk for a very long period produced four small peaks which are not present in the chromatogram of the solvent. These peaks occur in the early region of the chromatogram and correspond to substances with retention times of less than 30 seconds.

Since it was suspected, for reasons to be given in the discussion later, that these peaks were caused by hydrocarbons, samples of isopropanol containing ethylene and others containing calor gas were chromatographed. The chromatograms showed peaks in the same region as the one observed in the irradiated sample, but it was not possible to identify the substances responsible for them.

Samples irradiated for much shorter periods on the optical bench did not give these peaks probably because the extremely low concentrations at which they can be expected to be present in such solutions were below the sensitivity of the flame ionization detector.

c) Propylene Oxide.

The chromatogram of the solvent had a very small peak with a retention time of about 6 minutes when the chromatograph was run at an attenuation of 20. An attempt to run the chromatograph at higher sensitivities in order to obtain a peak that could be measured with some accuracy failed because the recorder pen became very unstable at sensitivities higher than those used for the detection and measurement of acetone. In bulk-irradiated solutions this peak showed an increase of about 2 per cent in relation to the same peak in the solvent.

The addition of propylene oxide to the solvent increased the area of this peak with respect to the main alcohol peak enabling its assignment to the epoxide to be made.

During the course of the experiments with solutions irradiated on the optical bench, it was found that degassing the solution with oxygen-free nitrogen caused the decrease of the acetone peak and the disappearance of the epoxide peak. After irradiation the acetone peak was considerably increased whereas the epoxide peak was just detectable

above the base line. It seems safe to say that the irradiated samples contained a small concentration of propylene oxide.

6.6. QUANTITATIVE ANALYSIS OF IRRADIATED SOLUTIONS.

The concentrations of the various compounds detected in the reaction mixture were estimated by spectrophotometric analysis using wavelengths of 450 nm, 365 nm and 290 nm.

Experiments done on pure quinones and hydroquinones in isopropanol showed that hydroquinones have zero extinction coefficients at 450 nm whereas Q III (trichlorohydroxyquinone) and Q I (chloranil) do absorb light, but the extinction coefficient of Q III is very much larger than that of Q I.

At 365 nm, again, the extinction coefficients of the hydroquinones are nearly zero, whereas Q III and Q I absorb significantly. In the ultraviolet region from 220 - 310 nm, the quinones and hydroquinones absorb strongly, but the peak extinction coefficients of the quinones are much larger than those of the hydroquinones.

The extinction coefficients used in the calculations in the present work are grouped in Table 6.1b.

Table 6.1b

Compound	Symbol	$\epsilon \times 10^2$		
		450 nm	365 nm	290 nm
Chloranil	Q I	0.20	2.75	144.1
Tetrachlorohydroquinone	QH ₂ I	0	0	19.92
Trichloroquinone	Q II	0.30	4.67	101.8
Trichlorohydroquinone	QH ₂ II	0	0	26.67
Trichlorohydroxyquinone	Q III	4.87	1.421	113.7
Trichlorohydroxyhydroquinone	QH ₂ III	0.60	0.25	32.2

Let the concentrations of the various substances present be denoted as follows

c_{10} = conc. of Q I at the start

c_1 = - do - at the end

c_2 = conc. of QH_2 II

c_3 = conc. of Q III

c_4 = conc. of QH_2 I

c_5 = conc. of chloride ions

in the irradiated
solution

The concentration of Q I at the end of the run (c_1) and the concentration of Q III in the irradiated solution (c_3) were calculated by measuring the absorbance of the solution at 450 nm and at 365 nm, and solving the simultaneous equations formed by substituting the appropriate figures in the expression

$$l (\epsilon_1 c_1 + \epsilon_3 c_3) = \text{Absorbance}$$

where ϵ_1 and ϵ_3 are the extinction coefficients of Q I and Q III respectively at a given wavelength and l is the path length of the cell.

The irradiated solution was then diluted tenfold and the absorbance measured at 290 nm, since this particular wavelength was found to be experimentally most convenient.

The irradiated mixture contains Q I, QH_2 I, QH_2 II and Q III. The concentrations of Q I (c_1) and Q III (c_3) were obtained from measurements in the visible region referred to earlier.

The concentrations of QH_2 II (c_2) and QH_2 I (c_4) were calculated from a knowledge of the concentration of chloride ions (c_5) in the irradiated mixture estimated by a potentiometric titration already described.

$c_2 = c_5 - c_3$ since both QH_2 II and Q III are formed by the loss of one chlorine atom

$c_{10} - c_1 = \text{Total loss of Q I}$

$c_4 = (c_{10} - c_1) - c_5$ since QH_2 II and Q III are the only two other products of the reaction of chloranil.

Since the concentration of each of the components of the mixture was known, as also their individual extinction coefficients at 290 nm, the value of the absorbance that the irradiated solution was expected to give at that wavelength was calculated. This value was then compared with the actual spectrophotometric measurement at 290 nm. Agreement between the calculated and measured value was taken as proof of the correctness of the analysis.

Acetone was estimated quantitatively, as described earlier, by G.L.C.

6.7. QUINONE - HYDROQUINONE INTERACTION.

Since the analysis of the irradiated solution revealed the presence of Q I, QH_2 I, QH_2 II and Q III only, the absence of trichloroquinone (Q II) and trichlorohydroxyhydroquinone (QH_2 III) had to be explained. It was thought that interaction between the

various quinones and hydroquinones could be responsible for their absence. To investigate this interaction the following mixtures were prepared and studied in an atmosphere of nitrogen;

- | | |
|----------------------------------|--------------|
| 1. Q I and QH ₂ I | } Table 6.2a |
| 2. Q III and QH ₂ III | |
| 3. Q II and QH ₂ II | Table 6.2b |
| 4. Q II and QH ₂ II | Table 6.2c |
| in the presence of Q III | |
| 5. Q I and QH ₂ II | Table 6.2d |
| 6. Q II and QH ₂ I | Table 6.2e |
| 7. Q I and QH ₂ III | } Table 6.2f |
| 8. Q II and QH ₂ III | |

After each table giving the concentration of the components of the mixture and the optical density at 290 nm, (and where helpful also at 450 nm), some obvious conclusions are noted. 4 cm cells were used for measurements at 450 nm and 1 cm cells for those at 290 nm.

Table 6.2a.

Compound	$c \times 10^4 \text{ mol l}^{-1}$	<u>Q I and QH₂ I</u>	
		Additive	Measured
Q I	0.3267		0.4705
QH ₂ I	0.6020		0.1195
Q I + QH ₂ I in concentrations as above		0.5900	0.5905
Q I	0.1638		0.2353
QH ₂ I	0.9030		0.1800
Q I + QH ₂ I in concentrations as above		0.4153	0.4150
<u>Q III and QH₂ III</u>			
Q III	0.2400		0.2730
QH ₂ III	0.3205		0.1035
Q III + QH ₂ III in concentrations as above			0.3768
Q III	0.2400		0.2730
QH ₂ III	0.6410		0.2075
Q + QH ₂ III in concentrations as above		0.4805	0.4800

No interaction takes place between Q I and QH₂ I and between Q III and QH₂ III as is seen from the additivity of the absorbances of the components of the mixture.

Table 6.2b Q II and QH₂ II

Compound	$c \times 10^4 \text{ mol l}^{-1}$	Absorbance at 290 nm l = 1 cm		$A_{\text{additive}} - A_{\text{measured}}$
		Additive	Measured	
Q II	0.4500		0.4600	
QH ₂ II	1.942		0.5180	
Q II + QH ₂ II in concentrations as above		0.9780	0.8400	0.1380
Q II	0.900		0.9150	
QH ₂ II	1.256		0.3350	
Q II + QH ₂ II in concentrations as above		1.050	1.05	0.2000

The significant difference between the additive absorbance and the measured one, points to an interaction between Q II and QH₂ II. This reaction was found to be slow. At the concentrations studied, it took about 90 minutes to attain equilibrium.

To determine whether the presence of traces of Q III catalyzes the process, a mixture of Q II and QH₂ II was studied in the presence and in the absence of Q III. Measurements were made immediately after mixing and at random intervals. (Table 6.2c).

Table 6.2c. The mixture consisted of 0.85×10^{-4} mol l^{-1} of Q II, 1.35×10^{-4} mol l^{-1} of QH₂ II and 0.0598×10^{-4} mol l^{-1} of Q III.

Time after mixing in minutes.	Absorbance at 290 nm, $l = 1$ cm	
	with Q III	without Q III
0	1.300	1.200
60	1.250	1.190
90	1.150	1.075
180	1.145	1.075
210	1.145	1.075

The value of the absorbance with or without Q III at zero time is additive for the components of the mixture. Values of absorbance at other times show that Q III does not catalyze the interaction between Q II and QH₂ II.

We shall return later to a discussion of the Q II - QH₂ II system.

Table 6.2a.

Q I and QH₂ II

Compound.	c x 10 ⁴ mol l ⁻¹	Absorbance at 290 nm l = 1 cm		A _{additive} - A _{measured}
		Additive	Measured	
Q I	0.3333		0.4800	
QH ₂ II	1.340		0.3500	
Q I + QH ₂ II in concentrations as above		0.8300	0.8150	0.0150
Q I	0.2220		0.3180	
QH ₂ II	2.01		0.530	
Q I + QH ₂ II in concentrations as above		0.8480	0.8260	0.0220

The small differences between the additive spectrum and the measured one indicate that the equilibrium of the reaction

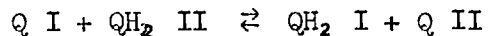
$Q I + QH_2 II \rightleftharpoons QH_2 I + Q II$ is almost entirely to the left in the circumstances of interest here.

Table 5.2e

Q II and QH₂ I

Compound	c x 10 ⁴ mol l ⁻¹	Absorbance at 290 nm, l = 1 cm		
		Additive	Measured	Calculated on basis of total conversion of Q II to QH ₂ II.
Q II	0.450		0.4600	
QH ₂ I	0.903		0.1800	
Q II + QH ₂ I in concentrations as above		0.6400	1.15	1.196
Q II	0.450		0.4600	
QH ₂ I	0.602		0.1195	
Q II + QH ₂ I in concentrations as above		0.5795	1.15	1.13

Table 5.2e confirms the previous conclusion that the equilibrium of the reaction



lies almost entirely to the left.

Since in irradiated solutions, an excess of QH₂ I relative to any Q II that may be formed is to be expected, the absence of Q II can be accounted for in terms of the above equilibrium.

Table 6.2f.

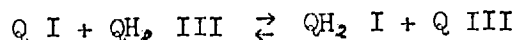
Q I and QH₂ III

Compound	c x 10 ⁴ mol l ⁻¹	Absorbance at 450 nm l = 4 cm	Absorbance at 290 nm, l = 1 cm		
			Additive	Measured	Calculated on basis of total conversion of quinone to hydroquinone
Q I	0.1638	0		0.2353	
QH ₂ III	0.4807	0		0.1550	
Q I + QH ₂ III in concentrations as above		0.0950		0.3200	0.3209
Q I	0.3267	0		0.4705	
QH ₂ III	0.3205	0		0.1035	
Q I + QH ₂ III in concentrations as above		0.0625		0.4350	0.4375
<u>Q II + QH₂ III</u>					
Q II	0.450	0		0.4600	
QH ₂ III	0.3205	0		0.1035	
Q II + QH ₂ III in concentrations as above		0.0600		0.600	0.5911
Q II	0.450	0		0.4600	
QH ₂ III	0.4807	0		0.1550	
Q II + QH ₂ III in concentrations as above		0.0950		0.6600	0.6620

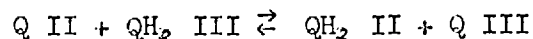
In every case, when the components were mixed, the characteristic orange-red colour of Q III appeared as soon as the solutions came in contact with one another. The absorbance of the mixture at 450 nm can be accounted for by that concentration of Q III which, in each individual case, would be obtained by the total oxidation of QH₂ III to Q III.

The absorbance at 290 nm can likewise be accounted for by the total reduction of quinone (either Q I or Q II) to the corresponding hydroquinone.

The evidence strongly suggests that the equilibrium position of the reactions



and



is entirely to the right in the circumstances relevant to the present work.

The absence of QH₂ III in the irradiated mixture has, therefore, a suitable explanation.

6.8. LIGHT ABSORPTION.

6.8.1. Actinometry.

The intensity of the light beam incident on the solution was measured using the potassium ferrioxalate actinometer developed by Hatchard and Parker ⁽¹¹⁴⁾. A $6 \times 10^{-3} \text{ mol l}^{-1}$ solution was

employed and the optical density was determined at the ferroin absorption peak, 510 nm.

Values used in this work are

$$\phi_{\text{Fe}^{2+}} = 1.26 \text{ at } 365 \text{ nm}$$

$$= 1.11 \text{ at } 437 \text{ nm}$$

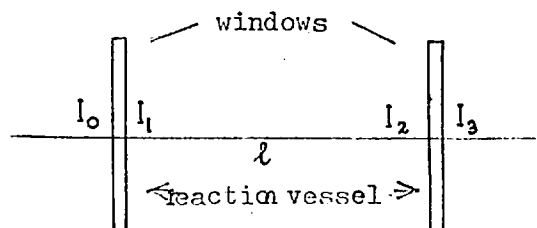
$$\epsilon_{\text{Fe}^{2+}} = 1.11 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1} \text{ at } 510 \text{ nm.}$$

Measurements of the intensity of the beam were carried out about once every four weeks.

6.8.2. Calculation Of Light Absorbed.

The symbols used are:

Photocell deflection for no cell in the beam	D_o
Photocell deflection for solvent in the cell	D_m
Photocell deflection for solution in the cell	D_n
Fraction of light lost at each window	α



Intensity of light absorbed

$$I_a = I_1 - I_2$$

$$I_o = \beta D_o \text{ and } I_3 = \beta D_n$$

where β is a constant whose value was determined by actinometry.

$$I_1 = I_0 (1 - \alpha) \text{ and } I_3 = I_2 (1 - \alpha)$$

For solvent in the cell $I_2 = I_1$

$$\text{Then } I_3 = I_1 (1 - \alpha) = I_0 (1 - \alpha)^2$$

Dividing by β ,

$$D_m = D_0 (1 - \alpha)^2 \text{ and } 1 - \alpha = \left(\frac{D_m}{D_0} \right)^{1/2}$$

This equation was used to calculate α .

Actinometer measurements gave the value of I_a which is the intensity of light absorbed by the solution in einsteins per second

$$\begin{aligned} \text{But } I_a &= I_1 - I_3 \\ &= I_0 (1 - \alpha) - \frac{I_3}{1 - \alpha} \\ &= (I_0 (1 - \alpha)^2 - I_3) \frac{1}{1 - \alpha} \\ &= \frac{\beta}{1 - \alpha} (D_m - D_n) \end{aligned}$$

This equation was used to determine β from actinometer measurements since $D_n = 0$ for $6 \times 10^{-3} \text{ mol l}^{-1}$ potassium ferrioxalate at 365 nm with a cell length greater than 1 cm.

Once β is known, the same equation was used to calculate I_a from D_n measured with the solution in the cell and D_m measured with the same solvent as that used to dissolve the quinone.

Photocell deflection of the reflected beam D_r

Time of irradiation in seconds t

Readings were taken during each run of D_n , D_r and t , and after each run of D_o and D_m . Since the intensity of the lamp, as represented by D_r , most of the time, fluctuated in a random manner during the run, a mean value of D_r was taken and the values of D_m and D_n were corrected to correspond to the mean value of D_r . A graph of D_n against t was plotted, the best curve was drawn through the points, and values of t were tabulated with values of D_n taken from the curve.

At each value of t , the following were calculated

$\log \frac{D_m}{D_n}$, the optical density of the solution

The fraction of quinone in moles per 25 ml remaining in the solution

The fraction of quinone in moles per 25 ml lost from the solution

$D_m - D_n$, the photocell equivalent of light absorbed by the solution

I_a , the amount of light absorbed in einsteins per second

Mean I in einsteins per second

For short periods of irradiation, the plot of I_a against time is linear, but not so for long periods when the concentration of quinone at the end of the run is significantly smaller than that at the start.

For short periods of irradiation, mean I_a is simply the mean value from $t = 0$ to $t = t_1$. For long periods of irradiation,

$$\text{mean } I = \left(\int_0^{t_1} I_a dt \right) / t$$

It in einsteins.

At time t , this gives the total amount of light absorbed by the solution up to time t .

A graph was plotted of the total amount of quinone lost, in moles, against I_t , in einsteins. The slope at any point on the curve represents the quantum efficiency for loss of quinone at that point.

Starting concentrations
 $a = 0.698 \times 10^{-3} \text{ mol l}^{-1}$
 $b = 0.349 \times 10^{-3}$
 $c = 0.2074 \times 10^{-3}$
 (see also fig. 6.8b on page 147)

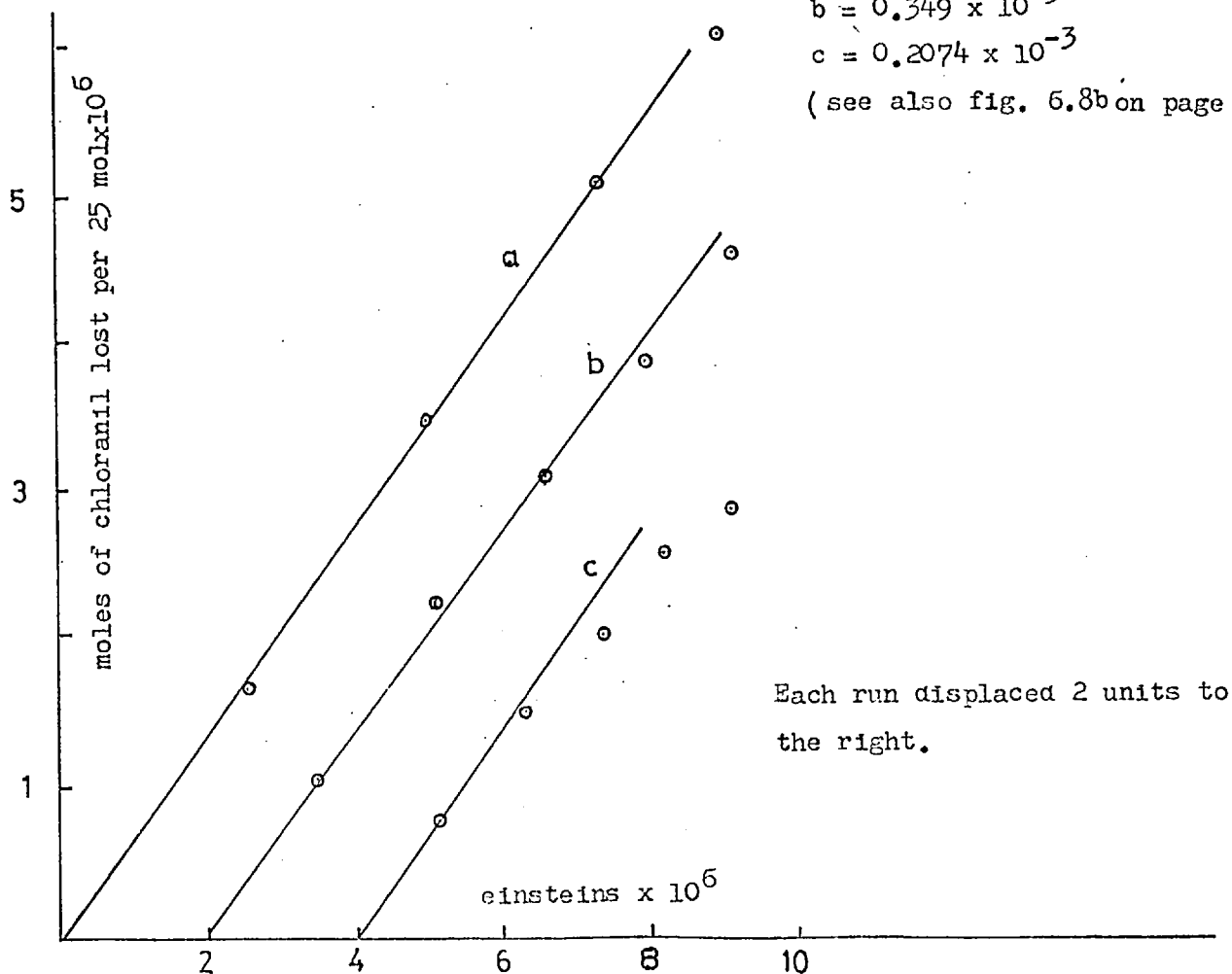


Figure 6.8a.

6.9. EXPERIMENTS WITH CHLORANIL.

6.9.1. Chloranil In Isopropanol - Anaerobic Solutions.

The first few runs with chloranil in isopropanol at 365 nm were carried out with a view to confirming the work done by Scrutton (115). The quantum efficiency for loss of quinone as shown in fig. 6.8_b decreases gradually as the reaction proceeds. The initial quantum efficiency, whatever the starting concentration of the quinone, is nearly 0.5. Since the intensity of light absorbed varies with chloranil concentration, and the quantum efficiency does not, this latter quantity must be independent of light intensity in the range studied. (See fig. 6.8a on page 145)

A second series of runs was carried out and an exhaustive analysis done of the products of irradiation by the methods already described. The results are tabulated in Tables 6.3 and 6.4. All concentrations are expressed in moles per litre.

Table 6.3.

$c_{10} \times 10^3$	$c_1 \times 10^3$	$c_{QIII} \times 10^3$	$c_{QH_2I} \times 10^3$	$c_{QH_2I} \times 10^3$	Absorbance at 290 nm; 1 cm path length; solution diluted tenfold	
					Calculated	Measured
0.5010	0.3265	0.0268	0.0473	0.1006	0.5339	0.5300
0.5010	0.2863	0.0334	0.0656	0.1186	0.4916	0.5000
0.5010	0.1716	0.0465	0.0983	0.1833	0.3627	0.3675
0.8726	0.4247	0.0621	0.1334	0.2468	0.7673	0.7545

Starting concentration of chloranil = $0.842 \times 10^{-3} \text{ mol l}^{-1}$

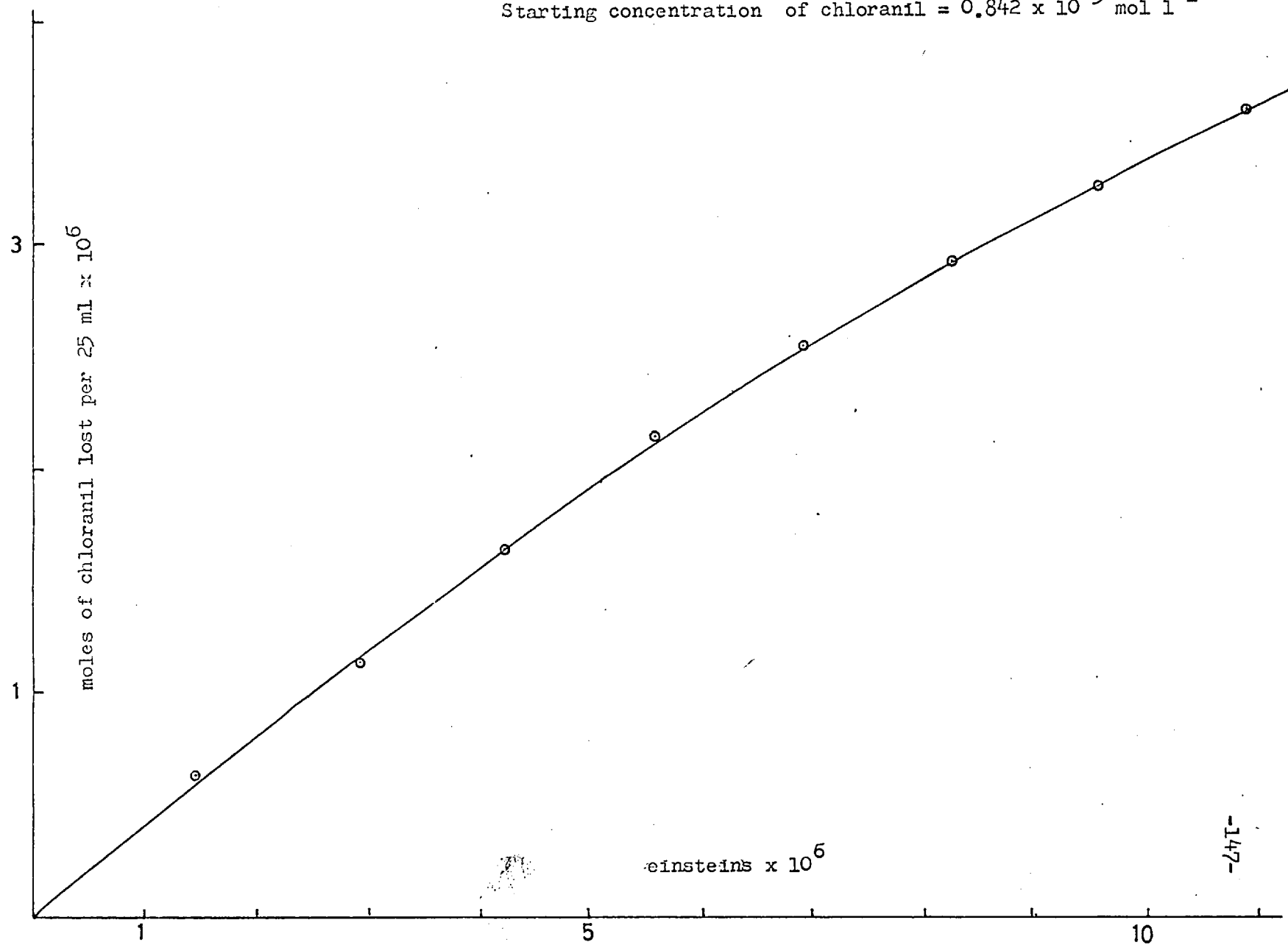


Figure 6.8b.

Extrapolation leads to values for initial quantum efficiencies, ϕ_1 , for loss of quinone and formation of various products given at the bottom of Table 6.4.

Table 6.4. Chloranil - Isopropanol Solutions. (Anaerobic)

$$\lambda = 365 \text{ nm } T = 20^\circ$$

$c_Q \text{ I} \times 10^3$	$\phi_{QH_2 \text{ I}}$	$\phi_{QH_2 \text{ II}}$	$\phi_Q \text{ III}$	ϕ_{Cl^-}	$\phi_{\text{loss } Q \cdot I}$	ϕ_{Acetone}	$It \times 10^5$ einsteins
0.5010	0.168	0.079	0.045	0.125	0.290	0.256	1.497
0.5010	0.141	0.078	0.0397	0.118	0.255	0.214	2.104
0.5010	0.138	0.074	0.035	0.108	0.248	0.207	3.321
0.8726	0.135	0.073	0.034	0.108	0.245	0.209	4.571
Extrapolated ϕ_1							
	0.252	0.132	0.066	0.199	0.45	0.383	

The amount of trichlorohydroxyquinone formed is, as can be seen from a comparison of ϕ_1 for loss of quinone and ϕ_1 for formation of Q III, 15 per cent of the total amount of chloranil lost. This relationship enabled a formula to be derived to determine the initial quantum efficiency for loss of quinone from the slope of the curve traced by the recorder. Q III is the only product of

irradiation which, together with unreacted chloranil absorbs at 365 nm.

$$\log \frac{D_o}{D_n} = 1 [\epsilon_1 c_1 + \{ \epsilon_3 (c_{10} - c_1) \} 0.15]$$

where ϵ_1 and ϵ_3 are the extinction coefficients of Q I and Q III respectively and c_{10} and c_1 are the concentrations of Q I at the beginning and at the end of the run.

$$- \frac{d D_n}{D_n} = 1 \left(\frac{\epsilon_1 - \epsilon_3 0.15}{2.303} \right) dc_1$$

$$- \frac{1}{D_n} \frac{d D_n}{dt} = 1 \left(\frac{\epsilon_1 - \epsilon_3 0.15}{2.303} \right) \frac{dc_1}{dt}$$

At $t = 0$, $D_n = D_{n_0}$, the recorder chart reading, at the beginning of the run, in inches.

$$\frac{d D_n}{dt} = \text{slope of the recorder chart in inches per second.}$$

Since $\frac{d D_n}{dt}$ can be measured, $\frac{dc_1}{dt}$ can be calculated.

The initial quantum efficiency for loss

$$\text{of quinone, } \phi_1 = \frac{dc_1}{dt} / I_a$$

where I_a is the amount of light absorbed in einsteins at zero time.

Quantum efficiencies calculated in this manner are compared with the figures obtained from the graph connecting quinone lost with einsteins absorbed for the same run (Table 6.5)

Table 6.5 ϕ_1 for loss of Quinone.

From Graph	From dDn/dt	Starting Concentration.
0.447	0.442	$0.5010 \times 10^{-3} \text{ mol l}^{-1}$
0.437	0.440	$0.8726 \times 10^{-3} \text{ mol l}^{-1}$
0.442	0.445	$0.5610 \times 10^{-3} \text{ mol l}^{-1}$
0.451	0.446	$0.2033 \times 10^{-3} \text{ mol l}^{-1}$
0.454	0.449	$0.4595 \times 10^{-3} \text{ mol l}^{-1}$

The very satisfactory agreement between the two values is valid proof of the correctness of the qualitative and quantitative analysis of the products of irradiation.

6.9.2. Chloranil In Isopropanol - Aerobic Solutions.

Quinones act as sensitizers in the photochemical oxidation of alcohols in the presence of air. The quantum efficiency for the formation of acetone in the irradiation of anthraquinone - 2-sulphonate in isopropanol in aerobic solutions was shown by Wells ⁽⁷⁶⁾ to be a good measure of the quantum efficiency for the formation of the photoexcited reactive species of the quinone.

With the intention of measuring the yield of acetone, undegassed solutions of chloranil in isopropanol were irradiated and air was bubbled through the solution taking care that the bubbles did not get into the path of the light beam. Fig. 6.9 shows the change in optical density at 365 nm in a typical run. The only products

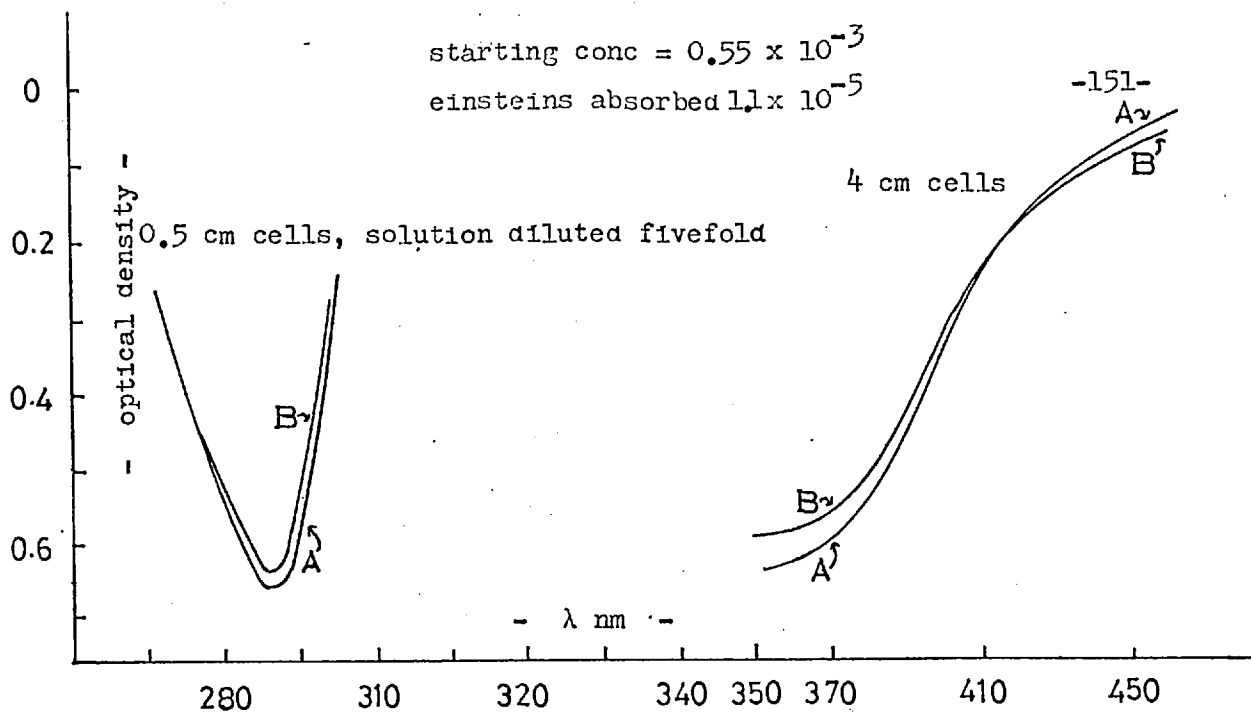


Figure 6.9.

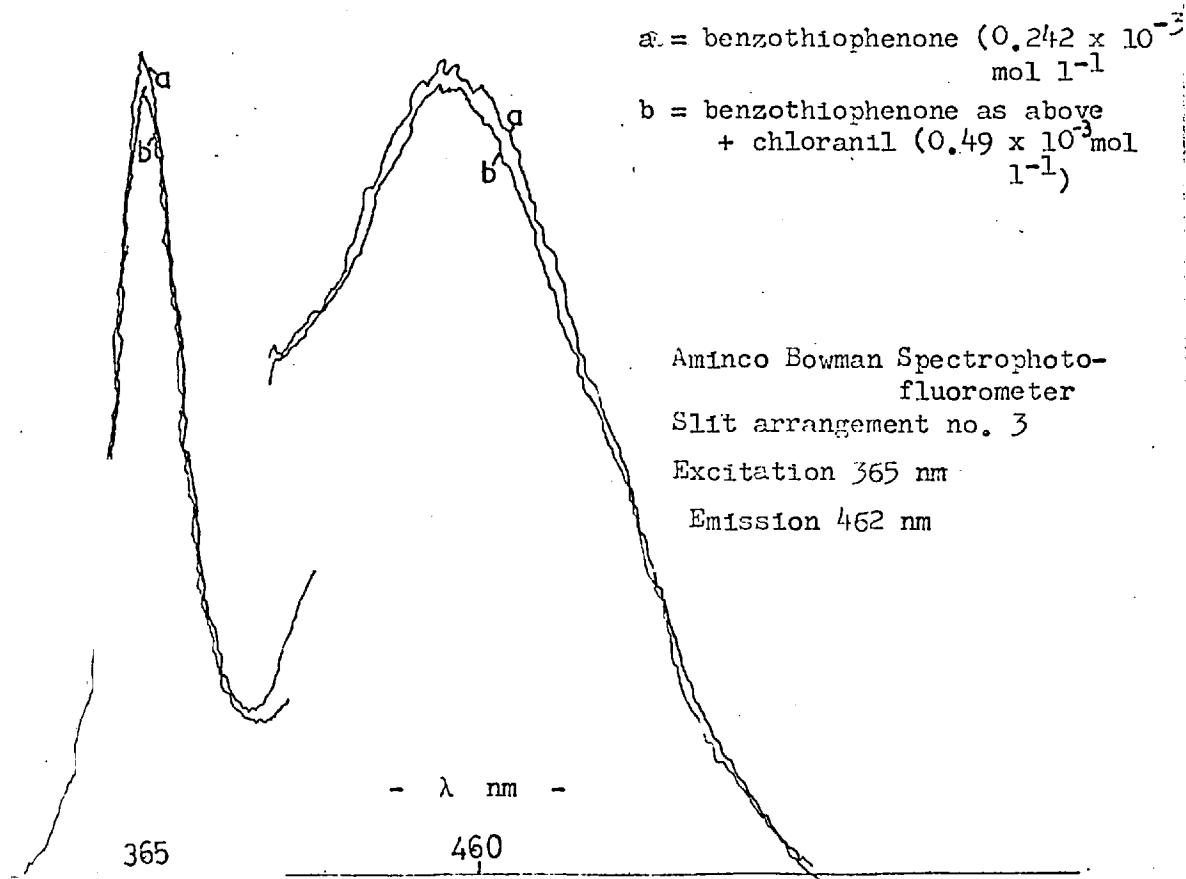


Figure 6.11.

of irradiation were found to be Q III and acetone. Results, including the quantum efficiency for formation of chloride ions are given in Table 6.6.

It is reasonable to conclude that the expulsion of a chlorine atom from chloranil, leading to the formation of Q III, is a primary photochemical reaction of the excited quinone.

The high quantum yield of acetone indicates that the photoreactive species of the quinone is produced with a quantum efficiency of nearly unity.

Table 6.6. Chloranil - Isopropanol Solutions (Aerobic)

$$\lambda = 365 \text{ nm} \quad T = 20^{\circ}\text{C}.$$

$c_{Q \text{ I}} \times 10^3$	$\phi_{Q \text{ III}}$	ϕ_{Cl^-}	$\phi_{\text{loss Q I}}$	ϕ_{Acetone}	$I t \times 10^5$ einsteins
0.5500	0.192		0.195		1.110
0.3660	0.197	0.189	0.190	0.98	0.5568
0.4910	0.196	0.190	0.194	0.976	0.4011
0.3660	0.199	0.193	0.199	0.973	0.2858

6.9.3. Irradiation In An Inert Solvent.

The expulsion of the chlorine atom from Q I may involve either a heterolytic or a homolytic rupture of the C - Cl bond.

To determine which of the two occurred during irradiation, an anaerobic solution of chloranil ($0.213 \times 10^{-3} \text{ mol l}^{-1}$) in

fluorochemical inert liquid FC - 75 (BDH) was irradiated at 365 nm. No reaction was detected. A slow current of air was bubbled through the solution for about 30 minutes before the beam of light was allowed to shine on it again. No reaction was detected in this case also.

Heterolytic rupture of the C - Cl bond is therefore suspected. Homolytic rupture of the bond would produce free radicals which, in an inert solvent, would be expected to dimerize. This would cause a change in the optical density.

FC - 75 is immiscible with water, ethanol or isopropanol. It was, therefore, not possible to investigate the photochemical behaviour of the quinone in dilute solutions of isopropanol or ethanol.

6.9.4. Irradiation With Sensitizers.

a) Chloranil - Anthracene Mixtures.

As will be shown later in the discussion that follows, there is reason to believe that the energy of the first excited triplet of chloranil lies between 40 - 42 kcal mol⁻¹. To determine whether the reaction proceeds via the triplet or not, anthracene ($E_T = 42$ kcal mol⁻¹) and benzothiophenone ($E_T = 40$ kcal mol⁻¹) were chosen as sensitizers.

Anthracene has a very strong absorption at 365 nm. The

Table 6.7a. Chloranil - Anthracene - Isopropanol Solutions (Anaerobic)

$\lambda = 365\text{nm}$ $T = 20^\circ\text{C}$.

Chloranil (Q I)			Anthracene			$\phi_{\text{loss Q I}}$	$I_t \times 10^5$ einsteins
$c \times 10^3$	Absorbance	% of Total Absorbance	$c \times 10^3$	Absorbance	% of Total Absorbance		
0.5093	0.1385	57.7	0.048	0.1050	42.3	0.69	0.4598
0.5000	0.1350	66.5	0.031	0.068	33.5	0.56	0.4581
0.0170	0.0047	2	0.105	0.2275	98	9.3	0.0409
0.0170	0.0047	2	0.105	0.2275	98	3.5	0.1566
0.5010	0.1355	100	0	0	0	0.29	1.497

Table 6.7c

$\lambda = 437 \text{ nm}$

1.10	0.044	100	0	0	0	0.276	1.141
1.00	0.040	100	0.1703	0	0	0.290	0.9073

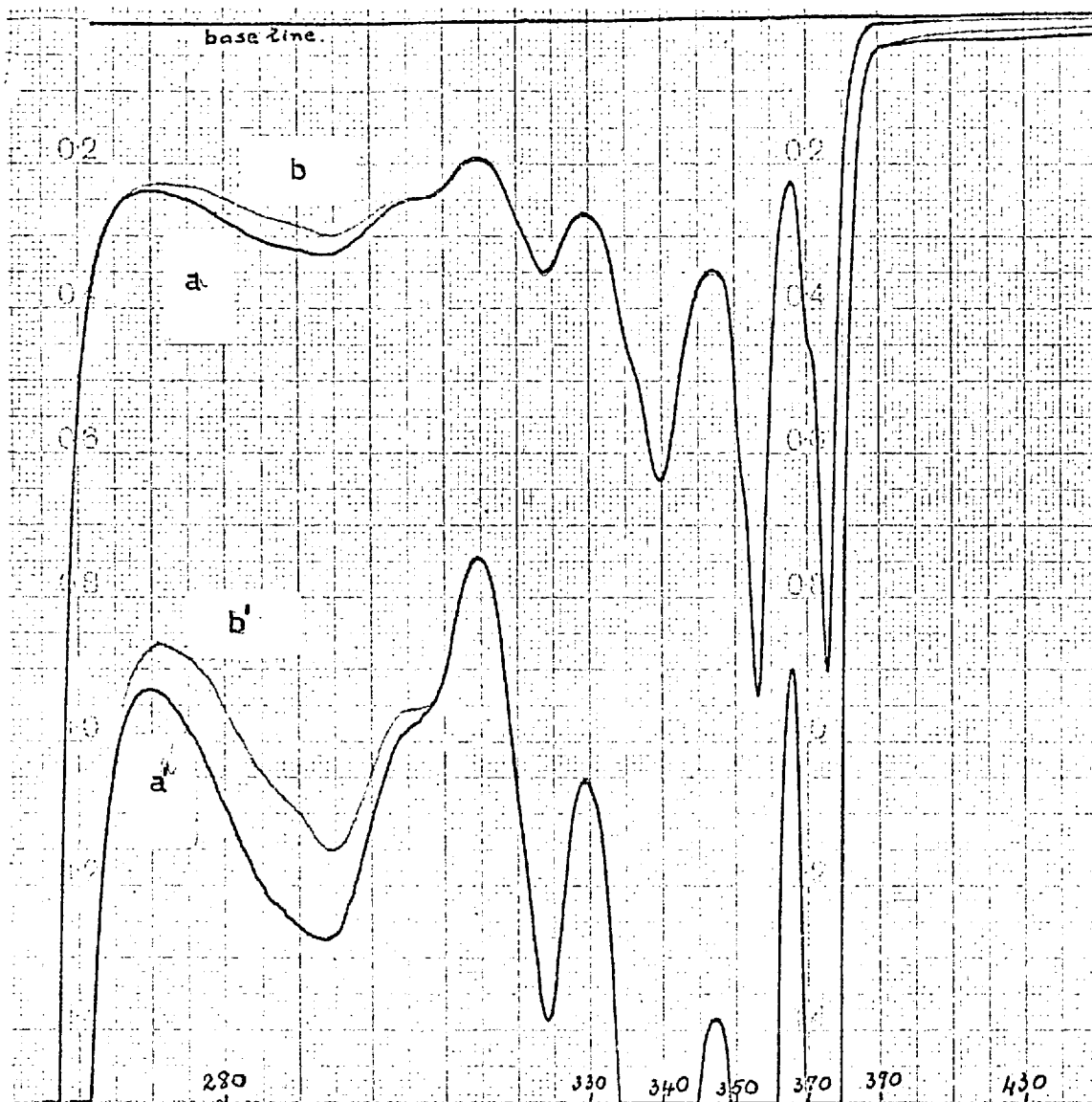


Figure 6.10a.

conc. of chloranil in the mixture = 0.017×10^{-3} mol l^{-1}

conc. of anthracene in the mixture = 0.105×10^{-3} mol l^{-1}

unirradiated mixture $\left\{ \begin{array}{l} a = 1 \text{ cm cells} \\ a' = 4 \text{ cm cells} \end{array} \right.$

irradiated mixture $\left\{ \begin{array}{l} b = 1 \text{ cm cells} \\ b' = 4 \text{ cm cells} \end{array} \right.$

einsteins absorbed = 0.0409×10^{-5} (45 minutes)

(slit width = 25 microns; speed = slow)



Figure 6.10b.

conc. of chloranil in the mixture = $0.017 \times 10^{-3} \text{ mol l}^{-1}$
 conc. of anthracene in the mixture = $0.105 \times 10^{-3} \text{ mol l}^{-1}$
 unirradiated mixture $\left\{ \begin{array}{l} a = 1 \text{ cm cells} \\ a' = 4 \text{ cm cells} \end{array} \right.$
 irradiated mixture $\left\{ \begin{array}{l} b = 1 \text{ cm cells} \\ b' = 4 \text{ cm cells} \end{array} \right.$
 einsteins absorbed = 0.1566×10^{-5} (3 hours)
 (slit width = 25 microns; speed = slow)

concentration of either component in the mixture of chloranil and anthracene was adjusted so that in some runs both chloranil and anthracene absorbed significantly, and in others anthracene alone absorbed almost 98 per cent of the incident light. The results are tabulated in table 6.7a and spectra before and after irradiation of the mixtures used in the last two runs which yielded the most revealing information are given in Fig. 6.10 a and b.

Anthracene fluoresces under ultraviolet irradiation. Correction for fluorescence was made as follows.

The optical density of the anthracene solution at the dilution used in the run was measured at 365 nm using a spectrophotometer. This value enabled the calculation of the value of the recorder chart reading to be made when the cell containing the same solution was placed on the optical bench.

$$\log \frac{D_m}{D_n} = \epsilon c l$$

Since D_m , ϵ , c and l were known, D_n was calculated. The actual recorder chart reading D'_n was noted. Then $D'_n - D_n =$ recorder equivalent of light transmitted due to fluorescence.

The concentration of anthracene varied very slightly during irradiation and hence the above correction for fluorescence was subtracted from every recorder chart reading during the run to get the true value of D_n at any time.

Fig. 6.10a and b representing runs in which the chloranil concentration was so low that the amount of light absorbed by the quinone was insignificant, show that the reduction of chloranil has indeed taken place as evidenced by the decrease in the absorption peak at 288 nm characteristic of chloranil and an increase at 308 nm characteristic of tetrachlorohydroquinone. Transfer of energy has undoubtedly taken place.

When the mixture was irradiated for longer periods the concentration of anthracene decreased slightly. The amount of chloranil that disappeared did not however differ very much from that reacted during shorter periods of irradiation. It would seem, therefore, that as the concentration of chloranil decreases the probability of collisions between excited anthracene molecules and quinone molecules decreases drastically thus increasing the probability of collision between anthracene molecules themselves, a process that probably leads to dimerization of anthracene.

Analysis of the spectra, as shown in Table 6.7b, revealed that a self-consistent picture is obtained only on the assumption that the only product formed by chloranil in this case is the tetrachlorohydroquinone.

The analysis was performed as follows:

Two different expressions can be written for the absorbance of

the irradiated mixture.

$$l [c_1 \epsilon_1 + (c_{10} - c_1) \epsilon_4 + c_6 \epsilon_6] = A \quad (I)$$

and

$$l [c_1 \epsilon_1 + c_4 \epsilon_4 + c_6 \epsilon_6] = A \quad (II)$$

where c_{10} = starting concentration of chloranil.

c_1 = final concentration of chloranil and ϵ_1 its extinction coefficient.

c_4 = concentration of tetrachlorohydroquinone and ϵ_4 its extinction coefficient.

c_6 = concentration of anthracene and ϵ_6 its extinction coefficient.

In both expressions, c_6 is calculated from absorbance measurements at 365 nm, since, particularly after irradiation, anthracene alone may be assumed to absorb at that wavelength.

In expression I, the concentration of tetrachlorohydroquinone (QH₂ I) in the irradiated mixture, is equated to the difference between the starting concentration and the final concentration of chloranil. Hence, only one equation is needed to calculate the value of c_1 .

In expression II, the concentration of QH₂ I is treated as a separate quantity unrelated to c_{10} and c_1 , and hence two equations are necessary to find c_1 and c_4 .

Table 6.7b.

Case I, $c_6 = 1.05 \times 10^{-4} \text{ mol l}^{-1}$

Duration of Irradiation = 3 hours.

Case II, $c_6 = 0.9635 \times 10^{-4} \text{ mol l}^{-1}$

Duration of Irradiation = 45 minutes.

Substance	Concentration, mol l^{-1}				
	From Expression I		From Expression II	From Expression III	
	From absorbance at 290 nm	From absorbance at 310 nm		From absorbance at 290 nm	From absorbance at 310 nm
Q I } Case I	0.1414×10^{-4}	0.1417×10^{-4}	0.1417×10^{-4}	0.1370×10^{-4}	0.152×10^{-4}
QH ₂ I }	0.0290×10^{-4}	0.0292×10^{-4}	0.0283×10^{-4}	0.033×10^{-4}	0.018×10^{-4}
Q I } Case II	0.1125×10^{-4}	0.1120×10^{-4}	0.1119×10^{-4}	0.106×10^{-4}	0.127×10^{-4}
QH ₂ I }	0.0579×10^{-4}	0.0576×10^{-4}	0.0582×10^{-4}	0.064×10^{-4}	0.043×10^{-4}

Measurements of absorbance made at 290 nm and 310 nm were introduced in expression I and II and the relevant concentrations calculated since ϵ_1 , ϵ_4 , and ϵ_6 were known at the above wavelengths.

The agreement is excellent.

The expression

$$1 [c_1 \epsilon_1 + (c_{10} - c_1) \{ 0.55\epsilon_4 + 0.3\epsilon_2 + 0.15\epsilon_3 \} + c_6 \epsilon_6] = A \quad (\text{III})$$

was derived from the knowledge obtained from runs using chloranil alone in which as Table 6.4 shows the concentrations of QH₂, II and Q III were 30 per cent and 15 per cent respectively of the total quinone lost. The values of c_1 calculated with the help of expression III using optical densities at 290 nm and 310 nm were, as can be seen from Table 6.7b beyond the limits of experimental error.

b) Irradiation of Chloranil-Anthracene Mixtures at 437 nm.

To verify that transfer of energy between the excited anthracene molecule and the quinone molecule does take place, mixtures of chloranil and anthracene were irradiated at 437 nm since at this wavelength anthracene does not absorb, but chloranil does, though very weakly. ($\epsilon = 40 \text{ l mol}^{-1} \text{ cm}^{-1}$) As Porter ⁽⁶³⁾ has reported, there was also the possibility that anthracene may act as a quencher in this reaction at this wavelength.

Chloranil alone, as well as a chloranil-anthracene mixture, as is shown in Table 6.7a, gave a normal overall quantum efficiency of nearly 0.3.

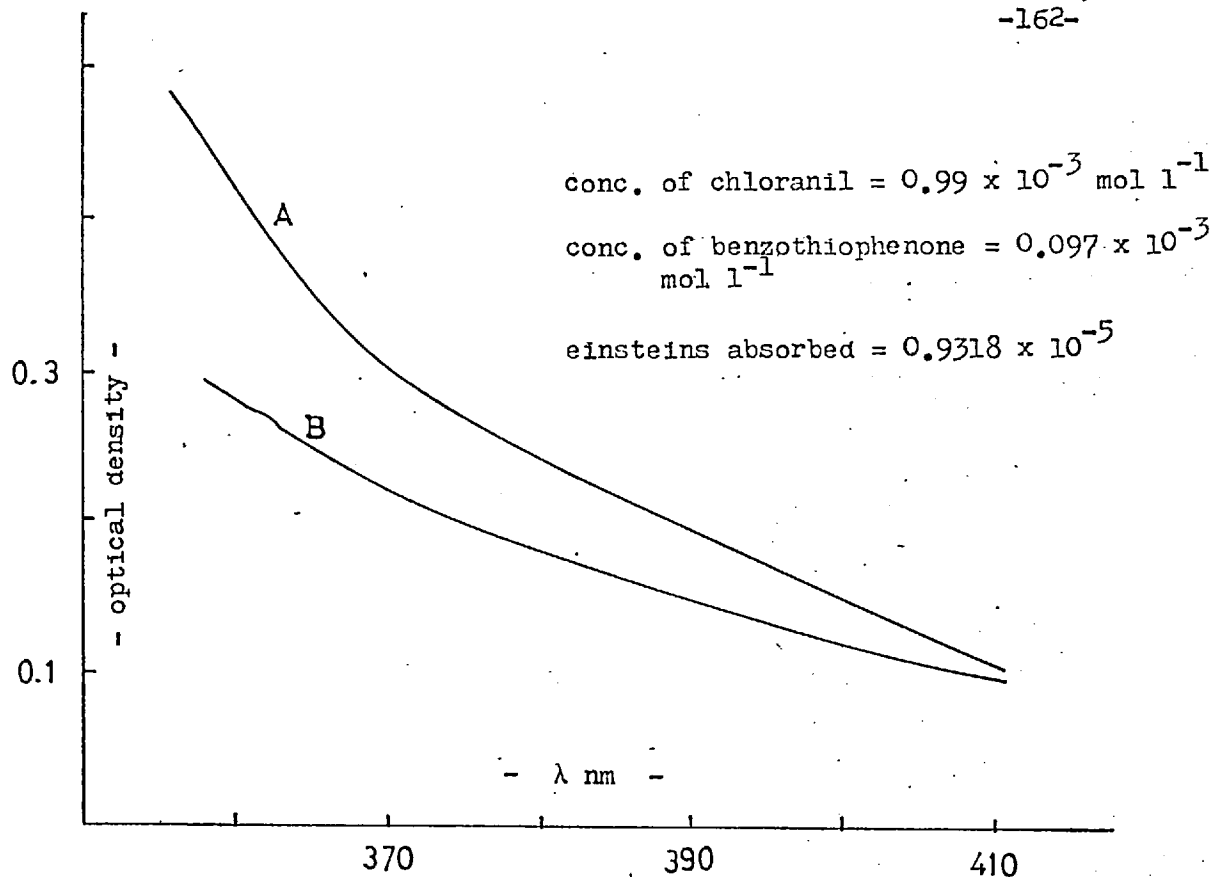


Figure 6.12a.

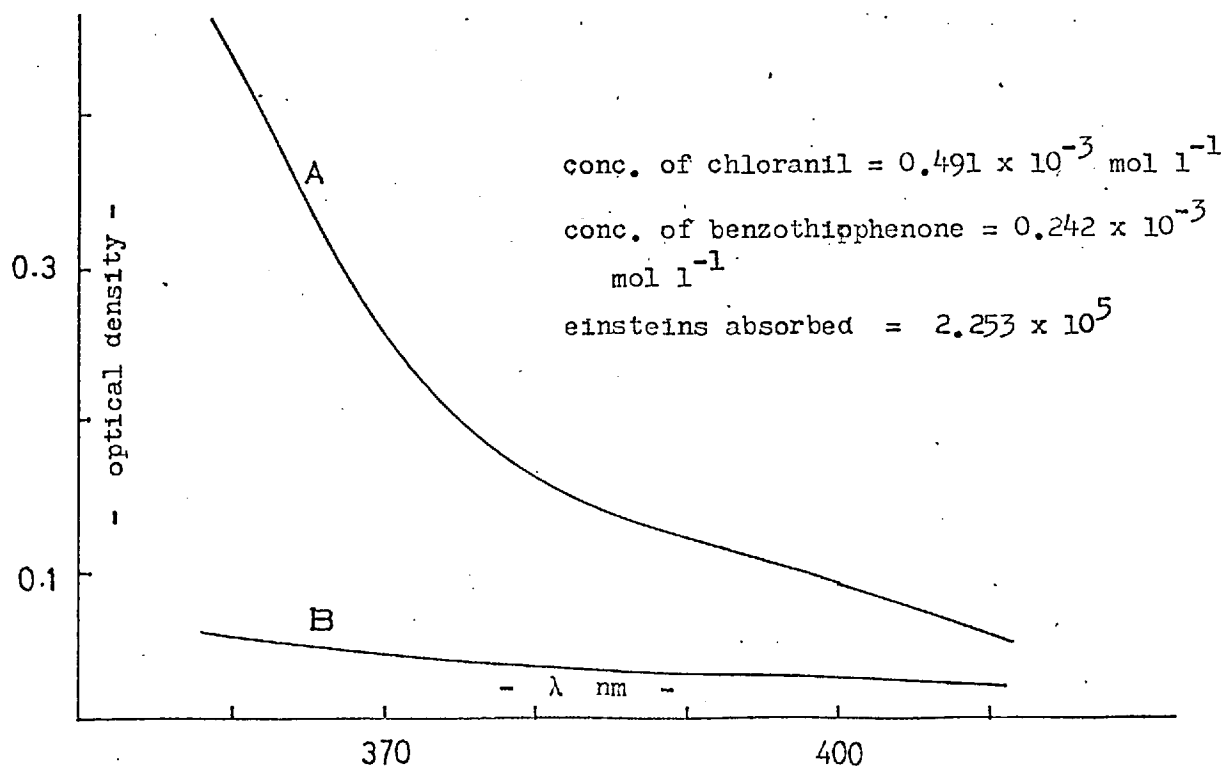


Figure 6.12b.

Excited anthracene, therefore, transfers its energy to chloranil, but ground-state anthracene does not act as quencher.

c) Chloranil-Thiobenzophenone Mixtures.

Thiobenzophenone absorbs strongly at 365 nm and fluoresces. According to data available in the literature,⁽¹¹⁶⁾ this ketone is reduced in isopropanol at 365 nm with a quantum yield of reduction of 0.047. This present work, however, found that the quantum efficiency for loss of ketone is 0.3. This figure is not strictly quantitative because no allowance was made in the measurement of light absorbed for the fluorescence of the compound.

Fig. 6.11 shows that the fluorescence of thiobenzophenone is not quenched by the addition of a significant amount of chloranil. (see page 151) Singlet - singlet energy transfer is, therefore, ruled out.

In the present series of runs, concentrations were adjusted so that in some cases, chloranil absorbed most of the light and in others thiobenzophenone absorbed most of it. Results are given in Table 6.8, and Fig. 6.12a and b give the spectra of two typical mixtures before and after irradiation.

Benzothiophenone has peak absorption at 315 nm which decreases rapidly to very nearly zero at longer wavelengths, thus making optical density measurements at 365 nm rather difficult to obtain with accuracy.

Quantum efficiencies for loss of quinone or ketone were calculated by obtaining the values of the concentration of chloranil and benzothiophenone left behind from two equations set up with

Table 6.8. Chloranil - Benzothiophenone - Isopropanol Solutions (Anaerobic)

$\lambda = 365 \text{ nm}$ $T = 20^\circ\text{C}$.

Chloranil (Q I)			Benzothiophenone (BTP)			$\phi_{\text{loss Q I}}$	$\psi_{\text{loss BTP}}$	$I t \times 10^5$ einsteins
$c \times 10^3$	Absorbance	% of Total Absorbance	$c \times 10^3$	Absorbance	% of Total Absorbance			
0.4909	0.1350	39	0.2424	0.2000	61	0.62	0.63	2.253
0.9907	0.2675	77	0.097	0.0818	23	0.82	0.06	0.9318
0.7270	0.2000	23.5	0.764	0.6500	76.5	0.027	0.85	3.4073
0.9150	0.2515	100	0	0	0	0.28	-	1.424
0	0	0	1.388	1.18	100	-	0.31	1.714

the help of optical density measurements made at 365 nm, and 380 nm assuming that the products of irradiation do not absorb at those wavelengths.

The actual values of the quantum efficiencies given in Table 6.8 should be smaller, since, as was mentioned earlier, allowances for the fluorescence of benzothiophenone were not made.

Table 6.8 shows that when chloranil was allowed to absorb two thirds of the incident light, the quantum efficiency for loss of quinone was higher than normal and that for loss of ketone very much lower than normal. The reverse is seen to be true when the ketone is allowed to absorb two thirds of the light.

By analogy with the results obtained with chloranil-anthracene mixtures, the conclusion that can be drawn is that there seems to be energy transfer between the quinone and ketone molecules but that the direction of transfer depends on their relative concentrations.

6.10. EXPERIMENTS WITH TRICHLOROQUINONE.

6.10.1. Interaction between Trichloroquinone and Trichlorohydroquinone.

The presence of trichlorohydroquinone (QH_2 II) in the irradiated solutions of chloranil indicated the relevance of an investigation of the photochemical behaviour of trichloroquinone (Q II).

Solutions of Q II in isopropanol were found to be unstable. A 0.87×10^{-3} mol l^{-1} solution stored for six weeks showed a 50 per cent decrease in optical density. The mass spectrum of the residue

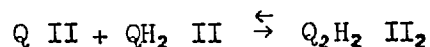
left after evaporation of solvent revealed the presence of QH_2 II and also QH_2 I (tetrachlorohydroquinone). The sample of Q II used to prepare the solution was analysed in the mass spectrometer and was found to contain less than 2 per cent of chloranil. The mass spectrum of the residue referred to above, however, showed a nearly 5 per cent chloranil content. There seemed to be, therefore, some basis to suspect that an interchange of chlorine atoms between molecules of Q II and QH_2 II had taken place.

Solutions of QH_2 II in isopropanol were also unstable. The optical density of solutions of QH_2 II in isopropanol kept standing for one or two weeks was found to increase, presumably due to oxidation of the hydroquinone.

Fresh solutions had to be made before every experiment. Solutions of Q II, as well as QH_2 II, were made with isopropanol degassed with oxygen-free nitrogen. The alcohol was gently warmed on a water bath when solutions of Q II had to be prepared. After dissolving the quinone or hydroquinone, oxygen-free nitrogen saturated with isopropanol was again passed through the solutions.

Evidence for an interaction between Q II and QH_2 II in solution was presented earlier. (Cfr Table 6.2b) It was at first thought that the interaction between the quinone and the hydroquinone led to the formation of a quinhydrone type of complex. On the basis of this assumption an attempt was made, making use of the optical

density measurements at 290 nm, to calculate the equilibrium constant k of the reaction



and the extinction coefficient of the complex at 290 nm.

However, when the suspicion arose that the interaction between the two seemed to consist in an interchange of a chlorine atom, the possibility of such an exchange was investigated. Known volumes of solutions of $Q \text{ II}$ and $QH_2 \text{ II}$ in isopropanol were mixed and stored under oxygen-free N_2 for three hours. The resulting concentrations in the mixture were

$$Q \text{ II} = 0.646 \times 10^{-3} \text{ mol l}^{-1}$$

$$QH_2 \text{ II} = 1.28 \times 10^{-3} \text{ mol l}^{-1}$$

Measurements of optical density of the mixture at 365 nm corresponded, within limits of experimental error, to $0.646 \times 10^{-3} \text{ mol l}^{-1}$ of the quinone. A portion of this mixture was exposed to air to allow the solvent to evaporate (Residue I) and another portion was distilled in vacuum (Residue II).

The mass spectrum of residue I was found to contain 16.5 per cent of tetrachlorohydroquinone, ($QH_2 \text{ I}$), and residue II had 32 per cent of the same. Percentages were calculated with respect to the 212 peak characteristic of $QH_2 \text{ II}$. No molecules heavier than $QH_2 \text{ I}$ were detected.

In residue I, the percentage of Q II was found to be less than 1 with respect to the 212 peak, whereas in residue II, it was nearly 10 per cent, still far below the 50 per cent that could be expected considering its starting concentration. Both mass spectra were run at 150°C and 70 V. It, therefore, became clear that the composition of the residue depended on the way the mixture was handled.

Unfortunately this insight into the behaviour of such mixtures was gained only later during the course of the work described in this section and hence the results recorded on the basis of evidence from mass spectra cannot be treated as quantitative.

However, the significant increase in the QH₂ I content of the mixture, compared to the maximum of 2 per cent that could be expected on the basis of 2 per cent impurity present in each of the components of the mixture, leads to the conclusion that an interchange of a chlorine atom seems to have taken place thermally in the mixture under the conditions described above. Such an interchange would be expected to lead to the formation of a dichloroquinone or dichlorohydroquinone.

The mass spectra of the two pure isomers of dichloroquinone, recorded under identical conditions as that of the above mixture, showed that these compounds have weak parent peaks, but a very strong breakdown peak of mass 88. In the mass spectrum of the mixture of Q II and QH₂ II, the 176 and 178 peaks characteristic

of dichloroquinone and dichlorohydroquinone showed only minor increases of about 2 per cent over the heights expected from the breakdown of Q II and QH₂ II. A very small peak of mass 88 was hardly measurable with any accuracy even at high amplifications. The virtual absence of this peak in the mass spectrum of the mixture makes it difficult to accept the presence of tetrachlorohydroquinone as conclusive evidence that the interchange of a chlorine atom has taken place in the mixture.

6.10.2. Irradiation Of Solutions Of Trichloroquinone.

Anaerobic solutions of trichloroquinone in isopropanol were irradiated at 365 nm and the reaction followed in exactly the same way as in solutions of chloranil. Figure 6.13, gives the plot of quinone lost against light absorbed. The initial quantum efficiencies obtained from a number of runs with different quinone concentrations are tabulated in Table 6.9.

Table 6.9.

Run	Starting Conc. of Q II $\times 10^3 \text{ mol l}^{-1}$	Φ_1
(1)	0.135	0.745
(2)	0.297	0.742
(3)	0.513	0.820
(4)	0.548	0.750

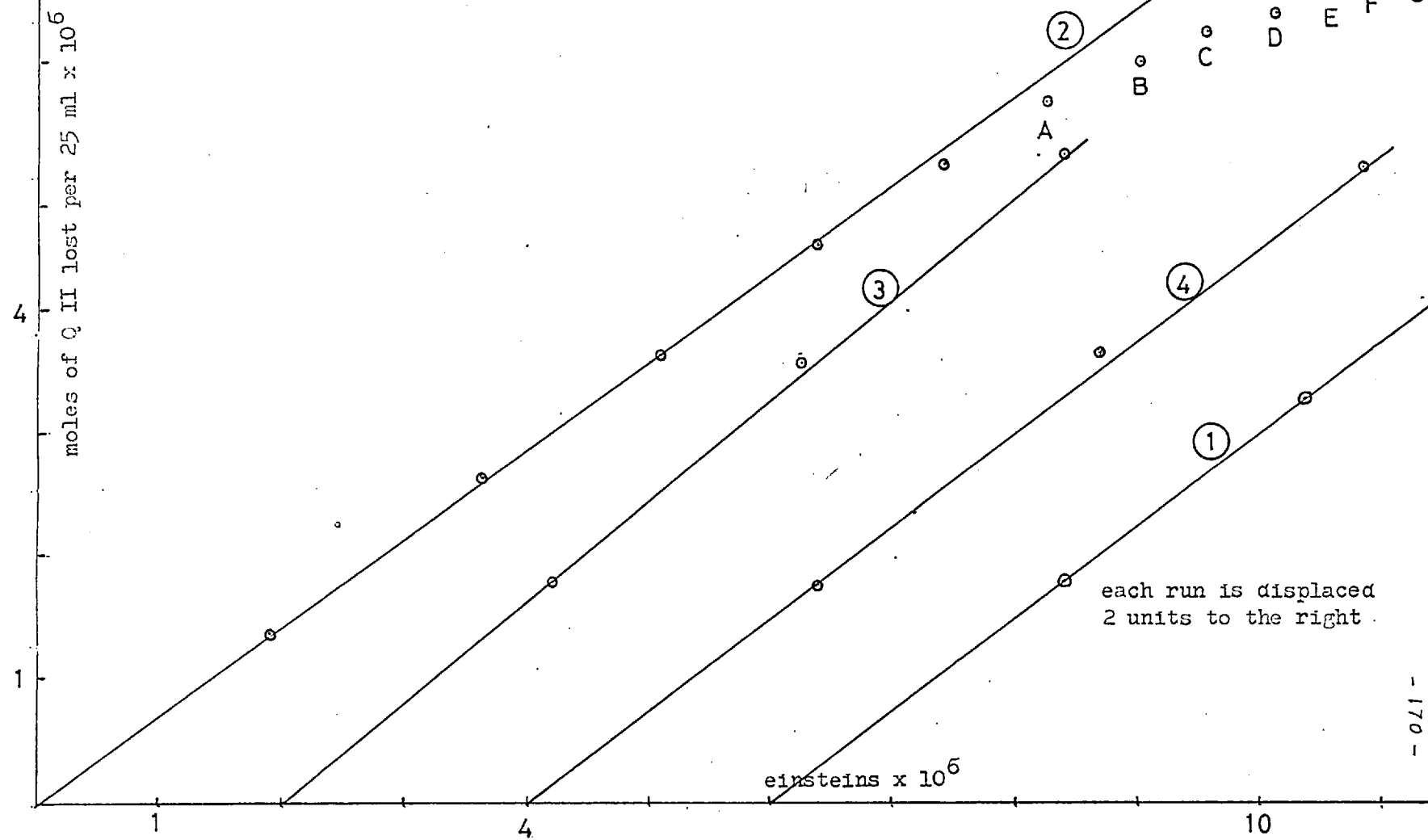
Starting concentrations $\times 10^3 \text{ mol l}^{-1}$

Run 1 - 0.135

2 - 0.297

3 - 0.513

4 - 0.548



The high quantum efficiency for run (3) was probably due to some undiscovered experimental error, since the values derived from the remaining three runs are in good agreement over the concentration range studied.

The quantum efficiency during the run does not seem to be noticeably affected by the formation of hydroquinone until about 70 per cent of the quinone has reacted.

Run (3) lasted for 3 hours, at which point reaction had virtually ceased although the optical density did not drop quite to zero. After irradiation, the solvent was distilled off under vacuum from a portion of the solution from this run using the same technique as with chloranil solutions. Potentiometric titrations of the solvent against silver nitrate did not reveal the presence of chloride ions.

Another portion of the irradiated solution was exposed to air and the residue left after evaporation was analysed in the mass spectrometer.

The spectrum showed the presence of QH_2 II and less than 2 per cent of QH_2 I. The 210 peak characteristic of Q II was hardly measurable even at high amplification. The ratio of peak heights, as Table 6.10 shows, did not correspond at all to the corresponding ratios in the mass spectrum of pure QH_2 II.

Table 6.10.

Ratio of peak heights.	Residue from irradiated solution	Pure QH ₂ II
180/212	0.026	0.20
178/212	0.073	0.37
176/212	0.055	0.13
141/212	0.022	0.05

The absence of a breakdown peak of mass 88 was a good confirmation of the conclusion that Q II does not lose an atom of chlorine on irradiation since a peak at 88 corresponding to C₇HClO is characteristic of 2,5 and 2,6-dichlorobenzoquinone.

6.10.3. Irradiation Of Mixtures Of Trichloroquinone And Trichlorohydroquinone.

Mixtures of solutions of Q II and QH₂ II in isopropanol were irradiated with a view to finding out whether the exchange of a chlorine atom takes place also under the influence of ultraviolet light, and to what extent the presence of the hydroquinone affects the quantum efficiency of reduction of the quinone.

Mixtures were prepared by pipetting directly into the cell known amounts of freshly prepared solutions of Q II and QH₂ II in isopropanol so that the total volume of the mixture was 25 ml.

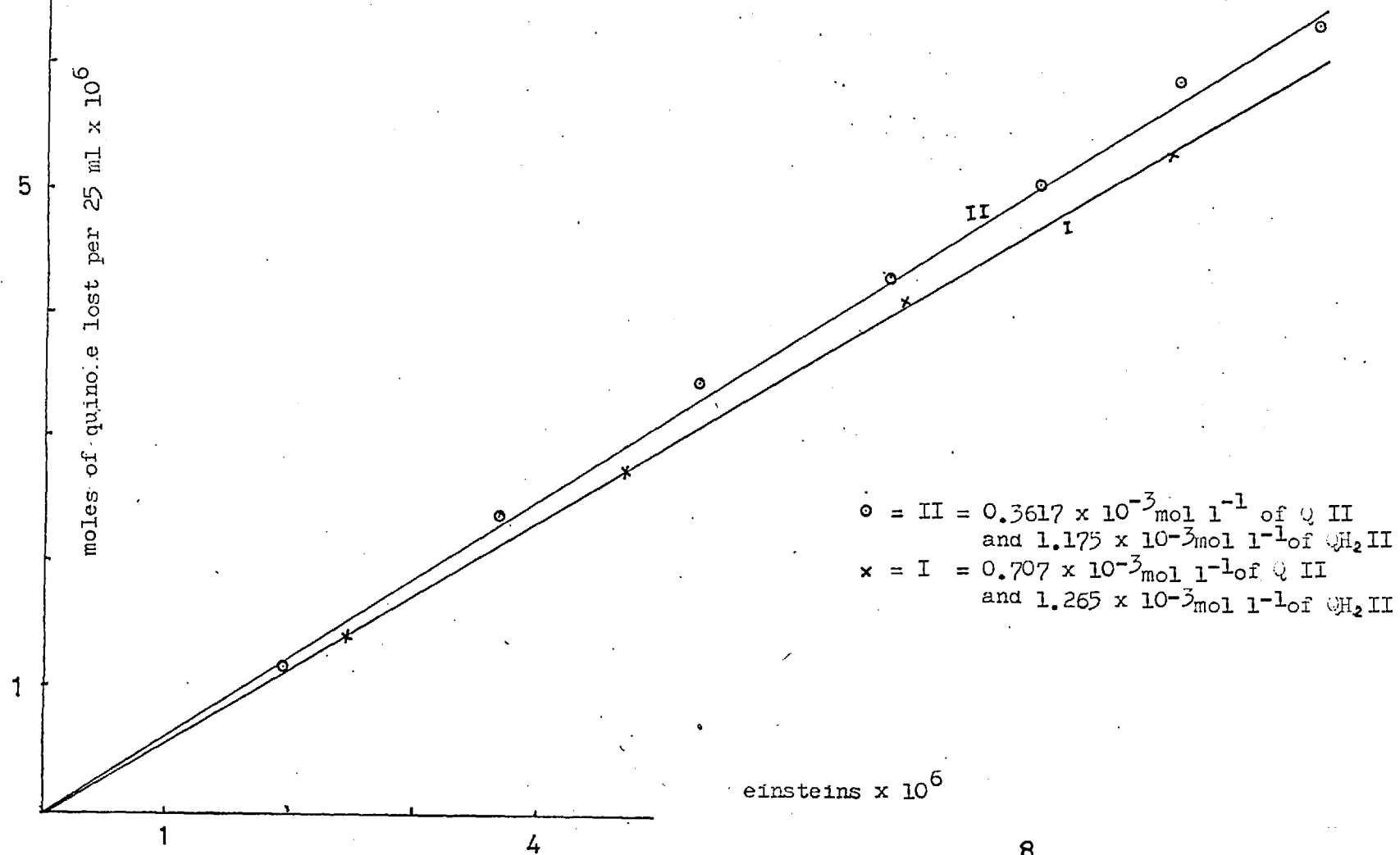


Figure 6.14.

The mixture was degassed with oxygen-free nitrogen for about 30 minutes and then allowed to stand for a further two hours to attain equilibrium. The reaction caused by irradiation was followed in the same way as with solutions of chloranil.

Fig. 6.14, which plots light absorbed against quinone reduced for two separate runs with different starting concentrations of quinone and hydroquinone, shows that the initial quantum efficiency of reduction has fallen from 0.75 to 0.637 and 0.595 in runs (1) and (2) respectively. Since the concentration of hydroquinone in both mixtures was nearly the same, the small variation of ± 3 per cent in the values of the quantum efficiency can be attributed to experimental error. An average value of 0.61 can be taken to represent the initial quantum efficiency of reduction of Q II in the presence of 1.2×10^{-3} mol l⁻¹ of QH₂ II.

The residue left after evaporating, by exposure to air, the solvent from the solution in run (2) was analysed in the mass spectrometer. The results of measurements of height of peaks in the mass spectra of Q II, QH₂ II and of the unirradiated as well as the irradiated mixture of Q II and QH₂ II are given in Table 6.11.

Q II in itself was found to give a weak mass spectrum and in mixtures of Q II and QH₂ II, with a large excess of the latter, the

position was found to be even worse.

Table 6.11.

Peak height Ratio	Q II	QH ₂ II	Mixture	
			Unirradiated	Irradiated
210/212	1.00	0.0	0.01	0.01
180/212	-	0.207	0.036	0.08
178/212	-	0.370	0.086	0.253
176/212	-	0.13	0.072	0.290
141/212	-	0.05	0.030	0.087
88/212	-	-	0.006	0.137

The ratios tabulated in 6.11 were measured with reference to the height of the 212 peak since this was the most intense peak in the spectra of mixtures.

For the calculation of the ratios in the table, the following ratios were first obtained from the mass spectra of the pure substances concerned.

248/212 from the mass spectrum of chloranil,

210/212 from the mass spectrum of trichloroquinone,

176/212 } from the mass spectrum of trichlorohydroquinone.
141/212 }

In conjunction with the relative abundance of chlorine isotopes given in the literature,⁽¹¹⁷⁾ these ratios enabled the contribution to the peaks in the mass spectrum of the mixture made by each of the substances present in it to be assessed. When all such contributions were subtracted from the actual heights of peaks in the spectrum of the mixture, the remainder served to give an indication of the new substances that were formed as a result of the interaction between the quinone and hydroquinone before and after irradiation, substances whose parent peaks happened to coincide with the breakdown peaks of heavier molecules.

The 176, 178 and 180 peaks were chosen because they are characteristic of the isomers of dichloroquinone and dichlorohydroquinone, the 141 peak because it appears prominently in irradiated mixtures, and the 88 peak because it is the strongest breakdown peak in the mass spectra of both isomers of dichloroquinone.

The method of calculation outlined above gave the value of the ratio of peaks 141/176 in the irradiated mixture as 0.23, and 88/176 as 0.51. The corresponding ratios in the isomers of dichloroquinone are given in Table 6.12.

Table 6.12.

Peak Height Ratio	2,5-dichloro	2,6-dichloro	Irradiated mixture
141/176	0.1	0.24	0.23
88/176	> 1	0.72	0.51

Experimental evidence, therefore, seems to indicate the formation of 2,6-dichloroquinone as a result of irradiation since the ratios 141/176 and 88/176 seem to be in better agreement with those obtained for this isomer rather than with those obtained for the 2,5 one.

New peaks after irradiation were found to appear at 106, 107, 108, 129, 131, 132, 95, 96, 74 and 75 mass units.

Measurements of heights of peaks characteristic of tetrachlorohydroquinone, i.e. 248, 246, + 244, however, did not indicate any increase in the concentration of this hydroquinone. In fact, there seemed to be a less than 1 per cent decrease, which, however, could be accounted for by instrumental variations.

CHAPTER 7

Discussion

7.1. CHLORANIL.

7.1.1. Summary of Experimental Evidence.

A summary of the experimental evidence obtained in the irradiation of solutions of chloranil is given below:

(a) Anaerobic solutions of chloranil in isopropanol irradiated at 365 nm gave as reaction products tetrachlorohydroquinone (QH₂ I) trichlorohydroquinone (QH₂ II) and trichlorohydroxyquinone (Q III). The initial quantum efficiencies of formation of these compounds are 0.252, 0.132 and 0.066 respectively. The initial quantum efficiency for loss of chloranil is 0.45. The main product formed from isopropanol, the substrate, was acetone. A small amount of unsaturated hydrocarbons and propylene oxide were also detected. The quantum efficiency of formation of acetone is 0.383.

(b) Aerobic solutions of chloranil in isopropanol irradiated at 367 nm, yielded from the quinone only trichlorohydroxyquinone (Q III), with an initial quantum efficiency of 0.199. The following relationship is found between the initial quantum efficiencies of the trichloro - products in anaerobic and aerobic solutions;

$$\phi_{Q \text{ III, aerobic}} = \phi_{QH_2 \text{ II, anaerobic}} + \phi_{Q \text{ III, anaerobic}}$$

In the aerobic solutions, isopropanol was oxidized to acetone with an initial quantum efficiency of 0.98.

(c) Aerobic as well as anaerobic solutions of chloranil in fluorochemical inert liquid FC-75, irradiated at 365 nm did not

show any reaction.

(d) Anaerobic solutions of chloranil in isopropanol containing enough anthracene to absorb 98 per cent of incident light at 367 nm, reacted with a quantum efficiency for loss of quinone very much larger than unity, the exact value depending upon the duration of irradiation. The spectrum of the irradiated mixture could be accounted for only on the assumption that tetrachlorohydroquinone is the sole product of the reaction.

(e) Anaerobic solutions of chloranil in isopropanol irradiated at 437 nm gave the same overall quantum efficiency for loss of quinone as solutions containing a mixture of chloranil and anthracene. Anthracene does not absorb at 437 nm.

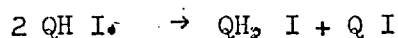
(f) Anaerobic solutions of chloranil and benzothiophenone in isopropanol irradiated at 365 nm gave an overall quantum efficiency for loss of quinone which varied directly with the percentage of light absorbed by the quinone in the mixture. When chloranil absorbed most of the light (75 per cent) the quantum efficiency for loss of quinone in the mixture was much higher than the normal overall quantum efficiency for the same duration of irradiation, and the quantum efficiency for loss of ketone was much lower than the normal quantum efficiency under the same conditions. The position was reversed when benzothiophenone absorbed most of the light (75 per cent).

7.1.2. Conclusions.

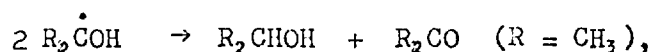
In view of the experimental evidence summarized above the following conclusions can be derived.

(1) The quantum efficiency of nearly unity for the formation of acetone in the irradiation of aerobic solutions of chloranil in isopropanol indicates that the quantum efficiency of formation of the photoexcited species is nearly unity.

(2) The initial quantum efficiency for loss of quinone in the absence of air is only 0.45. Hence ^{semi}quinone radicals, in anaerobic solutions, disproportionate thus



The initial quantum efficiency for the formation of acetone in the absence of air is only 0.383. This suggests not only that, under the conditions of the experiment, 2-hydroxyprop-2-yl radicals disproportionate thus

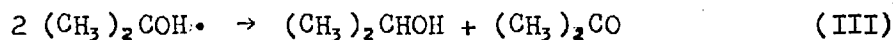
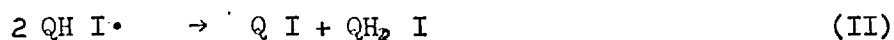
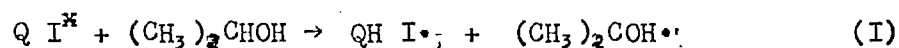


but also that acetone is not the only product of oxidation of the substrate.

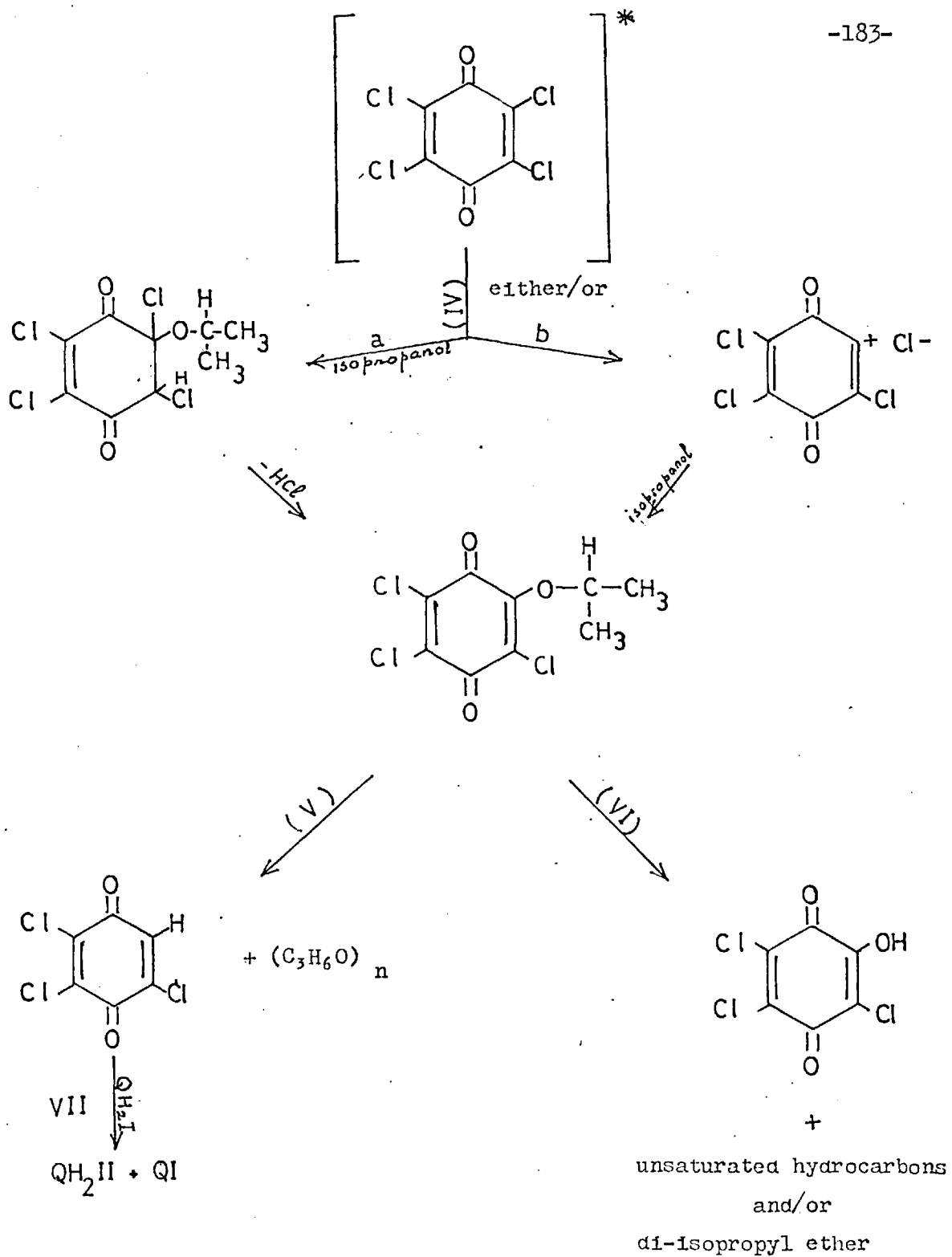
(3) The mechanism of the reaction clearly includes the formation of the semiquinone free radical from chloranil and its subsequent disproportionation. In the presence of oxygen the semiquinone radical is oxidized back to chloranil. Products containing only three chlorine atoms in the aromatic ring are formed with an efficiency close to 0.2

in both aerobic and anaerobic solutions. They must arise from a common precursor which is not the semiquinone of chloranil.

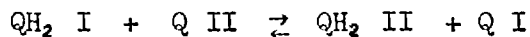
There are two distinct reactions of the excited state of chloranil, one leading to the formation of tetrachlorohydroquinone and the other to the formation of the trichloro products. In the mechanism given below tentative suggestions are made as to possible intermediates in the reactions by which chloride is formed.



(P.T.O. for other reactions in the mechanism)

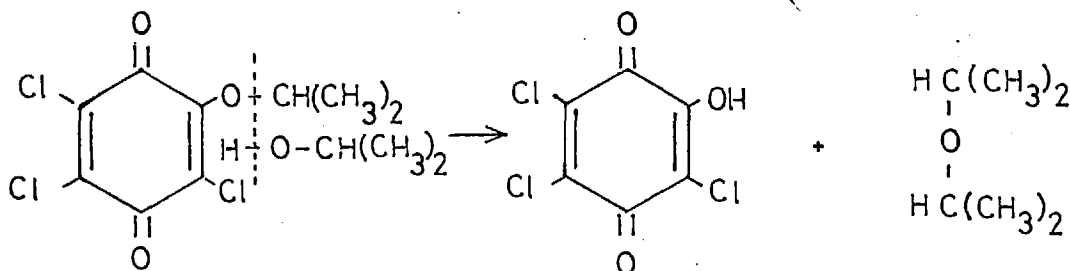


Reaction VII is justified by the evidence presented in Chapter 6, (Cfr Table 6.2 d and e), where it was shown that the equilibrium of the reaction



is almost entirely displaced to the right.

The formation of di-isopropyl ether can readily be envisaged as arising from the hydrolysis of the intermediate ester by isopropanol.



If in the above mechanism, the product of reaction(V) is acetone,

$$\phi_{\text{acetone}} = \phi_{QH_2 \text{ I}} + 2 \phi_{QH_2 \text{ II}}$$

since an amount of $QH_2 \text{ I}$ equal to the concentration of $QH_2 \text{ II}$ has been used up in reaction (VII). The experimental results, however, show that

$$\phi_{\text{acetone}} = \phi_{QH_2 \text{ I}} + \phi_{QH_2 \text{ II}} \text{ precisely.}$$

It must be noted that the figure for ϕ_{acetone} was obtained not indirectly but by direct measurement in which there were no reasons to suspect any deviations beyond the limits of experimental error.

On the basis of evidence of the presence of propylene oxide and hydrocarbons in bulk-irradiated samples it is suggested that reaction (V) produces propylene oxide rather than acetone.

The epoxide and hydrocarbons were not quantitatively estimated because in solutions irradiated on the optical bench, they seemed to be present in such minute concentrations that it was impossible to estimate them with the equipment available.

The fact that the hydrocarbons in such solutions did not make their presence felt in the chromatogram is understandable given the ease with which they are liable to be lost, but the failure of the epoxide to lend itself to measurement cannot be easily explained. According to the extrapolated values of the initial quantum efficiencies (Cfr. Table 6.4) of the various products of irradiation, the area of the epoxide peak would be expected to be about 35 per cent of the acetone peak. The upper limit of sensitivity, above which the chromatogram was too unsteady to be of any value, was still not high enough to produce a measurable epoxide peak. It may be possible, in future investigations, to find a different packing material for the column which will separate quantitatively the epoxide from the alcohol at lower sensitivities.

The breaking up of the epoxide, under the conditions of the experiment, to give various products in small concentrations, may be another reason why the epoxide peak fell below the working limits of the sensitivity of the chromatograph.

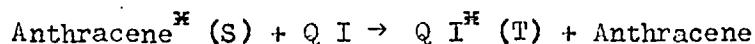
Possibly the chromatographic column was not suitable for the detection and separation of di-isopropyl ether, which again can be expected to be present only in very small concentrations.

(4) It is now necessary to consider the nature of the excited state of chloranil in the photochemical reactions (I) and (IV).

Experimental evidence referred to in Section 7.1 (d), (e) and (f) suggests the transfer of energy from anthracene and benzothiophenone to chloranil.

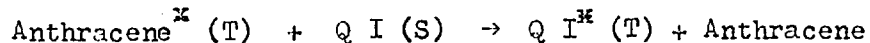
A singlet-singlet excited state transfer from the donor to the acceptor molecule is ruled out in this case because chloranil was found to be ineffective in quenching the fluorescence of benzothiophenone.

A singlet-triplet transfer as



is highly unlikely because of lack of spin conservation.

The only reasonable assumption is therefore, that a triplet-triplet energy transfer has taken place from excited anthracene or benzothiophenone to ground state chloranil thus



Recent spectroscopic studies ⁽¹¹⁸⁾ have established that there are two triplet states (T_1 , T_2) of anthracene with energies less than that of the lowest excited singlet state. The intersystem crossing from the excited singlet to the lowest triplet T_1 proceeds via the second triplet T_2 . T_1 lies at 14800 cm^{-1} ($42.5 \text{ kcal mol}^{-1}$) and T_2 lies at 25440 cm^{-1} ($74.4 \text{ kcal mol}^{-1}$).

T_2 has a short lifetime, of the order of 10^{-10} s, but that does not prevent it from taking part in fast energy transfer processes as was shown by Liu and Edman (119) who used anthracene and its substituted derivatives to sensitize the rearrangement of rigid molecules like norbornadiene and benzonorbornadiene, whose triplets have energies of about 72 kcal mol^{-1} and where the concept of "nonvertical excitation" (120) is inapplicable due to geometric restriction arising from the rigidity of the molecule.

That T_2 is not the triplet involved in the triplet-triplet energy transfer from anthracene to chloranil can be argued from the fact that T_2 has an energy of $74.4 \text{ kcal mol}^{-1}$ which is far in excess of what can reasonably be expected for chloranil considering that the $n\pi^*$ triplet of parabenzoquinone has an energy of 50 kcal mol^{-1} . The addition of chlorine to the aromatic ring, as was pointed out in Chapter 2, does increase the energy of the $n\pi^*$ states, but a jump of over 20 kcal mol^{-1} for the addition of four atoms of chlorine is improbable.

The fact that benzothiophenone which, as far as is known, produces only its lowest $n\pi^*$ triplet at 14000 cm^{-1} , sensitizes the photoreduction of chloranil also argues against T_2 of anthracene being involved in the energy transfer.

The choice of anthracene and benzothiophenone as sensitizers was based on conclusions arrived at by putting together theoretical and

experimental data supplied by Sidman (33) and Giacometti and co-workers (35).

The singlet-triplet splitting, ΔE_{ST} , in the $n\pi^*$ state of parabenzoquinone has been experimentally determined and found to be equal to 3200 cm^{-1} .

In the $\pi_3\pi_5^*$ state, according to Sidman's calculations for parabenzoquinone ΔE_{ST} is about 10500 cm^{-1} and in the $\pi_4\pi_5^*$ state, it is about 21000 cm^{-1} . If the theoretical values for ΔE_{ST} in the above states are assumed to apply to the molecule under experimental conditions, the $\pi_3\pi_5^*$ and $\pi_4\pi_5^*$ triplet levels of parabenzoquinone should lie at 25000 cm^{-1} and 20000 cm^{-1} respectively.

Now, if the assumption is made that ΔE_{ST} in the $n\pi^*$ and $\pi\pi^*$ states of chloranil is nearly the same as in the corresponding states of parabenzoquinone, the triplet levels of the states concerned can be fixed.

That ΔE_{ST} in the $n\pi^*$ state of chloranil is the same as in the corresponding state of parabenzoquinone is supported by evidence presented in Table 1.4 where ΔE_{ST} for a number of quinones is shown to be between $2000 - 3000 \text{ cm}^{-1}$, and by spectroscopic studies of the complex formed by parabenzoquinone and its chloroderivatives when dissolved in a mixture of alcohol and toluene. (121) These studies also lend support to the assumption that ΔE_{ST} in the $\pi\pi^*$ states of chloranil is the same as in the corresponding states of parabenzoquinone. The value of ΔE_{ST} for the $\pi_3\pi_5^*$ state of parabenzoquinone, according to Sidman, is

about 10500 cm^{-1} and the value obtained from spectroscopic studies of the complex referred to above is 10090 cm^{-1} .

Table 7.1 summarizes the conclusions. Values in brackets are arrived at on the basis of the assumptions described above.

Table 7.1.

State	p-Benzoquinone		Chloranil	
	Experimental	Theoretical	Experimental	Theoretical
	in cm^{-1}		in cm^{-1}	
$n\pi_5^*$ (S)	21780	31450	22000	
(T)	18550	23400	(19500)	
$\pi_3\pi_5^*$ (S)	35490	45980	26500	24400
(T)	(25000)	35490	(16000)	(14000)
$\pi_4\pi_5^*$ (S)	41130	50800	35000	36150
(T)	(20000)	29840	(14000)	(15000)

All values in Table 7.1, with the exception of the value for the $n\pi_5^*$ chloranil singlet, have been taken from Sidman ⁽³³⁾ and Giacometti ⁽³⁵⁾ and refer to molecules in the vapour phase. The value for the $n\pi_5^*$ chloranil singlet was taken from a recent paper by Trommsdorf and co-workers. ⁽¹²²⁾ Working with a crystal of chloranil at liquid helium temperature, they recorded a spectrum which showed two distinct zones of absorption, a very feeble one from 21200 cm^{-1}

to 21900 cm^{-1} and a much more intense one from $21900 - 23500\text{ cm}^{-1}$. This last value for the $\pi\pi^*$ singlet was chosen because of its greater intensity of absorption and because it fits in well with the expectation that the addition of chlorine to the aromatic ring will raise the energy of the $\pi\pi^*$ state of chloranil over that of the parent quinone.

Table 7.1 shows that whereas in parabenzoquinone the lowest triplet is a $\pi\pi^*$ triplet at 18550 cm^{-1} , in chloranil the lowest triplet is a $\pi\pi^*$ triplet lying between $14000 - 1600\text{ cm}^{-1}$. The experimental data presented in this work suggests that the chloranil triplet is nearer the 14000 cm^{-1} level since anthracene has its lowest triplet at 14800 cm^{-1} and benzothiophenone at 14000 cm^{-1} .

Recalling the principles discussed in Chapter 1 it must be noted that the chloranil triplet does not behave like a pure $\pi\pi^*$ triplet, since the quantum efficiency of formation of the semiquinone, a reaction that is taken to be characteristic of the $\pi\pi^*$ state, appears to be quite high.

Reference to Table 7.1 and Table 2.6 in Chapter 2 shows that the level of the $\pi_3\pi_5$ singlet estimated on the assumption that the red shift in this transition varies linearly with the number of chlorine atoms in the ring, lies close to the $\pi\pi^*$ singlet. This proximity of the two levels coupled with the fact that both transitions involve a B_{1g} state as the terminus ad quem, makes mixing of the $\pi\pi^*$ and $\pi\pi^*$ states in their singlet manifolds a virtual certainty. Mixing of the

two is more difficult to envisage in the triplet manifolds because of the wider gap between the triplet levels of the $\pi\pi^*$ and $\pi\pi^*$ states of chloranil but, again, the fact that the B_{1g} state is involved in both the triplet manifolds will facilitate the process.

(5) Reactions (I) and (IV) in the proposed mechanism are essentially different and, therefore, cannot be taken to involve identical photoreactive species of the quinone.

Addition or substitution at the carbon ring is characteristic of the $\pi\pi^*$ states of aromatic carbonyl compounds which, as has been stated in Chapter 1, have one of the carbon atoms of the ring as the most electrophilic atom. But, if reaction (IV) involved a $\pi\pi^*$ state of the quinone, one would expect the α -hydrogen of the alcohol to be abstracted as is normally the case with $\pi\pi^*$ states of carbonyl compounds.

The loss of a chlorine atom in products arising from reaction (IV) entails the weakening of the carbon-chlorine bond. Using the theoretical data given by Giacometti and co-workers⁽³⁵⁾ on the MOs of chloranil, it is possible to calculate the strength of the C-Cl bond in the excited $\pi\pi^*$ and $\pi\pi^*$ state of the molecule. Table 7.2 summarizes the results.

It is seen that whereas $\pi\pi^*$ excitation weakens the C-Cl bond, $\pi\pi^*$ excitation strengthens it slightly.

Granted that, as was stated earlier in this chapter, the chloranil

triplet in the reaction is a mixture of $\pi\pi^*$ and $\pi\pi^*$ configurations, it is still difficult to see why a considerable proportion of the excited molecules should react differently with the alcohol. If weakening of the C-Cl bond can be explained in terms of $\pi\pi^*$ excitation, the addition to the ring cannot, since the $\pi\pi^*$ state has oxygen as the most electrophilic atom.

Table 7.2.

State of Chloranil molecule	Charge Densities at				Bond Strengths			
	C ₁	C ₂	O	Cl	C ₁ -O	C ₁ -C ₂	C ₂ -C ₃	C ₂ -Cl
Ground	0.713	1.003	1.382	1.948	0.842	0.298	0.868	0.210
$\pi\pi_5^*$	0.831	1.107	1.033	1.958	0.710	0.409	0.764	0.178
$\pi_3\pi_5^*$	0.831	0.952	1.533	1.864	0.710	0.409	0.609	0.299
$\pi_4\pi_5^*$	0.831	0.998	1.384	1.842	0.713	0.409	0.655	0.267

The strongest argument against labelling the excited species in reaction (IV) as a $\pi\pi^*$ triplet, is the absence of any trichloro-products in dilute solutions of chloranil photolysed in the presence of anthracene as photosensitizer.

Taking all the experimental evidence into consideration, it is suggested that the excited species in reaction (IV) is a $\pi\pi^*$ singlet and that the trichloroproducts are formed via reaction (IV b)

The suggestion is based on the work of Fukui and co-workers (123) who, having studied the relation between the half-wave reduction

potentials of polyhalogenated compounds and their lowest unoccupied σ levels, concluded that in such compounds, the lowest unoccupied σ level lies below the lowest unoccupied π level. They supported their conclusion with theoretical calculations of π and σ electron systems in these compounds using the LCAO ASMO CI method. Their data shows that the probability of the lowest unoccupied σ level being found below the lowest unoccupied π level increases with the number of halogen atoms in the molecule.

Again, their theoretical calculations showed that the electron distribution of the lowest unoccupied level is greatly localized on the C-Cl bond, and the bond order of the level on the bond is negative and large in value. This suggests that delocalization of an electron to this antibonding level will cause a weakening of the C-Cl bond.

The substitution of hydrogen atoms in the aromatic ring by atoms of chlorine lowers the energy of the antibonding π orbitals as is evinced by the red shift in the allowed $\pi \rightarrow \pi^*$ transition of polyhalogenated aromatic compounds with respect to the position of the $\pi \rightarrow \pi^*$ transition of the parent compound. The work of the above-mentioned authors suggests that the unoccupied, i.e. antibonding σ levels, are also lowered in energy to such an extent that the lowest antibonding σ level actually falls below the lowest antibonding π level

with increasing number of chlorine atoms in the ring.

Table 7.3 shows the close resemblance in the lowering of the lowest unoccupied π orbital of the polychlorinated benzenes and the polychlorinated benzoquinones as judged from the position of the maximum absorption in the ultraviolet region corresponding to the formally allowed $\pi \rightarrow \pi^*$ transition.

Table 7.3. Solvent = Ethanol ; λ in nm.

Number of chlorine atoms	Position of chlorine atoms	$\lambda_{\max} (\pi \rightarrow \pi^* \text{ allowed transition})$	
		benzene	p-benzoquinone
0	-	255	243
1	-	264	253
2	ortho; 2,3	267 ^(a)	255
	meta ; 2,6	267 ^(a)	267
	para ; 2,5	266	266.5
3	1, 3, 5 ; -	273	273.5
	1, 2, 3 ;	273	
	1, 2, 4 ;	273	
4	1, 2, 3, 4 ; -	280	283
	1, 2, 3, 5 ; -	281	
	1, 2, 4, 5 ; -	285	
5		288	
6		291	

(124)
(a) Solvent - isooctane.

It can now be argued that since the work of Fukui and others⁽¹²³⁾ shows that the lowest unoccupied σ level in polychlorinated benzenes lies below the lowest unoccupied π level, it is logical to assume that the same is the case with polychlorinated p-benzoquinones. A $\pi \rightarrow \sigma^*$ transition is, therefore, quite probable in chloranil.

The excited state in reaction (IV) is taken to be a singlet since rupturing of bonds, a process that requires fairly high energy, is associated with singlet states. This view is strengthened by the failure of anthracene to sensitize, by triplet energy transfer, that excited state of chloranil which leads to the formation of the trichloro-products.

The rupture of the C-Cl bond in this case is not a homolytic process. Such a process would yield two free radicals which would abstract the α -hydrogen from the substrate and the resulting 2-hydroxyprop-2-yl radicals would disproportionate to give isopropanol and acetone. The value obtained for the quantum efficiency of formation of acetone clearly rules out this possibility.

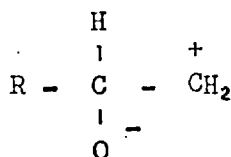
Homolytic rupture of the C-Cl bond can also be discarded on the basis of the failure to detect any reaction when solutions of chloranil in an inert solvent (FC-75) were irradiated at 365 nm. Free radicals formed by a homolytic rupture would lead to dimerization and consequently to a change in the optical density of the solution.

(6) A more definite mechanism can now be suggested for the reaction in anaerobic solutions:

The mechanism assumes that the weakening of the C-Cl bond in the $\pi \sigma^*$ excited state leads to a rupture of the same bond in the presence of the alcohol. It must be recalled here that Q III was isolated and identified as one of the reaction products in the irradiation of solutions of chloranil in ethanol. (111)

In anaerobic solutions, judging from the value of the quantum efficiency for the formation of QH_2 II as compared to that of Q III the migration of a hydride ion from a methyl group seems to be the favoured process.

The closing of the heterocyclic three-membered ring to produce the epoxide finds analogy in the reactions of aldehydes with diazocompounds where the intermediate (125) formed by the addition of the diazo compound to the carbonyl compound breaks up to give nitrogen and



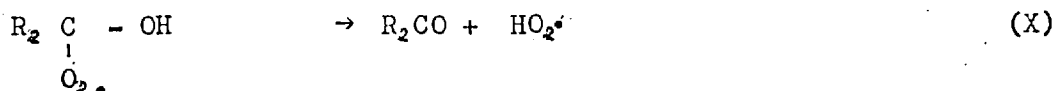
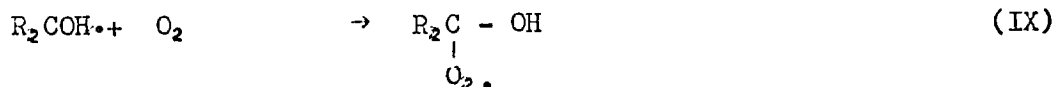
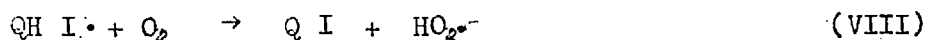
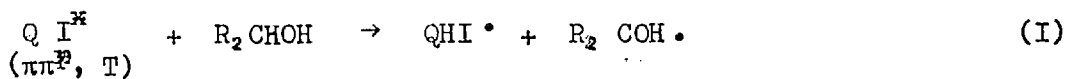
which subsequently gives a ketone and an epoxide. Since all the acetone quantitatively measured has been accounted for in other reactions, it has to be assumed that under the conditions of the experiments carried out in the course of this work, the epoxide alone is formed.

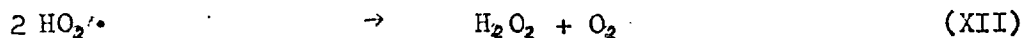
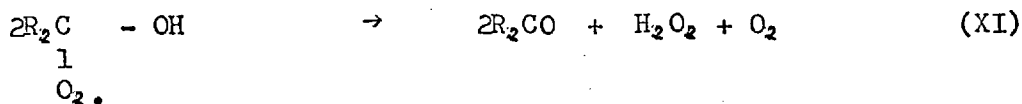
The aryl ether formed as an intermediate may either break up because of instability or undergo hydrolysis. Since no reliable experimental data as to the product derived from the substrate in this reaction is available, no choice can be made between paths (A) and (B).

(7) The high quantum efficiency of formation of acetone in aerobic solutions suggests that disproportionation of the 2-hydroxyprop-2-yl radical does not take place in the presence of oxygen. This is in agreement with the work of Wells (76) who reported a quantum yield of unity for the oxidation of isopropanol using anthraquinone derivatives as photosensitizers.

In the present work, however, a quantum yield of acetone of 0.98 implies that in aerobic solutions, the reaction of the triplet of chloranil as well as of the $\pi \sigma^{\pi}$ singlet with isopropanol leads to the formation of acetone.

The regeneration of the quinone and the formation of acetone from triplet chloranil and isopropanol follows from the standard reaction steps given below:



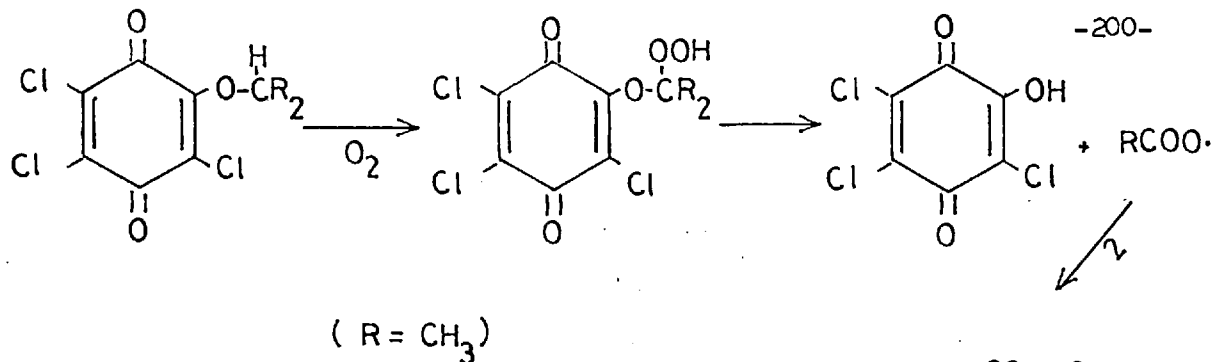


The absence of trichloroquinone in irradiated aerobic solutions indicates that oxygen prevents the migration of the hydride ion from the methyl group as postulated in anaerobic solutions. The only side-product obtained in such solutions was Q III which, it must be assumed, is formed via the aryl ether intermediate. The aryl ether may then break up via path (A) or path (B) as in anaerobic solutions.

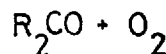
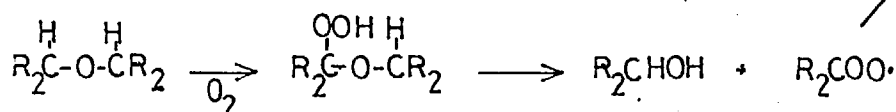
Ethers autoxidize with marked facility ⁽¹²⁶⁾. In particular, the reaction of di-isopropyl ether with oxygen has been reported to show the characteristic autoacceleration and susceptibility to added radical sources or inhibitors of a radical chain. ⁽¹²⁷⁾

The concentrations of Q III and acetone in irradiated aerobic solutions can be accounted for by the autoxidation of either the aryl ether or of di-isopropyl ether. This autoxidation may take place either by the straightforward addition of oxygen to the ether followed by decomposition of the hydroperoxide, or by a more complex chain reaction mechanism.

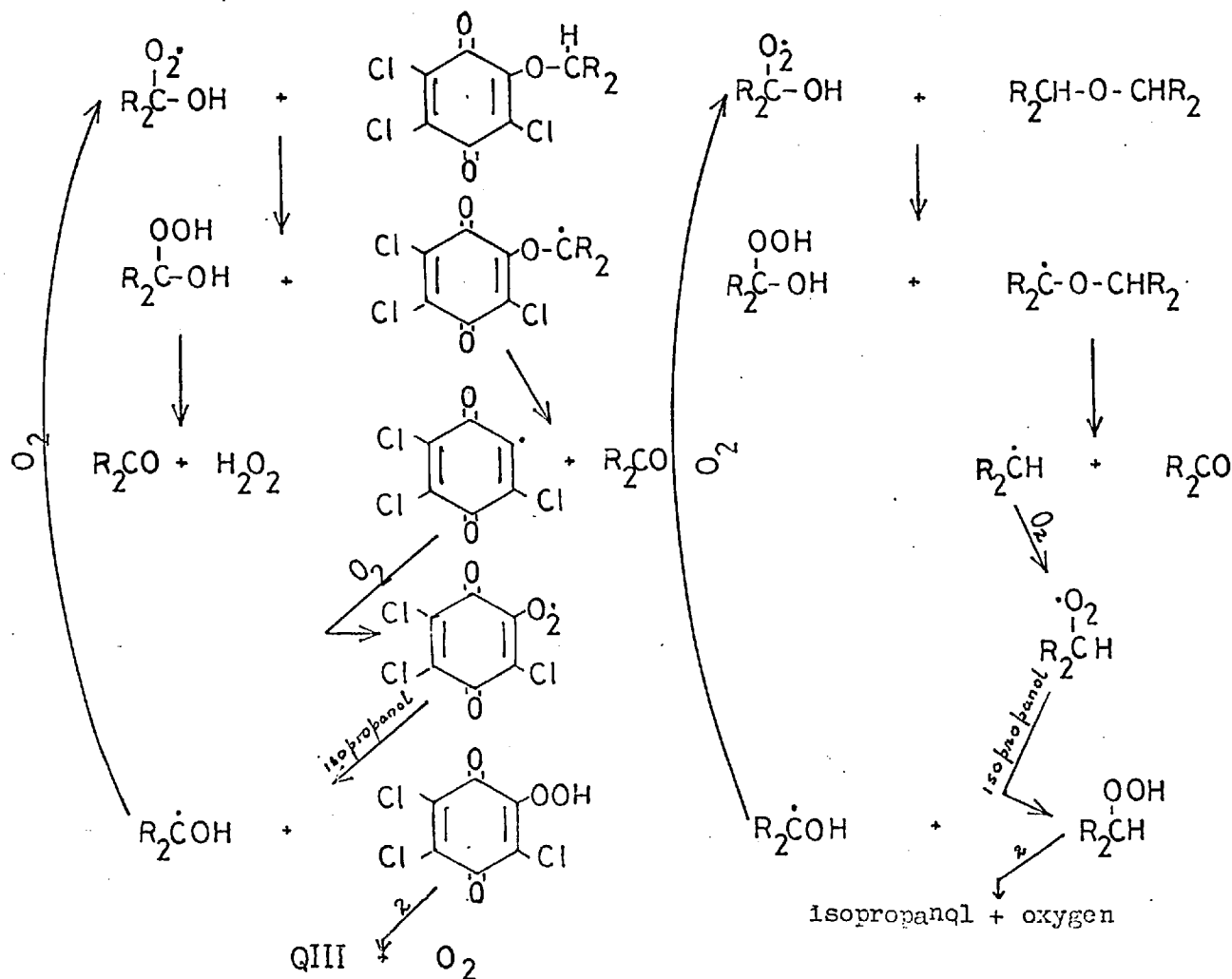
A simple autoxidation would proceed via the following steps:



or



A chain reaction mechanism would involve the following reactions in addition to the standard reactions mentioned earlier.



(8) Putting together the information reported by Kemp and Porter (63) who assigned the 500 nm transient observed at very short times after laser flash photolysis (347 nm) of chloranil in outgassed ethanol to the triplet state of the quinone, and the evidence obtained in the present work, the energy level scheme for the molecule of chloranil can be constructed as in Fig. 7.1.

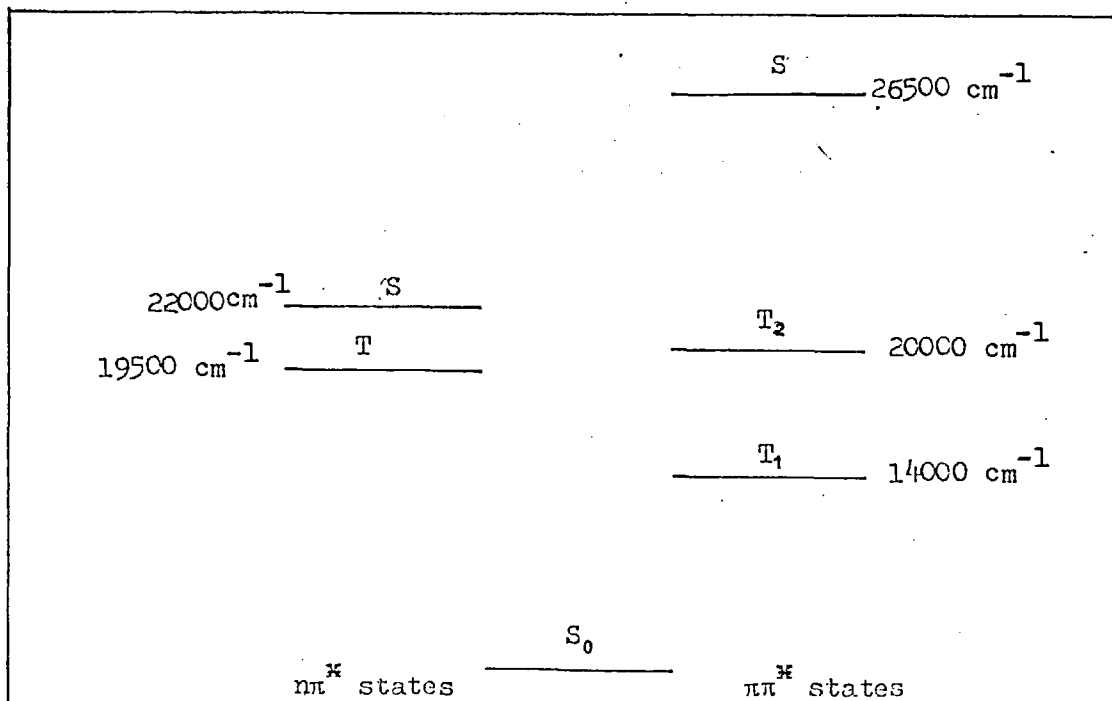


Figure 7.1.

T₁ and T₂ refer to the first and the second excited triplet respectively.

The $\pi \sigma^*$ singlet would lie below S_{ππ}* and above T₁ ππ*.

By analogy with the anthracene molecule where the presence of T_1 and T_2 has been established, (118) and considering that $T_{2\pi\pi}^*$ lies below both $S_{\pi\pi}^*$ and $S_{\pi\pi}^*$, it is possible to suggest that T_1 in chloranil is attained via T_2 .

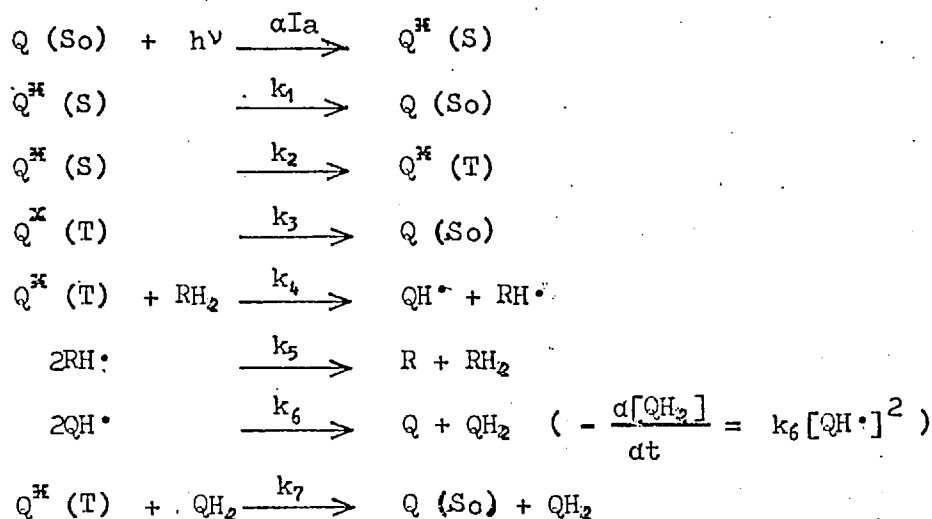
The proximity of $T_{1\pi\pi}^*$ and $T_{2\pi\pi}^*$ does not seem to be the predominant contributing factor to the mixed $\pi\pi^*$ and $\pi\pi^*$ character of the chloranil triplet, since photosensitization with anthracene, which as has been argued earlier, can only be via the lowest triplet, gave tetrachlorohydroquinone as the sole product of reduction of the quinone.

The $\pi\pi^*$ triplet state is spin-orbitally coupled with the $\pi\pi^*$ singlet (19) and vibronically coupled with the $\pi\pi^*$ triplet. (17) As was pointed out in Chapter 1, the experiments of Yang and co-workers (15b) showed that the increased reactivity with respect to photoreduction - a characteristic of the $\pi\pi^*$ triplet - of some methylated acetophenones whose lowest triplet is a $\pi\pi^*$ triplet, could not be accounted for solely by the spin-orbit coupling between the $\pi\pi^*$ triplet and the $\pi\pi^*$ singlet, since the $\pi\pi^*$ singlet level of acetophenone does not vary very much with methylation of this ketone. Their data suggested that the vibronic coupling between the $\pi\pi^*$ and $\pi\pi^*$ triplet states played a more significant role in the mixing of the two states.

Table 7.1 shows that the $\pi\pi^*$ singlet of chloranil does not vary very much relative to the $\pi\pi^*$ singlet of p-benzoquinone.

It is, therefore, reasonable to assume, by analogy with methylated acetophenones, that the mixing of the $\pi\pi^*$ and $\pi\pi^*$ states is mostly due to the vibronic coupling between the two triplet states, in addition to the spin-orbit coupling between the $\pi\pi^*$ triplet and the $\pi\pi^*$ singlet.

(9) For the purpose of assessing the rate constant for the abstraction of hydrogen from isopropanol by the chloranil triplet, only the reactions given below need be considered. Q represents the quinone, QH₂ the hydroquinone, and RH₂, isopropanol.



where α is the fraction of light which, on being absorbed, produces that excited state which ultimately yields the triplet responsible for hydrogen abstraction.

The inhibition of the reaction by the hydroquinone formed during the run, is introduced in the mechanism to account for the steady decrease in the quantum efficiency as the irradiation proceeds.

Direct evidence that the hydroquinone is indeed an inhibitor in this reaction was reported by Scrutton ⁽⁷⁷⁾ who obtained lower quantum efficiencies when tetrachlorohydroquinone was added before irradiation.

Applying steady-state assumptions to this mechanism, gives,

$$\frac{d [QH_2]}{dt} = \frac{k_4 [RH_2] \phi_T \alpha I_a}{2 (k_3 + k_4 [RH_2] + k_7 [QH_2])}$$

where ϕ_T = quantum yield of triplet

formation from the excited singlet

$$\text{i.e. } \phi_T = \frac{k_2}{k_1 + k_2} = 1$$

Rearranging and integrating,

$$It = \int_0^t I_a dt = \frac{k_7}{\alpha k_4 [RH_2]} [QH_2]^2 + \frac{2(k_3 + k_4 [RH_2])}{\alpha k_4 [RH_2]} [QH_2]$$

which can be written as

$$It = a [QH_2]^2 + b [QH_2]$$

where

$$a = \frac{k_7}{\alpha k_4 [RH_2]}$$

$$\text{and } b = \frac{2}{\alpha} \left(1 + \frac{k_3}{k_4 [RH_2]} \right)$$

The above equation predicts a parabolic curve of the form found experimentally (Cfr. fig. 6.8b.)

From the mechanism proposed in 7.2 (6),

$$\phi_{1,\text{semiquinone}} = 2 \phi_{1,\text{acetone}} = 0.775$$

The value of α , therefore, cannot be smaller than 0.775

Since,

$$\phi_{1,\text{photoreactive species}} = \phi_{1,\text{acetone in aerobic solutions}} = 1$$

and

$$\phi_{1, \pi \sigma^* \text{ singlet}} = 0.2,$$

the value of α cannot be significantly larger than 0.775.

Hence,

k_3 is nearly zero,

and

$$b = \frac{2}{\alpha} = 2.6$$

Using this value of b and parameters taken from the curve in Fig. 6.8b the value of a is found to be $7.675 \times 10^3 \text{ l mol}^{-1}$.

For the above calculation, the total number of einsteins, I_t , absorbed at any given time and the corresponding concentration of chloranil lost, $c_{10} - c_1$, were taken from the graph. Table 6.4 shows that the relevant concentration of hydroquinone in the system for purposes of this calculation is $\frac{0.383}{0.45} (c_{10} - c_1)$

Table 7.4 summarizes the results.

Table 7.4.

It $\times 10^5$ einsteins	c_1 $\times 10^5$ mol l^{-1}	$\frac{0.383}{0.45} c_1$ $\times 10^5$ mol l^{-1}	a $\times 10^3$ l mol $^{-1}$
8	3.34	2.84	7.350
12	4.80	4.08	8.000
16	6.20	5.48	8.025
28	10.20	8.67	7.370
36	14.40	10.54	7.650

$$\text{Average } a = 7.675 \times 10^3 \text{ l mol}^{-1}$$

Introducing the values of α , a , and $[RH_2]$ in the relevant equation, ($[RH_2] = 13.08 \text{ mol l}^{-1}$)

$$k_7/k_4 = 7.73 \times 10^4.$$

The quenching of the chloranil triplet by tetrachlorohydroquinone can be assumed to be diffusion controlled. This diffusion-controlled rate constant can be estimated from the expression

$$k_{\text{diff.}} = \frac{1}{4} \left(2 + \frac{d_1}{d_2} + \frac{d_2}{d_1} \right) \frac{8RT}{3 \times 10^3 \eta}$$

where k_{diff} is in $\text{l mol}^{-1} \text{ s}^{-1}$ when η , the viscosity of the solvent is in poise units, $R = 8.31 \times 10^7 \text{ ergs mol}^{-1} \text{ degree K}^{-1}$, and d_1 and d_2 are the diameters of the reacting species which are assumed to be spherical. For isopropanol $\eta = 23.7 \times 10^{-3}$ poise at 20°C , and for the chloranil and tetrachlorohydroquinone molecules it is reasonable to assume that $d_1 \approx d_2$. Hence,

$$k_{\text{diff}} = 2.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1} \text{ in isopropanol.}$$

The measured rate constant for the quenching of duroquinone by durohydroquinone is, according to Nafisi-Movaghar and Wilkinson⁽¹⁰⁰⁾, $2.1 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ which is in good agreement with the calculated value.

If k_7 is taken to be $2.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$,

$$k_4 = 3.5 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$$

The rate constant for the decay of the chloranil triplet as a result of its reaction with isopropanol is

$$k_{\text{decay}} = k_4 [\text{RH}_2] [\text{Q}^{\cdot\cdot}(\text{T})],$$

from which

$$k_{\text{decay}} = 4.6 \times 10^5 \text{ s}^{-1}$$

This value may be compared with the value of $8.4 \times 10^5 \text{ s}^{-1}$ for the corresponding rate constant measured by Kemp and Porter⁽⁶³⁾ in outgassed ethanol using laser flash-photolysis. Since the rate constant of decay of the triplet can, in these cases, be considered a measure of the ease with which hydrogen abstraction proceeds, one would reasonably expect k_{decay} in isopropanol to be larger than k_{decay} in ethanol. However, it is probable that the bulk of the isopropanol molecule makes proper orientation for reaction more difficult and consequently retards the process of abstraction.

There is reason to believe that the chloranil triplet does not behave in exactly the same way in the two alcohols. Kemp and Porter⁽⁶³⁾ reported that, on addition of anthracene, the rate

constant of decay of the triplet was increased to $10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ whereas, in the present work, anthracene was not found to inhibit the photoreduction in isopropanol (Cfr. Table 6.7a). One possible explanation of this discrepancy is based on a suggestion made earlier in this discussion that in chloranil, as in anthracene, the lowest triplet (first excited triplet, T_1) is attained via the second excited triplet, T_2 . This second excited triplet of chloranil ($E_{T_2} = 57.2 \text{ kcal mol}^{-1}$) is possibly stabilized in ethanol relative to T_1 and could be involved in an energy-transfer to the lowest triplet of anthracene ($E_{T_1} = 42.5 \text{ kcal mol}^{-1}$). This process cannot be an entirely efficient one because of the rather significant energy gap between T_2 of chloranil and T_1 of anthracene.

Pulse radiolysis studies ⁽¹²⁸⁾ have shown that disproportionation of 2-hydroxyprop-2-yl radicals is almost diffusion controlled, making

$$k_5 \text{ (in isopropanol)} \approx 2.7 \times 10^9 \text{ mol}^{-1} \text{ s}^{-1}$$

The rather low value for the rate constant of the reaction of chloranil with isopropanol compared to $1.3 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ for the same reaction of the benzophenone triplet ($\pi\pi^*$) is probably related

to the predominantly $\pi\pi^*$ character of the chloranil triplet where the electron distribution does not favour a fast abstraction of hydrogen from the alcohol molecule. Steric factors arising from the bulk of the chloranil as well as the isopropanol molecule can be expected to make proper orientation of the reacting molecules more difficult, thus slowing down the reaction. The net result may well be that the abstraction of hydrogen by the chloranil triplet needs rather more than the 7 kcal mol^{-1} in activation energy normally required for such a process.

7.2. TRICHLOROQUINONE.

7.2.1. Summary Of Experimental Evidence.

The following is a summary of the experimental evidence obtained during the irradiation of solutions of trichloroquinone in isopropanol and of mixtures of trichloroquinone and trichlorohydroquinone.

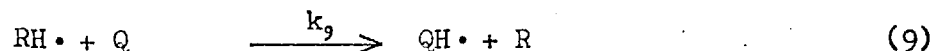
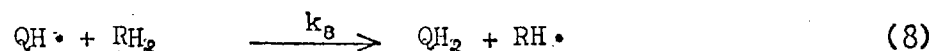
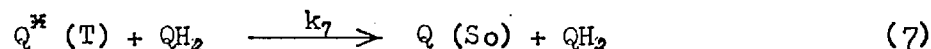
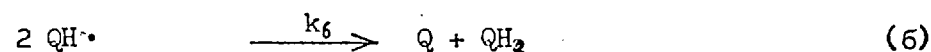
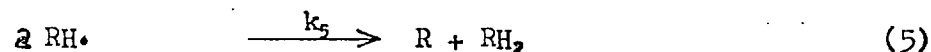
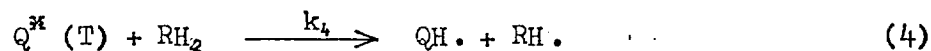
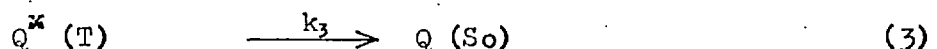
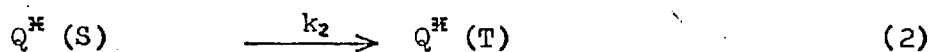
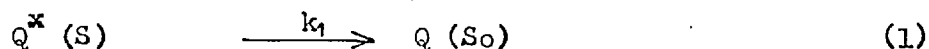
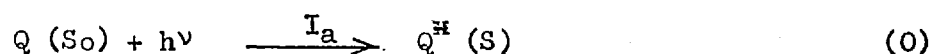
(a) The initial quantum efficiency of reduction of trichloroquinone in anaerobic solutions in isopropanol irradiated at 365 nm is 0.75, and is independent of the concentration of the solution.

(b) Trichlorohydroquinone when present in relatively high concentrations lowers the initial quantum efficiency.

(c) There is an interaction between the quinone and the hydroquinone under certain conditions. This interaction seems to result in the formation of a "tetrachloro" and a "dichloro" product.

7.2.2. Conclusions.

(1) The high quantum efficiency of reduction suggests the mechanism outlined below. By analogy with chloranil and other aromatic carbonyl compounds and according to principles discussed in Chapter 3, the abstraction of hydrogen from the substrate is assumed to proceed via the triplet quinone.



Reaction (9) would make the initial quantum efficiency of reduction concentration dependent, and since experimental evidence is to the contrary, it may be left out. Reaction (6) competes with reaction (8), but in pure alcohol, as in the present work, k_6 is expected to be very much smaller than k_8 . Reaction (6) can, therefore, also be neglected in the derivation of the equation for I_t using

steady state assumptions. For the above mechanism

$$I t = \int_0^t I_a dt = a [QH_2]^2 + b [QH_2]$$

$$\text{where } a = \frac{k_7}{k_4 [RH_2]} \quad \text{and } b = \left(1 + \frac{k_3}{k_4 [RH_2]}\right)$$

When no hydroquinone is present, $k_7 = 0$ and

$$b = \frac{1}{\phi_1} = \frac{1}{0.75} = 1.33$$

$$I t = a [QH_2]^2 + b [QH_2]$$

can also be written as

$$\frac{d(I t)}{d[QH_2]} = \frac{1}{\phi} = a [QH_2] + b$$

where ϕ = initial quantum efficiency with a known amount of hydroquinone present.

Taking 0.61 as the average value of ϕ for two runs with 1.2×10^{-3} mol l^{-1} of hydroquinone present, and b as 1.33, the value of a was found to be $0.252 \times 10^3 \text{ l mol}^{-1}$

From the values of a and b ,

$$\frac{k_7}{k_4} = 3.3 \times 10^3$$

$$\text{and } \frac{k_3}{k_4} = 4.31 \text{ mol l}^{-1}$$

and from these two

$$\frac{k_7}{k_3} = 7.6 \times 10^2 \text{ l mol}^{-1}$$

If the quenching action of the hydroquinone is assumed to be diffusion controlled, $k_7 = 2.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ and then

$$k_4 = 8.2 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$$

$$\text{and } k_3 = 3.5 \times 10^6 \text{ s}^{-1} \text{ in isopropanol.}$$

The rate of abstraction of hydrogen by the trichloroquinone triplet is found to be much higher than the corresponding rate for the chloranil triplet. The difference is probably due to

- (1) the larger energy of the trichloroquinone triplet as can be predicted from the larger extinction coefficient at 365 nm, (Cfr. Table 6.1b.)
- (2) the greater $\pi\pi^*$ character of the triplet, since it is reasonable to assume that the lowering of the $\pi\pi^*$ orbitals is not so marked with only three chlorine atoms in the aromatic ring as it is with four,
- and (3) the reduction of steric factors affecting proper orientation of the reacting molecules with the removal of one atom of chlorine.

(2) Figure 6.13 shows that the plots are linear until about 70 per cent of the quinone has disappeared. The deviation from linearity is then very noticeable. From the decrease in the initial quantum efficiency measured in the presence of $1.2 \times 10^{-3} \text{ mol l}^{-1}$ of hydroquinone, the decrease in $\frac{[QH_2]}{It}$ that could be expected at a given time, after deviation from linearity, during the run represented in Fig. 6.13 (2) was calculated. Points are labelled A, B, C, etc. in Fig. 6.13 for identification in Table 7.5 which shows clearly that the decrease

in $\frac{[QH_2]}{I_t}$, once the system begins to behave non-linearly, is not wholly accounted for by the formation of hydroquinone during the run. This seems to confirm that trichloroquinone and trichlorohydroquinone indeed interact, under certain conditions, to give products that are responsible for the absorption of light at that stage.

Experimental evidence obtained during the course of this work is too scanty to allow firm conclusions to be drawn as to the nature and the mechanism of the interaction.

Q II

Table 7.5.

$$c = 0.2973 \times 10^{-3} \text{ mol l}^{-1}$$

Point

$$\left(\frac{[QH_2]}{I_t} \right)^{t=0} - \left(\frac{[QH_2]}{I_t} \right)^{t=t}$$

Calculated

Measured from
plot in Fig. 6.13 (2)

A	0.026	0.051
B	0.028	0.057
C	0.029	0.084
D	0.0295	0.106
E	0.0304	0.112
F	0.0307	0.126
G	0.0308	0.144

7.3. Some Suggestions For Future Work.

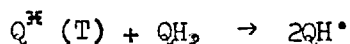
By way of conclusion, there follow a few suggestions that may prove useful in any future investigation of the photochemical reactions of chloranil and trichloroquinone.

a) The photochemical reaction of chloranil in 100 per cent isopropanol seems to take place via two distinct processes, one fast and the other slower. The fast process leading to the rupture of the C-Cl bond probably involves a higher-lying singlet state and the slow process leading to hydrogen abstraction involves a lower lying triplet state. Excitation with wavelengths lower than 365 nm may be used to observe whether there is any alteration in the ratio of products. It may be possible to discover that there is a threshold below which only tetrachlorohydroquinone is formed because the energy of excitation is not high enough to produce the singlet responsible for the fast process.

The irradiations performed in the course of this work seemed to indicate that the formation of trichloroproducts is linear with time, but it is probable that this was so because periods of irradiation were too short for any non-linear behaviour to be detected. Long periods of irradiation of chloranil in isopropanol in the presence of a sufficient amount of tetrachlorohydroquinone to inhibit the photoreduction of the triplet would probably help to confirm that the trichloroproducts are formed from a different photoreactive species.

It would be interesting to repeat Kemp and Porter's laser flash

photolysis to record the absorption spectrum of the chloranil triplet in isopropanol and detect any difference in its behaviour relative to that in ethanol. Flash photolysis in the presence of tetrachlorohydroquinone using flash duration of 1 μ s or less would enable the observation to be made as to whether the quenching of the triplet by the hydroquinone proceeds, as was found in the case of duroquinone (100) via a chemical reaction of the type



Since trichlorohydroquinone is formed during the irradiation of chloranil, flash photolysis in the presence of trichlorohydroquinone alone as also in the presence of a mixture of trichlorohydroquinone and tetrachlorohydroquinone would perhaps provide very helpful insight into the mechanism of quenching of the triplet by hydroquinone or hydroquinones.

Quantitative measurements of the semiquinone transient can be undertaken with a view to determining the quantum yield of triplet formation.

Extremely short flash duration of the order of 10 ps or less would probably be required to detect the presence of the excited species responsible for the formation of the trichloro products, which it has been suggested here is the $\pi\sigma^*$ singlet.

The discovery of an inert solvent which is miscible with alcohols and in which chloranil dissolves appreciably would be invaluable in

making a more accurate assessment of the rate constant of hydrogen abstraction by the chloranil triplet.

b) More rigidly controlled experiments would possibly yield more revealing information as to the interaction between trichloroquinone and trichlorohydroquinone. Mixtures containing known amounts of the two could be used for purposes of calibration of the mass spectra provided all mixtures are made and handled under strictly identical conditions.

The use of the highly sensitive and accurate Perkin-Elmer 402 spectrophotometer may shed light on the small changes in optical density at certain wavelengths that seem to accompany the interaction.

An investigation of the photochemical reactions of dichloroquinones in isopropanol is in progress in this laboratory.

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