RADIATION CHEMISTRY OF CARBON MONOXIDE

by

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A thesis submitted for the

Ph.D. Degree

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Imperial College,
The experiments described in this thesis were designed primarily to determine the mechanism of carbon dioxide production during gamma radiolysis of carbon monoxide.

Radiolysis of CO/C\textsubscript{2}H\textsubscript{6} mixtures results in the formation of propene oxide and propanal which are products characteristic of the reaction of O(\textsuperscript{3}P) with C\textsubscript{3}H\textsubscript{6}. Addition of C\textsubscript{2}H\textsubscript{2} to a CO/C\textsubscript{3}H\textsubscript{6} mixture results in a reduction in the formation rates of propene oxide and propanal to an extent which is proportional to the velocity constant ratio for reaction of O(\textsuperscript{3}P) with C\textsubscript{3}H\textsubscript{6} and C\textsubscript{2}H\textsubscript{2}.

It is concluded that in the gas phase at 22\textdegree{}C and 1 atm that GO(\textsuperscript{3}P) is 1.41 \pm 0.22 atoms per 100 eV and that O(\textsuperscript{3}P) atoms account for about 75\% of the CO\textsubscript{2} yield. It is suggested that electronically excited states of CO and CO\textsuperscript{+} account for the remaining 25\% of the CO\textsubscript{2} yield.
It is argued that the $O(3P)$ atoms are produced as the result of either the production of electronically excited states or a neutral dissociative process which accompanies ionisation. Further it is concluded that the experiments performed do not preclude the possibility that either $O(^1D)$ or $O(^1S)$ atoms are the precursors of the "observed" $O(3P)$ atoms.

$G(CO_2)$ and the reaction stoichiometry were studied in the gas at s.t.p density in the range 22°C to -196°C and in liquid CO at -196°C. Under all conditions studied it was found that the reaction stoichiometry does not deviate from:

$$4n \text{ CO} \rightarrow n \text{ CO}_2 + (C_3O_2)_n$$

It is argued that it is possible to explain the reduction in $G(CO_2)$ on lowering the temperature below 22°C in the gas phase in terms of the competing reactions $O + C_2O \rightarrow 2CO$, $C_2O + CO \rightarrow C_3O_2$ and $O + CO \rightarrow CO_2$.

A number of ways in which the experiments described here could be extended are indicated.
ACKNOWLEDGEMENTS.

The author is grateful for helpful tuition and direction from Dr. P.G. Clay and Professor G.R. Hall, also for the award of a grant from the Science Research Council.

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A **Introduction**

Radiolysis of carbon monoxide results in the formation of carbon dioxide and a carbonaceous deposit. Very little experimental work designed to determine the mechanism of formation of the observed products has been published. Past work has been reviewed by Anderson (1) thus an extensive background is not given here.

Anderson (1) found that during proton radiolysis, under ambient conditions, that $G(CO_2)$ fell from 2 to 0.5 molecules per 100eV as the dose rate increased from $2 \times 10^{12}$ to $1.3 \times 10^{18}$ eV cc$^{-1}$ sec$^{-1}$. Further the ratio $G(C)/G(CO_2)$ remained constant in the dose rate dependent range. The following mechanism was suggested to explain this effect:

$$\text{CO} \rightarrow \text{C} + \text{O}$$
$$\text{C} + \text{CO} \rightarrow \text{C}_2\text{O} \rightarrow \text{polymer}$$
$$\text{O} + \text{CO} \rightarrow \text{CO}_2$$
$$\text{O} + \text{C}_2\text{O} \rightarrow 2\text{CO}$$

Anderson (1) further suggested that neutralization of positive ions by electrons was not a dissociative process at atmospheric pressure. The recombination energy was postulated to be dissipated among molecules clustered around the positive ion. A neutral dissociative process yielding oxygen atoms was therefore postulated to accompany ionisation.
The following sections review the published work on oxygen atoms which has been used by the author as the basis for a diagnostic technique for oxygen atom formation during gamma radiolysis of carbon monoxide.

A review of the reactions of ionic and electronically excited states of carbon monoxide, carbon atoms and C2O radicals is also presented. The polymerisation of carbon suboxide is discussed.

B Reactions of ground state oxygen atoms.

The published literature on oxygen atom reactions is extensive, a comprehensive review will not be given here. Some aspects of oxygen atom reactions are discussed in detail in the experimental data assessment section. The following section presents an outline of the relevant literature and its application to the design of experiments described in this thesis.

1 Reaction with olefins.

Studies on the reaction of O(3P) with olefins have been performed and reviewed by Cvetanovic (2). The 2537 Å mercury sensitised photolysis of nitrous oxide yields oxygen atoms in the triplet ground state. It was shown that these atoms could add to double bonds to form biradicals which rearrange to form isomeric epoxides and carbonyl compounds. These addition compounds are formed with 4.3 eV per molecule excess energy.
The addition complex fragments at pressures below atmospheric.

A similar study, using a different technique, was made by Avramenko (3). Low pressure electrode discharges of H₂O and of O₂ were used as sources of oxygen atoms. It is doubtful if the former source does in fact produce oxygen atoms (4). Avramenko (3) found that the major products of the O(3P) + C₃H₆ reaction, in a low pressure O₂ discharge were HCHO, CH₃CHO, C₂H₄, and CO. This contrasts with Cvetanovic's analysis which showed that propene oxide and propanal were the major products. The products obtained by Avramenko (3) were very probably due to the combined effects of low pressure and the presence of molecular oxygen. Under such conditions the addition biradical can fragment and the fragmentation products react with molecular oxygen.

Hughes et al (5) and (6) used the dissociation of molecular oxygen on a rhenium wire heated to 2300°K as a source of O(3P). They reacted the atoms with condensed olefins at 77°K. These authors confirmed Cvetanovic's product analysis.

2 Reaction with acetylene

The mechanism of room temperature oxidation of acetylene by O(3P) has been postulated by Brown and Thrush (7) to be:
The reaction between atomic oxygen and acetylene is known however to produce chemiluminescence in the vacuum ultraviolet. Becker (8) postulated this to be due to the reaction:

\[ ^3P_0 + O_2 \rightarrow CO(Alr) + CO(X^1\Sigma) \]

which suggests that \( ^3P_0 \) must react with \( C_2H_2 \) as follows:

\[ O + C_2H_2 \rightarrow C_2O + H_2 \]

However, Marmo et al (9) studied the chemiluminescence quantitatively. These authors concluded that 1 photon was produced for every \( 10^4 \) molecules oxidised.

3 Rate constants.

Comparative rate constants were obtained by Cvetanovic (2) using the method of competition kinetics. Absolute values were obtained by Elias (10) from oxygen flow discharge experiments, where \( ^3P_0 \) concentrations were measured by titration with NO at various points along the flow reactor. Callear and Smith, (11), (12) measured the absolute velocity constants of the reaction:

\[ ^3P_0 + CS_2 \rightarrow SO + CS \]

and \( ^3P_0 + \) butenes. The appearance of CS was measured spectro photometrically during the flash photolysis of \( NO_2/CS_2 \) mixtures with and without the addition of butene. Lower values than those determined by Elias (10) were found.
It was suggested that removal of oxygen atoms in second order reactions occurs in the low pressure discharge flow technique used by Elias. This conclusion was substantiated by Brown and Thrush (7).

Table 1 Some Velocity Constants for Reaction of $O(3P)$ atoms at 25°C

<table>
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<tr>
<th>Material</th>
<th>$k$(cc/mole sec)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>$O_2$</td>
<td>$(9.0 \pm 3.1) \times 10^6$</td>
<td>14</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>$(1.8 \pm 0.6) \times 10^7$</td>
<td>7</td>
</tr>
<tr>
<td>$C_2H_6$</td>
<td>$(7.24 \pm 0.75) \times 10^8$</td>
<td>13</td>
</tr>
<tr>
<td>$C_2H_2$</td>
<td>$(9.2 \pm 0.4) \times 10^9$</td>
<td>7</td>
</tr>
<tr>
<td>$C_2H_4$</td>
<td>$(3.2 \pm 0.4) \times 10^10$</td>
<td>7</td>
</tr>
<tr>
<td>$C_3H_6$</td>
<td>$(1.85 \pm 0.23) \times 10^11$</td>
<td>7 and 2</td>
</tr>
<tr>
<td>but-1-ene</td>
<td>$(1.9 \pm 0.3) \times 10^12$</td>
<td>12</td>
</tr>
<tr>
<td>iso-butene</td>
<td>$(7.6 \pm 1.2) \times 10^12$</td>
<td>12</td>
</tr>
</tbody>
</table>

These authors used a flow discharge technique and estimated $O(3P)$ concentrations by E.S.R. measurements. The source of $O(3P)$ atoms was the reaction:

$$N(^4S) + NO(^2Π) \rightarrow O(3P) + N_2 (^1Σ)$$

Studies of the rate of $O(3P)$ uptake as a function of olefin concentration allowed an estimate of the reaction stoichiometry to be made.
Some velocity constants for $O(3P)$ reactions are shown in Table 1.

4 Reaction with paraffins.

The reaction of $O(3P)$ with alkanes is generally thought to involve H atom abstraction:

$$O + RH \rightarrow R + OH$$

The reaction mechanism has been discussed and the velocity constants determined (7), (13). The simple alkanes react with $O(3P)$ atoms far more slowly than do the simple alkenes.

5 Experiment Design.

This section outlines the design of the diagnostic technique used by the author to detect the formation of $O(3P)$ atoms during gamma radiolysis of carbon monoxide gas.

There are two approaches whereby $O(3P)$ may be diagnosed using hydrocarbon $O(3P)$ scavengers and end product analysis. The formation rate of $CO_2$ or, product to which the hydrocarbon is oxidised, may be measured as a function of mixing ratio. The velocity constant ratio may then be estimated from the derived scavenger plot.

The alkanes are not suitable scavengers. The OH radicals produced react rapidly with CO to form $CO_2$ via the reaction:
\( k_s, k_{CO} \) = velocity constant for reaction of \( O(3P) \) with scavenger and carbon monoxide respectively.

\( [S], [CO] \) concentrations of scavenger and carbon monoxide respectively.
OH + CO → CO₂ + H

at room temperature (15).

The olefins react rapidly with O(³P) and yield characteristic oxidation products.

Consider a simple competition between CO and scavenger for O(³P).

When the scavengeable CO₂ yield is cut by half:

\[ k_s \left[ S \right] = k_{CO} \left[ CO \right] \]

If N_{CO₂} is the least number of CO₂ moles which can be measured then the number of moles scavenger (Nₖ) which must be added is at least 10 N_{CO₂}. Thus at atmospheric pressure the vessel volume which has to be used is:

\[ V = \frac{k_s}{k_{CO}} \times 10 N_{CO₂} \ RT \ litres. \]

By gas chromatography N_{CO₂} is about 5 x 10⁻⁵ moles (p 71), thus for \( C_2H_4 \) V is about 400 litres! By mass spectroscopy, much smaller quantities of CO₂ can be measured. However the quantity 10 N_{CO₂}, in the equation above now becomes the least amount of condensable material which can be reproducibly extracted from a vessel of about 100 cc capacity by a refrigerated scrubbing loop and is about 10⁻⁶ moles. Thus V is about 0.24 litres for acetylene but again inconveniently high for most olefins. The detection limit for epoxides and carbonyl products with a flame ionisation detector is low, about 10⁻⁹ moles. However preconcentration is required to prevent over-
loading of the V.P.C. thus the amount of scavenger which can be added is again not less than $10^{-6}$ moles.

When the experiments to be described in this thesis were being designed a mass spectrometer was not available and the rate constant for reaction of $O(3P)$ with acetylene had not been reliably determined. Thus although the formation of oxidation products from an olefin could be used to diagnose the presence of $O(3P)$ the consistency of the diagnosis could not be checked by measuring comparative velocity constants in a static reaction system. Such a consistency check was essential since at the time of preliminary design the work of Hughes et al (5) had not been published. The products characteristic of $O(3P)$ reaction with olefins were thus not well established. This problem was solved by the addition of a second scavenger. The rate of formation of oxidation products from the primary scavenger was then measured as a function of secondary to primary scavenger mixing ratio.

Propylene-acetylene mixtures were the scavenger combination finally chosen. Propylene was chosen because the $(C_3H_6O)$ complex does not undergo extensive fragmentation at atmospheric pressure. Acetylene because it does not yield products which interfere with the chemical analysis of the products to which propylene is oxidised.
6 Surface Recombination.

O(\(^3\)P) atoms recombine on surfaces by a process which is first order with respect to the concentration of O(\(^3\)P).\(^{(4)}\) The association between O(\(^3\)P) and CO to form CO\(_2\) is however spin forbidden and slow \(^{(14)}\). The purpose of this section is to discuss the influence of varying surface/volume ratio on G(CO\(_2\)).

a Theory.

Assuming a homogeneous distribution of O(\(^3\)P) throughout a reaction vessel, the total number of atoms which hit the wall in one second \(16\ p\ 146\) is:

\[
N_w = \frac{1}{4} \bar{c} [0] S \text{ atom sec}^{-1}
\]  

\([0] = \text{atoms cc}^{-1}\)

\(\bar{c} = \text{root mean square velocity cm sec}^{-1}\)

\(S = \text{surface area (cm}^2)\)

The rate of wall recombination is defined by:

\[- \frac{d[0]}{dt} = k_w [0] \text{ atom (cc sec)}^{-1}\]  

\(\gamma\) is defined as the fraction of total atoms colliding with the surface which are lost. Thus combining (1) and (2):

\[k_w = \frac{\gamma}{4} \frac{S}{V} \bar{c}\]  

\(k_w = \text{velocity constant for surface recombination}\)

The mean life of an O(\(^3\)P) atom with respect to wall recombination \(t_w\) is the reciprocal of (3).
For the rate of wall recombination not to be hindered by diffusion to the walls; the diffusion time \( t_D \) from the centre of the reactor to the surface, must be less than \( t_w \). The time required by a molecule to diffuse a distance \( x \) is given by the Einstein diffusion formula (16):

\[
t_D = \frac{3}{2} \frac{x^2}{c\lambda}
\]

\( \lambda = \) mean free path (cm)

In the pressure range \( 10^{-3} \) to 20 atm., \( c\lambda \) may be defined by the expression (16):

\[
\eta \sim 0.5 \rho \bar{c}\lambda
\]

\( \eta = \) viscosity poise
\( \rho = \) density gm cc\(^{-1}\)

Combining (4) and (5)

\[
t_D = \frac{3}{4} x^2 \frac{\rho}{\eta}
\]

b **Application.**

Assuming that oxygen atoms are produced during gamma radiolysis of CO, the conditions under which the \( \text{CO}_2 \) yield will be surface-volume dependent may be calculated. If a simple competition exists between reaction with CO and wall recombination the reaction may be defined by the conservation equation:

\[
R_o = [O(3\text{P})] \left( k_H [\text{CO}] + k_w \right)
\]

\( R_o = \) rate of \( O(3\text{P}) \) production.
\( k_H = \) velocity constant for reaction of \( O(3\text{P}) \) with CO
The reaction will be demonstrably surface-volume dependent when:

\[ t_D < t_w = t_H \]

\[ t_H = \text{mean life for homogeneous reaction of } O(3p) \text{ with CO} \]

For a long cylinder the ratio of the volume to the surface area (V/S) approximates to \( r/2 \) (\( r = \text{radius} \)) thus the condition stated above occurs when:

\[ 0.75 r^2 \frac{\rho}{\eta} < \frac{2r}{v} = \frac{1}{k_H [CO]} \]

Table 2 shows \( t_D, t_w \) and \( t_H \) calculated as a function of \( r \) for CO gas at 1 atm and 25ºC. Clearly the wall reaction does not become free from diffusion control until \( r \) is less than \( 10^{-1} \text{cm} \). Further variation of the surface material in vessels of usual dimensions is unlikely to alter \( G(\text{CO}_2) \) because of diffusion control.
<table>
<thead>
<tr>
<th>Surface</th>
<th>θ</th>
<th>t_D</th>
<th>t_W</th>
<th>t_D</th>
<th>t_W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrex</td>
<td>1.2 x 10^{-4}</td>
<td>2.7 x 10^{-2}</td>
<td>2.7 x 10^{-1}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>7.1 x 10^{-4}</td>
<td>4.5 x 10^{-3}</td>
<td>4.5 x 10^{-2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbO</td>
<td>5.8 x 10^{-3}</td>
<td>5.5 x 10^{-4}</td>
<td>5.5 x 10^{-3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>3.6 x 10^{-2}</td>
<td>8.9 x 10^{-5}</td>
<td>8.9 x 10^{-4}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>1.7 x 10^{-1}</td>
<td>1.9 x 10^{-5}</td>
<td>1.9 x 10^{-4}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ t_H = 2.5 \times 10^{-3} \text{ secs} \]

θ values taken from ref (4)
Reactions of \( \text{O}^*(1D) \) atoms

Two singlet excited states of the oxygen atom are known, \( \text{O}^*(1D) \) and \( \text{O}^*(1S) \) which are 2 eV and 4.2 eV above the ground state respectively. \( \text{O}^*(1D) \) gives an emission at 6300 Å and 6364 Å while \( \text{O}^*(1S) \) has an emission at 5577 Å. The radiative lifetimes of \( \text{O}^*(1D) \) and \( \text{O}^*(1S) \) are 100 sec and 1 sec respectively, relaxation to the triplet ground state being spin forbidden. Little work has been published on the chemical reactions of \( \text{O}^*(1S) \), however it has been suggested that it is formed during the 1470 Å photolysis of \( \text{N}_2\text{O} \) (18).

1 Reaction Mechanisms and Products.

a Reaction with carbon monoxide.

Raper (19) studied the oxidation of CO during the 2537 Å photolysis of \( \text{O}_3/\text{CO} \) mixtures dissolved in liquid argon at 87 K. A very small \( \text{CO}_2 \) quantum yield was observed. This was postulated to be due to pre-dissociation of a vibrationally excited state of \( \text{CO}_2 \), lower than that formed in the initial association reaction, which is formed by collisional deactivation of the initial association complex:–

\[
\begin{align*}
\text{O}^*(1D) + \text{CO} & \rightleftharpoons \text{CO}_2^* & (1) \\
\text{CO}_2^* + M & \rightarrow \text{CO}_2^{**} + M & (2) \\
\text{CO}_2^{**} & \rightarrow \text{CO} + \text{O}^*(3P) & (3) \\
\text{CO}_2^{**} + M & \rightarrow \text{CO}_2 & (4)
\end{align*}
\]
The reaction stoichiometry:

\[ \text{O}_3 + \text{CO} \rightarrow \text{O}_2 + \text{CO}_2 \]

was explained in terms of the reaction

\[ \text{O}(^{3}P) + \text{O}_2 \rightarrow \text{O}_3 \]

Verdurmen (20) showed that during 1849 Å photolysis of N\textsubscript{2}O in the presence of CO\textsubscript{18} at room temperature and in the pressure range 6-48 torr, that molecular oxygen formed by the reaction:

\[ \text{O}(^{1}D) + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2 \]

contains O\textsubscript{18} thus substantiating the formation of a labile association complex.

Product CO\textsubscript{2} detection in N\textsubscript{2}O based on the m/e = 22 peak was understandably inaccurate. Although it was concluded that between 3-10% of O\textsubscript{1}D formed was converted to CO\textsubscript{2}, it is difficult, if not impossible, to calculate the fraction of O\textsubscript{1}D formed converted to CO\textsubscript{2}, and thus to estimate the relative importance of reactions 3 and 4 of Raper's mechanism.

Clerc (21)(22) explained the lack of O\textsubscript{2} formation during 1240 Å flash photolysis of CO\textsubscript{2} at 3 torr and room temperature in terms of the rapid reaction:

\[ \text{O}(^{1}D) + \text{CO} \rightarrow \text{CO}_2 \]

The only evidence for O(1D) formation given was the appearance of a CO\textsubscript{2} absorption at 1152 Å. Direct evidence of O(1D) formation such as observation of the 6300, 6364 Å
emission was not reported. \( \text{O}_2 \) loss could also be explained by the occurrence of the following reactions in the high intensity flash:

\[
\begin{align*}
\text{O}^{(1D)} + \text{CO}_2 & \rightarrow \text{CO}_3 \\
\text{CO}_3 + \text{CO} & \rightarrow 2 \text{CO}_2
\end{align*}
\]

It may be concluded that direct experimental evidence, confirming or challenging the experiments and conclusions of Raper (19) has yet to be published.

b Reaction with other simple molecules.

Norrish and Wayne (23) studied the reaction of \( \text{O}^{(1D)} \) produced by 2537 Å \( \text{O}_3 \) gas phase photolysis with various simple molecules. \( \text{CO}_2 \) and \( \text{N}_2 \) were found to decrease the \( (-\text{O}_3) \) quantum yield and \( \text{H}_2\text{O}, \text{H}_2, \text{CH}_4, \text{NH}_3 \) and \( \text{HCl} \) induce a chain \( -\text{O}_3 \) quantum yield probably initiated by

\[
\text{O}^{1D} + \text{RH} \rightarrow \text{OH} + \text{R}
\]

Evidence for insertion at high densities and cryogenic temperatures was however found by De More and Raper (24) who studied the reaction of \( \text{O}^{(1D)} \) with \( \text{CH}_4 \) using the technique described above (19). Methyl alcohol was formed presumably via:

\[
\text{O}^{1D} + \text{CH}_4 + \text{M} \rightarrow \text{CH}_3\text{OH} + \text{M}
\]

with \( \text{H}_2 \) however (25) the major reaction path was found to be abstraction to form \( \text{OH} \) under the same conditions.
Evidence for association of $O(1^D)$ with $CO_2$ forming $CO_3$ under cryogenic conditions has been found by Weissberger et al (26).

The gas phase reaction of $O(1^D)$ with $O_2$ has been studied by Young and Black (27) who find evidence for the rapid reaction:—

$$O(1^D) + O_2 \rightarrow O_2 (b^1\Sigma^+) + O_3^P$$

Preston, Cvetanovic and Yamazaki (28, 29) studied the reaction of $O(1^D)$ with propane using the 1850 Å photolysis of $N_2O$. $O(1^D)$ was found to insert into the CH bonds to form "hot" alcohols which require pressures of the order of 10 atm for stabilisation.

The ratio of n-propyl to iso propyl alcohol formed is about 3. $O(3P)$ atoms do not insert into CH bonds, but abstract to form OH as already discussed. No evidence for fragmentation processes forming aldehyde such as

$$O(1^D) + C_3H_6 \rightarrow (C_3H_8O)^+ \rightarrow C_3H_6O + H_2$$

was reported.

2 Rate Constant Data.

By a study of propyl alcohol formation from propane during the photolysis of $NO_2$ at 2288 Å and $N_2O$ at 1850 Å in the presence of various additives Yamazaki, Cvetanovic and Preston (28, 29), obtained comparative rate constants for reaction of $O(1^D)$. $Xe, N_2, CO_2, N_2O, NO_2$ and $C_3H_8$ were all
found to react rapidly, whereas He, Ar, Kr and SF₆ react slowly.

Snelling and Blair (30) estimated the following absolute rate constants during a study of the 2537 Å gas phase photolysis of O³ in cc (mole sec)⁻¹ units:

\[
\begin{align*}
0_3 & (2.0 \pm 1) \times 10^{14} \\
N_2 & (1.3 \pm 0.6) \times 10^{13} \\
Xe & (3.5 \pm 1.7) \times 10^{13} \\
Ar & \sim 5 \times 10^{10}
\end{align*}
\]

The maximum gas kinetic rate constant for bimolecular collisions is of the order of \(10^{14}\) cc (mole-sec)⁻¹, thus it is apparent that these reactions are extremely fast.

Claimed comparative reaction rates from a study of 1477 Å O₂ photolysis (31) are invalid because the 6300 Å 0(1D) emission was mistaken for the 7618 Å band of O₂(b¹Σ g⁺) (32).

The rate constant suggested by Clerc (22) for \(O^{1}D + CO + M\), \(10^{19}\) cc² mole⁻² sec⁻¹, must be regarded with suspicion since it was not demonstrated that it was in fact \(O^{1}D\) reacting with CO as already discussed above.
An estimate of the comparative rate of reaction of 0(1D) with N₂O, CO₂ and C₃H₈ from E.A. Th. Verdurmen's data.

The velocity constant ratio for reaction of 0(1D) with carbon monoxide and hydrocarbons is not known.

The purpose of this section is to make an estimate of this ratio for the case of carbon monoxide and propane. Such a calculation allows the interceptor level of propane which has to be added to CO to detect 0(1D) formation during gamma radiolysis to be predicted.

Consider the reaction sequence:

\[ \begin{align*}
N₂O & \rightarrow N₂ + O(1D) & R₀ \\
O(1D) + N₂O & \rightarrow N₂ + O₂ & k₁ \\
O(1D) + CO & \rightarrow CO₂^\# & k₂ \\
CO₂^\# & \rightarrow O(1D) + CO & k₃ \\
CO₂^\# + M & \rightarrow CO₂^\#^\# & k₄
\end{align*} \]

The rate of removal of 0(1D) due to reaction with CO is given by the expression:

\[ -\frac{d(O(1D))}{dt} = + \frac{dCO₂^\#}{dt} = k₄ (CO₂^\#) (M) \quad ---- (1) \]

The stationary state expression for CO₂^\#^\# is:

\[ (CO₂^\#^\#)_{ss} = k₂ (O(1D))(CO)/(k₃ + k₄(M)) \quad ---- (2) \]

Since exchange takes place it may be postulated that:

\[ k₃ > k₄ \quad ---- (3) \]
combining equations 1, 2 and 3:
\[
d(\text{CO}_2)/dt = (O(^1D)) k_6(M)(\text{CO})
\]
where \( k_6 = k_2k_4/k_3 \)
Thus reactions 2, 3 and 4 may be considered as a single reaction which does not yield \( \text{N}_2 \):
\[
O(^1D) + \text{CO} + M \rightarrow \text{products} \quad \cdots \quad k_6
\]
The mass conversion equation for \( O(^1D) \) is thus:
\[
d(O(^1D))/dt = 0 = R_0 - (O(^1D)) [k_4(N_2O) - k_6(\text{CO})(M)]
\]
The rate of \( \text{N}_2 \) formation is given by:
\[
d(\text{N}_2)/dt = R_0 + R_0 \left(1 + \frac{k_6(\text{CO})(M)}{k_1(N_2O)}\right)^{-1}
\]
which rearranging yields
\[
\frac{k_6(\text{CO})(M)}{k_1(N_2O)} = \left[\left(\frac{d(\text{N}_2)/dt}{R_0} - 1\right)^{-1} - 1\right] \quad \cdots \quad (5)
\]
It should be noted that \( R_0 \) refers to half the \( \text{N}_2 \) quantum yield thus the relative formation rates given by Th. Verdurmen should be doubled.

A similar expression for \( \text{CO}_2 \) quenching may be derived if the mechanism for reaction of \( O(^1D) \) with \( \text{CO}_2 \) proposed by Baylch (33) is assumed i.e.
\[
\begin{align*}
\text{CO}_2 + O(^1D) &\rightarrow \text{CO}_3^x \\
\text{CO}_3^x &\rightarrow \text{CO}_2 + O^3P \quad \cdots \quad k_5
\end{align*}
\]
Kinetic Analysis of $N_2$ formation data obtained by Verdetmèn (20) for 1850 Å photocysis of $N_2O$ in the presence of CO and CO$_2$.

\[ \frac{[N_2/(R_0)]^{-1} - 1}{[N_2/(R_0)]^{-1} - 1} \]

\[ \frac{(CO)(M)}{(N_2O)} \text{ moles litre}^{-1} \times 10^2 \]

\[ \dot{N}_2 = \frac{d(N_2)}{dt} \]

\[ \frac{(CO_2)/(N_2O)} \]
i.e.

\[ \frac{k_5}{k_1} \frac{\text{CO}_2}{\text{N}_2\text{O}} = \left( \frac{\frac{d(N_2)}{dt}}{R_0} - 1 \right)^{-1} \] ........ (6)

It should be clearly noted that the subscripts on the velocity constants (k) in equations (5) and (6) refer to steps in the reaction mechanism written on pages 25 and 26 with the exception of \( k_6 \) which is defined on page 26. \( R_0 \) mean rates of production of \( O(1^D) \) atoms.

Data plots of equations 5 and 6 are shown in graph (1).

Clearly

\[ \frac{k_6}{k_1} = 2 \times 10^4 \text{ cc/mole,} \quad \frac{k_5}{k_1} = 2.5 \times 10^{-1} \]

Preston (29) obtained values of \( k(O(1^D) + \text{CO}_2)/k(O(1^D) + \text{N}_2\text{O}) \) ranging between 0.42 and 1 in reasonable agreement with the ratio \( k_5/k_1 \) stated above. Preston (29) further obtained a value for \( k(O(1^D) + \text{N}_2\text{O})/k(O(1^D) + \text{C}_3\text{H}_8) \) of about 3. Thus \( k(O(1^D) + \text{CO})(M)/k(O(1^D) + \text{C}_3\text{H}_8) \) is about 2.8 at 1 atm and 25°C if the above analysis is correct.
Formation and reactivity of ions produced during gamma radiolysis of carbon monoxide.

The recombination energy of CO⁺, 14 eV is greater than the dissociation limit of carbon monoxide, 11.1 eV. It is thus conceivable that oxygen atom production during gamma radiolysis of carbon monoxide results from neutralisation of CO⁺ ions by thermalised electrons. If this were the case and if the CO⁺ ions reacted with the oxygen atom scavenger added to the system before neutralisation, then oxygen atom formation would not be detected. The following section considers the type of ions that are formed in carbon monoxide by electron impact, secondly the possible reactions of CO⁺.

Dissociation of carbon monoxide by electron bombardment.

Total cross sections for ionisation and attachment in gases by electron impact have been measured by Rapp (34). Ionisation cross section is defined by the relation:

\[ \sigma = \frac{i_i}{i_e} n l \]

\( i_i, i_e = \) ion and electron currents
\( n = \) target gas number density
\( l = \) effective path length.

Cross sections for positive ionisation:

\[ e^- + CO \rightarrow CO^+ + 2e^- \]

and dissociative attachment:

\[ e^- + CO \rightarrow CO^- \rightarrow C + O^- \]
were measured. The two processes have resonance peaks at (100 - 120 eV) and 9.9 eV respectively. At these two energy maxima the ratio of cross sections, (dissociative attachment to positive ion formation) was found to be $7.64 \times 10^{-4}$. The cross section for negative ion formation:

$$e^- + CO \rightarrow CO^- \rightarrow C^+ + O^- + e^-$$

was not measured accurately, it was found however to have a resonant peak of about 30 eV and a cross section of a comparable order of magnitude to dissociative attachment. CO$^+$ ions are therefore the major product of electron impact of carbon monoxide.

2 Reactions of CO$^+$

Leventhal (35) has discussed the energetics of the following collision induced dissociative and reaction processes of CO$^+$:

$$CO^+ + CO \rightarrow C^+ + O + CO \quad (1)$$
$$CO^+ + CO \rightarrow C^+ + CO_2 \quad (2)$$
$$CO^+ + CO \rightarrow C_2O^+ + O \quad (3)$$

Heats of reaction as a function of the electronic excitation energy of CO$^+$ are shown below:
<table>
<thead>
<tr>
<th>Term</th>
<th>Ionisation Symbol</th>
<th>Reaction Heat $\Delta H$ (eV)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>eV 1 2 3</td>
<td></td>
</tr>
<tr>
<td>$X^2\Sigma^+$</td>
<td>14.009</td>
<td>8.4 1.9 8.4 - D$^+$</td>
<td></td>
</tr>
<tr>
<td>$A^2\Pi$</td>
<td>16.538</td>
<td>5.9 -0.6 5.9 - D$^+$</td>
<td></td>
</tr>
<tr>
<td>$B^2\Sigma^+$</td>
<td>19.665</td>
<td>2.75 -3.75 2.75 - D$^+$</td>
<td></td>
</tr>
</tbody>
</table>

D$^+$ = bond dissociation energy of CO-C$^+$ ($\sim$5 eV)

See ref (36) for ionisation potentials.

Reaction (1) does not occur with thermalised ions.
R2 can occur with $A^2\Pi$ and $B^2\Sigma^+$. R3 occurs with $B^2\Sigma^+$ only. The reaction:-

$$CO^+ + CO \rightarrow CO_2^+ + C$$

was shown experimentally not to occur.

With thermalised ions therefore CO$_2$ can only be formed directly via reaction (2). R3 is a possible source of oxygen atoms.

b  Reaction with CH$_4$ and O$_2$

The purpose of this section is to estimate the amount of additive which must be added to intercept the primary ions CO$^+$.

Consider the two step dissociation and recombination sequence:-

R1, R2 and R3 refer to the reactions 1, 2 and 3 on page 30.
\[
\begin{align*}
\text{CO} & \xrightarrow{R_0} \text{CO}^+ + e^- \\
e^- + \text{CO}^+ & \leftrightarrow \text{CO} \\
\text{e}^- + \text{CO}^+ & \xrightarrow{k_r} \text{CO} 
\end{align*}
\]

By mass and charge conservation at stationary state:

\[
R_0 = k_r [e^-] [\text{CO}]
\]

\[
[e^-] = [\text{CO}^+] 
\]

thus:

\[
[e^-]_{SS} = [\text{CO}^+]_{SS} = \left( \frac{R_0}{k_r} \right)^{1/2}
\]

The mean electron and positive ion lifetimes are equal and may be estimated from the relation:

\[
t_m = \frac{1}{k_r} \left( \frac{R_0}{k_r} \right)^{1/2}
\]

At atmospheric pressure, electron-positive ion recombination processes are pseudo bimolecular (37) a representative velocity constant is; \(5 \times 10^{17}\) cc/mole sec. The maximum gamma dose rate used in the experiments to be described was \(2.8 \times 10^{13}\) eV/sec. Assuming that the energy required to form an ion pair in carbon monoxide is 30.6 eV, this absorbed dose rate is equivalent to a primary ion production rate of \(1.57 \times 10^{-12}\) moles/cc sec., thus:

\[
[e^-]_{SS} = 1.76 \times 10^{15}\text{ moles/cc}
\]

and \(t_m = 1.11 \times 10^{-3}\)

The rate of the reaction:

\[
\text{CO}^+ + \text{CD}_4 \rightarrow \text{COD}^+ + \text{CD}_3
\]

has been determined by low pressure mass spectrometry (38) to be; \(5.5 \times 10^{14}\) cc/mole sec. Clearly the mean lives of \(\text{CO}^+\) in reactions (2) and (3) are equal when:

\* \text{stationary state}
\[ \frac{k_r [e^-] [CO^+]}{[CD_4]} = \frac{k_3 [CD_4]}{[CO^*]} \]

i.e. \[ [CD_4] = \left( \frac{k_r}{k_3} \right) [e^-] \]

\[ = 1.76 \times 10^{-12} \text{ moles/cc} \]

Thus \[ \frac{[CD_4]}{[CO]} = 3.9 \times 10^{-8} \text{ for stp CO} \]

Therefore if it can be assumed that there is no significant isotope effect, secondly, that ion molecule reactions of \( CO^+ \) with other hydro-carbons have similar velocity constants, \( CO^+ \) should be intercepted at all practicable mixing ratios.

Confirmation of this prediction may be found by considering the effect of \( O_2 \) addition on \( G(CO_2) \) during radiolysis of carbon monoxide.

\( G(CO_2) \) is known to be very sensitive to traces of oxygen. Clay et al (39) postulated the existence of an ionic chain mechanism to explain the dependence of \( G(CO_2) \) on \( O_2/CO \) ratio. Anderson (1) found the enhancement of \( G(CO_2) \) caused by addition of \( O_2 \) to be reduced at high dose rates. For example at a dose rate of \( 6 \times 10^{15} \text{ eV/cc sec} \), yield enhancement was not observed until \( O_2 \) was greater than 10 ppm, at a total pressure of 1 atm.

Consider then that the ion molecule reaction postulated by Clay et al:

\[ CO^+ + O_2 \rightarrow CO_3^+ \] (4)
to initiate the ionic chain, competes with volume recombination, reaction 2. Clearly as:

\[ \kappa_4 [O_2] \rightarrow \kappa_2 \left( \frac{R_0}{k_2} \right)^{1/2} \]

\( G(CO_2) \) will be enhanced. At a dose rate of \( 6 \times 10^{15} \text{ eV/cc sec} \), assuming that \( k_1 \) is about \( 5 \times 10^{17} \text{ cc/mole sec} \):

\[ k_2 \left( \frac{R_0}{k_2} \right)^{1/2} \sim 1.3 \times 10^4 \]

10 ppm \( O_2 \) in s.t.p CO corresponds to \( 4.5 \times 10^{-10} \) moles/cc, thus \( k_4 \) must be about \( 3 \times 10^{13} \text{ cc/mole sec} \). This is about 10 times less than the usual velocity constant for ion-molecule reactions measured in low pressure mass spectrometers. However, because of the practical difficulty of measuring ppm quantities of \( O_2 \) in CO, secondly the approximations involved in the above calculation the original prediction may be considered to be confirmed.

On the basis of the evidence presented above, it may be concluded that if oxygen atom formation results from neutralisation of \( CO^+ \) by thermalised electrons, oxygen atoms cannot be detected by addition of oxygen atom scavengers.
A energy level diagram for carbon monoxide is given by Herzberg. (40) The purpose of this section is to consider whether oxygen atoms can be formed from such reactions as:

$$\text{CO}^* + \text{CO} \rightarrow \text{C}_2\text{O} + \text{O}$$

Secondly to discuss the possible interception of CO* by an oxygen atom scavenger before it undergoes such a reaction.

1. **Triplet Excitation.**

The heat of formation of C₂O may be estimated as follows. The onset of photochemical reactivity of C₃O₂ is about 3100 Å (8). The heat of formation of C₃O₂ is -1.05 eV (41). Thus the heat of formation of C₂O is about +4.1 eV. Thus the least excitation energy for CO* is 8.96 eV (1380 Å). The reaction is thus only possible with the $b^{3}Σ^+$ state.

Liuti et al (42) have demonstrated that the CO($a^3Π$) (6 eV) state may be produced by energy transfer from Hg ($6^3P_1$) (1849 Å photolysis). Addition of water during 1849 Å mercury sensitised photolysis of carbon monoxide was found to result in methanol formation. It is not known if the methanol resulted from reaction of CO ($a^3Π$) with water, or the reaction of carbon atoms produced via the reaction:

$$\text{CO}^* + \text{CO} \rightarrow \text{CO}_2 + \text{C}$$
with water. No other studies concerned with the reactivity of triplet electronically excited states of carbon monoxide have been published.

2 Singlet Excitation.

Very little is known about the chemical reactivity of CO \((A^1\Sigma^+)(8.065 \text{ eV})\). It has a very short radiative lifetime \((\tau \approx 10^{-8} \text{ sec})\) \((43)\). Early work on the 1295 and 1470 Å photochemistry is reviewed by McNesby \((44)\). Photolysis of CO/H\(_2\) mixtures at these wavelengths results in the formation of \((\text{HCO})_2\) and HCHO. This has been postulated to be due to:

\[
\text{CO}^3 + \text{H}_2 \rightarrow \text{CO} + 2\text{H}
\]

It is not known if CO\((A^1\Sigma^+)\) undergoes a transition to a triplet state before this reaction occurs.
Formation of carbon suboxide during radiolysis of carbon monoxide gas.

Anderson (1) demonstrated that the reaction stoichiometry of the gas phase radiolysis of carbon monoxide is:

\[ 4n \text{CO} \rightarrow n \text{CO}_2 + (\text{C}_3\text{O}_2)_n \]

where \((\text{C}_3\text{O}_2)_n\) is polymeric carbon suboxide.

Formation mechanism.

Dondes (45) reports that polymerisation of monomeric \(\text{C}_3\text{O}_2\) takes place in a 3:1 Helium/\(\text{C}_3\text{O}_2\) mixture on exposure to polonium - 210 - \(\alpha\) radiation. The polymerisation rate is about 10 times as fast as in an equivalent mixture heated to 50°C and not exposed to ionising radiation. Experiments designed to characterise the difference in the polymer prepared by these two methods were not however completed.

Blake (46) studied the gamma radiolysis of carbon suboxide gas. Products of the radiolysis were found to be polymer and \(\text{CO}\). In contrast to the thermal polymerisation which produces a uniform film over the surface of the reaction vessel, the polymer collected at the base of the reactor indicating that it was formed in the gas phase. Homogeneous gas phase formation of \(\text{C}_3\text{O}_2\) polymer has been clearly demonstrated during radiolysis of carbon monoxide by Anderson (1). Blake (46) also demonstrated that radiolysis of 50:50 \(\text{C}_3\text{O}_2/\text{C}_2\text{H}_4\) mixtures did
not produce allene, further addition of oxygen did not reduce the rate of polymerisation. Liuti et al (42) found that the 1849 Å mercury sensitised photolysis of CO results in the formation of CO₂, monomeric C₃O₂ and polymeric C₃O₂.

The experiments described above suggest that polymerisation of monomeric C₃O₂ proceeds readily under the influence of ionising radiation. Monomeric C₃O₂ has not been detected during radiolysis of CO gas in contrast to the photolysis of CO gas. It may therefore be tentatively concluded that formation of polymeric C₃O₂ during radiolysis of CO is preceded by formation of monomeric C₃O₂, the polymerisation process being initiated by charge transfer from the primary ion CO⁺ to monomeric C₃O₂ (I.P. = 10.6 eV) (47).

2 The influence of monomeric C₃O₂ formation on G(CO₂)

Von Weyssenhoff et al (48) studied the reaction of O(3p) with C₃O₂ gas in a fast flow system. They suggested that the principal reaction was:

\[ \text{O}(3p) + \text{C₃O₂} \rightarrow 3\text{CO} \]

The velocity constant of this reaction was not estimated. The authors however suggested that competition for O(3p) between CO and C₃O₂ could influence the kinetics of CO₂ formation during radiolysis of carbon monoxide. Such a competition could possibly explain why G(CO₂) is less than the theoretical
maximum calculated on the assumption that:-

a) CO\(^+\), e\(^-\) recombination

b) dissociation accompanying ion pair formation.

Both produce oxygen atoms which react with CO to form CO\(_2\).

Consider now the sequence:

\[
\begin{align*}
\text{CO} & \rightarrow \text{C} + \text{O} & & \text{---} & R_0 \\
\text{C} + \text{CO} & \rightarrow \text{C}_2\text{O} & \rightarrow & \text{C}_3\text{O}_2 \\
\text{O} + \text{CO} & \rightarrow \text{CO}_2 & & \text{---} & (1) \\
\text{O} + \text{C}_3\text{O}_2 & \rightarrow 3\text{CO} & & \text{---} & (2)
\end{align*}
\]

Since it is well established experimentally that CO\(_2\) formation is straight line to 0.1% conversion in the dose rate independent region (1), it may be postulated that:

\[
(C_3O_2)_{ss} = R_0 / k_2(0)_{ss}
\]

i.e. \[
\frac{d(CO_2)}{dt} = \frac{k_1}{k_2} \frac{(CO)}{(C_3O_2)_{ss}} \times R_0
\]

or \[
\frac{(C_3O_2)_{ss}}{CO} = \frac{k_1}{k_2} \times \frac{10^2}{W_{CO} G(CO_2)}
\]

\[
k_2 = (4 \pm 2) \times 10^{11} \text{ cc/mole sec at 25°C (49)}
\]

thus \[
(C_3O_2)_{ss} / CO = 4.5 \times 10^{-5}
\]

The subscripts 1 and 2 in the equations on page 39 refer to reactions 1 and 2 of the mechanism written on page 39. 

\(R_0\) means rate of production.
However there is evidence (vide supra) to support the idea that polymeric C$_3$O$_2$ is formed from monomeric C$_3$O$_2$ by charge transfer from the primary ion CO$^+$. Further it was shown on page 33 that an ion interceptor:carbon monoxide ratio of $3.9 \times 10^{-8}$ would intercept about half of the positive ions before ion-electron recombination at a dose rate of $2.8 \times 10^{13}$ eV/cc sec.

The theory that G(CO$_2$) is influenced by monomeric C$_3$O$_2$ formation is thus not compatible with the theory that C$_3$O$_2$ polymerisation is initiated by CO$^+$ ion interception.
Reactions of \(C_2O\) and \(C\)

\(C_2O\) and \(C\) may clearly be postulated to be intermediates in the production of carbon suboxide during carbon monoxide radiolysis. The purpose of the following section is to discuss the reaction characteristics of these species with both hydrocarbons and carbon monoxide.

1 Reaction of \(C_2O\) with hydrocarbons.

The reactions of \(C_2O\) have been studied using the photolysis of carbon suboxide. When \(\lambda > 2900 \text{ Å}\) triplet \(C_2O\) is formed, however when \(\lambda \approx 2540 \text{ Å}\) singlet \(C_2O\) is formed.

a) Reaction products and mechanisms.

When \(\lambda > 2900 \text{ Å}\) the following mechanism was proposed by Bayes (50)

\[
\begin{align*}
C_3O_2 + h\bar{\nu} & \rightarrow C_2O + CO \\
C_2O + C_2H_4 & \rightarrow C_3H_4 + CO \\
C_2O + C_3O_2 & \rightarrow \text{polymer} + CO
\end{align*}
\]

\(C_3H_4 = 80\%\) allene + \(20\%\) methyl acetylene

This work was extended (51) to include propylene, cis-2-butene, trans-2-butene and isobutene. In every case the corresponding allene was found to be formed. The allene yield was found to be decreased as pressure increased. This was rationalised in terms of the mechanism:
\[
\begin{align*}
C_2O + \text{olefin} &\rightarrow I^\# \\
I^\# &\rightarrow \text{allene + isomers} \\
I^\# + M &\rightarrow \text{non allene products.}
\end{align*}
\]

In the case of 2,3 dimethyl 1-2-butene a dimer \((C_6H_{12}C_2O)_2\) is claimed as a reaction product at high pressures (52), stabilisation of the initial association complex is thus indicated.

The reaction of triplet \(C_2O\) with paraffins has been studied by Baker et al (53) who claim that the photolysis products in the presence of methane, ethane, propane and neopentane are ethylene, propylene, isobutene and 3,3 dimethyl but-1-ene respectively. The dependence of the product yields on pressure was not studied.

**Singlet \(C_2O\)** When \(\lambda \sim 2450 \, \text{Å}\) singlet \(C_2O\) is formed. Extensive studies of its mechanism of reaction have not been reported. Formation of allene from ethylene has however been demonstrated (54)

b) **Evidence for the existence of two electronic states of \(C_2O\)**

Bayes (54) found that the addition of oxygen when 2900 Å supressed allene formation in \(C_3O_2/C_2H_4\) mixtures. No such effect was observed when \(\lambda > 2540\, \text{Å}\). The mechanism proposed was:-
A radiation less transition

\[ C_3O_2 \rightarrow C_3O_2(s) \rightarrow \text{radiation less transition} \]

\[ C_3O_2 \rightarrow C_3O_2(T) \]

\[ C_2O(T) + CO \]

\[ \lambda \sim 2540 \text{ Å} \]

\[ C_3O_2 \rightarrow C_3O_2(s) \rightarrow C_2O(s) + CO \]

Cundall et al (55) claim to have demonstrated triplet state formation during 2540 Å photolysis. During the photolysis of C_3O_2/cis-butene-2 mixtures the quantum yield of CO decreases as the partial pressure of cis-C_4H_8-2 increases and that trans C_3H_8 is formed. The mechanism proposed was:

\[ C_3O_2 (T) + \text{cis C_4H_8 - 2} \rightarrow \text{cis C_4H_8 - 2 (T) + C_3O_2} \]

\[ \downarrow \]

\[ \text{cis C_4H_8 - 2 + trans C_4H_8} \]

Mercury contamination of the additive could also explain this result; both by preferential absorption of the incident quanta and by energy transfer to the butene.

c) Rate Constants.

Triplet C_2O was found to react with NO at 135 times the velocity of O_2 and 10^{14} times the velocity of ethylene (49). The comparative velocity constant data obtained by Willis (51) are quite different from those obtained by Baker et al (56). The reason for the discrepancy has not yet been
resolved. It can only be suggested that Baker (56) did not take into account the known pressure dependence of the reactions. Comparative velocity constant data for paraffins were reported by Baker (53). It may be tentatively concluded that C₂O reacts with alkanes more slowly than with alkenes.

Comparative rate constant data for singlet C₂O is not so extensive as for the triplet. Morrow (57) studied the flash photolysis of C₃O₂ in the λ range 2300 – 2900 Å and found an absorption at 40 50 Å. This was thought to be due to a C₃ intermediate. Assuming that this radical is formed by reaction of C₂O with C₃O₂, the quenching order for C₃ suppression and thus C₂O reaction velocity with the following additives was found to be

\[ C₂H₄ > C₂H₂ > NO > O₂ > CO \]

2 Reaction of carbon atoms with hydrocarbons.

a Reaction products.

The reactions of hot carbon atoms, produced by such techniques as the N¹⁴(np) C¹⁴ reaction, have been extensively reviewed and discussed by Wolfgang (58) and Wolf (59).

High yields of acetylene and other unsaturated products are characteristic of the reaction of C atoms with hydrocarbons in the gas phase. Sckell (60) used carbon vapour as a source of atomic carbon for a study of the
reaction of C atoms with condensed olefins at 77°K. Under such conditions acetylene is not formed, reactions of the primary association complex are observed.

Both the techniques described above are very complex and sources of experimental error will not be discussed here.

A more convenient source of carbon atoms is probably the 1470 Å photolysis of C\textsubscript{3}O\textsubscript{2} \cite{61}. For 1470 Å photolysis of C\textsubscript{3}O\textsubscript{2}/CH\textsubscript{4} mixtures the following mechanism has been proposed \cite{61}

\[
\begin{align*}
C\textsubscript{3}O\textsubscript{2} + h\nu &\rightarrow C + 2CO \\
C + CH\textsubscript{4} &\rightarrow C\textsubscript{2}H\textsubscript{4}^x \\
C\textsubscript{2}H\textsubscript{4}^x + M &\rightarrow C\textsubscript{2}H\textsubscript{4} + M \\
C\textsubscript{2}H\textsubscript{4}^x &\rightarrow C\textsubscript{2}H\textsubscript{2} + H\textsubscript{2}.
\end{align*}
\]

Higher n-alkanes absorb 1480 Å light \cite{62}, this could possibly limit the extension of this technique to include other n-alkanes. For ethylene, acetylene, propylene and butene-1 \cite{63,64} the same argument would appear to hold true.

b Rate Constants.

Meaburn and Ferner \cite{65} have found an optical absorption at 2478 Å during pulse radiolysis of carbon dioxide and carbon monoxide, this was ascribed to the 1\text{P} \rightarrow 1\text{S} transition of the carbon atom. Addition of small quantities of CH\textsubscript{4} and C\textsubscript{3}H\textsubscript{6} reduced the half life of the optical absorption thus indicating the occurrence of fast insertion reactions.
Summary.

The dominant mechanism of reaction of C<sub>2</sub>O and C with hydrocarbons is carbon insertion. In the case of C<sub>2</sub>O this results in the formation of allene at low pressure and low carbon number. When either the total system pressure or the carbon number of the interceptor hydrocarbon is increased, stabilisation of the associated complex is favoured. Carbon atom insertion results in a less stable association complex and acetylene is a characteristic fragmentation product. Velocity constant data is not extensive and is often conflictory, it is clearly an area for future research.
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Section 2 Experimental Techniques and Data

The author does not claim that the techniques described below are the most suitable for every experiment described. The final technique evolved was often a compromise between the availability of materials and the time which could be allotted to the experiment. The above statement applies especially to the choice of columns for the chromatograph, the design of the reaction vessels used for pressures above atmospheric and the procedure used for making up 3 component gas mixtures.

A Safety Considerations.

The following section lists the main sources of hazard and precautions taken.

Pyrex glass was used extensively in the construction of the vacuum gas handling system and reaction vessels. This was because it is chemically inert and does not brittle fracture on cycling between room and cryogenic temperature, also because of the ease with which apparatus may be constructed by a skilled glass blower. An eye shield was worn when working with glass apparatus under high vacuum or at pressures above atmospheric.

Liquid Oxygen was used because:

a) Carbon monoxide may be safely distilled from $-183^\circ C$ to $-196^\circ C$. 
b) It is the only readily available cryogenic fluid to cool a trap which will quantitatively extract "mass spectroscopically pure" CO\textsubscript{2} from a CO\textsubscript{2}/CO mixture.

Clearly fracture of a Pyrex vessel containing CO and immersed in liquid oxygen could cause a spark and thus an explosion. Such a mishap did not occur during the course of the experiments. Liquid oxygen was not used to condense large quantities of hydrocarbons. Both liquid oxygen and liquid nitrogen were used in the Co-60 source to cool irradiation vessels. Large quantities of ozone were produced when liquid oxygen was used. Irradiation of liquid nitrogen produced nitrogen oxides due to combination between N\textsubscript{2} and O\textsubscript{2}. Dewars containing liquid oxygen or nitrogen under these conditions were not allowed to boil dry, the remaining liquid after irradiation was dumped on waste ground.

**Carbon Monoxide.** All the experiments were performed in a well ventilated lab. The exhaust from the gas handling apparatus was fed to the ventilation extract.

**B Irradiation Source and Reaction Vessels.**

The work described in this report was performed with the Imperial College 17,000 Ci Co-60 source. The design of this source is described in outline by Spalding et al (1).

The gas phase experiments were mostly performed with cylindrical vessels of about 145 cc capacity constructed of
The method of calculation described here is explained in greater detail in the appendix. The method of dosimetry using tritium β particles ($\text{H}_3^2\beta$) is also explained in the appendix.
Pyrex. For filling pressures up to about 3 atm (abs.), A.D. Wood spring loaded stopcocks were found to be unsuitable. The holding bolt sheared off the key on tightening. The Springham design was more satisfactory, however fracture of the key was sometimes observed on tightening.

For pressures of about 10 atm; 10 cc capacity, cylindrical Pyrex vessels having a wall thickness of 2.5 mm were used. These were fitted with Hoke International 482 bellows seal valves via a Jencon's 1/4" Kovar-Pyrex graded seal, the connection was soft soldered (diag. 5). The maximum pressure attainable was 200 psi.

Pyrex stopcocks were lubricated with Apiezon M grease. Pyrex vessels were cleaned by reannealing after use.

Experiments with cryogenic liquid carbon monoxide (77°K) were performed in a 3-4 cc Pyrex or silica vessel. The vessels had long narrow necks (~ 20 cm) and were immersed in liquid nitrogen contained in a 500 cc capacity narrow neck Dewar.

Dosimetry

In solids and liquids Co-60 photons are absorbed by Compton interaction. In small gas phase reaction assemblies however, photon absorption occurs mainly at the boundary and the gas cavity is irradiated by scatter electrons when the pressure is low. A technique is therefore required to
estimate the energy absorption in the gas from Fricke
dosimetry.

The method of calculation adopted was first described
by Johnson (2). The dose rate in the vessel boundary is
first calculated by multiplying the measurements obtained
from Fricke dosimetry by the ratio of the electron density
of the wall to the water. The dose rate in the gas is then
estimated using the Bragg-Gray relation.

Boundary/gas, electron stopping power ratios may be
estimated from the equations given by Baily (3). The
following relation may be derived:

\[ E_{CO} = E_{H2O} \left( \begin{array}{c}
\frac{\varepsilon_{CO}}{\varepsilon_{H2O}} \\
1.336 - 0.1642 \ln Z_{W}
\end{array} \right) \]

\[ Z_{W} \]

\[ E = \text{rate of energy absorption per gram} \]
\[ \varepsilon = \text{electron density (electrons/gm)} \]
\[ Z = \text{mean atomic number (electrons/atom)} \]
\[ Z_{W} \text{ for Pyrex may be estimated from the composition data} \]
\[ \text{in Ref. 4. It may be shown that:} \]
\[ E_{CO} = 0.95 E_{H2O} \text{ eV/gm time (at stp.)} \]

As the gas cavity pressure increases direct photon
absorption in the gas becomes an important energy transfer
mechanism. Thus the absorbed dose rate becomes a function of
(density)\(^2\) rather than density and the Bragg-Gray law no
longer holds. Toi(5) estimated dose rates in dense ammonia,con-
tained in a small stainless steel pressure vessel, by \( H_{3}P \)
and Fricke dosimetry. It was found that Fricke dosimetry underestimates the true dose rate.

Substitution into the equation:

\[ E_{\text{NH}_3} = \frac{\epsilon_{\text{NH}_3}}{\epsilon_{\text{H}_2\text{O}}} \cdot E_{\text{H}_2\text{O}} \left[ \frac{1.336 - 0.1642 \ln Z_{\text{NH}_3}}{1.336 - 0.1642 \ln Z_{\text{Fe}}} \right] \]

gives a value of 1.47 for the bracketed term. This value is in good agreement with the dose rate ratio \( H^3^\beta/\text{FeSO}_4 = 1.55 \) in the density range \( 5.5 \times 10^{-4} - 2.5 \times 10^{-2} \text{ gram cc}^{-1} \). Thus for small reaction vessels, it may be concluded that the method of calculation described above is valid for quite high densities \( (2.5 \times 10^{-2} \text{ gm/cc}) \).

Dose rates in cryogenic liquid CO were determined by Fricke dosimetry. Water replaced the cryogenic cooling boundary during this operation.

D. U.V. Light Source (2537 Å + 1849 Å)

The light source consisted of two opposed Engelhard-Hanovia Bactericidal Unit 12 lamps.

The photolysis vessel was a blanked off square cylinder of silica 3.2 cm id and 29.5 cm long (248 140 cc). A Pyrex stopcock was attached to a vessel via a black waxed B10 cone and socket joint. To filter the 1849 Å photons, the vessel was immersed in a cylindrical silica tank (8 cm id) containing an aqueous saturated solution of sodium chloride.
E Construction, Operation and Performance of an A.E.I
MSIO Mass Spectrometer.

During the course of the work an A.E.I MSIO mass spectrometer became available. This instrument was used to measure as little as $2.5 \times 10^{-9}$ moles of CO$_2$ (p 71). The instrument can be operated in many different ways depending on the type of sampling system and a variety of control systems can be used. During construction and operation of the instrument it was found that the instruction manual was often misleading. The following notes describe the features of the instrument used by the author.

1) Auto. control system. This system was designed to:-
a) Switch off all systems in the case of cooling water failure.
b) Switch off the MS10 filament in the case of the system pressure rising above $10^{-4}$ torr.
c) Seal off the stack (the term stack refers to the total assembly of components comprising analyser tube, cold trap and diffusion pump) and switch off the diffusion pump in the case of rotary pump failure.

The lay-out of the system is shown in diag. (1). The flow controlled switch follows the design described by Conlon (6). The pump and backing line control is as described in (7).

2) Sample Inlet System.

A batch sampling system designed as described in (8) was constructed as shown in diag. (2).

3) Pumpdown.

The orifice was set to give a pumping speed of 1 litre/sec.

The attainment of initial vacuum $10^{-2}$-$10^{-3}$ torr was indicated by:-
Electromagnetic control system used with the A.E.I. M.S.10 mass spectrometer unit

1) Transformer 240/12 volts
2) Rectifier 200 ma 40 piv
3) Flow controlled switch
4) Relay 12v 120 A
5) Pump and backing line auto. control
6) Manual switch board
7) Ion gauge control
8) Vacuum control relay
9) M.S.10. control
10) Protection link switch
11) Stack heaters
Sample injection system used with the A.E.I. MS10 mass spectrometer unit.

1) To pumps
2) Sprinham high vacuum glass stopcocks
3) Sample holder connexion
4) Cone and Socket connector
5) Reservoir volume
6) Pirani vacuum gauge
7) A.E.I. pipeline valve (nylon diaphtaqm)
8) A.E.I. sample inlet valve (type X23)
9) To MS10 stack
a) blackout of the discharge tube mounted on top of the rotary pump oil receiver.
b) condensation not forming on the cold trap when filled with liquid nitrogen.

Because the ion gauge filament readily burns out at pressures in excess of $10^{-3}$ torr it was found useful to fit a Pirani gauge during test pumping runs. An Edwards G5B-2 gauge was attached to a $1\frac{1}{2}''$ flange via a brass/Pyrex cone socket connection, and bolted to the adaptor tube in place of the ion gauge.

To prevent ion gauge filament burn-out the gauge must not be turned on for at least 2 hours after the diffusion pump is switched on.

15 hours pumping was sufficient to reduce the system pressure to about $10^{-5}$ torr.

4) Bakeout

All stack flange bolts were smeared with moly-graphite grease to prevent seizure during bakeout.

The stack was heated by attaching band heaters to the flanges and heavily lagging the metal surfaces with asbestos string. Temperatures of about $350^\circ$C could be attained.

The leak valve contains polythene gaskets and was water cooled during baking periods.
After the initial baking period (about 6 hours) the flanges had to be retightened.

After about a week of continuous pumping and baking the system pressure was reduced to about $2 \times 10^{-8}$ torr.

Baking causes oxidation of the source plug pins. The pins were carefully cleaned and the filament potential (1.6v AC) checked before operation.

5) Leak testing.

Two types of dynamic leak test were performed. For rough vacuum leaks the suspected component was covered with Apiezon sealing compound Q. For high vacuum leaks argon tracer gas was used. To prevent false results during this test caused by the instrument drifting off the $m/e = 40$ setting; the sampling system was filled with argon and periodic injections of argon were made.

6) Ion gauge filament pumping and desorption.

The ion gauge filament had a marked effect on the parent mass height and cracking spectra of compounds injected into the analyser. The effect is illustrated in the table 3. To minimise this effect the vacuum protection circuit was cut out during test sample injection. After reconstruction (see next section) the effect was no longer observed.
Table 3 The effect of the ion gauge on the observed cracking pattern of carbon dioxide.

Injection $\sim 2.54 \times 10^{-6}$ moles
Reservoir volume $\sim 500$ cc
Pumping speed 1 litre (sec)$^{-1}$

<table>
<thead>
<tr>
<th>m/e</th>
<th>Range</th>
<th>Meter reading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>nd</td>
</tr>
<tr>
<td>12</td>
<td>100</td>
<td>0.46</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>16</td>
<td>100</td>
<td>0.68</td>
</tr>
<tr>
<td>28</td>
<td>1000</td>
<td>0.12</td>
</tr>
<tr>
<td>44</td>
<td>1000</td>
<td>0.9</td>
</tr>
</tbody>
</table>

a) Initial injection with ion gauge off
b) ion gauge switched on
c) ion gauge turned off again
Reconstruction

The unit was modified to make it as an MS10 Argon Dating System 1(9). This system has the advantage that the analyser tube can be shut off at high vacuum. Further, the ion gauge is shielded from the analyser tube by the orifice plate, the mass flow rate from the ion gauge is thus greater than from the analyser tube. These latter considerations probably account for the lack of effect of the ion gauge on the observed cracking pattern with this system. The ultimate vacuum attained ($\sim 5 \times 10^{-8} \text{ torr}$) was the same as that attained with the standard system.

Reaction Product Collection Trap.

Before injection into either the MS.10. or V.P.C. units, both scavenger and reaction products were fractionated from the carbon monoxide by means of the spiral trap shown in diag. 3. The lower portion of the trap was immersed in liquid $N_2$ or $O_2$. The flow through the trap was regulated by a Metheson microflow valve (model 150) fitted with B14 brass cones.

Preparation and purification of materials.

Carbon monoxide was prepared by the dehydration of deaerated formic acid with degassed acetic anhydride containing $0.5\%$ concentrated sulphuric acid. It was purified by distillation from liquid oxygen to liquid nitrogen.
Sampling Loop

1) 1/8" o.d. stainless steel tube
2) backing plate
3) compression spring
4) B14 brass cone 5) B14 pyrex socket
6) clamp
7) Springham 4mm H.V. spring loaded valve
8) by-pass loop 9) ample loop
Acetylene. Matheson C.P. acetylene was further purified to remove traces of acetone as follows. 5 litres of the gas were equilibrated with 50 cc of a solution of 2, 4-dinitrophenyl hydrazine in 30% perchloric acid. The scrubbed gas was then cryo pumped through a packed bed of phosphorous pentoxide and deaerated by multiple freeze thaw cycles.

Nitrous Oxide. B.O.C. Medical grade N₂O was deaerated by multiple freeze thaw cycles.

Propylene and Propane.

Initially crude industrial grades of these materials were used. Reasonably pure preparations could be made by flowing the gas through an annular trap refrigerated to -78°C. This step removed most low boiling impurities. The middle fraction was subsequently collected and deaerated by multiple freeze thaw cycling. Later experiments were performed with Matheson CP grade gas without further purification.

H Preparation of Gas Mixtures.

Note on mixing times.

It was shown on page 17 that the time taken for a molecule to travel a distance \( x \) by diffusion in the gas phase is given by the relation:

\[
 t_D = 0.75 \frac{x^2}{\Gamma} \rho / r
\]
If the minor condensible component of a gas mixture is condensed at the base of the reaction vessel, then the time taken for this component to diffuse to the top of the vessel on warming to room temperature, may be considered to be the mixing time.

The 145 cc vessels used in many of the experiments described here were about 16 cm long. Thus at 3.3 atm and 25°C \( t_D \) is about 2 hrs. An "overnight" mixing time is therefore adequate.

**CO/C_2H_2/C_3H_6 mixtures.**

The essential features of the apparatus are shown in diag. 4. The \( C_2H_2 \) and \( C_3H_6 \) are first premixed as follows:

a) Fill 8 to the required partial pressure with \( C_3H_6 \). Cryopump contents of 8 into 7

b) Fill 8 to the required partial pressure with \( C_2H_2 \). Refrigerate 8 and transfer contents of 7 into 8.

c) Shut off 8 and allow to mix overnight at room temperature.

The final mixture is then made as follows:

d) Fill reaction vessels to the required partial pressure with premixed \( C_2H_2/C_3H_6 \)

e) Refrigerate the reaction vessels with liquid oxygen.

f) While still refrigerated fill reaction vessels with carbon monoxide.
Assembly for making 3 component gas mixtures at 3.3 atm.

1) to vacuum pump  2) seal off valve  
3) Pirani gauge head  4) traps at -78° C  
5) mercury manometer  6) gas inlet port  
7) mixing vessel B  8) mixing vessel A  
9) needle valve  
10) stacked reaction vessel seal off valves  
11) manifold  12) to reaction vessels.
When filling with CO an absolute filling pressure of 1 atm produces an absolute internal pressure of 3.3 atm on warming to room temperature.

**CO/C₃H₈ mixtures at 10 atm.**

In the absence of a high pressure supply of these two materials 50:50 mixtures were made by cryopumping from a ballast volume (diag. 5). Clearly the pressure of each component in the reaction vessel is given by the expression:

\[ P_R = \frac{V_B}{V_R} (P_1 - P_2) \]

\( P_R \) = partial pressure of each component in the reaction vessel after warming to room temperature.

\( V_B, V_R \) = Ballast and reactor capacity respectively.

\( P_1, P_2 \) = pressure of each component in the ballast volume before and after refrigeration of the reaction volume respectively.

For the first component \( P_2 \) must be zero.

**CO - C₃H₆ mixtures (1 - 3.3 atm).**

These were made by freezing "known PVT quantities" of propene into the reaction vessels and adding CO while keeping the vessels refrigerated in liquid oxygen.
150 p.s.i. Reaction vessel and filling arrangement.

1) Pyrex 6mm stopcock
2) Ballast volume
3) B14 Pyrex socket
4) B14 brass cone
5) Copper tube (1/4"
6) Hoke 482 bellows seal valve
7) Kovar - Pyrex graded seal (1/4"
8) Reaction volume
I Chemical Analysis.

1 Carbonyl, Epoxide and Ketone products.

The total yields of carbonyl and ketone products were estimated by reaction with 2,4-dinitrophenyl hydrazine (10). The optical density of the coloured complex obtained using this technique was measured on a Unicam SP-500 spectrophotometer.

The individual yield of each component was measured on a Perkin-Elmer 452 unit using a flame ionisation detector. A 2 metre column of polyethylene glycol on 'Chromosorb P' and a 2 metre pre-column of tetra ethylene glycol dimethyl ether on 'Chromosorb P' were used. The pre-column ensured a good separation between scavenger and reaction products. The operating temperature was 40°C. The carrier gas was argon, 40 cc per min., and the splitting ratio was 1:9 (F.I.D. to effluent).

Calibration of the spectrophotometer was achieved by preparing standard solutions by mixing quantities of purified vapour of known P.V.T with water. The gas chromatograph was calibrated by injecting aliquots of known P.V.T. via the sampling loop. Representative calibration factors are shown in table 4. The calibration factors are defined as follows:
For the gas chromatograph:

\[ CF = \frac{\text{No. moles} \times \text{Range}}{\text{Peak Area}} \]

For the spectrophotometer

\[ CF = \frac{\text{OD at 430 nm}}{\text{No. moles}} \quad (1 \text{ cm path-length}) \]

Table 4 Calibration Factors.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calibration Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VPC x 10^8</td>
</tr>
<tr>
<td>Propanal</td>
<td>3.69 ± 0.31</td>
</tr>
<tr>
<td>Acetone</td>
<td>3.44 ± 0.12</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>6.42 ± 0.10</td>
</tr>
<tr>
<td>Propene Oxide</td>
<td>2.8 ± 0.44</td>
</tr>
</tbody>
</table>

2 Carbon Dioxide.

3 techniques have been used:–

a) PVT measurement. The operation was performed with a gas burette of conventional design. The CO₂ was first separated from the CO by passing the mixture through a spiral trap half immersed in liquid oxygen. The CO₂ was then transferred to the gas burette via a single stage diffusion pump and a Toepler pump.
b) **Gas Chromatography.** The following conditions were used. Hydrogen carrier at 20 cc/min, 2 metre silica gel column, a temperature of 35°C and a thermistor detector.

c) **Mass Spectrometry.** The most sensitive conditions were: A reservoir volume of 500 cc and a pumping speed of 1 litre per second.

Table 5 summarises the least detectable limits.

5 **Carbon Suboxide.**

The yield and composition of the carbonaceous deposit formed during radiolysis was determined by vacuum pyrolysis followed by burn off of the residual carbon.

Table 5 Least Detectable Limits.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Technique</th>
<th>LDL (moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>DNPH, VPC</td>
<td>1.24 x 10⁻⁷, 6.3 x 10⁻⁹</td>
</tr>
<tr>
<td>Propanal</td>
<td>DNPH, VPC</td>
<td>1.64 x 10⁻⁷, 3.7 x 10⁻⁹</td>
</tr>
<tr>
<td>Propene Oxide</td>
<td>VPC</td>
<td>2.9 x 10⁻⁸</td>
</tr>
<tr>
<td>Acetone</td>
<td>DNPH, VPC</td>
<td>8.5 x 10⁻⁷, 3.5 x 10⁻⁹</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>VPC, FVT</td>
<td>5 x 10⁻⁵, 10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>MS</td>
<td>2.5 x 10⁻⁹</td>
</tr>
</tbody>
</table>
Reaction vessels were constructed of silica to withstand the pyrolysis temperature, 1000°C. The vessels had long necks which terminated in a Pyrex glass stopcock via a cone-socket connection. A water cooled jacket below the connection and an asbestos thermal radiation shield below the water jacket, prevented pyrolysis and oxidation of the tap grease during analysis.

**Experimental Data**

Throughout the section errors are expressed as the average deviation from the arithmetic mean. During the operations of addition or subtraction errors are added. During the operations of multiplication or division the percentage error is added.

**Gamma Radiolysis of carbon monoxide-propylene mixtures.**

The yields of propanal, propene oxide, acetaldehyde and acetone formed during the radiolysis of carbon monoxide propene mixtures were measured as a function of the following variables.

- a) Total Dose
- b) Mixing Ratio and Pressure
- c) Temperature and Addition of SF$_6$
- d) Addition of C$_2$H$_2$
Throughout this section total dose is calculated by multiplying the dose rate by the vessel volume, filling pressure and irradiation time.
a) Total Dose At total doses greater than $2 \times 10^{19}$ eV in the dose rate range $(4.75 - 10.2) \times 10^{16}$ eV (cc-hr)$^{-1}$ the yield of each product falls off sharply. Data for propanal are presented in graph 2. There is a systematic difference between the preliminary and latter data. This was due to the incorporation of a pre-column into the gas chromatography unit. The pre-column caused better fractionation between scavenger, other products and propanal thus allowing reliable peak area estimates to be made. The following variables were shown not to affect the yield fall off: mixing ratio, vessel size, pressure and the addition of SF$_6$. Subsequent data were obtained in the range $0 - 2 \times 10^{19}$ eV.

b) Mixing Ratio and Pressure. G-values obtained as a function of mixing ratio and pressure, and estimated from V.P.C measurements are shown in table 6.

To ensure that quantitative separation of the reaction products had been obtained with the scrubbing loop described on page 62, the following consistency check was designed. Total aldehyde and ketone was extracted with water and reacted with D.N.P.H., the optical density as a function of dose was measured. The theoretical rise in optical density as a function of dose was calculated from the V.P.C data using the calibration factors listed in Table 4.
Gamma Radiolysis of CO/C₃H₆ gas mixtures at 22°C

Yield Propanal vs Total Dose

<table>
<thead>
<tr>
<th>Symbol</th>
<th>( V_V ) (cc)</th>
<th>( d_t ) eV/cc h⁻¹</th>
<th>( C_3H_6/CO ) %</th>
<th>( p ) (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>□</td>
<td>100</td>
<td>( 4.75 \times 10^{16} )</td>
<td>6.3</td>
<td>1</td>
</tr>
<tr>
<td>△</td>
<td>340</td>
<td>( 4.75 \times 10^{16} )</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>○</td>
<td>145</td>
<td>( 10.2 \times 10^{16} )</td>
<td>2.5</td>
<td>3.3</td>
</tr>
<tr>
<td>•</td>
<td>85</td>
<td>( 10.2 \times 10^{16} )</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

□ Preliminary Data  + + 3% SF₆
△ ○ ● later Data

Estimated from detailed study in total dose range 0 - \( 2 \times 10^{19} \) eV

** \( V_V \) = vessel volume
*** \( d_t \) = dose rate
Table 6: G(oxidation products) as a function of pressure and mixing ratio. (gamma radiolysis of CO/C₂H₆ mixtures)

<table>
<thead>
<tr>
<th>Product</th>
<th>G (molec. per 100 eV)</th>
<th>Mixing Ratio Range(%)</th>
<th>Pressure Range (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>propene oxide</td>
<td>0.58 ± 0.09</td>
<td>0.03</td>
<td>1 - 3.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>propanal</td>
<td>0.61 ± 0.07</td>
<td>0.03</td>
<td>1 - 3.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>acetaldehyde</td>
<td>0.135 ± 0.040</td>
<td>0.03</td>
<td>1 - 3.3</td>
</tr>
<tr>
<td>acetone</td>
<td>0.40 ± 0.04</td>
<td>2.5</td>
<td>1 - 3.3</td>
</tr>
<tr>
<td></td>
<td>0.08 ± 0.016</td>
<td>0.03</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.185</td>
<td></td>
</tr>
</tbody>
</table>

Dose Rate = 1.04 x 10¹⁷ eV/cc hr
Vessel Volume = 145 cc
Total Dose Range 0 - 2 x 10¹⁹ eV
Temperature 22°C
The following result was obtained:

\[
\frac{(OD)_{\text{expt}}}{eV} = (8.6 \pm 1.8) \times 10^{-21}
\]

\[
\frac{(OD)_{\text{calc}}}{eV} = (8.96 \pm 1.28) \times 10^{-21}
\]

c) **Temperature and SF6 addition.** Total aldehyde and ketone formation was measured in 3\% C3H6/OO mixtures at 1 atm a) with the addition of 3\% SF6 at room temperature b) at -78°C. The average OD/eV ratio for both conditions was found to be (9.5 \pm 1.8) \times 10^{-21}. No significant effect of these operators was therefore detected within experimental error.

d) **Addition of C2H2.** The G-values of propanal and propene oxide were investigated (Tables 7 and 8). The data are presented in the form:

\[
\left( \frac{R_0}{R} - 1 \right) \text{ as a function of } \frac{(C_2H_2)}{(C_3H_6)}
\]

\(R_0, R:\) are the rates of formation of propene oxide and propanal in the absence and presence of C2H2 respectively.

The data were obtained under the following conditions:

- **Dose rate =** 1.04 x 10^{17} eV/cc hr
- **Pressure =** 3.3 atm. (abs) **Temp. 22°C**
- **Vessel Volume 145 cc. Total C2H2 5\%.**

The data are presented in the order in which the experiments were performed. R0 was redetermined before data were collected at \((C_2H_2)/(C_3H_6)\) ratios of 20 and 10.
Table 7  Formation kinetics of propanal during gamma radiolysis of CO/C_{2}H_{2}/C_{3}H_{6} mixtures.

<table>
<thead>
<tr>
<th>No. obs.</th>
<th>( \frac{(C_{2}H_{2})}{(C_{3}H_{6})} )</th>
<th>R</th>
<th>( \frac{R_{0} - 1}{R} )</th>
<th>( \frac{(b)}{(a)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>-</td>
<td>44.0</td>
<td>( \pm 5.5 )</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>27</td>
<td>17.5</td>
<td>( \pm 1.6 )</td>
<td>0.055 ( \pm 0.021 )</td>
</tr>
<tr>
<td>2</td>
<td>81</td>
<td>7   ( \pm 1 )</td>
<td>5.3 ( \pm 1.4 )</td>
<td>0.065 ( \pm 0.018 )</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>12 ( \pm 3 )</td>
<td>2.7 ( \pm 1.4 )</td>
<td>0.053 ( \pm 0.026 )</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>20 ( \pm 1 )</td>
<td>1.2 ( \pm 0.4 )</td>
<td>0.080 ( \pm 0.024 )</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>34 ( \pm 1 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>18 ( \pm 3 )</td>
<td>0.9 ( \pm 0.4 )</td>
<td>0.045 ( \pm 0.020 )</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>21 ( \pm 2 )</td>
<td>0.6 ( \pm 0.2 )</td>
<td>0.062 ( \pm 0.020 )</td>
</tr>
</tbody>
</table>

Average \( \frac{(b)}{(a)} \) = 0.060 \( \pm 0.021 \)
Table 8 Formation kinetics of propene oxide during gamma radiolysis of CO/C$_2$H$_2$/C$_3$H$_6$ mixtures.

<table>
<thead>
<tr>
<th>No. obs.</th>
<th>(C$_2$H$_2$)/(C$_3$H$_6$) (a)</th>
<th>R</th>
<th>(R$_0$/R - 1) (b)</th>
<th>(b)/(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>-</td>
<td>55 ± 6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>27</td>
<td>20 ± 2</td>
<td>1.75 ± 0.58</td>
<td>0.065 ± 0.020</td>
</tr>
<tr>
<td>2</td>
<td>81</td>
<td>5.9 ± 0.2</td>
<td>8.3 ± 1.3</td>
<td>0.101 ± 0.014</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>14.5 ± 4.6</td>
<td>2.8 ± 1.6</td>
<td>0.056 ± 0.032</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>26 ± 4</td>
<td>1.1 ± 0.4</td>
<td>0.073 ± 0.025</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>47 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>22 ± 3</td>
<td>1.10 ± 0.34</td>
<td>0.055 ± 0.017</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>30 ± 4</td>
<td>0.57 ± 0.24</td>
<td>0.057 ± 0.024</td>
</tr>
</tbody>
</table>

Average (b)/(a) = 0.067 ± 0.023
The total acetylene content was 5%. It should be noted that the response of the instrument changed during the course of the experiment. This was later diagnosed to be due to an obstruction in the stream splitter.

2 Mercury-sensitised photolysis of N₂O/C₃H₆ mixtures.

The yields of aldehyde, measured by the DNPH technique, and product non condensable at 77°K were measured as a function of time. The results are shown in Table 9. The rate of formation of 'non condensable' product was

\[(6.9 \pm 0.33) \times 10^{-6} \text{ moles/min.}\]

The rate of formation of propanal was:

\[(3.5 \pm 0.5) \times 10^{-6} \text{ moles/min.}\]

3 Gamma Radiolysis of Carbon Monoxide - Acetylene Mixture.

G(CO₂) was measured as a function of the ratio \(\frac{C_2H_2}{CO}\). The carbon dioxide yields were measured with a mass spectrometer and the identification confirmed by the observed "removal" of the m/e 44 peak by absorption onto sofnolite. Ketene could not be detected. After several experiments a yellow deposit could be seen coating the walls of the product collection trap. An attempt was made to repeat the experiment at 1 atm. after the mass spectrometer had been reconstructed. No reproducible data was obtained. G(CO₂) estimates are shown in table 10.
Table 9. 2537 Å Mercury Sensitised Photolysis of \( \text{N}_2\text{O/C}_3\text{H}_6 \) mixtures.

<table>
<thead>
<tr>
<th>Time (mins)</th>
<th>n NC moles x (10^6)</th>
<th>(b) x (10^6)</th>
<th>OD at 430 nm</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>(b)</td>
<td>(a)</td>
<td>(c)</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>3.25</td>
<td>6.5</td>
<td>0.87</td>
<td>1.74</td>
</tr>
<tr>
<td>1</td>
<td>6.57</td>
<td>6.57</td>
<td>2.44</td>
<td>2.44</td>
</tr>
<tr>
<td>1.75</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>2.3</td>
</tr>
<tr>
<td>2.0</td>
<td>14.6</td>
<td>7.3</td>
<td>-</td>
<td>2.3</td>
</tr>
<tr>
<td>2.5</td>
<td>17.7</td>
<td>7.1</td>
<td>5.7</td>
<td></td>
</tr>
</tbody>
</table>

Average 6.9 ± 0.33  Average 2.20 ± 0.22

Total Pressure = 760 torr  Temp = 22°C

p.p. \( \text{C}_3\text{H}_6 \) = 20 torr

Vessel Volume = 248 cc

NC = product non condensable at 77°K

OD = optical density (1 cm light path)
4 Gamma Radiolysis of Carbon Monoxide-Propane Mixtures.

Yields of normal and iso propyl alcohol formed during gamma radiolysis of carbon monoxide-propane mixtures are shown in Graph 3 and Tables 11 and 12. G "aldehyde" refers to a product detected by the DNPH test. Two propane preparations were used. Crude B.O.C. propane was purified by the author. Matheson C.P. propane was used without further purification. In the 10 atm experiments, fractional sampling refers to expanding the vessel contents into the reservoir (Diag. 5) and injecting the residual vessel contents into the gas chromatograph. Total sampling refers to freezing the liquid nitrogen consensable product into the V.P.C. sampling loop (Diag. 3) and injecting the 50 stp cc of propane into the chromatograph. This large propane load passed through the unit (Perkin-Elmer 452) in a few seconds under the following conditions:

2m column of polyethylene glycol on 'Chromosorb P'
Temp 60°C Argon flowrate. 50cc min⁻¹.

No peak tailing was observed, however the flame was extinguished and had to be reignited after passage of the propane. It must be noted that the G(alcohol) estimates summarised in Table 13 are approximate since detailed calibration data were not obtained.
Table 10 Gamma Radiolysis of Carbon Monoxide -

Acetylene Mixtures.

<table>
<thead>
<tr>
<th>Mixing Ratio ($C_2H_2$)/(CO)</th>
<th>No. determinations</th>
<th>$G(CO_2)$ molec. 100eV$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8 \times 10^{-5}$</td>
<td>4</td>
<td>$2.5 \pm 0.25$</td>
</tr>
<tr>
<td>$1.66 \times 10^{-4}$</td>
<td>3</td>
<td>$2.4 \pm 0.24$</td>
</tr>
<tr>
<td>$4 \times 10^{-4}$</td>
<td>3</td>
<td>$1.72 \pm 0.22$</td>
</tr>
<tr>
<td>$8 \times 10^{-4}$</td>
<td>5</td>
<td>$1.23 \pm 0.13$</td>
</tr>
<tr>
<td>$1.6 \times 10^{-3}$</td>
<td>2</td>
<td>$1.02 \pm 0.07$</td>
</tr>
</tbody>
</table>

Total Pressure = 3.3 atm Temp 22°C

Vessel Volume = 145 cc

Dose Rate = $1.04 \times 10^{17}$ ev/cc hr.
Product of dose rate eV gm\(^{-1}\) hr\(^{-1}\) and vessel content (gm)
1849 Å photolysis of N₂O - C₃H₈ mixtures.

A single experiment was performed on the 1849 Å photolysis of N₂O - C₃H₈ mixtures under the following conditions:
- Temp 22°C
- Pressure 1 atm
- C₃H₈:N₂O = 3
- Vessel Volume 80cc.

The total vessel contents were injected into the V.P.C. unit for the purpose of analysis. The result of the experiment was
- Yield iso-propyl alcohol ~ 5 x 10⁻⁷ moles.
- Ratio, normal: iso-propyl alcohol ~ 0.47

A blank run in which the vessel was surrounded in an aqueous solution of sodium chloride to filter the 1849 Å photons showed that no products were formed indicating that mercury had been excluded during vessel filling.

Table 11 Gamma Radiolysis of liquid CO + 3% Propane at -196°C

* Dose Rate ~ 1.2 x 10²⁰ eV/hr

Vessel Volume ~ 3cc.

BOC Propane

Ratio normal/iso-propyl alcohol as a function of dose

<table>
<thead>
<tr>
<th>Total Dose eV x 10⁻¹⁹</th>
<th>N/I</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>0.64</td>
</tr>
<tr>
<td>13</td>
<td>0.26</td>
</tr>
<tr>
<td>25.6</td>
<td>0.38</td>
</tr>
</tbody>
</table>
Gamma Radiolysis of CO + 3% C₃H₈ at 22°C

Dose Rate $1.02 \times 10^{17}$ eV/cc hr
Vessel Vol. 85 ml
B.O.C. C₃H₈

Iso Propyl Alcohol

Normal Propyl Alcohol

3.3 atm.  ○  1 atm.

3.3 atm.  □  1 atm.
Table 12 Gamma Radiolysis of 50:50 CO:C₃H₈ mixtures at
10 atm and 22°C

N/I
Ratio normal/iso propyl alcohol as a function of dose, propane preparation and sampling.

<table>
<thead>
<tr>
<th>Total Dose</th>
<th>Propane Source</th>
<th>Sampling Method</th>
<th>N/I</th>
</tr>
</thead>
<tbody>
<tr>
<td>eV x 10⁻¹⁹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.16</td>
<td>B.O.C</td>
<td>Fractional</td>
<td>2.8</td>
</tr>
<tr>
<td>1.95</td>
<td>Matheson</td>
<td>&quot;</td>
<td>0.54</td>
</tr>
<tr>
<td>2.7</td>
<td>Matheson</td>
<td>&quot;</td>
<td>0.51</td>
</tr>
<tr>
<td>2.28</td>
<td>B.O.C</td>
<td>&quot;</td>
<td>0.58</td>
</tr>
<tr>
<td>3.3</td>
<td>B.O.C</td>
<td>Total</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Dose Rate 1.04 x 10¹⁷ eV/cc Hr

Vessel Volume = 10 CC
Table 13 Gamma Radiolysis of CO/C₃H₈ mixtures.

G estimates of isopropyl alcohol (I) n-propyl alcohol (N) and uncharacterised aldehyde ('ald') as a function of state, mixing ratio and pressure.

<table>
<thead>
<tr>
<th>State</th>
<th>Temp °C</th>
<th>Pressure atm.</th>
<th>C₃H₈/CO</th>
<th>G (I)</th>
<th>G (N)</th>
<th>G &quot;ald&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liq</td>
<td>-196</td>
<td>-</td>
<td>0.03</td>
<td>0.17</td>
<td>0.005</td>
<td>0.17</td>
</tr>
<tr>
<td>Gas</td>
<td>22</td>
<td>1</td>
<td>0.03</td>
<td>1.46</td>
<td>0.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Gas</td>
<td>22</td>
<td>3.3</td>
<td>0.03</td>
<td>1.46</td>
<td>0.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Gas</td>
<td>22</td>
<td>10</td>
<td>1</td>
<td>1.2</td>
<td>0.64</td>
<td>nd</td>
</tr>
</tbody>
</table>

6. **G (CO₂) as a function of temperature and dose-rate.**

G (CO₂) was measured as a function of temperature in the range 22°C to -196°C. Some measurements as a function of dose rate at low temperatures were also made; Table 14. G(C) in table 14 refers to the G value of carbon contained in the polymer which is formed during radiolysis of pure carbon monoxide.
Table 14. $G(\text{CO}_2)$ as a function of temperature and dose rate in CO gas (vessels filled to 1 atm. (abs) at 22°C

<table>
<thead>
<tr>
<th>Dose Rate eV/cc sec</th>
<th>Vessel Volume (cc)</th>
<th>$G(\text{CO}_2)$ molec. (100 eV)$^{-1}$</th>
<th>$G(\text{C}) / G(\text{CO}_2)$</th>
<th>Temp °C</th>
<th>No. Obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.56 x $10^{13}$</td>
<td>145</td>
<td>2.0 ± 0.1</td>
<td>nd</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>1.45 ± 0.02</td>
<td>nd</td>
<td>-78</td>
<td>2</td>
</tr>
<tr>
<td>&quot;</td>
<td>85</td>
<td>0.66 ± 0.09</td>
<td>nd</td>
<td>-183</td>
<td>3</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>0.60 ± 0.07</td>
<td>nd</td>
<td>-196</td>
<td>3</td>
</tr>
<tr>
<td>5.65 x $10^{12}$</td>
<td>273</td>
<td>2.0 ± 0.2</td>
<td>3.3 ±0.2</td>
<td>22</td>
<td>3</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>1.58 ± 0.11</td>
<td>3.25±0.18</td>
<td>-78</td>
<td>5</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>0.80 ±0.03</td>
<td>3.16±0.02</td>
<td>-183</td>
<td>2</td>
</tr>
<tr>
<td>2.08 x $10^{11}$</td>
<td>560</td>
<td>0.77 ±0.05</td>
<td>nd</td>
<td>-183</td>
<td>2</td>
</tr>
</tbody>
</table>

nd = $G(\text{C})$ not determined.

7 $G(\text{CO}_2)$ and polymer composition in liquid carbon monoxide at -196°C.

The $G$ value of $\text{CO}_2$ and the composition of the polymer formed during gamma radiolysis of carbon monoxide at -196°C were estimated. The technique whereby the polymer composition was determined is described on pages 71 and 72. The data collected are shown in tables 15 and 16.
**Table 15 CO₂ yields and polymer composition.**

Liquid CO at -196°C.

Dose Rate 2.86 x 10¹⁷ eV gm⁻¹ min⁻¹

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Total Dose eV x 10⁻²⁰</th>
<th>Radio lytic CO₂ moles x 10⁶</th>
<th>Vacuum Pyrolysis CO₂ moles x 10⁶</th>
<th>Burn off CO₂ moles x 10⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.68</td>
<td>1.11</td>
<td>0.93</td>
<td>0.61</td>
</tr>
<tr>
<td>2</td>
<td>5.10</td>
<td>2.14</td>
<td>1.55</td>
<td>1.06</td>
</tr>
<tr>
<td>3</td>
<td>7.85</td>
<td>3.00</td>
<td>1.81</td>
<td>1.62</td>
</tr>
<tr>
<td>4</td>
<td>21.1</td>
<td>8.15</td>
<td>6.20</td>
<td>4.4</td>
</tr>
<tr>
<td>5</td>
<td>31.0</td>
<td>11.5</td>
<td>10.0</td>
<td>5.25</td>
</tr>
</tbody>
</table>

**Table 16 Mass balance and solid composition ratios calculated from the data in table 15.**

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>( \frac{x}{y} ) in ( C_x O_y )</th>
<th>C in products</th>
<th>O in products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.62</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.48</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.43</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.46</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>1.49±0.05</td>
<td>0.98±0.03</td>
<td></td>
</tr>
</tbody>
</table>
Addition of Methane to CO at 1 atm.

The methane used for this experiment was originally thought to be free of oxygen. Product analysis after irradiation (Table 17), however, indicated the presence of oxygen.

Table 17 G oxidation products in CO + CH₄ mixtures.

<table>
<thead>
<tr>
<th>Product</th>
<th>G molec 100 ev⁻¹</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCHO + peroxide</td>
<td>0.345</td>
<td>Chromatrophic acid</td>
</tr>
<tr>
<td>HCHO peroxide</td>
<td>0.033</td>
<td>DNPH</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>iodide reagent</td>
</tr>
</tbody>
</table>

Dose Rate $6.3 \times 10^{12}$ ev/cc sec  
Vessel Vol = 340 cc  
Total Dose = $1.6 \times 10^{20}$ eV  
Temp = $22^°C$

The decay characteristic of the peroxide on reaction with I⁻ was determined by measuring the formation of $I_3^-$ with a Unicam SP500 spectrophotometer. The pseudo first order velocity constant was found to be (graph 4) $2.3 \times 10^{-2}$ min⁻¹. This is in good agreement with the constant for methyl hydrogen peroxide ($1.6 \times 10^{-2}$ min⁻¹) (11). The formation of the products under discussion was presumably due in the presence of oxygen in the system. Addition of O₂ did not alter the G values reported in Table 18.
90

Gamma radiolysis of CO/CH4/O2 mixtures.

Pseudo first order decay characteristic of product peroxide on reaction with I- in acid solution.

\[ t_{\frac{1}{2}} = 29 \text{ mins} \]

\[ k = 2.3 \times 10^{-2} \text{ min}^{-1} \]
Table 18  \( G(\text{CO}_2) \) as a function of total dose and methane content

<table>
<thead>
<tr>
<th>% CH(_4)</th>
<th>Total Dose eV x 10(^{-19})</th>
<th>( G(\text{CO}_2) ) molec. (^{-1}) 100 eV(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.25</td>
<td>2.23</td>
</tr>
<tr>
<td>5</td>
<td>6.25</td>
<td>2.17</td>
</tr>
<tr>
<td>5</td>
<td>3.13</td>
<td>2.42</td>
</tr>
<tr>
<td>3</td>
<td>9.38</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>6.55</td>
<td>2.06</td>
</tr>
<tr>
<td>5</td>
<td>7.2</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Dose rate 2.56 x 10\(^{13}\) eV/cc sec.

Vessel Volume = 340 cc  filling pressure = 1 atm.

Temp = 22°C

At a later date when a purer source of CH\(_4\) was available, \( G(\text{CO}_2) \) was measured in CO/CH\(_4\) mixtures. Table (18). The liquid oxygen condensable fraction of the reacted mixture was measured by P.V.T. This fraction was shown:
a) to be totally adsorbed on to sofrolite

b) not to contain peroxide or HCHO.

c) to contain only very small quantities of C₂H₆.
References


2) G.R.A. Johnson
   J. Inorganic and Nuclear Chemistry 80 6183 1962

3) N.A. Baily and G.C. Brown
   Rad. Res. 11 745 1959

4) J.A. Jobling and Co. Ltd. Handbook "Pyrex" Industrial Glass

5) Y. Toi, D.B. Peterson and M. Burton
   Rad. Res. 17 399 1962


7) Associated Electrical Industries (AEI) Technical Information Sheet A 193

8) AEI Technical Information Sheet A 522

9) AEI Publication 2032-891

10) G.R.A. Johnson and G. Scholes, Analyst 79 217 1954

11) J.A. Hearne and R.W. Hummel
    UK Atomic Energy Authority Report AERE R - 4581 and R-4871 1964
Section 3  Data Assessment and Discussion.

A  Gas Phase Studies, $O(^3P)$ characterisation.

1  Mass Balance

It was shown on page 76 that the yield of aldehyde and ketone calculated from both V.P.C and D.N.P.H. data were in good agreement. Thus no aldehyde or ketone other than propanal, acetaldehyde and acetone were formed. Further quantitative separation of the reaction products from excess CO was obtained prior to injection into the chromatography unit.

Cvetanovic (1) has discussed the formation of propene oxide and propanal as a function of total pressure during the mercury sensitised 2537 Å photolysis of $N_2O/C_3H_6$ mixtures. Both pressure dependent and pressure independent fragmentation processes, steps 1a and 3 respectively, of the initial association complex were postulated to occur. In the case of propanal formation, the reaction sequence postulated was:

$$Hg^+ + N_2O \rightarrow N_2 + O(^3P) + Hg \quad (R_0)$$

$$O(^3P) + C_3H_6 \rightarrow (C_3H_6O) \quad \text{decomposition} \quad (k_3)$$

$$C_2H_5CHO^+ \quad (k_4)$$

$$CH_3CH-CH_2^+ \quad (k_2)$$

steps of the mechanism written below.
The subscripts on the velocity constants \( (k) \) in the equations on page 95 refer to the reactions in the mechanism written on pp 94-95. \( R_0 \) means rate of reaction \( \text{H}_2 \text{O}^* + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}(^3\text{P}) + \text{H}_2\text{O} \).
\[ \text{C}_2\text{H}_5\text{CHO}^* \rightarrow \text{decomposition} \ (k_{1a}) \]
\[ \text{C}_2\text{H}_5\text{CHO}^* + \text{M} \rightarrow \text{C}_2\text{H}_5\text{CHO} + \text{M} \ (k_{1b}) \]

Stationary state analysis of this mechanism produces the rate expression.

\[ \frac{d\left[\text{C}_2\text{H}_5\text{CHO}\right]}{dt} = \left( \frac{k_1R_0}{k_1 + k_2 + k_3} \right) \left( \frac{k_{1b}(\text{M})}{k_{1a} + k_{1b}(\text{M})} \right) \]

clearly:

\[ \frac{k_1R_0}{k_1 + k_2 + k_3} = \text{fraction of oxygen atoms consumed in reaction 1} \]

\[ \frac{k_{1b}(\text{M})}{k_{1a} + k_{1b}(\text{M})} = \text{fraction of } \text{C}_2\text{H}_5\text{CHO}^* \text{ stabilised.} \]

Rearranging

\[ \left( \frac{d(\text{C}_2\text{H}_5\text{CHO})}{dt} \right)^{-1} = \frac{1}{\alpha} + \frac{k_{1a}}{k_{1b} \alpha (\text{M})} \]

where \( \alpha = \frac{k_1R_0}{(k_1 + k_2 + k_3)} \)

The presentation of Cvetanovic's data in the form of relative formation rates, however makes it impossible to estimate \( \alpha \) from these data. Further, nitrogen quantum yield data were not presented, thus the relation between \( O(3p) \) atom and addition product formation could not be determined.
directly from experimental data. Finally Cvetanovic stated that there was no certainty that all the addition products were recovered during preliminary fractionation of the reacted mixture prior to analysis.

For the reasons discussed above Cvetanovic's experiment was repeated. To avoid possible experimental error during preliminary fraction by low temperature distillation in a Le Roy still, the aldehyde formed was directly extracted with water and estimated by its reaction with D.N.P.H. reagent. The results of this experiment are shown in table 9. The rate of formation of aldehyde which may be assumed to be substantially propanal, was found to be \((3.5 \pm 0.5) \times 10^{-6}\) moles/min. The rate of formation of the "non-condensable" product was \((6.90 \pm 0.33) \times 10^{-6}\) moles/min at 1 atm and 22°C. It can be assumed that the propanal yield is equal to the propene oxide yield. Thus it can be concluded that the "non-condensable" product yield was substantially nitrogen and that all the \(O(3P)\) atoms produced during the photolysis reacted with the propene to form carbonyl and epoxide products.

The \(SF_6\) molecule has a considerable number of degrees of freedom and is known to be an efficient collisional deactivator of vibrational energy (2). Unimolecular fissions are well known to have quite large activation energies.
No effect, within experimental error, was observed on the rate of formation of total aldehyde and ketone when the temperature was lowered to -78°C or SF₆ was added to CO/C₃H₆ mixtures at 22°C. (page 76)

The G values of addition products were shown to be independent of pressure in the range 1 - 3.3 atm at 22°C. Table 6.

\[ G(0^3P) \] may thus be taken to be the sum of the G (oxidation products) in Table 6. when C₃H₆ is less than 0.185% because the yield ratios are similar to those found by Cvetanovic (1) and no evidence for fragmentation of the addition complex to give products other than those listed in Table 6 could be found.

It may be concluded that:

\[ G(0^3P) = 1.41 \pm 0.22 \text{ atoms per 100 eV.} \]
during gamma radiolysis of carbon monoxide gas in the pressure range 1 - 3.3 atm at 22°C.

\[ \text{Mixing Ratio } (\text{C}_3\text{H}_6)/(\text{CO}) \]

From table 3 in ref. 3 it may be estimated that:

\[ k_0(3P) + \text{CO} = (9.0 \pm 3.1) \times 10^6 \text{ cc mole}^{-1} \text{ sec}^{-1} \text{ at } 25°C \]

The velocity constant was measured in the pressure range 0.51 to 1.23 torr. The reaction was shown to be bimolecular. A velocity constant of about ten times the above
value has been reported (4). The conditions under which it was determined were not however made clear.

Combining the comparative velocity constant ratio for reaction of \( \text{O}(^3\text{P}) \) with \( \text{C}_2\text{H}_4 \) and \( \text{C}_3\text{H}_6 \) (5) with the absolute velocity constant for \( \text{O}(^3\text{P}) + \text{C}_2\text{H}_4 \) (6) it may be shown that:

\[
k_0(^3\text{P}) + \text{C}_3\text{H}_6 = (1.85 \pm 0.23) \times 10^{12} \ 	ext{cc mole}^{-1} \text{sec}^{-1} \text{ at } 25^\circ\text{C}
\]

Thus no significant effect due to competition between CO and \( \text{C}_3\text{H}_6 \) for \( \text{O}(^3\text{P}) \) is expected until:

\[
(\text{C}_3\text{H}_6)/(\text{CO}) = (4.9 \pm 2.3) \times 10^{-6}
\]

The lowest ratio used was \( 3 \times 10^{-4} \). No effect was observed which could be ascribed to competition between CO and \( \text{C}_3\text{H}_6 \) for \( \text{O}(^3\text{P}) \) at this ratio. Thus it may be concluded that the rate constants discussed above are essentially correct.

At mixing ratios \( (\text{C}_3\text{H}_6/\text{CO}) \) above \( 1.85 \times 10^{-3} \) the yield of acetone becomes non characteristic of the reaction between \( \text{O}(^3\text{P}) \) and \( \text{C}_3\text{H}_6 \). Table 6.

The reaction:

\[
\text{CO} + \text{C}_3\text{H}_6 \rightarrow (\text{CH}_3)_2 \text{CO} + \text{C}
\]

is 6.13 eV endothermic. With the \( a^3\Pi \) state of \( \text{CO}(6\text{eV}) \) the reaction becomes almost thermoneutral. The reaction becomes exothermic for all other electronically excited states of CO. The occurrence of the reaction however has not been demonstrated experimentally in an isolated system. (See page 35).
The reaction:

\[ \text{CO}^+ + \text{C}_3\text{H}_6 \rightarrow (\text{CH}_3)_2\text{CO} + \text{C}^+ \]

is 3.35 eV endothermic but is exothermic for electronically excited states of CO\(^+\) (p.31). The occurrence of the reaction has not been demonstrated experimentally in an isolated system.

As well as the appearance of a large acetone yield at mixing ratios above 1.85 \(\times 10^{-3}\) other products appear in the chromatographic spectrum. These products had retention times intermediate between propene and the \(0(3^P) + \text{C}_3\text{H}_6\) reaction products. The peaks were not well resolved and no attempt was made to identify them.

3 Yield-Dose.

Yields of \(0(3^P) + \text{C}_3\text{H}_6\) reaction products were shown to be linear with dose to \(2 \times 10^{19}\) eV. At the lowest mixing ratio used (3 \(\times 10^{-4}\)) this dose corresponds to an 8% conversion of \(\text{C}_3\text{H}_6\) by \(0(3^P)\) oxidation. No significant consumption of \(\text{C}_3\text{H}_6\) could be determined by V.P.C. Thus no evidence was obtained of a chain \(\text{C}_3\text{H}_6\) polymerisation initiated by charge transfer from \(\text{CO}^+\). At higher mixing ratios \(\text{C}_3\text{H}_6\) consumption could not be measured because the amount of \(\text{C}_3\text{H}_6\) was sufficient to swamp the detector.

At total doses greater than \(2 \times 10^{19}\) eV the yield of \(\text{C}_3\text{H}_6\) oxidation products starts to fall off. The fall off
could not be arrested by addition of SF6 which has a high
electron affinity and thus was not due to the scavenging of
thermalised electrons by the reaction products. Further at
high doses and mixing ratios a deposit could be seen collect-
ing on the wall of the vessel. This observation suggests
that C3H6 polymerisation does take place at high mixing ratios.

4 Competition Kinetics CO/C3H6/O2H2 mixtures.

The results of this experiment are shown in Tables 7
and 8. The velocity constant ratio for reaction of O(3P) with
C2H2 and C3H6 may be estimated from two recent sets of data.

Saunders and Heicklen (7) studied the reaction of O(3P)
atoms with C2F4 using the 2537 Å mercury sensitised photo-
lysis of N2O as an atom source. Comparative rate constant
data were obtained by a study of the competing reactions:

$$\text{O}(3\text{P}) + \text{hydrocarbon} \rightarrow \text{products} \quad k_c$$
$$\text{O}(3\text{P}) + \text{C}_2\text{F}_4 \rightarrow \text{CF}_2\text{O} \quad k_d$$

at 25°C $k_c/k_d$ ratios for C2H2 and C2H4 were found to be
0.193 ± 0.020 and 0.91 ± 0.12 respectively.

Brown (6) measured the absolute rate of reaction of
O(3P) with C2H2 and C2H4.

These two sets of data may be combined with the com-
parative velocity constant ratio for reaction of O(3P) with
C2H4 and C3H6 (5)
From (7) and (5) it may be concluded that the ratio of velocity constants for reaction of $0(^3P)$ with $C_2H_2$ and $C_3H_6$ are:

$$0(^3P) \left[ \begin{array}{cc} C_2H_2 \\ C_3H_6 \end{array} \right] = 0.037 \pm 0.009$$

Whereas combining (6) and (5)

$$0(^3P) \left[ \begin{array}{cc} C_2H_2 \\ C_3H_6 \end{array} \right] = 0.050 \pm 0.009$$

The ratio obtained from the authors experiments was $0.06 \pm 0.02$ and $0.067 \pm 0.023$ from measurements made on the yields of propanal and propene oxide respectively. The ratio agrees best with that calculated from the data in (6) and (5).

The error in estimating $(\frac{R_0}{R})^{-1}$ is $(x\% + y\%)$ where $x$ and $y$ are the errors in $R_0$ and $R$. Clearly as $\frac{R_0}{R}$ approaches 1 the error is large whereas when $\frac{R_0}{R}$ is much greater than 1 the error is less. However at high $(C_2H_2)/(C_3H_6)$ ratios it becomes far more difficult to measure $R$ because of peak tailing. This latter consideration probably accounts for the deviation from linearity at high $(C_2H_2)/(C_3H_6)$ ratios. The data in Tables 7 and 8 is represented in Graphs 5 and 6.

The peak areas due to acetone and acetaldehyde were too small for the yield of these compounds to be measured as a function of $(C_2H_2)/(C_3H_6)$

References (5) (6) and (7)
Kinetics of formation of propanal during gamma radiolysis of CO/C₂H₂/C₃H₆ mixtures

Comparison of data with published velocity constant ratios.

1) Saunders + Heicklen
2) Brocon + Thrush
Kinetics of formation of propene oxide during gamma radiolysis of CO/C₂H₂/C₃H₆ mixtures

Comparison of data with published velocity constant ratios

1) Saunders + Heicklen
2) Brown + Thrush
5 Competition Kinetics CO/C2H2 mixtures.

The experimental data described so far supports the hypothesis that the CO2 yield is produced as the result of the reaction of O(3P) atom with CO. The yield of oxygen atoms however is less than the yield of CO2. As a general consistency check on this hypothesis it seemed instructive to see if the kinetics of CO2 formation would comply with the following mechanism.

\[
\begin{align*}
\text{CO} & \rightarrow \text{CO}_2 G_0 \\
\text{CO} & \rightarrow \text{O} (3P) G_s \\
\text{O} + \text{CO} & \rightarrow \text{CO}_2 k_1 \\
\text{O} + \text{C}_2\text{H}_2 & \rightarrow \text{CH}_2 + \text{CO} k_2
\end{align*}
\]

By stationary state analysis of the above mechanism

\[
\frac{k_1(CO)}{k_2(C_2H_2)} = \frac{G_s}{\Delta G} - 1
\]

where

\[
\Delta G = G_p = G_T - G(\text{CO}_2)_{\text{expt}}
\]

\[
G_T = G_0 + G_s
\]

\[
G(\text{CO}_2)_{\text{expt}} = G_0 + G_s - G_p
\]

and G_p = G of products from reaction 2.

The data obtained is shown in Table 10. k1/k2 ratios calculated by substitution into the formula above are about 10 times higher than that which may be calculated from data.
given in (6) and (3). Detailed analysis of these data is not worthwhile because:

a) The maximum $G(\text{CO}_2)$ measured was greater than the well established value of 2. This was presumably due to a calibration error.
b) The product characteristic of reaction 2 ($\text{CH}_2\text{CO}$) could not be detected.
c) No reproducible data could be obtained when an attempt was made to repeat the experiment at a total pressure of 1 atm. The reasons for this are not understood.

After several runs a yellow deposit, presumably cuprene, was seen building up in the product collection trap. A detailed study of the cuprene formation was not made since such a study is unlikely to provide any diagnostic information about the nature of the reactive species formed during the radiolysis of carbon monoxide. It is known that acetylene polymerisation can be initiated by $\beta$ particle radiation (8), 1849 Å light (9) and mercury photosensitisation (10). Further the polymerisation is known to be pressure dependent below 70 torr (9) and the exact nature of the pressure dependence has not been investigated in detail.

6 Addition of Propane.

The purpose of this experiment was to detect the formation of $O(^1D)$ atoms by the insertion of the atoms into
propane to form normal and iso propyl alcohols in the ratio 3:1 (2).

It should be noted that the primary aim of the experiments was to detect the 3:1 alcohol formation ratio. The experiments were not primarily designed to obtain velocity constant ratios for reaction of O(1D) with CO and C3H8.

a) Yield Ratio of Alcohols

The yield ratio normal: iso propyl alcohol of at least 3 found by Yamazaki (2) was not found in any of the experiments performed by the author. Table 11 Graph 3.

However, the N/I ratio found by the author for 1849 Å photolysis of N2O/C3H8 mixture (page 83) was similar to that found during gamma radiolysis of CO/C3H8 mixtures.

Hummel (11) has found N/I ratios of less than 3 for N2O/C3H8 1849 Å photolysis. N/I ratios varying from 0.14 to 2.4 for 1 and 5 hr. exposure times respectively were found. A dependence of N/I ratio on exposure time was therefore suggested, however neither Hummel (11) nor Yamazaki (2) report molar yields, thus the work of these authors and the present author cannot be directly compared.

No rigid interpretation of the CO/C3H8 gamma radiolysis runs may be made until the oxidation of propane in an O(1D) isolated system is fully understood.
The subscripts on the velocity constants \( k \) used in the discussion (pp 107 and 108) refer to the reaction mechanism written on page 107.
Inspection of Yamazaki's (12) data reveals that a systematic study of the photodissociative N₂ yield as a function of the total propyl alcohol yield was not made. Clearly such a study as a function of total pressure and the exposure time is required to resolve the discrepancy discussed above.

b) Mixing Ratio \( \frac{(C_3H_8)}{(CO)} \) and Total Pressure.

The mechanism of reaction of \( O(^{1}D) \) with CO has already been discussed in some detail (pp 20, 25); the formation of alcohols is claimed to be pressure dependent (2). The following mechanism may therefore be postulated.

\[
\begin{align*}
\text{CO} & \rightarrow \text{C} + O(^{1}D) \quad \text{R0} \\
O(^{1}D) + CO + M & \rightarrow \text{products 1} \\
O(^{1}D) + C_3H_8 & \rightarrow C_3H_8O^* \quad \text{2} \\
C_3H_8O^* + M & \rightarrow C_3H_8O \quad \text{3} \\
C_3H_8O^* & \rightarrow \text{products 4}
\end{align*}
\]

Clearly the rate of formation of stable alcohol will be a complex function of mixing ratio and total pressure. It was suggested on page 27 that \( k_1(M)/k_2 \) is 2.8 at 1 atm. In a 50:50 \( C_3H_8/CO \) mixture at 10 atm if it is assumed that \( GO(3P) \) is equal to \( GO(1D) \) the \( G \) total alcohol should be much less than \( G O(3P) \) if the \( C_3H_8O^* \) is stabilised. A \( G \) total alcohol of 1.84 molecules per 100 eV was however found (Table 13) in
complete contradiction to the argument developed above.

The only consistent way to explain the yields of alcohol observed in the gas phase experiments on the assumption that it is formed by reaction of \( \text{O}(^{1}\text{D}) \) with \( \text{C}_3\text{H}_8 \), secondly that \( G \, \text{O}(^{3}\text{P}) \) is equal to \( G \, \text{O}(^{1}\text{D}) \), is to postulate that \( k_2 > k_1 \) (M) and that the addition complex \( \text{C}_3\text{H}_8\text{O}^\# \) is stabilised at pressures of 1 atm. and above.

The formation of aldehyde (Table 13) is difficult to explain in terms of reaction of \( \text{O}(^{1}\text{D}) \) with \( \text{C}_3\text{H}_8 \). Yamazaki (2) states that no oxygen containing compounds other than the two propanols were detected in his experiments. Since propanol formation was claimed to be pressure dependent other oxygenated products must have been formed. It cannot, therefore, be concluded from Yamazaki's experiments that such processes as:

\[
\text{C}_3\text{H}_8\text{O}^\# \rightarrow \text{C}_3\text{H}_6\text{O} + \text{H}_2
\]

do not occur.

However, because the total propanol \( G \) value during gamma radiolysis of \( \text{CO}/\text{C}_3\text{H}_8 \) mixtures correlates with \( G \, \text{O}(^{3}\text{P}) \), it may be postulated that the aldehyde formation observed by the author does not occur by a fragmentation process such as that above.

Since the type of aldehyde formed was not determined secondly, since it has not been established that propanol formation is due to \( \text{O}(^{1}\text{D}) \) reaction, further speculation as to the mechanism of aldehyde formation is unprofitable.
The results of the experiments discussed above do not permit a conclusion to be made as to the initial electronic state of the oxygen atoms formed during gamma radiolysis of carbon monoxide. The yield ratio of propanols and the dependance of propanol yield on mixing ratio and pressure during gamma radiolysis of CO/C\textsubscript{2}H\textsubscript{8} mixtures are not in agreement with previously determined physico-chemical characteristics of O(\textsuperscript{1}D) reaction. For reasons discussed above Yamazaki's experiment requires re-investigation. It is perhaps worth mentioning that there is another possible way of detecting O(\textsuperscript{1}D) formation during gamma radiolysis of carbon monoxide. From Table 1 it is clear that O(\textsuperscript{3}P) reacts with CO and CH\textsubscript{4} with nearly the same velocity constant at room temperature. It should therefore be possible to add large quantities of CH\textsubscript{4} to CO/C\textsubscript{2}H\textsubscript{6} mixtures without inhibiting the scavenging of O(\textsuperscript{3}P) by C\textsubscript{2}H\textsubscript{6}. A decrease in the rate of C\textsubscript{2}H\textsubscript{6} oxidation product formation in the presence of CH\textsubscript{4} may be taken as indicative of O(\textsuperscript{1}D) preceding O(\textsuperscript{3}P) formation. An independent assessment of the velocity constant ratio for reaction of O(\textsuperscript{1}D) with CO and CH\textsubscript{4}, presently not available, is however required for a confident diagnosis to be made.
7 Conclusions

a Yield of $O(^3P)$ atoms.

It has been shown that $G(O(^3P))$ is $1.41 \pm 0.22$ atoms per 100 eV. $G(CO_2)$ is however $2.05 \pm 0.15$ molecules per 100 eV (12). The dose rate dependence of $G(CO_2)$ (12) suggests that these atoms are intermediates in $CO_2$ production. However, because of the lack of correlation between $G(O(^3P))$ and $G(CO_2)$, other intermediates must be involved in $CO_2$ production. This conclusion is substantiated by the fact that experimentally determined $G(CO_2)$ values at high dose rates (12) are higher than those calculated assuming that $G(O(^3P)) = G(CO_2)$.

It was shown (pp 30, 35) that it is possible for electronically excited states of both $CO$ and $CO^+$ to react with $CO$ to form $CO_2$. Further it was shown on page 98 that it is thermochemically feasible for such intermediates to react with $C_3H_6$ to form acetone. Further analysis is not possible since independent studies of the reaction characteristics of these intermediates have not been reported, secondly $G(CO_2)$ in the presence of $C_3H_6$ was not measured by the author because of the complexity of the product spectrum.

b Mechanism of $O$ atom formation.

On page 33 it was shown that ratios of additive/CO as small as $4 \times 10^{-8}$ should in theory be sufficient to scavenge all $CO^+$ ions. It was argued that $CO^+$-electron recombination
was a possible mechanism of O atom production and that addition of a CO$^+$ interceptor should inhibit O atom production via this route. No product characteristic of the interception of CO$^+$ with either propene or acetylene was measured during the course of these experiments. However it seems reasonable to assume, especially in the CO/C$_2$H$_2$/C$_3$H$_6$ experiments where 5% additive levels were used that the CO$^+$ ions were being intercepted. Under these conditions the formation kinetics of propene oxide and propanal were as those expected from the reaction characteristics of O($^3P$) determined in isolated systems. It is thus possible to conclude that O atom formation is substantially the result of a neutral dissociative process accompanying innisation, or possibly the reaction

$$\text{CO}(b^3\Sigma^+)+\text{CO}(X^1\Sigma) \rightarrow \text{C}_2\text{O}(X^3\Sigma) + \text{O}(^3P).$$

Rudolph and Lind (13) suggest that the addition of more than 6% CO$_2$, a known CO$^+$ interceptor, reduces the rate of CO consumption during $\alpha$ particle radiolysis by about half. This again suggests that a substantial part of the radiolysis proceeds via non ionic pathways. However since Rudolph's CO uptake estimates depend on measurements of total pressure drop as a function of time and an assumed reaction stoichiometry: $3\text{CO} \rightarrow \text{CO}_2 + \text{solid}$ his results and conclusions must be regarded with caution.
c. Initial electronic state of the O atom.

Two considerations establish that it was not singlet oxygen atoms reacting with the propene to give the observed reaction products.

(i) the kinetics of propanal and propene oxide formation as a function of C\textsubscript{2}H\textsubscript{2}/C\textsubscript{3}H\textsubscript{6} were those characteristic of 0(3\textpi)

(ii) if the propene oxidation products were due to singlet reaction, the initial association reaction would become at least 2eV per molecule more exothermic. It would therefore be reasonable to expect the addition product formation to be pressure dependent. No such pressure dependence was observed in the range 1 - 3.3 atm.

continued on page 113
The experiments designed to detect $O(^1D)$ formation directly by addition of propane were inconclusive.

The possibility exists therefore that if the mechanism of $O(^1D)$ reaction with CO is as described on page 20, secondly if $O(^1D)$ reacts with CO and $C_3H_6$ with similar velocity constants, that $O(^1D)$ could be formed initially and react first with CO to form $O(^3P)$ which subsequently reacts with $C_3H_6$.

If $O(^1D)$ is formed initially, deactivation rather than predissociation, following partial vibrational deactivation of the initial excited association complex between $O(^1D)$ and CO could account for $GO(^3P)$ not being equal to $G(CO_2)$.

B Gas Phase Studies. Effect of Temperature and Dose Rate.

The effect of temperature in the range 22°C to -183°C on $G(CO_2)$ and reaction stoichiometry during gamma radiolysis of CO in vessels filled to 1 atm at 22°C is shown in Table 14. The carbon deposit to CO$_2$ yield ratios indicate that reduction in temperature does not result in a deviation from a reaction stoichiometry described by the equation:

$$4n \text{ CO} \rightarrow n \text{ CO}_2 + (C_3O_2)_n$$

The velocity constant for reaction of $O(^3P)$ with CO is low and has a large activation energy, 4 kcal/mole (3). At -183°C the mean life of $O(^3P)$ with respect to reaction with
\( R_o = \text{rate of production of oxygen atoms} \)
CO to form CO₂ is about $1.2 \times 10^4$ secs for s.t.p density.
The velocity constant for recombination of $O(^3P)$ atoms is however large, is dependent on the 3rd body concentration and probably increases as temperature decreases. At room temperature the velocity constant ($k_R$) for:

$$2O(^3P) + M \rightarrow O_2 + M$$
is $9.5 \times 10^{14}$ cc²/mole² sec (14). Assuming that $O(^3P)$ atoms are produced and recombine as described by the equation above, the mean life of $O(^3P)$ with respect to recombination may be estimated from the equation:

$$[k_R \left[\frac{R_O}{k_R \left[CO\right]}\right]^\frac{1}{2} ]^{-1}$$

The rate of production of oxygen atoms is to first approximation equal to the rate of production of CO⁺ ions. Thus at the dose rate and CO density used by the author the mean life of $O(^3P)$ with respect to recombination (8.7 secs) is less than that for reaction with CO. It may be concluded that if $O(^3P)$ is produced the reaction sequences which may be postulated to explain the decrease of $G(CO_2)$ with temperature, cannot include an $O(^3P)$ recombination step because the reaction stoichiometry remains the same as at room temperature.

The following discussion will consider if the mechanism proposed by Anderson (12) to explain the decrease of $G(CO_2)$ as the dose rate is increased can also explain the temperature
The subscripts 1, 2 and 3 in equations 1 and 2 (p115) and in the discussion (pp 116-119) refer to reactions 1, 2 and 3 of the reaction mechanism on page 115.
effect. Consider the mechanism proposed by Anderson (12):

\[
\begin{align*}
\text{CO} & \rightarrow C + O \quad (R_0) \\
C + CO & \rightarrow C_2O \\
C_2O + CO & \rightarrow \text{polymer} \\
O + CO & \rightarrow CO_2 \\
O + C_2O & \rightarrow 2CO
\end{align*}
\]

Stationary state treatment of these reaction steps yields the relation:

\[
\frac{k_3}{k_1k_2} = \left( \frac{\text{(CO)}^2}{\frac{d(CO_2)}{dt}} \right)^2 \left( R_0 - \frac{d(CO_2)}{dt} \right) \\
R_0 = \text{rate of formation of } O(3P)
\]

Transformation of Eq. 1 to Arrhenius parameters yields the expression:

\[
\log_{10} \left( \frac{A_3}{A_1A_2} \right) + \frac{(E_1 + E_2 - E_3)}{2.3RT} = \log_{10} \left[ \left( \frac{\text{(CO)}^2}{\frac{d(CO_2)}{dt}} \right)^2 \left( R_0 - \frac{d(CO_2)}{dt} \right) \right]
\]

\[
A = \text{frequency factor} \\
E = \text{activation energy}
\]
Clearly if \((E_1 + E_2) > E_3\) the R.H.S. of Eq 2 will increase as the temperature decreases. Graph 7 shows the \(G(CO_2)\) data obtained in the temperature range 0°C to -196°C at a dose rate of \(2.56 \times 10^{13}\) ev/cc sec plotted in the form of Eq 2. The shape of the curve depends on the value assumed for \(G_0(3P)\) when calculating \(R_0\). The relation is linear if \(G_0(3P)\) is assumed to be 1.5. The slope corresponds to an activation energy of about 1.5 kcal per mole.

However if both temperature and dose rate effects can be explained in terms of the same reaction mechanism, then the \(G(CO_2)\) values obtained at low temperature are expected to be dose rate dependent. Graph 8 shows Anderson's (12) and the author's data. The sparsity of the author's data is due to:

a) lack of a homogeneous high dose rate facility,

b) the practical difficulty of maintaining temperatures of -78°C over long periods of time at low dose rates in large reaction vessels.

Clearly if Anderson's 22°C dose rate profile applies to all temperatures then the plot of the Arrhenius equation (2) should have a dose rate dependent curvature. If dose rate dependence at low temperatures is assumed then the observed dependence of \(G(CO_2)\) on dose rate at -183°C confirms the suggestion that \(G_0(3P)\) is less than \(G(CO_2)\). However since the slope and curvature of the plot of Eq 2 is expected to be
$G(\text{CO}_2)$ as a function of temperature in s.t.p. density carbon monoxide

Dose Rate $2.56 \times 10^{13} \text{ eV/cc sec}$

1. $G(\text{O}^{3p}) = G(\text{CO}_2) = 2$
2. $G(\text{O}^{3p}) \neq G(\text{CO}_2) = 1.5$

\[ \text{CO}_2 = \frac{d(\text{CO}_2)}{dt} \]

\[ \left( \frac{1}{T(\text{K})} \right) \times 10^2 \]
$G_1(CO_2)$ as a function of dose rate and temperature

- $G_1(CO_2)$ at 22°C (Anderson's Data)
- $G_1(CO_2)_{\text{expt}}$ at -78°C
- 'sketched' - 78°C dose rate profile
- $G_1(CO_2)_{\text{expt}}$ at -183°C
- observed -183°C dose rate profile

$G_1(CO_2)$
molec. (100eV)$^{-1}$

$\log_{10}$ dose rate (eV/cc sec)
dose rate dependent it is probably fortuitous that it becomes straight line when it is assumed that \( \text{GO}(^3\text{P}) \) is 1.5 rather than 2.

Because of the lack of experimental data other considerations are clearly required to decide whether Anderson's mechanism can explain the effect of low temperature.

The velocity constant ratio \( \frac{k_3}{k_1k_2} \) calculated from Anderson's data is about \( 3 \times 10^{-1} \) mole sec/cc. It may be argued that \( k_3 \) cannot be greater than the velocity constant of for example methyl radical recombination (\( \approx 10^{13} \) cc/mole sec) (15) \( k_2 \) is known (\( \approx 10^7 \) cc/mole sec at 25\(^\circ\)C) (3) thus \( k_1 \) must be about \( 10^6 \) cc/mole sec.

Jacox et al (16) concluded that \( \text{C}_2\text{O} \) reacts with carbon monoxide with little or no activation energy. The electronic state of the \( \text{C}_2\text{O} \) radical observed by Jacox et al, and the \( \text{C}_2\text{O} \) radical intermediate in production of \( \text{C}_2\text{O}_2 \) in CO radiolysis is unknown.

It is of interest to note here that the rate of the addition reaction:

\[
\text{O}(^3\text{P}) + \text{NO} \rightarrow \text{NO}_2 + \text{h}\nu
\]

is defined by the velocity constant \( k = 3.2 \times 10^6 \exp(+1.5/RT) \) cc/mole sec. (17). Addition reactions with high steric factors and low activation energies are therefore known.

It has already been mentioned p.99 that during radiolysis
of C$_3$H$_6$/CO mixtures, the product spectrum contains components other than those which may be ascribed to the O($^3P$) + C$_3$H$_6$ reaction, when C$_3$H$_6$/CO $> 2 \times 10^{-3}$. Let it be assumed that these components are due to the reaction between triplet C$_2$O and C$_3$H$_6$. Thus:

$$k(C_2O + CO) \sim 2 \times 10^{-3} k(C_2O + C_3H_6)$$

Bayes (18,19) have found that velocity constant for reaction of triplet C$_2$O with NO is $2 \times 10^3$ greater than with C$_3$H$_6$. NO is by far the most effective scavenger for C$_2$O($^3\Sigma^+$) known. If it is assumed that the reaction has negligible activation energy, and that reaction occurs at one in every 100 collisions then it may be seen that:

$$k_{C_2O} (^3\Sigma^+) + CO \sim 10^6 \text{ cc/mole sec.}$$

The above argument clearly supports the concept that Anderson's mechanism can explain the effect of low temperature on G(CO$_2$) and reaction stoichiometry.

There is however another feasible mechanism which may explain the effects of temperature and dose rate:

\[
\begin{align*}
\text{CO} & \rightarrow \text{CO}^+, \text{e}^- \\
\text{CO}^+ + \text{e}^- & \rightarrow \text{CO} \\
\text{CO}^+ + C_3O_2 & \rightarrow \text{polymer} \\
0 + C_3O_2 & \rightarrow 3\text{CO} \\
0 + \text{CO} & \rightarrow \text{CO}_2
\end{align*}
\]
Table 19 shows \((\text{C}_3\text{O}_2)/(\text{CO})\) calculated as discussed on pp 33 and 39 as a function of dose rate and temperature, it is assumed that \(0(3\text{P}) + \text{C}_3\text{O}_2\) has an activation energy of 2.5 kcal per mole. The high value of \(k_x\) refers to a typical velocity constant for an ion molecule reaction as determined in a low pressure mass spectrometer. The low value of \(k_x\) refers to the velocity constant for interception of \(\text{CO}^+\) by \(\text{O}_2\) at 1 atm as discussed on p 34.

Inspection of Table 19 shows that if it is assumed:

a) that the reaction of \(0(3\text{P})\) with \(\text{C}_3\text{O}_2\) has an activation energy of about 2.5 kcal per mole.

b) that the velocity constant for interception of \(\text{CO}^+\) by \(\text{C}_3\text{O}_2\) in a gaseous system at 1 atm is 100 times lower than that for ion molecule reactions at low pressure.

Then it is possible to explain the reduction in \(G(\text{CO}_2)\) by either increasing the dose rate above \(10^{15}\) eV/cc sec at 22°C, or reducing the temperature below 22°C at dose rates below \(10^{15}\) eV/cc sec in terms of \(0(3\text{P})\) and \(\text{CO}^+\) competing for \(\text{C}_3\text{O}_2\).

Summary.

During gamma radiolysis of CO gas at s.t.p density no evidence for a deviation from a reaction stoichiometry described by the equation:

\[ 4n \text{CO} \rightarrow n\text{CO}_2 + (\text{C}_3\text{O}_2)_n. \]
Table 19

A) \( \frac{(\text{C}_3\text{O}_2)}{(\text{CO})} \) as a function of dose rate and velocity constant for \( \text{CO}^+ \) ion interception.

<table>
<thead>
<tr>
<th>Dose Rate eV/cc sec</th>
<th>* ( k_x ) cc/mole sec</th>
<th>( \frac{(\text{C}_3\text{O}_2)}{(\text{CO})} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8 x 10^{13}</td>
<td>5.5 x 10^{14}</td>
<td>3.9 x 10^{-8}</td>
</tr>
<tr>
<td></td>
<td>5.5 x 10^{12}</td>
<td>3.9 x 10^{-6}</td>
</tr>
<tr>
<td>5 x 10^{16}</td>
<td>5.5 x 10^{14}</td>
<td>1.66 x 10^{-6}</td>
</tr>
<tr>
<td></td>
<td>5.5 x 10^{12}</td>
<td>1.66 x 10^{-4}</td>
</tr>
</tbody>
</table>

B) \( \frac{(\text{C}_3\text{O}_2)}{(\text{CO})} \) as a function of temperature

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>( k^0(3p) \left[ \frac{\text{CO}}{\text{C}_3\text{O}_2} \right] )</th>
<th>( \frac{(\text{C}_3\text{O}_2)}{(\text{CO})} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>2.25 x 10^{-5}</td>
<td>4.5 x 10^{-5}</td>
</tr>
<tr>
<td>-183</td>
<td>6.25 x 10^{-8}</td>
<td>1.25 x 10^{-7}</td>
</tr>
</tbody>
</table>

\[ k_x = k(\text{CO}^+ + \text{C}_3\text{O}_2) \]
on lowering the temperature to -183°C was found.

Because of the lack of dose rate dependence on $G(CO_2)$ at -183°C it is suggested that the observed CO$_2$ yield is not derived from O($^3P$) intermediates. This conclusion is supported by the CO/$C_3H_6$ experiments from which it was concluded that $G(0(^3P)) = 1.41 \pm 0.22$ which indicates a "residual" $G(CO_2)$ of 0.6.

It is demonstrated that it is feasible to explain the effect of temperature in terms of the reaction $O + C_2O \rightarrow 2CO$ competing with $C_2O + CO \rightarrow C_3O_2$ and $O + CO \rightarrow CO_2$. However it is suggested that it is also feasible to explain the effect in terms of both O($^3P$) and CO$^+$ competing for monomeric $C_3O_2$. Independently derived velocity constant data are required to resolve this problem.

C Cryogenic Liquid Studies, $G(CO_2)$ and reaction stoichiometry.

$G(CO_2)$ and the reaction stoichiometry were measured during gamma radiolysis of liquid carbon monoxide at 77°K. The polymer yield and composition was estimated as described on page 71. Table 15 shows the result of the analysis. $G(CO_2)$ estimated from this data is $0.24 \pm 0.01$ molecules per 100 eV about 25% higher than that previously reported (20).

If the reaction stoichiometry is:-

$$4nCO \rightarrow nCO_2 + (C_3O_2)_n$$
then the C:O ratio for all the reaction products is unity and the C:O ratio for the solid is 1.5. These two ratios calculated from the data in Table 15 are shown in Table 16.

The experimental data indicates that the solid has the composition \((C_3O_2)_n\) and that the overall stoichiometry is that discussed above and is identical to that reported by Anderson (12) for gamma and proton radiolysis of carbon monoxide gas at 1 atm and 22°C. This result strongly contrasts with the finding of Buschmann (20) who found that gamma radiolysis of pure liquid CO at 77K results in the formation of CO\(_2\) and a solid deposit consisting mainly of carbon. The reason for this discrepancy is not clear. It can only be suggested that Buschmann (20) used reaction vessels constructed of Pyrex (softening point 820°C), thus pyrolysis temperatures of 1000°C obtained by the author with silica reaction vessels (softening point 1594°C) could not be attained.

The result that the deposit formed during gamma radiolysis of liquid carbon monoxide at 77K is carbon suboxide makes the effects observed when methane is added to the system (20) easier to explain. Buschmann (20) observed monomeric \(C_3O_2\) formation on addition of methane, and was unable to propose a satisfactory mechanism to explain this effect.
It was suggested p 38 that the polymerisation of monomeric $\text{C}_3\text{O}_2$ could be initiated by charge transfer from CO$^+$, thus initiation should be inhibited by addition of a CO$^+$ interceptor. Anderson (12) however found that addition of 0.5% CO$_2$ (a known CO$^+$ interceptor) did not affect G(C) solid under ambient conditions. CO$_2^+$ however has an I.P. of 13.26 eV which is higher than the C$_3$O$_2$ I.P. (10.6 eV). Clearly a two step charge transfer sequence can be postulated to make the theory and observation above compatible.

The following ion molecule reaction may be postulated to occur on interception of CO$^+$ by CH$_4$:

\[
\text{CO} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HCO}^+ 
\]

HCO$^+$ has an I.P. of 9.87 eV (21) and will therefore not transfer charge to C$_3$O$_2$. Thus it is reasonable to propose that CH$_4$ will inhibit C$_3$O$_2$ polymerisation if the initiation process can be explained in terms of simple charge transfer reactions.

On page 120 it was suggested that monomeric C$_3$O$_2$ would successfully compete with CO for O($^3\text{P}$). The reaction of O($^3\text{P}$) with CH$_4$ has a large activation energy (6), it may be shown that O($^3\text{P}$) will react with CO rather than CH$_4$ at low temperature.

Thus it has to be postulated that O($^3\text{P}$) atoms are caged and that monomeric C$_3$O$_2$ is formed from such processes as:

\* Ionisation Potential
D Cryogenic Liquid Studies. Oxygen Atom Formation.

a) Cage Effects.

An argument identical to that on page 113 shows that if oxygen atoms are formed during radiolysis of cryogenic liquid CO at 77°K recombination to form molecular oxygen is faster than association with CO to form CO₂.

From the measured solid composition and mass balance ratios it is clear that molecular oxygen is not formed during radiolysis under liquid state conditions. The homogeneous reaction, O + C₂O → 2CO may be postulated to explain the reduction in G(CO₂) in the gas phase at 77°K. However in the liquid it is presumably possible for the primary dissociation fragments to be trapped in a solvent cage.

A preliminary experiment by the author indicated that G(aldehyde) during gamma radiolysis of liquid CO + 1% C₃H₆ at 77°K was about 0.33. If propene oxide formation is assumed then a G(O₃P) of about 0.66 is indicated. This supports the cage hypothesis. Noyes(23) has considered theoretically the competition between reassociation of a photodissociated molecule trapped in a liquid cage and reaction of the photodissociation
fragments with an added interceptor. It may be predicted theoretically that the products of the fragment interceptor reaction will increase linearly in the square root of interceptor concentration. This experiment needs to be performed before the argument stated above may be advanced.

Buschman (20) studied the gamma radiolysis of liquid CO + CH₄ mixtures at 77°C. At high mixing ratios, CH₄/CO = 0.3 acetylene formation was detected and explained in terms of the reaction:

\[ \text{C} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 \]

The maximum \( G(\text{C}_2\text{H}_2) \) detected was however 0.097 which does not support the liquid cage effect proposed above if \( \text{C}_2\text{H}_2 \) formation has been correctly rationalised.

b) \( \text{O}(^1\text{D}) \) formation.

The mechanism of reaction of \( \text{O}(^1\text{D}) \) with CO has been discussed on page 20. A similar mechanism for reaction of \( \text{O}(^1\text{D}) \) with \( \text{N}_2 \) may be proposed (22). It may also be shown that velocity constants for reaction of \( \text{O}(^1\text{D}) \) with \( \text{N}_2 \) and CO at 77°C are similar (22).

If the mechanism proposed for \( \text{O}(^1\text{D}) \) reaction is correct, secondly if the \( \text{CO}_2 \) yield during gamma radiolysis of liquid CO at 77°C is due to \( \text{O}(^1\text{D}) \) reaction, then in a 50:50 mixture of liquid CO and \( \text{N}_2 \) at 77°C a yield composed of a 50:50 mixture of \( \text{CO}_2 \) and \( \text{N}_2\text{O} \) is to be expected.
A preliminary experiment by the author demonstrated the following:

(i) The rate of formation of CO$_2$ during gamma radiolysis of liquid CO and a liquid 50:50 N$_2$/CO mixture were found to be $1.9 \times 10^{-7}$ moles per hr and $2.3 \times 10^{-7}$ moles per hour respectively at the same dose rate.

(ii) The "CO$_2$" formed in the CO/N$_2$ mixture was found to be CO$_2$ by sorption on to sofnilite.

(iii) A deposit was formed during radiolysis of N$_2$/CO mixtures. The LOX condensable fraction of the gas produced during vacuum pyrolysis of this deposit could not be sorbed on to sofnilite and was therefore not CO$_2$.

It may be concluded that gamma radiolysis of liquid 50:50 CO/N$_2$ mixtures:

(i) does not result in N$_2$O formation

(ii) charge or energy transfer from N$_2$ to CO occurs

(iii) a deposit containing nitrogen is formed.

Buschman (20) also states that N$_2$O is not formed during gamma radiolysis of liquid CO/N$_2$ mixtures at 77ºK. The same author did not detect CH$_3$OH formation during gamma radiolysis of liquid CO/CH$_4$ mixtures at 77ºK. Under such conditions the reaction:

$$\text{O}^{(1)} \text{D} + \text{CH}_4 \rightarrow \text{CH}_3\text{OH}$$

is expected to take place (page 22) if O$^{1}$D is formed.
Propyl alcohol formation was detected during gamma radiolysis of liquid CO + propane mixtures, Table 13 and page 107. The significance of this observation is uncertain on page 109.

**Summary.**

Although the yield of products per unit energy input during gamma radiolysis of liquid CO at 77°K is less than the yield in the gas phase under ambient conditions the products formed and the overall reaction stoichiometry are identical.

Preliminary evidence for a cage effect during gamma radiolysis of liquid CO at 77°K was obtained. Positive evidence for O(1D) formation was not obtained.
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Section 4  Proposed Research Programme.

There are many ways in which the project described in this thesis could be usefully extended. Several have already been discussed:-

a) The reaction of $O(^{1}D)$ with propane at low quantum inputs with measurements concomitant to the propyl alcohol formation rate and yield ratio such as the rates of formation of nitrogen and aldehyde p 109 .

b) Extension of the low temperature gas phase experiments to higher dose rates p 116 .

c) Isolation of cage effects during radiolysis of cryogenic liquid CO by measuring yields as a function of $O(^{3}P)$ interceptor concentration p 126 .

d) Identifying those components of the gas chromatographic spectrum between the peaks due to propene and $(O(^{3}P) + C_{3}H_{6})$ addition products p 99 .

These products may well be at least partly due to the reaction of $C_{2}O$ with $C_{3}H_{6}$. Independently determined velocity constants for $C_{2}O$ reaction are required to resolve the discrepancy stated on page 46 .

Three further topics will be discussed.
Reactions of CO⁺

Ion interception velocity constants have apparently not been measured in atmospheric systems. A method of doing this is to measure such constants relative to the ion-electron recombination velocity constant \( v_33 \). An effect due to positive ion interception first has to be isolated. The interception of CO⁺ by O₂ probably initiates a complex ionic chain reaction. Study of such a complex system is unlikely to provide information about the velocity constants of single reaction steps. A simple one step reaction is clearly required. The reaction of CO⁺ with CH₄ will be discussed below.

The minimum energy requirement corresponding to the appearance potential of the fragments for charge transfer and dissociative charge transfer to methane have been listed (1) and are:

\[
\begin{align*}
\text{CH}_4^+ & \quad 13.1 \text{ eV}, \\
\text{CH}_3^+ + \text{H} & \quad 14.4 \text{ eV}, \\
\text{CH}_2^+ + \text{H}_2 & \quad 15.6 \text{ eV}, \\
\text{CH}_2^+ + 2\text{H} & \quad 20.1 \text{ eV}, \\
\text{CH}^+ + 3\text{H} & \quad 22 \text{ eV}, \\
\text{C}^+ + 4\text{H} & \quad 26.8 \text{ eV}.
\end{align*}
\]

The recombination energy of ground state CO⁺ and the electronically excited states of CO⁺ \( (A^2Π \text{ and } B^2Σ^+ \text{)} \) are 14, 16.54 and 19.7 eV respectively (2). The electronically excited states of CO⁺ have very short life times (3). If it is valid to assume that transition to the ground state take place before charge transfer, secondly that the CO⁺ ions do not have excessive translational energy, then CH₄⁺ may be postulated.
to be formed as a result of charge transfer from CO\(^+\) to CH\(_4\). CH\(_4^+\) if formed could probably react as follows (4):

\[
\begin{align*}
\text{CH}_4^+ + \text{CH}_4 & \rightarrow \text{CH}_5^+ + \text{CH}_3 \\
\text{CH}_5^+ + e^- & \rightarrow \text{CH}_3 + \text{H}_2
\end{align*}
\]

The ion molecule reactions:

\[
\begin{align*}
\text{CO}^+ + \text{CD}_4 & \rightarrow \text{COD}^+ + \text{CD}_3 \\
\text{CD}_4^+ + \text{CO} & \rightarrow \text{COD}^+ + \text{CD}_3
\end{align*}
\]

have been shown to occur with high efficiency in a mass spectrometer (5).

The interception of CO\(^+\) by CH\(_4\) is for the reasons outlined above, expected to result in the formation of CH\(_3\). Before the detection of CH\(_3\) is discussed the reaction of other intermediates produced during radiolysis of CO with CH\(_4\) is first reviewed.

Both O\((3P)\) and O\((1D)\) can react with CH\(_4\) to produce CH\(_3\). O\((3P)\) will not react with CH\(_4\) at low CH\(_4\)/CO ratios at room temperature; an experiment to demonstrate the presence of O\((1D)\) eg in a CO/CH\(_3\)\(_2\)/CH\(_4\) mixture (p 109) has yet to be performed.

The reactions of C and C\(_2\)O with CH\(_4\) are expected to yield C\(_2\)H\(_2\) and C\(_2\)H\(_4\) respectively p 46.

The reactions of CO\((a^3\Pi)\) will be discussed p 138. It
The subscripts on the velocity constants \( k \) on p135 refer to the numbered steps in the reaction mechanism written on p135.
will be suggested that CH$_4$ can accept electronic excitation energy and decomposes to H$_2$ and CH$_2$.

It may be concluded that O(1D) is the only other intermediate likely to produce CH$_3$ at low CH$_4$/CO ratios. The detection of CH$_3$ will now be discussed.

CH$_3$ radicals may be detected by either of two processes:

$$2 \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$$

or

$$\text{CH}_3 + \text{CO} \rightarrow \text{CH}_3\text{CO}$$

$$2 \text{CH}_3\text{CO} \rightarrow (\text{CH}_3\text{CO})_2$$

The CH$_3$CO radical is stable with respect to fragmentation at 1 atm. and 22°C (6). The relative velocity constant ratio $k_1/k_2$ has been measured (7)

$$k_2/(k_1)^{1/2} = 81.3 \exp (-3.9/RT) \text{ (cc/mole sec)}^{1/2}$$

The recombination constant, $k_1$, has been estimated to be $2.34 \times 10^{13}$ cc/mole sec (8). Combining these two estimates:

$$k_2 \sim 5 \times 10^5 \text{ cc/mole sec at 22°C}$$

Thus assuming the mechanism above, the mean life of CH$_3$ in step 2 is about $5.6 \times 10^{-2}$ secs at 1 atm. At the maximum dose rate available to the author ($\sim 2.8 \times 10^{13}$ eV/cc sec) the mean life of CH$_3$ in step 1 is 0.164 secs. Thus biacetyl formation is to be expected. Ethane however would be formed at lower temperatures or higher dose rates.

Some preliminary experiments performed by the author
suggest that CH$_3$ radicals are indeed formed during gamma radiolysis of CO/CH$_4$ mixtures, page 89. Methyl hydrogen peroxide was found to be formed, presumably due to the accidental presence of oxygen. The mechanism of formation of CH$_3$OOH is reviewed by Rosen (9). For the system under discussion CH$_3$OOH is unlikely to be formed via the reaction sequence:

\[
\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2
\]

\[
\text{CH}_3\text{O}_2 + \text{CH}_4 \rightarrow \text{CH}_3\text{OOH} + \text{CH}_3
\]

because this is a chain mechanism, it should be noted however that a yield dose plot was not constructed.

The measured peroxide/aldehyde yield ratio indicates that the following reactions do not occur in the system under discussion:

\[
2 \text{CH}_3\text{O}_2 \rightarrow 2 \text{CH}_3\text{O} + \text{O}_2
\]

\[
\text{CH}_3\text{O} + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{OOH} + \text{HCHO}
\]

A feasible mechanism is probably:

\[
\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2
\]

The source of HO$_2$ in the system under discussion is not clear. Hydrogen atoms could perhaps be formed by decomposition of such intermediates as HCO, or perhaps HCO can act as a donor as HO$_2$.

The reason why the estimated G(CH$_3$OOH) yield is about a tenth of G(CO$^+$) is not clear. It might be due to dissociative
charge transfer to CH_4 not yielding CH_3. However a yield dose plot and a study of oxygen consumption has to be made to substantiate the observed G (peroxide).

In another brief series of experiments addition of water vapour was found to increase G(CO_2). This effect could possibly be explained in terms of the mechanism:

\[
\text{CO}^+ + \text{H}_2\text{O} \rightarrow \text{HCO}^+ + \text{OH} \\
\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}
\]

O(^1\text{D}) however reacts with H_2O to form 2(OH).

\section{Polymerisation of carbon suboxide.}

This subject has already been discussed on pages 37, 125.

It has been suggested that the polymerisation process can be initiated by charge transfer from CO^+ to monomeric C_3O_2. Preliminary experiments (p 91) have indicated that G(CO_2) is not influenced by the presence of about 5% methane under ambient conditions in the gas phase. A search for both monomeric and polymeric C_3O_2 in this system would clearly be useful.

\section{Chemical Reactivity of Electronically Excited States of CO.}

This subject was introduced on page 35. On page 98 it was suggested that electronically excited states of CO might react with propene to form acetone.

A number of techniques exist for producing electronically
excited states of CO, these will be listed below:-
a) An iodine lamp which emits 2062 Å photons and can thus produce CO (a$^3\pi$) is described by Harteck et al (10) b) Liuti (11) has demonstrated that CO(a$^3\pi$) may be produced during 1849 Å mercury sensitised photolysis. c) Meisels (12) has demonstrated that the acceleration of electrons by means of an applied electrostatic field during radiolysis accentuates the formation of products from electronically excited states while the formation of products from ionic intermediates remains unaffected.
d) Williams (13) describes a reactor in which electrons produced by UV light falling on a photo sensitive surface are accelerated by application of an electrostatic field. Product yields per electron collected were found to be greater than the ion pair yield in radiolysis. The production of electronically excited states was therefore indicated.

The reaction of electronically excited states of CO with CH$_4$ is of interest since CH$_4$ has been suggested as a CO$^+$ interceptor (vide supra). Gover (14) suggests that the mechanism of 1849 Å iodine sensitized photolysis of methane may be described in terms of the following reactions:

\[ I_2^{\text{exc}} + CH_4 \rightarrow I_2 + CH_4^{\text{exc}} \]
\[ CH_4^{\text{exc}} \rightarrow H_2 + CH_2 \]
\[ CH_2 + CH_4 \rightarrow C_2H_6 \]
It would clearly be of interest to see if CH₄ will accept electronic excitation energy from CO. In the presence of excess CO, CH₂ is expected to react with CO to form ketene (7). The fission reaction could also be diagnosed by measuring the production of H₂ and D₂ from a CO + CH₄/CD₄ mixture.
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Appendix (I)

Calculation of dose rates

This section is intended to describe the derivation of the formula on page 54 in greater detail.

The dose rate in water contained in the reaction cavity is first determined by Fricke dosimetry. The rate of energy absorption per unit mass of wall (W) is then calculated from the relation:

\[ E_W = \frac{\varepsilon_W}{\varepsilon_{H_2O}} \cdot E_{H_2O} \quad (1) \]

where:
- \( E \) = rate energy absorption per gram (eV/sec gm)
- \( \varepsilon \) = electron density (electrons/gm)

The dose rate in the gas (G) is then estimated using the Bragg-Gray relation:

\[ E_W = \frac{S_W}{S_G} \cdot E_G \quad (2) \]

where:
- \( S \) = mass stopping power eV cm\(^2\) gm\(^{-1}\)

For \( \beta \) particles (\( E_{max} = 0.167 \text{ MeV} \)) the following relation was derived experimentally by Baily for calculating the mass stopping power ratio of a compound X relative to air.

For \( \beta \) particles (\( E_{max} = 0.167 \text{ MeV} \)) the following relation was derived experimentally by Baily for calculating the mass stopping power ratio of a compound X relative to air.
\[ \frac{S_X}{S_{\text{air}}} = \frac{\epsilon_X}{\epsilon_{\text{air}}} \left( 1.336 - 0.1642 \ln Z_X \right) \]

\( Z = \text{mean atomic number} \) (electrons per atom)

thus:

\[ \frac{S_{\text{CO}}}{S_W} = \frac{\epsilon_{\text{CO}}}{\epsilon_W} \left( \frac{1.336 - 0.1642 \ln Z_{\text{CO}}}{1.336 - 0.1642 \ln Z_W} \right) \quad \ldots \ldots \quad (3) \]

combining equations 1, 2 and 3

\[ E_{\text{CO}} = E_{\text{H}_2\text{O}} \frac{\epsilon_{\text{CO}}}{\epsilon_{\text{H}_2\text{O}}} \left( \frac{1.336 - 0.1642 \ln Z_{\text{CO}}}{1.336 - 0.1642 \ln Z_W} \right) \]

this is the formula stated in the script.

Typical Pyrex brand borosilicate glass has the following composition:

\( \text{SiO}_2, 80.6\%; \text{B}_2\text{O}_3, 12.6\%; \text{Na}_2\text{O}, 4.15\%; \text{Al}_2\text{O}_3, 2.12\%; \)

thus \( Z_W \) is about 9.5. \( Z_{\text{CO}} \) is 7. Substitution of these numbers into the derived equation yields:

\[ E_{\text{CO}} = 0.95 E_{\text{H}_2\text{O}} \]

The validity of this equation was not tested by direct experimental estimates of ionisation currents etc. in the reaction vessels used by the author.
Appendix (2)

H³⁻³⁻ Dosimetry

H³⁻³⁻ dosimetry refers to adding known quantities of tritium (half life 12.46 years, maximum p energy from 0.018 MeV) and calculating the dose rate, the known specific activity and range of the p particles.