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THE PHOTOCHEMISTRY OF FORMALDEHYDE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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* * * * * *

The Ohio State University
1965

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ACKNOWLEDGMENTS

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INTRODUCTION

In discussing this and previous work on the photochemistry of formaldehyde, continued reference will be made to the detailed spectroscopy of the molecule. As an aid to understanding the photochemistry of formaldehyde, a brief review of the relevant results from spectral investigations are presented here.

Spectroscopy

Formaldehyde

The spectrum of formaldehyde has been observed in both absorption (1-6) and emission (7-10). The major band system extends from 3700-2300Å. The f value of this system is about $2.4 \times 10^{-4}$ (11) indicating a "forbidden transition." A second and much less intense ($f \approx 1.2 \times 10^{-6}$) series of bands has been observed in the 4000 to 3600Å region (12-14). Most workers agree that these are the $1_{A_2} - 1_{A_1}$ and $3_{A_2} - 1_{A_1}$ electronic transitions respectively. These assignments agree well with predictions made from simple molecular orbital considerations. Thus the ground state ($1_{A_1}$) of formaldehyde can be represented by

$$(1_{a_1})^2(2_{a_1})^2(1_{b_2})^2(3_{a_1})^2(1_{b_1})^2(2_{b_2})^2(2_{b_1})^0$$
where the letter with the subscript denotes the symmetry species
of the orbital and the superscript denotes the number of electrons
in the orbital. The first excited state is then

\[ \cdots \cdot \cdot \cdot (2b_2)^1(2b_1)^1 \quad A_2 \]

The \(2b_2\) orbital correlates roughly with the \(2p_z\) non-bonding
orbital of oxygen while the \(2b_1\) orbital is roughly the same as the
CO \(\pi\) antibonding orbital. The transition is commonly denoted as
an \(n-H^*\) type and is similar to the first absorption system of most
small aldehydes and ketones. As expected, the promotion of an
electron from the oxygen atom to the CO \(\pi\) antibonding orbital re-
results in a weaker CO bond. This is shown experimentally; the CO
bond distances in the \(1A_1\) and \(1A_2\) states are 1.22 and 1.32 Å
respectively.

Both the \(1A_2 - 1A_1\) and \(3A_2 - 1A_1\) electronic transitions are
forbidden due to symmetry. However, theoretical considerations (15)
indicate that the \(1A_2 - 1A_1\) transition is a vibronic transition in-
volving the out-of-plane bonding mode \(v_4\) (see Figure 1). Thus the
vibronic species is \(B_2\) and the transition should give rise to \(A\)
bands. Moreover, Sidman (16) concludes that the \(3A_2 - 1A_1\) transition
is due to spin-orbit perturbations of the \(3A_1\) state with \(1A_1\) excited
states.

Formaldehyde undergoes a rather pronounced change in geometry
in the transition to \(A_2\) excited state. The ground state has been
shown to be of \(C_{2v}\) symmetry (17). However, on excitation the planar
configuration is destroyed and a nonplanar upper state results
Figure 1. Normal vibrations for H$_2$CO.
(C$_S$ symmetry). The barrier to inversion is quite low (about 650 cm$^{-1}$) and this results in large splittings of the v$^4$ mode.

As the transition is accompanied by a change in the CO bond distance and a change from planar to nonplanar configuration, the Franck-Condon principle predicts that the observed bands should involve progressions involving v$^2$ and v$^4$. Experimentally this was found to be the case. The first strong band in absorption (A-band, see Figure 2) near 3530 cm$^{-1}$ is the first member in a regular series with spacing of 1177 cm$^{-1}$. This corresponds to the CO stretching frequency in the excited state. Rotational analysis of the A band showed that the transition moment was perpendicular to the C$_2$ axis and thus the transition could be represented as a vibronic transition of species $^1B_2 ^1A_1$. This is in complete accord with theory.

Further work showed the presence of a "hot" band* about 1280 cm$^{-1}$

---

* The term "hot band" denotes a band whose origin is a vibrationally excited ground state. Since at room temperature the majority of molecules are in their ground vibrational state, the intensity of such bands is usually quite small. However, if the temperature of the sample is raised, the upper vibrational levels are populated according to Boltzman's law. Due to the exponential nature of the Boltzman factor, small changes in temperature may produce significant changes in the population of the higher vibrational levels; and, correspondingly product dramatic change in the intensity of the bands originating from those levels. The pronounced sensitivity to temperature of this type of band is the reason for the term "hot band."

---

to the red of the A-band (18-20). While this band is quite weak in absorption it is the first predominant band observed at the violet end of the emission spectra. Dyne (19) concluded from a rotational analysis of the so-called a band that the transition represented had
Figure 2.---Energy level diagram for some of the bands of CH$_2$O.
neither an upper nor a lower state in common with the A-band. The transition was assigned by Brand (20) and corroborated by Dyne as $0^+ - v_n$ with a vibronic species $A_2 - B_1$. At the long wave-length end of the $\alpha$ band, both workers observed a second weaker component which was assigned to the $0^+ - v_n$ transition.

A vibrational analysis of the $3A_2 - 1A_1$ system indicated that it was very similar to the singlet system (21,22). A rotational analysis of the two bands involving $0^+$ and $1^+$ levels in the upper state showed that the transition moment was parallel to the CO axis in agreement with Sidman's predictions. As with the excited singlet state, the triplet molecule has a nonplanar configuration.

With the analysis of many of the bands of H$_2$CO and D$_2$CO, considerable information about the vibrational frequencies and geometries of the excited states could be determined. Since reference will be made to these quantities, the information is summarized in Table 1.

Even a brief discussion of the formaldehyde spectrum would not be complete without mention of the emission spectra and its relation to the question of the first dissociation energy of the molecule. The fluorescence spectra of formaldehyde can be observed and this fact argues for an excited state with a finite lifetime. However, only the singlet-singlet transition is observed. This may indicate a rapidly dissociating triplet or that no perturbation was present to permit so-called "intersystem crossing." Typical of most polyatomic molecules, transitions from only a few of the lowest lying excited states are observed. Presumably this is due to the rapid
<table>
<thead>
<tr>
<th>Constant</th>
<th>( v_1 )</th>
<th>( v_2 )</th>
<th>( v_3 )</th>
<th>( v_4 )</th>
<th>( v_5 )</th>
<th>( v_6 )</th>
<th>( \angle_{HCH} )</th>
<th>( V_\circ ) (C-H)</th>
<th>( r_\circ ) (C=O)</th>
<th>out-of-plane angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{A_1} )</td>
<td>2766.4</td>
<td>1746.1</td>
<td>1500.6</td>
<td>1163.5</td>
<td>2843.4</td>
<td>1247.4</td>
<td>120°</td>
<td>1.09</td>
<td>1.22</td>
<td>0°</td>
</tr>
<tr>
<td>( \frac{1}{A_2} )</td>
<td>2851</td>
<td>1177</td>
<td>1321</td>
<td>683</td>
<td>--</td>
<td>899</td>
<td>122°</td>
<td>1.09</td>
<td>1.32</td>
<td>20°</td>
</tr>
<tr>
<td>( \frac{3}{A_2} )</td>
<td>--</td>
<td>1251</td>
<td>--</td>
<td>643</td>
<td>--</td>
<td>--</td>
<td>120°</td>
<td>--</td>
<td>1.31</td>
<td>35°</td>
</tr>
<tr>
<td>Units</td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
<td>( \AA )</td>
<td>( \AA )</td>
<td>°</td>
</tr>
</tbody>
</table>

**TABLE 1**

Molecular Constants for \( \text{H}_2\text{CO} \) and \( \text{D}_2\text{CO} \) in Their Ground and Excited States (23)
depopulation of the higher vibrational levels by deactivating collisions.

Robinson has investigated the emission spectra under discharge tube conditions (24) and found that emission occurs strongly from the vibronic ground level and also from the level in which one quantum of $v_2$ has been excited. Weaker transitions occur from the first overtone $v_2$ level and also from the $0^+$ member of the first inversion doublet. In agreement with the Franck-Condon principle only $v^*$ and $v_2^*$ are observed as ground state fundamentals.

Robinson argued that the vanishing small intensity from the $1^+$ doublet is strong evidence for predissociation in this region. This would set an upper limit on $D(H-COH)$ of 82.1 kcal/mole. He also pointed out that absorption of 3650 Å radiation from a mercury arc results in the population of high rotational sublevels of the $0^+$ or $0^+ + v_2^*$ states. These states lie about 82 kcal/mole above the ground state. Hence the use of the energy of the incident photon as a measure of $D(H-CHO)$ results in a value about 4 kcal/mole too low ($E_{\text{photon}} = 78$ kcal/einstein).

**Formyl**

The ultraviolet spectrum of formyl has been studied by Ramsay (25), Herzberg and Ramsay (26), and Johns, Priddle, and Ramsay (27). While all the facets of the spectra cannot, as yet, be explained, valuable information about the structure of the radical has been gained. The following discussion is taken largely from the work of Johns, Priddle, and Ramsay.
The absorption band system of formyl extends from 7500Å to about 4500Å. Vibrational and partial rotational analysis showed the transition was from a bent ground state ($\angle \text{HCO} = 119^{\circ} 30'$) to an essentially linear excited state. As expected from the Franck-Condon principle, the bands are due largely to $v_2$ progressions. However, only the alternate bands of the progression are sharp. These are associated with $K'' = 1, K' = 0$ (i.e., $\Sigma$-vibronic levels).

* In this discussion $v_1$ denotes C-H or C-D stretching frequency, $v_2$ the HCO or DCO bending frequency, and $v_3$ the CO stretching frequency.

** In the earlier work it was not possible to establish a definite vibrational numbering, and hence it was impossible to definitely assign the vibronic transition as $\Sigma^+ - \Sigma^-$, or $\Sigma - \Pi$. Herzberg and Ramsay favored the former assignment. However, on the basis of derived correlation diagrams, Walsh (28) argued that the electronic transition should be $2\Sigma^+ - 2\Pi$. Ramsay later concluded that this was indeed possible (29).

Johns, et al. reinvestigated the spectrum and were unable to show that the transition was $2\Sigma^+ (\Pi) - 2\Pi$ as predicted. They were also able to show definite evidence for an absorption continuum from 5000-7000Å. The maximum intensity of absorption was about 50%.

Since more bands of lower vibrational quanta were observed in
this study, the vibrational numbering of the bands could be made with some confidence. In addition, the large vibronic splittings due to the Renner effect were observed. Through the usual method of combination of differences, the rotational and vibrational constants for HCO and DCO were obtained. The observation of several "hot" bands allowed determination of \( v^2 \) and \( v^3 \) for HCO and \( v^2 \) for DCO. The relevant spectral data are summarized in Table 2.

From the position of the first observed diffuse band the authors derive \( D(H-C) < 12400 \text{ cm}^{-1} \) (<35.4 kcal/mole). However, this value does little to resolve the controversy over \( E_a \) for \( \text{HCO} \rightarrow \text{H} + \text{CO} \). From a correlation diagram it was evident that both stable states of HCO cannot be generated from \( \text{H}(^2\Sigma) + \text{CO}(^1\Sigma^+) \). The authors feel that the state generated by this combination is likely repulsive and may account for the observed continuum.

Prior to the work of Johns, Friddle, and Ramsay; Pimentel, et al. (30) had produced HCO and DCO in a matrix at 20°K. These investigators photolyzed HX and DX in a CO matrix and observed the product by infrared spectroscopy. Their results are also included in Table 2. While the two sets of values for the ground state vibrational frequencies are not in perfect agreement, the differences can justifiably be attributed to matrix shifts. That the radical observed by Pimentel was the same as that seen by Ramsay was definitely established by observing the electronic spectra of the product produced in the matrix. The bands observed compared favorably with those reported by Ramsay.
<table>
<thead>
<tr>
<th>State</th>
<th>Constant</th>
<th>HCO</th>
<th>DCO</th>
<th>Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2A''(\Pi)$</td>
<td>$\gamma_e$ (CH)</td>
<td>1.06&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>Å</td>
<td>(27)</td>
</tr>
<tr>
<td></td>
<td>$\gamma_e$ (CO)</td>
<td>1.18</td>
<td></td>
<td>Å</td>
<td>(27)</td>
</tr>
<tr>
<td></td>
<td>$\angle$ HCO</td>
<td>180°</td>
<td></td>
<td></td>
<td>(27)</td>
</tr>
<tr>
<td></td>
<td>$\omega_1 \times 11$</td>
<td>3316.2</td>
<td>2547.7</td>
<td>cm&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>(27)</td>
</tr>
<tr>
<td></td>
<td>$\omega_2$</td>
<td>805.5</td>
<td>641.7</td>
<td>cm&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>(27)</td>
</tr>
<tr>
<td></td>
<td>$\omega_3 \times 33$</td>
<td>1813.4</td>
<td>(1713)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>cm&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>(27)</td>
</tr>
<tr>
<td></td>
<td>$T_{100}$</td>
<td>9294.0</td>
<td>9161.2</td>
<td>cm&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>(27)</td>
</tr>
</tbody>
</table>

| $^2A^+$   | $\nu_2$     | 1083.0    | 847.4    | cm<sup>-1</sup> | (27) |
|           |            | 1091      | 839.0    | cm<sup>-1</sup> | (30) |
|           | $\nu_3$     | 1860      | 1849     | cm<sup>-1</sup> | (30) |
|           | $1820.2$    |           | --       | cm<sup>-1</sup> | (27) |
|           | $\gamma_0$ (CH) | 1.08      |          | Å     | (27)   |
|           | $\gamma_0$ (CO) | 1.19      |          | Å     | (27)   |
|           | $\angle$ HCO | 119°30'   |          |       | (27)   |

<sup>a</sup> Assumed value

<sup>b</sup> From Teller-Redlich product rule
Thus the geometry of the upper and lower stable states, and
the nature of the transition involved have been fairly well
elucidated for the formyl radical.

**Photochemistry**

The photolytic and pyrolytic decomposition of formaldehyde has
been studied by many investigators using a wide variety of tech­
niques. While a considerable amount of data have been reported;
there appears to be no general agreement on the mechanism or
energetics of decomposition. A brief survey of the research
reported to date will illustrate the divergency of opinion.

**Early work**

Norrish and Kirkbride (31) investigated the photolysis of
formaldehyde at 100°C using manometric analysis techniques. Three
wave-length regions were studied: 3650-3340Å; 3130-3030Å, and
2650-2540Å. While the actinometry was only qualitative, they were
able to estimate decomposition quantum yields of 0.7, 1.1, and 0.9
respectively for the three regions. Since the quantum yields were
not significantly greater than unity, the authors concluded that a
chain process was not operative; and hence, no free hydrogen atoms
were formed in the primary act. Since the purpose of the investi­
gation was to determine what photochemical significance, if any,
could be attached to the onset of observable predissociation
(λ < 2750Å), the authors speculated that
\[
\begin{align*}
\lambda < 2750 \, \text{Å} & \quad \text{H}_2\text{CO} + h\nu \rightarrow \text{H}_2 + \text{CO} \quad [\text{\(\phi_{II}\)}] \\
\lambda > 2750 \, \text{Å} & \quad \text{H}_2\text{CO} + h\nu \rightarrow \text{H}_2\text{CO}^* \quad [\text{I}] \\
& \quad \text{H}_2\text{CO}^* + M \rightarrow \text{H}_2 + \text{CO} + M \quad [\text{II}]
\end{align*}
\]

Patat (32) and Patat and Locker (33) investigated the decomposition of formaldehyde in the presence of oxygen. They reasoned that hydrogen atoms produced in the primary process would react with the oxygen to eventually produce water. These observers followed the \(\text{H}_2/\text{CO}\) ratio as a function of wave-length. At 80°C, they found the ratio unchanged by oxygen addition using wave-lengths greater than 2750 Å. However, when wave-lengths of less than 2750 Å were used, the \(\text{H}_2/\text{CO}\) ratio decreased to 0.66. These facts lead the authors to conclude that molecular hydrogen and carbon monoxide were produced directly at wave-lengths above 2750 Å.

The reactions occurring below 2750 Å in the presence of oxygen were reinvestigated by Norrish and Carruthers (34). Using the full arc, they found that little of the formaldehyde was decomposed directly, but that the predominant reaction was the oxidation of the aldehyde to formic acid. At 100°C the formic acid was subsequently photolyzed as follows:

\[
\begin{align*}
\text{HCOOH} + h\nu & \rightarrow \text{H}_2 + \text{CO}_2 \quad [\text{3}] \\
& \rightarrow \text{H}_2\text{O} + \text{CO} \quad [\text{4}]
\end{align*}
\]

Thus the change in the \(\text{H}_2/\text{CO}\) ratio did not demand the presence of free hydrogen atoms but could readily be attributed to the preceding reactions. It was also found that the oxidation of the aldehyde proceeded by a chain mechanism.
A short time later, the direct photolysis of formaldehyde was reinvestigated by Akeroyd and Norrish (35). The same manometric analytical technique was used, but the rate of decomposition was studied as a function of temperature and pressure. At higher temperatures the quantum yield increased rapidly, pointing to a chain process. The chain carrier was thought to be hydrogen atoms and the initiation process was taken to be

$$H_2CO + h\nu \rightarrow H^+ + HCO.$$ \[\text{[\text{I}]}\]

The overall observed activation energy was 16.0 kcal/mole and this was assigned to the reaction

$$H + H_2CO \rightarrow H_2 + HCO.$$ \[\text{[5]}\]

However, later investigations showed this assignment was incorrect.

The photolysis of formaldehyde at very short wave-lengths (Schuman region) was investigated by Norrish and Noyes (36). The products were almost entirely hydrogen and carbon monoxide. No evidence was found for

$$\text{CH}_2\text{O} + h\nu \rightarrow \Phi : (3\text{P}) + \text{CH}_2.$$ \[\text{[6]}\]

Most of the decomposition in these experiments was caused by \(\lambda < 1600\text{Å}\), where formaldehyde absorbs some of the Lyman bands of hydrogen.

The iodine-inhibited photolysis of formaldehyde was investigated by Gorin (37) at wave-lengths 3660Å, 3130Å, and 2537Å. Hydrogen iodide was observed at all three wave-lengths. Only traces of
hydrogen were found at 2537Å and 3130Å. However, at 3660Å, a HI/H₂ ratio of 2.4 was observed. Thus it appeared that two processes were operative with one or the other predominant according to the wavelength. Quantum yields were also reported, but these were based on formaldehyde as an actinometer with an assumed quantum yield of unity. This assumption has been shown to be incorrect. Gorin reasoned that since light of 3660Å wave-length could produce hydrogen atoms, as shown by the formation of HI, then the first C-H bond dissociation energy of formaldehyde must be equal to or less than 78 kcal/mole. From thermal data it is known that

\[ H₂CO → 2H + CO \quad ΔH° \quad 298 = 105 \text{ kcal/mole}. \]  

Hence \( E_a \) for formyl decomposition must be about 27 kcal/mole.

It should be mentioned that others have tried to repeat various portions of Gorin's work. Specifically, the work with acetone (38) and acetaldehyde (39,40) has been repeated. Unfortunately repetition of his results has not proved possible. Also, the deactivating effect of iodine on the decomposition of small carbonyl compounds is well established (41-44). Hence, Gorin's work must be viewed with some skepticism.

Blacet and coworkers (45) used the Paneth mirror removal technique to test for the presence of free radicals in the photolysis of several simple compounds. Using 2537Å radiation, no removal was observed for either formaldehyde or acetaldehyde. However, the mirrors were removed by both compounds using light in the 2770Å and 3170Å region. Later experiments at 2537Å using a more intense
light source resulted in rapid mirror removal. While only CH$_3$CHO was tested using the stronger light, the earlier failure of both acetaldehyde and formaldehyde was thought to be due to the low intensity of the light source used.

Considerable evidence now pointed to the occurrence of at least two primary processes; one which produced hydrogen atoms and one which apparently produced molecular hydrogen. These were thought to be

$$H_2CO + h\nu \rightarrow H + HCO \quad [\phi_1]$$

$$\rightarrow H_2 + CO \quad [\phi_{II}]$$

**Energetics**

The energetics of the decomposition of formaldehyde have been the subject of considerable controversy. Norrish (46) and later Style and Summers (47) reported observed activation energies of 16.0 and 12.0 kcal/mole respectively for the photolysis of formaldehyde. Style and Summers assigned this energy to

$$HCO + M \rightarrow H + CO + M. \quad [8]$$

These values were in sharp contrast to that obtained by Gorin for the same process.

Calvert and Steacie (48) studied the high temperature photolysis of formaldehyde at 3130$\AA$. The high values obtained for quantum yields and the sharp lowering of the hydrogen quantum yield by the addition of propene left little doubt that a chain mechanism was operative and that hydrogen atoms were involved.

An accelerating effect on the rate of hydrogen formation by
the addition of "inert gases" was also observed. This, plus the observed first order intensity dependence of the hydrogen formation rate lead the authors to postulate the following mechanism:

\[
\begin{align*}
\text{CH}_2\text{O} + h\nu &\rightarrow H + \text{HCO} \quad [\text{I}] \\
\text{H} + \text{H}_2\text{CO} &\rightarrow \text{H}_2 + \text{HCO} \quad [\text{II}] \\
\text{HCO} &\rightarrow \text{H} + \text{CO} \quad [\text{VII}] \\
\text{HCO} + \text{Wall} &\rightarrow \text{products} \quad [\text{IX}]
\end{align*}
\]

On the assumption that the chain terminating step was of low activation energy, the observed activation energy was assigned to the reaction

\[
\text{HCO} \rightarrow \text{H} + \text{CO}. \quad [\text{VII}]
\]

The authors also investigated the activation energy for reaction \([\text{II}]\) by indirect methods. Based on relative rate of the competing reaction

\[
\text{H}^* + \text{C}_3\text{H}_6 \rightarrow \text{C}_3\text{H}_7^* \quad [\text{X}]
\]

they concluded that \(E_5\) was less than or equal to 5 kcal/mole.

Somewhat later Schoen (49) performed a series of experiments involving the photolysis of formaldehyde in the presence of deuterium. Since HD was formed in these experiments at 300°C using 3650Å radiation, he concluded that \(D^*(\text{H-COH})\) must be less than or equal to 78 kcal/mole. Combining this value with \(\Delta H^0_{f298}(\text{CH}_2) = 105\pm1.5\) kcal/mole (50) leads to \(D^*(\text{H-CO}) \geq 27\) kcal/mole. This observation was in agreement with Gorin's work.
Klein and Schoen (51) photolyzed mixtures of formaldehyde and formaldehyde-d₂ at 300°C using 3650Å radiation. Again HD was formed, indicating the presence of free hydrogen atoms.

Dorman and Buchanan (52) attempted to calculate the activation energy for formyl decomposition using an improved Bawn method of constructing potential energy surfaces. They obtained a value for \( E_\theta \) of 26 kcal/mole. However, the error limits for such an estimate are very large. Also, the method is very sensitive to the choice of values for the relative positioning of the vibrational and collisional energy surfaces. Experimentally this value corresponds to \( \Delta H_r \) for HCO \( \rightarrow \) H + CO. Since the authors derived this value from a thermal cycle involving the C-C bond dissociation energy of acetaldehyde which is by no means established, little weight can be given to the results.

In a second paper (53) the same authors criticized the mechanism of Calvert and Steacie as being too simple. They proposed a ten step mechanism which included

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

as a chain carrying step. By using several simplifying assumptions, they derived an expression for the overall observed activation energy. They contended that \( E_{\text{obs}} = E_\theta - E_\text{II} \), and that \( E_\text{II} \) was about 10 kcal/mole. Thus \( E_\theta \approx 23 \) kcal/mole.

To support their contention, the photolysis of formaldehyde at high temperatures was repeated using wavelengths greater or equal to 3100Å. A plot of \( 10^\text{log}_{10} \) (rate of formaldehyde decomposition)
vs. $1/T$ gave a non-linear curve over the temperature range 198-352°C. This was claimed to be evidence for a changing mechanism; and, hence the assignment of $E_{\text{obs}}$ to a specific step was unjustified. However, the authors made no mention of a dark reaction which is known to occur at temperatures greater than 150°C. Also, they reported some condensation of the monomer during the experiments. Thus their interpretation of the observed curvature is open to question.

Calvert reviewed the various data available on the decomposition of the formyl radical (54). He revised his mechanism to take account of the primary molecular rearrangement.

$$H_2CO + h\nu \rightarrow H_2 + CO,$$

and the probable bimolecular nature of the decomposition of formyl. From the derived expression for the rate of hydrogen formation; using the usual Arrhenius plot, the overall activation energy was found to be 14.6 kcal/mole. If $E_a$ for the chain terminating step was small, then $E_a (HCO + M \rightarrow H + CO + M)$ was about 14.6 kcal/mole.

Calvert also analyzed the data from the photolysis of several aliphatic aldehydes. Using the generally accepted mechanism, he derived a rate function for the formation of hydrogen which allowed an estimation of $E_0$. The value obtained was 15.3 kcal/mole. The work of Klein, Klein and Schoen, and Dorman and Buchanan was also reviewed. It was concluded that no clear choice between the "high" and "low" values for $E_0$ was possible. However, Calvert felt that the most reliable evidence favored the "low" value.

Klein and Schoen (55) disputed this viewpoint. They pointed
out that the evidence for the "low" value was based entirely on kinetic data; and, more specifically on the assignment of an observed activation energy to a particular step. They contended that the wide variety of techniques by which the "high" value was obtained (56) should give added proof of its validity.

Kutschke and Venugopalan (57) repeated the work of Klein and Schoen using chemical filters to assure monochromatic radiation. They found, as before, that HD was formed at both 3130Å and 3650Å. Thus the experimental fact seemed well established. However, the interpretation was by no means established.

To the present, the question of the correct value of $D$ (H-COH) and $D$ (H-CO) has not been resolved.

One other point of interest should be considered in the energetics of formaldehyde decomposition. Two species have been suggested as chain carriers (58,59), hydrogen atoms and formyl radicals.

Several estimates for the activation energy for

$$H + H_2 CO \rightarrow H_2 + HCO$$

[5]

can be found. Calvert and Steacie set the upper limit for $E_5$ at 5 kcal/mole. Blake and Kutschke (60) decomposed di-tert. butyl peroxide for a source of methyl radicals and obtained $E_a = 6.6$ kcal/mole for the reaction

$$CH_3 + H_2 CO \rightarrow CH_4 + HCO.$$ [12]

Klein, Scheer, and Schoen (61) pyrolyzed mixtures of CH$_2$O and CD$_2$O and followed the production of the various isotopes. From the data
they derived \( k_5 \) as \( 7 \times 10^4 \, \text{mm}^{-1} \, \text{sec}^{-1} \). By using a \( Z \) value calculated from collision theory, they derived \( E_5 \leq 5.7 \, \text{kcal/mole} \). Later, Klein, et al. (62) photolyzed mixtures of \( \text{CD}_2\text{O} \) and \( \text{H}_2 \). From their results at temperatures of 250-350\(^\circ\text{C} \), they concluded that

\[
\text{DCO} + \text{D}_2\text{CO} \rightarrow \text{D}_2 + \text{CO} + \text{DCO} \quad [13]
\]

was unimportant. From the known activation energy of

\[
\text{H} + \text{H}_2 \text{ (para)} \rightarrow \text{H}_2 \text{ (ortho)} + \text{H} \quad [14]
\]

and a suitable isotope correction, they were able to calculate that \( E_5 \) was about \( 3.0 \pm 0.2 \, \text{kcal/mole} \) for \( \text{D} \) atoms reacting with \( \text{D}_2\text{CO} \). This would suggest that \( E_a \) for the corresponding protonated species is about 2.1-2.5 kcal/mole.

Thus it appears that hydrogen atoms are the chain carriers and that \( 2.2 < E_5 < 5.5 \, \text{kcal/mole} \).

**Primary processes**

Information concerning the relative importance of the two primary processes, \( \phi_1 \) and \( \phi_\text{II} \) at various wave-lengths is scarce and most of doubtful validity. Gorin's work suggested a preference for the molecular rearrangement (\( \phi_\text{II} \)) at longer wave-lengths. Thus, he found only small amounts of hydrogen at 2537\(\AA\) and 3130\(\AA\) in his iodine inhibition studies; whereas the \( \text{HI}/\text{H}_2 \) ratio at 3660\(\AA\) was about 2.5. As later work showed that, contrary to his assumption, formyl did react with iodine to produce HI and CO; the corrected value for \( \phi_\text{II}/\phi_1 \) is 0.8. However, as previously stated there are several reasons to doubt the interpretation of these findings.
Klein and Schoen (63) used the deviation of the equilibrium value found for \((\text{HD})^2/(\text{H}_2)(\text{D}_2)\) in their formaldehyde-formaldehyde-\(\text{D}_2\) experiments as an indication of the relative importance of the two processes. At 300°C they observed isotopic equilibrium in the products. However, at 140°C there was a distinct deviation from this value. From the deviation, the authors derived an expression for the relative probabilities of the two processes. Their values are \(P_{\text{II}}/P_{\text{I}} = 0.2\) at 3650° with an initial total pressure of 221.0 mm.

* The results are expressed in terms of the relative probability of the two processes.

Hg, and \(p_{\text{II}}/p_{\text{I}} = 2.0\) at 3130° with an initial total pressure of 219 mm. Hg, and \(p_{\text{II}}/p_{\text{I}} = 2.0\) at 3130° with an initial total pressure of 26.8 mm. Hg. The initial \(\text{H}_2\text{CO}/\text{D}_2\text{CO}\) ratio was unity. They assumed that the sum of \(\phi_{\text{I}}\) and \(\phi_{\text{II}}\) was unity. Based on the low pressure experiment at 3130°, they conclude that \(\phi_{\text{II}}\) is favored at 3130°. The reason for choosing that experiment in preference to the other was explained as being due to the shorter chain length at lower pressure. It should be noted that at 140°C any apparent deviation from the "equilibrium value" will be very sensitive to differences in the activation energies for abstraction by H and D atoms from the aldehydes.

Lossing and Harrison (64) decomposed \(\text{CH}_2\text{O}, \text{CD}_2\text{O}\) and mixtures of the two by mercury photosensitization, at low pressures in a flow system. Mass spectrometry was used as the means of analysis. By using a fixed amount of \(\text{CH}_2\text{O}\) and increasing the mole fraction of
the authors assumed that a point would be reached where any
H₂ produced would have to come from intramolecular rearrangement.
They found values of 0.4 and 0.6 for \( \phi_{II} \) and \( \phi_I \) respectively.
Thus it appeared that the intramolecular process was important
even at 2537 Å. The same technique was used on acetaldehyde with
results which indicated the intramolecular process was not im-
portant under their conditions. Apparently this is not the case in
the direct photolysis of acetaldehyde. Hence, the values found by
Lossing and Harrison must be treated only as an indication. This
work will be discussed in more detail in the Discussion.

Recently, Calvert and McQuigg (65) applied the technique of
flash photolysis to mixtures of formaldehyde and formaldehyde-d₂.
By use of various glass filters, they were able to show that the
amount and also the mode of decomposition was a function of incident
wave-length. Assuming that only radical-radical reactions were im-
portant, they were able to fit the data to a reaction scheme which
indicated a predominance of the intramolecular process, \( \phi_{II} \), at
longer wave-lengths. However, there seems to be some question about
the validity of the assumed mechanism.

In view of the conflicting data as to the relative importance
of \( \phi_I \) and \( \phi_{II} \), it is of interest to consider similar processes* for

* For this discussion \( \phi_I \) implies \( \text{RCHO} + \text{hv} \rightarrow \text{R} + \text{CHO} \), and \( \phi_{II} \)
denotes \( \text{RCHO} + \text{hv} \rightarrow \text{RH} + \text{CO} \).

other aldehydes. Blacet and coworkers (66-69) have used iodine
inhibition to study the relative importance of the various primary
processes as a function of wave-length for acetaldehyde, propionaldehyde, and the two butyraldehydes. Also, more recently Paramenter and Noyes (70) completed a reinvestigation of acetaldehyde using a somewhat different technique. All these results are summarized in Table 3.

The data indicate the increasing importance of the concerted process \((\phi_{12})\) at shorter wave-lengths. Also, it is apparent from a comparison of Blacet's and Noyes' value for \(\phi_{12}\) for acetaldehyde in the 2654-2537Å region that the effect of I\(_2\) and NO on the course of photolysis is not completely understood. However, the values do illustrate the trend.

Pyrolysis

To gain further insight into the various modes of decomposition of formaldehyde and the energetics involved, the literature on the pyrolysis of CH\(_2\)O was searched. Unfortunately, there is no general agreement here either.

Fletcher (71) pyrolyzed formaldehyde in a quartz vessel (packed and unpacked) at temperatures in the 510-607\(^\circ\) range. At fairly low CH\(_2\)O pressures the products were almost exclusively hydrogen and carbon monoxide in a ratio of CO/H\(_2\) = 1.07. However, an analysis of the product gases at high initial formaldehyde pressures showed CO/H\(_2\) = 1.37. The reaction, as measured by the pressure rise, had two distinct stages. The second and slower stage was not observed at CH\(_2\)O pressures of less than 40 mm. Hg. At high initial pressures of CH\(_2\)O, the first stage produced more CO than H\(_2\), while
<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Process</th>
<th>( \lambda(\AA) )</th>
</tr>
</thead>
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<td></td>
<td></td>
<td>3130</td>
</tr>
<tr>
<td>CH(_3)CHO</td>
<td>I</td>
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</tr>
<tr>
<td></td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>II</td>
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</tr>
<tr>
<td>n-C(_3)H(_7)CHO</td>
<td>I</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.017</td>
</tr>
<tr>
<td>iso-C(_3)H(_7)CHO</td>
<td>I</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.03</td>
</tr>
</tbody>
</table>

* The majority of the data taken from a summary in reference 68

* Data taken from reference 70 (Parmenter and Noyes).
the reverse was true of the second stage. Fletcher argued that these facts were consistent with the following:

\[
\begin{align*}
2 \text{H}_2\text{CO} & \xrightarrow{\text{fast}} \text{CH}_3\text{OH} + \text{CO} \\
\text{CH}_3\text{OH} & \xrightarrow{\text{slow}} \text{CO} + 2 \text{H}_2 \\
2 \text{CH}_2\text{O} & \rightarrow \text{H}_2 + \text{CO} + \text{H}_2\text{CO}.
\end{align*}
\]

Patat and Sachase (72) observed the pyrolysis of formaldehyde at 823°C in the presence of 600 mm Hg of para hydrogen. Since no increase in the ortho content of the hydrogen was observed, the authors concluded that the pyrolysis of the aldehyde proceeded by a non-free radical mechanism.

Steacie and Alexander (73) pyrolyzed mixtures of acetone-d6 and dimethyl ether at 590°C. They assumed the mechanism

\[
\begin{align*}
\text{CD}_3\text{COCD}_3 & \rightarrow \text{CH}_4 + \text{CD}_2\text{CO} \rightarrow \text{CO} + 1/2\text{C}_2\text{D}_4 \\
\text{CH}_3\text{OCD}_3 & \rightarrow \text{CH}_4 + \text{CH}_2\text{O} \rightarrow \text{H}_2 + \text{CO}.
\end{align*}
\]

They argued that HD should appear as a product if formaldehyde decomposition involved free radicals. However, within experimental error, (2%), they found that all the hydrogen produced was "light."

Longfield and Walters (74) investigated the thermal decomposition of CH2O at 400-475°C with and without ethylene oxide as a sensitiser. Results from the experiments with pure aldehyde showed the important reaction was

\[
2 \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{OH} + \text{CO}. \quad \text{E}_{15} \approx 31.0 \text{ kcal/mole} \quad (15)
\]
The sensitized reaction appeared to follow the same chain mechanism as the direct photolysis. A pronounced enhancement of the rate of decomposition of the aldehyde with the addition of inert gases was also noted.

Klein, Scheer, and Schoen (75) examined the pyrolysis of formaldehyde at 547°C with an initial pressure of 140 mm Hg. Carbon monoxide and hydrogen were formed in accord with second order kinetics. Methanol was also formed in a bimolecular process, but at a slower rate than the chain decomposition of the aldehyde. Using mixtures of CH₂O and CD₂O, they were able to establish that a chain mechanism was operative. But, the low observed activation energy lead them to conclude that the initiation step was probably heterolytic. The surface to volume ratio had little effect, but the rate of decomposition was very sensitive to the previous history of the vessel.

Anisonyan, et al. (76) studied the oxidation and pyrolysis of CH₂O under industrial conditions. The pyrolysis experiments were done at 600-900°C in a flow system with methane as a diluent. The surface to volume ratio and previous history of the vessel had no effect. Surprisingly, the addition of up to 0.8% NO had no effect on the rate.

While it may be inferred from some of the data that the high temperature pyrolysis of formaldehyde proceeds by an intramolecular mechanism, this is by no means established. In view of the variety of results obtained by different workers, it is not possible from
the pyrolysis data to ascertain whether the intra- or intermolecular mode of decomposition is energetically favored.

The foregoing discussion emphasizes the number of unanswered questions concerning the mechanism and energetics of formaldehyde decomposition. This work was undertaken in the hope of providing at least partial answers to the questions: 1) what is the relative importance of $\phi_1$ and $\phi_2$ at various wave-lengths? 2) From which excited state does each of these processes arise? 3) Can the spectroscopic and kinetic data concerning the energetics of decomposition be reconciled?
EXPERIMENTAL PROCEDURE

Apparatus

Optical system

The light source was a Hanovia S-500, Type A mercury arc mounted axially in a brass cylinder which was cooled by circulating water through copper tubing soldered to the outside of the cylinder. A stable 250 volt A.C. potential was provided for the arc circuit by passing the 115 volt house current through a Sorensen Model 1000-S voltage regulator to a Hanovia Model 20651 transformer. The output of the arc was controlled by adjusting a 50 ohm, 500 watt Ohmite variable resistor connected in series with the arc.

Light from the arc (A) (see Figure 3) was collimated by a quartz lens (L1), passed through a stop (S1), and then passed through a filter system (FS and CF) to isolate the desired wavelength. The filter systems used were those recommended by Calvert and Pitts (1). All filter combinations were satisfactory except the one used to isolate the 2654Å region. This particular filter was extremely unstable.*

* The potassium iodide solution was very unstable to ultraviolet radiation. Even though this component was situated last in the filter combination, considerable color change was observed during a standard photolysis (colorless changing to red-brown). Intensity drops of 10% or greater were not uncommon. Fortunately the purity of the transmitted light did not change appreciably with use.
Figure 3. — The photolysis system.
The emergent beam was rendered nearly parallel by a long focus quartz lens \( L_2 \). The cross section of the light beam was then reduced to about the size of the cell window by a stop \( S_2 \). Having passed through a quartz window \( W_1 \), the photolysis cell, and a second quartz window \( W_2 \); the transmitted light was focused by quartz lens \( L_3 \) on the cathode of an R.C.A. 935 phototube \( P \).

The phototube was operated at a 45 volt potential which was provided by batteries. The tube was housed in a compartment which was insulated from the box by a quartz window \( W_4 \) and a shutter \( Sh \). The tube was well shielded \( Sd \) and shielded cable was used throughout the photometer circuit. No spurious signals or "dark current" occurred with this arrangement. The output from the phototube was passed through a decade resistance box connected in series with the phototube. The potential drop across the resistor was measured on a 0-16 mv. Honeywell recorder. Thus a permanent record of both incident and transmitted light intensities was obtained. This type of photometer system was most helpful in detecting filter aging and other intensity changes.

**Photolysis system**

The photolysis system consisted of a quartz photolysis cell and the necessary devices for introducing and measuring samples. Two cells were used in this work. At 3130\( \lambda \) a 5-cm cell with 3-cm (diameter) windows was used. A 25-cm cell with 3-cm windows was used at all other wave-lengths.

The pressure in the photolysis system was determined with the aid of a spoon gage used as a null device. When a sample was
admitted to the cell, the deflection of the spoon gage was observed through a Gaertner long focus microscope. By admitting air to one side of the manometer (M) (see Figure 3) through a three-way stopcock (T2), the pointer of the spoon gage was returned to its original position. The resulting difference in the two column heights of the manometer equaled the pressure in the cell.

When more than one gas was used for an experiment, complete mixing was necessary to avoid any local concentration effects. This was accomplished by means of an all-glass, inline circulating pump (Pu). The pump, solenoid and timing device have been described in detail elsewhere (2).

Gases were admitted or removed from the photolysis system through one of two Granville-Phillips #64181 metal valves (V1 and V2). These valves were very satisfactory for this type of application.

The formaldehyde monomer and propylene were both stored at liquid nitrogen temperature on the vacuum line. A sym-tetrachloroethane slush (m.p. -43.8°C) was used to warm the formaldehyde monomer to provide adequate sample pressure. Solid carbon dioxide in isopropyl alcohol was used as a warming bath for the propylene. Other gases were added through a tap adjacent to the photolysis system. This tap was connected to the outside of valve V1, and was also used to remove the residual material at the end of an experiment.
**Temperature control system**

To avoid polymerization of the formaldehyde, the entire photolysis system was enclosed in an air thermostat. All tubing outside this thermostat which had contact with the aldehyde was wrapped with #20 nichrome wire (1.65 ohms per foot). By trial and error a current was found that maintained this tubing at about 100°C.

The air thermostat, or box, was of sandwich wall construction. The outer layer was Masonite; the inner wall was Transite. A one inch thick layer of commercial fiberglass insulation separated the two walls. While this material provided good thermal insulation, it possessed one particularly annoying characteristic. The fibers were held together by a binder which bled out badly even at moderate temperatures. Because of this, it was necessary to clean lens L₂ immediately before each experiment. Fortunately, no other part of the optical train was affected.

The box was heated by a 1000 watt fin heater which operated continuously. The fine control was provided by a 500 watt cone heater which was actuated by a Fenwal thermostat. The air inside the box was rapidly circulated by a Dayton blower. With this arrangement less than 5°C temperature gradient was observed between the coolest and warmest areas. A thermocouple was placed in the coolest portion of the box to provide a minimum reading. This was a necessary safeguard to avoid polymerization of the aldehyde.

The 5 cm cell used in the early part of the work was enclosed in a high mass oven. It was similar to the type used previously in this laboratory and the details of its construction are described.
in full elsewhere (3). Thermocouples were placed at the lower front and upper rear of the cell. The average temperature was reported. With this oven the temperature gradient along the cell was never greater than 0.5°C.

In later experiments it became necessary to replace the 5-cm cell with one 25 cm in length. Unfortunately, the oven was too short for the longer cell and had to be removed. However, since only one temperature was used in these later experiments, this resulted in only a minor inconvenience. Good temperature control was still possible at the relatively low temperature used. Without the oven the temperature gradient along the cell was less than 1.1°C. During the course of a photolysis, the average temperature never varied by more than 0.2°C.

As previously mentioned, the temperature in the cell and box were obtained by means of thermocouples (copper-constantan). The e.m.f. was read on a Rubicon potentiometer. The millivolt readings were converted to degrees Centigrade by means of a chart published by Leeds and Northrup Company. An ice-water slush (0°C) was used for the reference junction.

High vacuum system

The high vacuum system consisted of a two stage mercury diffusion pump, mechanical forepump, liquid nitrogen cooled trap, and the usual taps and tubing. Pressures of 10^{-6} mm Hg. as indicated by a McLeod gage, were readily obtained. Taps which were not heated were greased with Apiezon N; all other stopcocks were greased with Dow-Corning silicone grease. Four Delmar mercury float valves were
used on the product removal portion of the system. These were not particularly satisfactory, but caused only minor inconvenience.

The non-condensable (liquid nitrogen temperature) photolysis products were pumped into sample thimbles by means of a Toepler pump. The condensable products were removed through a tap connected to the photolysis system. A Ward-LeRoy still was also included in the system, but was not used in this work.

Analytical system

The analytical system consisted of a high vacuum sample introduction line (see Figure 4), an Aerograph A-90-P-2 gas chromatograph, and a Bristol strip chart recorder.

The sample introduction system was evacuated by a single stage, oil diffusion pump backed by a mechanical forepump. The sample loop was demountable and could be evacuated by means of the three-way stopcocks, \( T_4 \) and \( T_5 \), without disturbing the carrier gas flow. In practice the sample loop was first evacuated; the stopcocks \( T_6 \) and \( T_7 \) were closed; and the loop was removed from the line.

The gas samples were stored over mercury in thimbles. To transfer the sample from the thimble to the sample loop, the capillary tip of the loop was inserted into the thimble and tap \( T_8 \) opened. After the sample was sucked into the loop, it was again placed in the vacuum train using joints \( J_1 \) and \( J_2 \). The loop was then pressurized with argon and the sample injected. A time pattern was followed in order to avoid errors due to different injection patterns.

The Aerograph instrument was used essentially "as received." However, it was necessary to remove the injector heater and improvise
Figure 4--The analytical system
a Swagelok fitting in order to attach the unit to the vacuum sample introduction system.

Many different sets of conditions were tried, but those shown in Table 4 proved most satisfactory. Using these conditions a mixture of hydrogen, oxygen, nitrogen, and carbon monoxide was readily resolved with at least 30 seconds between the closest component.

**TABLE 4**

**V.P.C. Operating Conditions**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Optimum condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>carrier gas</td>
<td>argon</td>
</tr>
<tr>
<td>flow rate</td>
<td>25 cc/min</td>
</tr>
<tr>
<td>column</td>
<td>5-A molecular sieve 30/60 mesh, 8 ft long</td>
</tr>
<tr>
<td>column temperature</td>
<td>105°C</td>
</tr>
<tr>
<td>detector temperature</td>
<td>105°C</td>
</tr>
<tr>
<td>filament current</td>
<td>150 milliamperes</td>
</tr>
</tbody>
</table>

Since no attempt was made to dry the carrier gas, it was necessary to bake out the column overnight at 300°C about every two months to retain maximum resolution.

The Bristol strip chart recorder had a signal range of 1.0 mv. This was quite satisfactory for this application.
Preparation of Reagents

Formaldehyde

Monomeric formaldehyde was obtained from the polymer by the method of Spence and Wild (4) as modified by McQuigg (5). The normal monomer (CH₂O) was generated from Eastman paraformaldehyde. Formaldehyde-d₂ was obtained from Merck & Sharpe, and Dohome, Ltd. with a stated purity of 99.4% deuterium.

Once the monomer was generated, it was stored at liquid nitrogen temperature. With this procedure the monomer can be stored almost indefinitely.

Biacetyl (2,3 butane-dione)

Eastman biacetyl was first outgassed at room temperature. After bulb to bulb distillation, the middle third was distilled from -78 to -196°C into a sample bulb containing a small amount of Drierite. The ketone was stored in the dark at -20°C until used.

Propylene, isobutylene (2-methyl propene), and neopentane (2,2 dimethyl-propane)

These gases were Phillips Research Grade and used without further purification. Mass spectral analyses showed the gases to be essentially pure.

Carbon monoxide

Carbon monoxide was supplied by Air Reduction Company. The gas contained nitrogen as the major contaminant in the amount of 510 ppm.
Hydrogen and nitrogen

Hydrogen and nitrogen were obtained from Liquid Carbonic cylinders and checked for impurities by mass spectrometry. Both gases contained less than 1% total impurities.

Deuterium

Deuterium was kindly furnished by Dr. Robert Lawrence. Mass spectral analysis showed less than 1% combined H$_2$ and HD impurity.

Acetone

Baker and Adamson Reagent Grade acetone was purified by preparative vapor chromatography.

Azomethane

Azomethane was supplied by Dr. E. D. Thomas of this laboratory. Mass spectral analysis showed it was of high purity.

Experimental Procedures

Actinometry

Chemical actinometry was used throughout this work. Acetone was used for wave-lengths 3130, 2654, and 2537Å. At 3340Å azomethane was used. The compounds have a quantum yield of unity for CO and N$_2$ respectively at these wave-lengths and our conditions. The experimental conditions are summarized in Table 5.

Since the chemical filters employed for isolating the various mercury lines showed a marked tendency to age, it was necessary to follow the day to day change in the incident intensity, I$_0$. Using chemical actinometry in conjunction with the photometer system
TABLE 5
Experimental Conditions for Actinometry

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cell (cm)</th>
<th>Pressure (mm Hg)</th>
<th>Temperature (°C)</th>
<th>λ(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>5</td>
<td>90-105</td>
<td>130</td>
<td>3130</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>32</td>
<td>125</td>
<td>3130</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>22-24</td>
<td>110</td>
<td>2654</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>22-24</td>
<td>110</td>
<td>2537</td>
</tr>
<tr>
<td>Azomethane</td>
<td>25</td>
<td>22-24</td>
<td>110</td>
<td>3340</td>
</tr>
</tbody>
</table>

already described, an accurate, permanent record of the changes in \( I_o \) was obtained. This system also allowed an accurate estimate of \( I_o \) on a daily basis. An example may better illustrate the system’s utility.

On 15 July 1965 actinometry at 3340 Å showed \( I_o \) was approximately \( 1.19 \times 10^{12} \) q/cc/sec. The photometer reading for the empty cell was 73.25 divisions. Thus the photometer constant for that wave-length was

\[
\frac{1.19 \times 10^{12} \text{ q/cc/sec}}{73.25 \text{ div.}} = 1.626 \times 10^{10} \text{ q/cc/sec/div.}
\]

One week later the photometer reading was 65.2 divisions. Thus the calculated value of \( I_o \) was \( 65.2 \times 1.626 \times 10^{10} \approx 1.060 \times 10^{12} \) q/cc/sec. Actinometry performed the same day indicated \( I_o = 1.047 \times 10^{12} \) q/cc/sec. Thus from the photometer reading taken before each experiment, a good estimate of \( I_o \) was obtained for that particular day.
As an added check, the $I_o$ values for 2537Å and 3340Å were calculated from photometer readings using actinometry performed at 2654Å. The photometer readings were corrected for differences in spectral response in accordance with the manufacturer's general specifications. The calculated results for 2537Å agreed within 4% and those at 3340Å within 7% of the values obtained by chemical actinometry. Since the phototube itself was not calibrated, these results were as good as could have been anticipated.

All actinometry experiments were done in duplicate when starting work at a new wave-length. If the two values did not agree within 3%, a second set was performed.

**Photolysis of formaldehyde**

The following is a description of the procedure used for a typical experiment. While certain procedures were modified from experiment to experiment, the general form of the procedure did not change appreciably for the bulk of the work.

The arc was first struck and brought to equilibrium operating conditions. As soon as the arc appeared stable, a photometer reading was taken; the front lens $L_2$ having been cleaned. Also during this warm up period a Dewar of liquid nitrogen was used to cool a trap immediately preceding the photolysis system. This procedure was used to remove the bulk of the mercury vapor present in the photolysis system.

The arc was allowed to stabilize for an additional twenty minutes and then a second photometer reading was made. If the two values did not disagree by more than 2% it was assumed that
arc had stabilized sufficiently to proceed. The second photometer reading was used to calculate $I_0$ for that experiment. If, as sometimes happened, the two readings did disagree, an additional twenty minutes was allowed. This sufficed in all cases.

After determining $I_0$, the pressure in the system was checked with the McLeod gage. If the pressure was less than $5 \times 10^{-6}$ mm Hg the experiment was continued. No problems were experienced in this respect. Valve $V_1$ was closed, sealing the photolysis system from the pumps. The two warming baths, sym-tetrachloroethane and solid $CO_2$-isopropyl alcohol, were positioned. The null position of the spoon gage was centered in the cross hairs of the microscope, and valve $V_2$ was opened to admit the aldehyde. Since the spoon gage was quite fragile, it was necessary usually, to pressurize the system in steps. About 50 mm of gas were added at a time; then air was bled into the opposite side of the gage to compensate. Using the procedure previously described, the pressure of formaldehyde was brought to the desired value. Valve $V_2$ was then closed and the warming bath on the monomer storage bulb replaced with liquid nitrogen.

The tap to the propylene storage bulb was then opened, putting a pressure of about 400 mm on the out side of valve $V_1$. This valve was then cracked and the photolysis system rapidly pressurized with propylene. When the required pressure of propene was achieved, valve $V_1$ was closed. The warming bath was replaced by liquid nitrogen, and the tap was closed. The two gases were then mixed by means of the in-line pump for at least 20 minutes. After mixing the spoon
was checked for possible pressure drop. In only two cases did this occur, and both these experiments were aborted. The temperature of the box and cell were then determined, and the photolysis was begun. Transmitted intensity, $I_t$, was measured every half hour and temperatures every hour. Also, at frequent intervals, the spoon gage was observed for pressure changes.

At the end of the experiment, a Dewar of liquid nitrogen was used to condense the gases in trap T (see Figure 3). The majority of the material was condensed within five minutes, but a period of at least 30 minutes was allowed before continuing. During this period a second $I_o$ reading was made in order to estimate the drop in intensity during the experiment. If the change was greater than 4% a correction was applied to the calculated value of $I_o$. It was assumed that the decrease in intensity was linear with time and the correction was made as follows:

$$\delta I_o = \text{observed change in photometer readings}$$
$$\text{in divisions}. $$

$$I_o(\text{eff}) = \text{the effective incident intensity (corrected).}$$

$$k = \text{photometer constant (q/cc/sec/div).}$$

$$I_o = \text{calculated incident intensity based on the initial photometer reading.}$$

Thus we have

$$I_o(\text{eff}) = I_o - \frac{\delta I_o k}{2}.$$

Since in almost every case the decrease in intensity was due to filter aging, the assumption of a linear time-decay relation is a
good first approximation. The correction was significant only for those experiments at 2654A; where filter aging was very pronounced.

After the condensing period, the pressure in the external system was checked. The product removal portion of the line was isolated from the pumps and valve $V_1$ opened. The non-condensable fraction was pumped into a sample thimble by means of a Toepler pump. When no more gas could be collected, the liquid nitrogen was removed from trap T and the condensable materials allowed to distil into a sample bulb cooled to -196°C. After a condensation time of 20 minutes, Toepler pumping was resumed. In every case, less than 1 µl of additional gas was obtained. The sample bulb containing the condensables was then removed and the contents vented into the hood. The experiments in which the condensable portion was analyzed will be described in detail elsewhere.

The photolysis and product removal systems were then opened to the pumps. Trap T was flamed to remove any residual formaldehyde.

For the experiments with added isobutylene or neopentane, the procedure was essentially the same. However, when biacetyl was the added gas, it was introduced first since only a few millimeters pressure were used.

Analysis

For most experiments only the non-condensable portion of the products was analyzed. A variety of procedures were used depending on the information desired. These procedures were used alone or in combination. They are described in the following.
The sample was first transferred to a Blacet-Leighton gas buret and the volume of the sample determined at ambient conditions. This volume was then corrected to S.T.P.

Next a standard mixture of H₂ (or D₂) and CO was measured and analyzed on the gas chromatograph. The sensitivity (peak area/μl*)‡

‡ The symbol μl* denotes micro-liters of gas corrected to S.T.P.

for each gas was determined and compared with that found for previous standards. If the value obtained fell within ±3% of the average value, it was assumed that the instrument was operating properly.

A portion of the experimental sample was then measured out and transferred to the sample loop of the chromatograph's injection system as previously described. The peak areas were integrated by use of the formula, Peak area = peak height x width at half height. The width at half height was measured by means of a Gaertner traveling microscope. Plots of sample volumes vs peak area were linear; and, hence the assumption of constant sensitivity was justified in the sample range used (2-100 μl*).

A second standard having the approximate composition of the experimental sample was then analyzed and the sensitivities obtained were used to refine the analysis of the experimental sample. An additional check on the performance of the instrument was provided by comparing the volume of the experimental sample measured on the gas buret with that found from the peak areas of the chromatogram. Usually the two volumes agreed within 2%.
Considerable effort was expended in an attempt to use the mass spectrometer for quantitative determination of $\text{H}_2$ (or $\text{D}_2$) and CO. However, due to the very different rates of diffusion of the two gases, the observed sensitivity of the instrument for each gas varied not only with time, but also with the composition of the mixture. Since the composition of the samples changed with each experiment, it was virtually impossible to carry out a meaningful analysis.

The mass spectrometer (Consolidated Engineering Company Model 21-620) was frequently used for qualitative checks, however. The sample holders were of the type described by Smith (6). Checks were made for $\text{CH}_4$ and $\text{C}_3\text{H}_6$ for reasons given in the Discussion.

For several experiments the $\text{HD}/\text{D}_2$ or $\text{HD}/\text{H}_2$ ratio was desired. These were obtained on a C.E.C. Model 21-620 mass spectrometer with isotopic ratio attachment. Assistance in these analyses by Dr. Robert Lawrence is gratefully acknowledged.

In an attempt to ascertain the presence of methyl alcohol in the condensable products of the photolyses, a Perkin-Elmer Model 21 long path infrared spectrometer was used. The sample was bled in through an auxiliary vacuum line and the pressure in the 55 liter sample tank was brought to 730 mm Hg with dry nitrogen. The spectral region scanned was $10,000$ to $650 \text{ cm}^{-1}$ at a speed of $20 \text{ min/micron}$. Sodium chloride optics were used. Dr. E. D. Thomas assisted with several of the analyses.
EXPERIMENTAL DATA

The experimental conditions used for this work are shown in Tables 6-8. Experiments 11 through 57-D were performed using the 5-cm cell. The remainder of the experiments were done with the 25-cm cell. The results of the "standard" photolyses are tabulated in Tables 9 and 10. The product quantities are reported in microliters corrected to S.T.P. (symbolized by μl*). To convert microliters to micro-moles, multiply by 4.464 x 10^-2. The results of the special experiments will be presented in the appropriate place in the Discussion.

The extinction coefficients observed for formaldehyde and formaldehyde-d2 at various wave-lengths are compiled in Table 11. For the most part, the data show little scatter; the exception is for 3340 Å. This particular value was redetermined on three separate occasions using at least five points each. The average value found was about the same for each determination, but the scatter of the individual points was always very pronounced. No reason is apparent for this phenomenon.

The results of actinometry are summarized in Table 12. At low external impedance (i.e., 1.7 kohms), the photometer response was not linear with intensity. Hence, no meaningful photometer constant could be derived. Therefore it was necessary to perform
TABLE 6
Experimental Conditions for the Photolyses of Formaldehyde

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Pressure (mm. Hg)</th>
<th>Avg. cell temperature (°C)</th>
<th>( I_a \times 10^{-11} ) q/cc/sec</th>
<th>( \lambda(\AA) )</th>
</tr>
</thead>
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<tr>
<td>CH₂O</td>
<td>C₂H₆</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>F-11</td>
<td>169.0</td>
<td>156.0</td>
<td>23.6₃</td>
<td>3130</td>
</tr>
<tr>
<td>F-15</td>
<td>161.0</td>
<td>127.8</td>
<td>22.8₈</td>
<td></td>
</tr>
<tr>
<td>F-16</td>
<td>159.0 112.5</td>
<td>128.2</td>
<td>21.7₀</td>
<td></td>
</tr>
<tr>
<td>F-17</td>
<td>160.5 47.5</td>
<td>128.5</td>
<td>21.9₆</td>
<td></td>
</tr>
<tr>
<td>F-18</td>
<td>159.0 205.5</td>
<td>128.7</td>
<td>21.7₀</td>
<td></td>
</tr>
<tr>
<td>F-19</td>
<td>159.5 308.5</td>
<td>128.7</td>
<td>21.5₈</td>
<td></td>
</tr>
<tr>
<td>F-20</td>
<td>160.0 290²</td>
<td>128.9</td>
<td>21.4₇</td>
<td></td>
</tr>
<tr>
<td>F-21</td>
<td>159.5 194.0 116²</td>
<td>128.9</td>
<td>21.5₀</td>
<td></td>
</tr>
<tr>
<td>F-23</td>
<td>199.0</td>
<td>128.9</td>
<td>25.4₃</td>
<td></td>
</tr>
<tr>
<td>F-24</td>
<td>78.0</td>
<td>129.1</td>
<td>10.1₄</td>
<td></td>
</tr>
<tr>
<td>F-25</td>
<td>78.0 23.5</td>
<td>129.2</td>
<td>9.3₅₉</td>
<td></td>
</tr>
<tr>
<td>F-26</td>
<td>78.0 51.0</td>
<td>129.3</td>
<td>9.2₇₁</td>
<td></td>
</tr>
<tr>
<td>F-27</td>
<td>78.0 102.0</td>
<td>129.2</td>
<td>9.4₁₅</td>
<td></td>
</tr>
<tr>
<td>F-30</td>
<td>78.0 155.5</td>
<td>129.6</td>
<td>9.1₄₉</td>
<td></td>
</tr>
<tr>
<td>F-31</td>
<td>78.0 102.0 53.0²</td>
<td>129.6</td>
<td>8.9₂₈</td>
<td></td>
</tr>
<tr>
<td>F-34</td>
<td>78.5 205.0²</td>
<td>129.5</td>
<td>7.5₈₂</td>
<td></td>
</tr>
<tr>
<td>F-35</td>
<td>79.0 102.5²</td>
<td>129.5</td>
<td>7.6₅₄</td>
<td></td>
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<td>F-36</td>
<td>80.0</td>
<td>91.0</td>
<td>8.4₉₉</td>
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<tr>
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<td>78.0</td>
<td>90.8</td>
<td>8.3₇₃</td>
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<tr>
<td>F-39</td>
<td>80.0 21.5</td>
<td>91.2</td>
<td>8.2₁₈</td>
<td></td>
</tr>
<tr>
<td>F-42</td>
<td>81.5 105.0 113.5²</td>
<td>91.0</td>
<td>7.9₅₇</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 6 (Cont'd.)

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Pressure (mm Hg) CH\textsubscript{2}OH C\textsubscript{3}H\textsubscript{6} other Avg. cell Temperature (^\circ\text{C})</th>
<th>(I_a \times 10^{-11}) q/cc/sec</th>
<th>(\lambda(\AA))</th>
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<tbody>
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<td>79.0</td>
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<td>21.20</td>
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<td>79.0</td>
<td>129.2</td>
<td>18.35</td>
</tr>
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<td>F-45</td>
<td>80.5 103.0</td>
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<td>F-49</td>
<td>82.5 106.0 408.0\textsuperscript{a}</td>
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<td>F-50</td>
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<td>Experiment number</td>
<td>Pressure (mm. Hg)</td>
<td>Avg. cell Temperature (°C)</td>
<td>$I_a \times 10^{-11}$ q/cc/sec</td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------</td>
<td>----------------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>F-75</td>
<td>109.0</td>
<td>108.5&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>F-97</td>
<td>63</td>
<td></td>
<td>109.3</td>
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<sup>a</sup> Neopentane ($C_5H_{12}$)

<sup>b</sup> Isobutylene ($C_4H_8$)
<table>
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<tr>
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<th>Pressure (mm. Hg)</th>
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<th>( I_a \times 10^{-11} ) q/cc/sec</th>
<th>( \lambda(A) )</th>
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<tr>
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\(^a\) Isobutylene
### TABLE 8

Experimental Conditions for Special Experiments

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<tr>
<th>Experiment number</th>
<th>Pressure (mm. Hg)</th>
<th>Avg. cell Temp. (°C)</th>
<th>$I_a \times 10^{-11}$ q/cc/sec</th>
<th>$\lambda$ (Å)</th>
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<tr>
<td>F-13</td>
<td>161.0 (CH$_2$O)</td>
<td>128.3</td>
<td>&quot;dark run&quot;</td>
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<tr>
<td>F-22</td>
<td>1.0 (D$_2$)</td>
<td>129.0</td>
<td>&quot;dark run&quot;</td>
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<tr>
<td>F-28</td>
<td>75.0 (CH$_2$O) 180.0 (C$_3$H$_6$)</td>
<td>129.6</td>
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<tr>
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<td>129.5</td>
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<td>129.2</td>
<td>19.12</td>
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<tr>
<td>F-82-D</td>
<td>67.0 (CD$_2$O) 34.5 (CH$_2$O) 94.0 (C$_3$H$_6$)</td>
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<td>a</td>
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### TABLE 8 (Cont'd.)

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*a See Discussion*
<table>
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<tr>
<th>Experiment number</th>
<th>Photolysis time $\times 10^{-3}$ (sec.)</th>
<th>Non-condensable products (µl$^*$)</th>
<th>$\phi_H^*$</th>
<th>$\phi_CO$</th>
<th>$\lambda$</th>
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<td>$\phi_{\text{H}_2}$</td>
<td>$\phi_{\text{CO}}$</td>
<td>$\lambda(\text{A})$</td>
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<td>( \phi_{D_2} )</td>
<td>( \phi_{CO} )</td>
<td>( \lambda(\AA) )</td>
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\[ a \frac{\sigma}{\bar{x}} \times 100 \] where $\sigma$ = standard deviation and $\bar{x}$ is the average value.
TABLE 12
Actinometry

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<th>Experiment number</th>
<th>External resistance (K ohms)</th>
<th>$\lambda$ (Å)</th>
<th>Photometer reading (divisions)</th>
<th>$I_0 \times 10^{-12}$ q/cc/sec</th>
<th>Photometer const. $\times 10^{-10}$ q/cc/sec/div</th>
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<td></td>
<td>87.20</td>
<td>6.343</td>
<td>7.27</td>
</tr>
<tr>
<td>A-21</td>
<td>1.7</td>
<td></td>
<td>91.40</td>
<td>16.75</td>
<td>a</td>
</tr>
<tr>
<td>A-22</td>
<td>1.7</td>
<td></td>
<td>91.65</td>
<td>16.83</td>
<td></td>
</tr>
<tr>
<td>A-23</td>
<td>1.7</td>
<td></td>
<td>78.50</td>
<td>15.50</td>
<td></td>
</tr>
<tr>
<td>A-24</td>
<td>6.0</td>
<td>2654</td>
<td>85.00</td>
<td>1.870</td>
<td>2.20</td>
</tr>
<tr>
<td>A-25</td>
<td>6.0</td>
<td></td>
<td>87.50</td>
<td>2.027</td>
<td>2.32</td>
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<tr>
<td>A-26</td>
<td>6.0</td>
<td></td>
<td>69.80</td>
<td>1.560</td>
<td>2.24</td>
</tr>
<tr>
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<td>6.0</td>
<td>2537</td>
<td>59.60</td>
<td>1.377</td>
<td>2.31</td>
</tr>
<tr>
<td>A-30</td>
<td>6.0</td>
<td></td>
<td>73.00</td>
<td>1.742</td>
<td>2.36</td>
</tr>
<tr>
<td>A-31</td>
<td>1.7</td>
<td>3130</td>
<td>68.90</td>
<td>3.180</td>
<td>a</td>
</tr>
<tr>
<td>A-32</td>
<td>1.7</td>
<td></td>
<td>59.50</td>
<td>3.071</td>
<td></td>
</tr>
<tr>
<td>A-33</td>
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<td>3340</td>
<td>73.25</td>
<td>1.191</td>
<td>1.63</td>
</tr>
<tr>
<td>A-34</td>
<td>6.0</td>
<td></td>
<td>65.20</td>
<td>1.047</td>
<td>1.61</td>
</tr>
</tbody>
</table>

*At low external impedance the photometer response was not linearly related to intensity.*
more actinometry experiments so that the value of $I_0$ could be estimated with a minimum of extrapolation.

In those experiments with added gases, there was sufficient scattering of the light beam that the fraction of the incident light absorbed was not determined directly.* The percentage absorp-

* The word scattered is probably not entirely correct. A series of photometer readings was taken at 3130Å using the 25-cm cell and various pressures of propylene. The change in transmitted intensity varied from 0-1%, depending on the pressure of the olefin. At 3130Å the observed and calculated values for the absorbed intensity with added propylene agreed within the uncertainty of the extinction coefficients. However, at 2654Å and 2537Å the difference between the calculated and observed values was somewhat greater (i.e. 4-6%). While scattering increases with shorter wave-lengths, it is difficult to blame the difference entirely on this. Since the observed value was always greater than the calculated value, pressure broadening may have occurred.

The percentage absorption was calculated from the known extinction coefficients and the observed pressure of pure formaldehyde.

Several experiments were discarded. These, with the reasons for their rejection, are listed in Table 13.
<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Reason for rejection</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-(1-10)</td>
<td>&quot;Shake down&quot; experiments</td>
</tr>
<tr>
<td>F-(12,14)</td>
<td>Material condensed prior to experiment. Not all material revaporized.</td>
</tr>
<tr>
<td>F-33</td>
<td>Faulty analysis</td>
</tr>
<tr>
<td>F-37</td>
<td>Circulating pump failure</td>
</tr>
<tr>
<td>F-(40,41)</td>
<td>Pressure drop after premixing components</td>
</tr>
<tr>
<td>F-53</td>
<td>Power failure</td>
</tr>
<tr>
<td>F-71</td>
<td>Faulty analysis</td>
</tr>
<tr>
<td>F-85D</td>
<td>Sample lost in handling</td>
</tr>
<tr>
<td>F-88-D</td>
<td>Air in sample</td>
</tr>
<tr>
<td>F-95</td>
<td>Operator error</td>
</tr>
</tbody>
</table>
DISCUSSION

Uninhibited Photolyses

Mechanism

The following kinetic mechanism appears to satisfy the conditions imposed by the experimental results.

\[
H_2CO + h\nu \rightarrow H_2CO^* \quad [I_a]
\]

\[
H_2CO^* \rightarrow H + HCO' \quad [I]
\]

\[
H_2CO^* \rightarrow H_2 + CO \quad [II]
\]

\[
H_2CO^* + H_2CO \rightarrow H_3CO + HCO \quad [III]
\]

\[
HCO' \rightarrow H + CO \quad [I]
\]

\[
HCO' + M \rightarrow HCO + M \quad [2]
\]

\[
H + H_2CO \rightarrow H_2 + HCO \quad [3]
\]

\[
HCO + M \rightarrow H + CO + M \quad [4]
\]

\[
2 HCO \rightarrow H_2CO + CO \quad [5]
\]

\[
\rightarrow (HCO)_2 \quad [6]
\]

\[
CH_3O + H_2CO \rightarrow CH_3OH + HCO \quad [7]
\]

Several steps need additional comment. The asterisk signifies only that the molecule has absorbed a quanta of incident radiation; nothing is implied as to the nature of the excited state involved. This point will be considered in a separate section of the Discussion. The prime \((HCO')\) denotes a radical that is not thermally
equilibrated. The remaining steps have all been suggested previously, or, as for reactions [III] and [7], are analogous to steps found for other aldehydes and ketones.

Several possible steps have been omitted. Thus

\[
\begin{align*}
H + H + M & \rightarrow H_2 + M \quad [8] \\
H + HCO & \rightarrow H_2 + CO \quad [9] \\
H + HCO & \rightarrow H_2CO \quad [10]
\end{align*}
\]

have not been included. These reactions are competing with [3] for H atoms. Since [8], [9], and [10] are all second order in radical concentration; whereas [3] is first order and has a very low activation energy, it seems likely that at the low intensities used (i.e., \( I_a = 5 \times 10^{11} \) q/cc/sec) reaction [3] would be the dominant mode of H atom removal. On the basis of Kutschke's work (1) with azomethane-formaldehyde mixtures, it is likely that [10] is not an important reaction. Very likely at higher intensities [9] and possibly [8] become important.

There are several other possible reactions which might be included, however, the above mechanism seems to fit the data and there is no need to complicate matters further.

Having presented the mechanism as a whole, it would be well to examine the individual steps and show how the data support them.

Hydrogen deficiency

Very early in this work it became apparent that under our experimental conditions the quantum yield of CO exceeded that of
H₂ for uninhibited photolyses. This was not unexpected as Calvert and Steacie (2) had observed a similar phenomenon in their investigation. However, McQuigg and Calvert (3) found an approximate balance of CO and H₂ in their flash photolyses studies. Since the difference between the quantum yield of H₂ and CO was well outside experimental error (see for example, experiment F-11), it seemed worthwhile to investigate the matter and see if the two previous observations could be reconciled with our own. The first possibility to be examined was that of a "dark reaction."

**Dark reaction**

Two dark experiments were performed (experiments F-13 and F-99). Experiment F-13 was done in the 5-cm cell, while F-99 was done using the 25-cm cell. Both experiments showed that at the temperatures used in this work, no dark reaction was occurring which gives rise to hydrogen or carbon monoxide.* Thus the thermal reaction

\[
\text{HCO} + \text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{CO}
\]  

[11]

found by Calvert and Steacie (4) and studied by Longfield and Walters (5) cannot account for the CO imbalance in our experiments. This is in accord with the findings of Calvert and Steacie that reaction [11] was negligible below 150°C.

---

* In both experiments some hydrogen and carbon monoxide was found. However, the quantity was so small (i.e., < 6 µL* total non-condensables in a 22 hour contact period) that its contribution can be neglected in the usual three hour photolysis.
Another possible "dark reaction" was the loss of H atoms on the cell wall. Thus atomic hydrogen produced in the photolyses might stick to the wall and not form molecular hydrogen. To test this, deuterium was placed in the photolysis system after a regular formaldehyde photolysis (see experiment F-22). The products and residual aldehyde were, of course, removed before introducing the D₂. It was thought that the reaction

\[ H + D₂ \rightarrow HD + D \]  \hspace{1cm} [12]

would occur and increase the HD content of the sample if an appreciable quantity of H atoms were present on the wall. After 22 hours in the photolysis system, the deuterium was pumped into a sample thimble and analyzed by mass spectrometry for HD content. Comparison of the sample's HD content with that of the original deuterium showed that no significant increase in HD had occurred. This fact, coupled with the large hydrogen deficit usually observed, argues against the loss of hydrogen atoms on the wall as the major reason for the imbalance of hydrogen and carbon monoxide.

The possible loss of molecular hydrogen in the photolysis system; and, in particular, on the metal valves, was also tested. A measured sample of hydrogen and carbon monoxide approximating a normal photolysis sample was introduced and held in the photolysis system for three hours. The sample of the original composition was recovered quantitatively using the usual sample removal techniques.
Thus it appeared some photolysis reaction was producing CO and not H₂. This implied that one of the photolysis products was in a reduced state relative to the aldehyde. Assuming this product contained only one carbon atom, the options were CH₃OH and CH₄. Methane could be ruled out at once since it would have been detected in the non-condensables by the analysis procedure used. Thus it seemed likely that methanol was being produced photochemically. Several attempts were made to show its presence in the condensable material.

**Methanol search**

The condensable material from a photolysis (F-23) was condensed with liquid N₂ into the side arm of a sample tube similar to that described by Blacet and Calvert (6). The sample tube was closed and removed from the line. The formaldehyde vapors were allowed to polymerize over KOH pellets contained in the second arm of the sample holder by replacing the liquid nitrogen cooling bath with solid CO₂. During this process the KOH pellets became colored by a bright yellow solid. After polymerization appeared complete the Dry Ice trap was removed and the residual vapors examined by mass spectrometry. Peaks at 31 and 32 in the correct ratio* were taken as evidence for methanol. A blank was then run in which pure CH₂O monomer was subjected to similar treatment. Here also 31 and 32 peaks in the correct ratio were observed. Thus it seemed this

* The ratio was determined by examining a known spectrum of CH₃OH taken on that machine.
procedure was not a reliable indication of photolytic methanol formation. Presumably what was taking place was

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

(i.e., a Carnizzaro reaction).

To circumvent this problem, the aldehyde was allowed to polymerize without the aid of KOH pellets. The residue from a photolysis so treated (F-24) gave 31 and 32 peaks. When unphotolyzed monomer was treated in this manner 31 and 32 peaks were also observed. However, in both cases the 32/31 peak ratio was distinctly different from that observed for pure methanol. In view of these difficulties, little faith could be put in an identification based on these peaks.

In the hope of providing a more positive means of identifying methanol in the products, the condensable material from several photolyses was examined via long-path infrared spectrophotometry. The usual procedure was to polymerize the excess aldehyde as previously described and then allow the residual vapor to expand into the 55 l. tank of the spectrometer. The tank was then pressurized to 730 mm Hg with dry nitrogen.

When the condensable material was polymerized with KOH, the spectrum of methanol was clearly visible (2850, 1050, and 1010 cm\(^{-1}\) badly broadened). However, as discussed earlier, the blank yielded a similar result. If the aldehyde was allowed to self-polymerize, no spectral features were observed which could be attributed to free methanol. However, several absorption peaks were found which could not be correlated with formaldehyde. The origin of these peaks
could be in dimeric and higher polymers of formaldehyde; but, this point was not pursued. In order to test if methanol could be detected in the presence of formaldehyde by this procedure, a quantity of formaldehyde monomer roughly equivalent to that used for a standard photolysis was condensed with one drop of anhydrous methanol. After allowing the excess formaldehyde to self-polymerize, the residual vapor was examined in the infrared region. The spectrum of free methanol could not be detected. Thus it appeared that methanol, if present, reacts with the aldehyde. One possible reaction would be:

\[ \text{CH}_3\text{OH} + \text{CH}_2\text{O} \rightarrow \frac{\text{QCH}_3}{\text{OH}} \text{HCH} \]  

This is quite reasonable since formaldehyde exists to a large measure as \( \text{CH}_2(\text{OH})_2 \) in aqueous solution.

Thus under our conditions neither infrared nor mass spectrometry provided a satisfactory means of detecting methanol. There is reported in the literature a test for methanol in the presence of formaldehyde (7). However, this test would have involved a disproportionate amount of time. Consequently the search for methanol in the condensables was discontinued.

Pressure dependence

It soon became evident that the pressure of formaldehyde had a pronounced effect on the \( \text{H}_2\text{-CO} \) imbalance (e.g., compare F-15 and F-24). Using the mechanism given at the start of the Discussion and applying the usual steady state approximation, it can be shown
\[ \phi_H^2 = \phi_{\text{II}} + \phi_{\text{I}} [1 + k_1/(k_1 + k_2[M])] + k_4[M] \left[ \frac{\phi_{\text{II}} + \phi_{\text{III}} k_o[H_2CO]}{(k_5 + k_6) I_a} \right]^{1/2} \]

where \( k_o \) is the pseudo rate constant for

\[ \text{CH}_2O^* + \text{CH}_2O \rightarrow \text{CH}_3O + \text{HCO} \]  \[\text{(III)}\]

and \( \phi_{\text{III}} \) denotes the fraction of excited molecules which can undergo reaction \[\text{(III)}\]. The subscripts relate the rate constants to their respective reactions.

It can also be shown that

\[ \phi_{\text{CO}} = \phi_{\text{II}} + \phi_{\text{I}} [k_5/(k_5 + k_6) + k_1/(k_1 + k_2[M])] + k_4[M] \left[ \frac{\phi_{\text{II}} + \phi_{\text{III}} k_o[H_2CO]}{(k_5 + k_6) I_a} \right]^{1/2} \]

\[+ k_5/k_5 + k_6 \left[ \phi_{\text{III}} k_o[H_2CO] \right], \]

and thus

\[ \phi_{\text{CO}} - \phi_{H^2} = (k_5/k_6 + k_5) \left[ \phi_{\text{III}} k_o[H_2CO] \right] + \phi_{\text{I}} \left[ (k_5/k_5 + k_6) - 1 \right]. \]

Hence a plot of \( \phi_{\text{CO}} - \phi_{H^2} \) vs. \( P_{\text{CH}_2O} \) should be linear. Figure 5 shows the data from experiments 90, 96, and 97 plotted in this fashion. These data were taken using light of 3340\( \AA \) and an average cell temperature of 109.0\( \pm \)0.5\( ^\circ \)C. Several points need amplification.

One reaction path is available which yields CO and not \( H_2^+ \):

\[ \text{H}_2\text{CO}^* + \text{H}_2\text{CO} \rightarrow \text{H}_3\text{CO} + \text{HCO} \]  \[\text{(III)}\]
\[ \text{H}_3\text{CO} + \text{H}_2\text{CO} \rightarrow \text{H}_3\text{COH} + \text{HCO} \]  \[\text{(7)}\]
\[ \text{HCO} + \text{HCO} \rightarrow \text{H}_2\text{CO} + \text{CO} \]  \[\text{(5)}\]
Figure 5—Pressure dependence of the hydrogen deficit.
Conversely, one path will produce H\textsubscript{2} and not CO:

\begin{align*}
H_2CO^* & \rightarrow H + HCO \quad [1] \\
H + H_2CO & \rightarrow H_2 + HCO \quad [3] \\
HCO + HOC & \rightarrow (CHO)_2^* \quad [6]
\end{align*}

The path which results in excess CO has a higher order dependence in CH\textsubscript{2}O than the other reaction series. At higher pressures of formaldehyde the first sequence should be favored. The negative intercept of Figure 5, an indication of a hydrogen excess at lower pressures, suggests that the second sequence predominates in the low pressure region. Thus, chain termination by reaction [6] must occur to some extent. The intercept, as determined by a least squares treatment, is -0.215. This should represent \( \phi_I(k_5/k_5+k_6 - 1) \); from which \( k_5/k_6 \) could be determined. Unfortunately the value of \( \phi_I \) is not known exactly. Since \( \phi_{II} = 0.4 \) it must surely be between 0.6 and 0.3*. Thus we find that \( 0.44 \leq k_5/k_6 \leq 1.8 \). However,

* These limiting values are obtained by assuming \( \phi_I + \phi_{II} + \phi_{III} = 1.0 \). Also, that \( \phi_{III} \) lies in the range 0 to 1/2 \( \phi_I \).

these values prove very little except that both reactions are occurring.

As previously discussed, no reliable evidence for methanol formation could be found. However, the absence of methane could definitely be established. Since mechanical loss of hydrogen appears unlikely, the photoreduction of the aldehyde represents the most plausible explanation of the H\textsubscript{2}-CO imbalance. And, the mechanism assigned to such a process does fit the data.
Reactions of this type are common in the liquid phase (8), but only one instance has been reported in the gas phase (9). Since collision frequencies are much smaller in the gas phase, one of two conditions must be met to allow photoreduction. Either a relatively long-lived excited state must be had or the hydrogen transfer reaction must be very efficient. In the case of perfluorobiacetyl (reference 9) the excited triplet is long lived and the carbonyl group of perfluoroketones is particularly susceptible to free radical addition (10). In the case of formaldehyde the hydrogen transfer reaction must be very efficient. This is compatible with the very low activation energies observed for abstraction of an H atom from formaldehyde.

Interestingly, the deuteroaldehyde does not show a serious CO-D₂₅ inbalance under our conditions. Two explanations seem plausible. It is possible that the photoreduction reaction occurs but that the ratio k_f/k_o is such that virtually no excess CO is produced. This does not seem likely since disproportionation/recombination ratios are generally not too sensitive to isotopic substitution. The second possibility is an isotope effect for the hydrogen abstraction reaction.

Presumably the first step in the photoreduction is the abstraction of a hydrogen atom by the excited molecule (assumed to be a triplet species). Thus either the difference in activation energies for abstraction is sufficiently high or the excited molecule sufficiently shorter lived as to preclude reaction for CD₂₀. Since deutero compounds generally have a longer excited life-time, it is probable
that the former explanation is correct. If the temperature were raised sufficiently, we should observe the same phenomenon for formaldehyde-d₂ as was found for the protonated aldehyde. The data of Kutschke and Venugopal (11) for CD₂O photolyzed at 300°C shows that this is the case. The deuterium deficit also showed qualitatively the same pressure and intensity dependence as we observed.

The H₂-CO imbalance also exhibits a positive temperature dependence (see experiments 11 and 15). If we assume, as is usually done, that the disproportionation/recombination ratio is independent of temperature, we can ascribe the temperature dependence to kₒ. Presumably, an activation energy could be calculated; however, the data are very limited and taken under different conditions. Thus such a calculation would be rather unreliable.*

*Calculation of E_a from the available data was made. However, the values obtained were not consistent. Values were found to range from 0 ≤ E_a ≤ 1.8 kcal/mole. This is an apparent activation energy and may or may not correspond to Eₒ depending on the validity of our previous assumptions.

Nothing has been said about the state of the activated molecule which is undergoing reaction. Comment on this matter will be reserved until later in the Discussion.

Full arc photolyses

Since McQuigg and Calvert did not observe a hydrogen deficit in their flash studies and since we wished to establish that the hydrogen deficit was not an artifact of our system, several experiments were carried out using a full arc in order to approximate
McQuigg's experimental conditions. The results of these experiments are summarized in Table 14. The equivalence of hydrogen and carbon monoxide is evident.

**TABLE 14**

Full Arc Photolyses of Formaldehyde

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Pressure (mm Hg)</th>
<th>Temperature (°C)</th>
<th>Time x 10^-2 (sec)</th>
<th>H_2/CO ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-92</td>
<td>24.0</td>
<td>109.2</td>
<td>36</td>
<td>1.01_2^c</td>
</tr>
<tr>
<td>F-93</td>
<td>24.5</td>
<td>109.1</td>
<td>18</td>
<td>1.05_6^c</td>
</tr>
<tr>
<td>F-94_b</td>
<td>24.0</td>
<td>109.2</td>
<td>180</td>
<td>1.01_6^c</td>
</tr>
<tr>
<td>F-98</td>
<td>121.0</td>
<td>109.1</td>
<td>6</td>
<td>1.03_2^c</td>
</tr>
</tbody>
</table>

^a Visible light removed by Corning #9863 filter. ^b Incident intensity reduced to 2% by neutral density filter. ^c Average of at least four determinations.

Thus the hydrogen deficit is not an artifact of this particular mechanical system. From the results of our study of the pressure dependence of the hydrogen deficit, the equivalence of H_2 and CO at low formaldehyde pressures is readily explained. The balance of the two at higher pressures deserves some comment. As shown earlier, the critical step in the mechanism producing a CO excess is

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

[5]

Also, at low intensities we neglected the reaction

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

[9]
It is likely that at high intensities \([9]\) becomes a major reaction. If this is true, then the amount of reaction leading to the excess CO will decrease as the square of the formyl radical concentration. In other words, at high intensities the photoreduction is still operative, but the observable effect, namely excess CO, is lost due to a change in mechanism.

**Carry over energy**

The mechanism presented earlier allows the possibility of "hot" radicals (reactions 1, 2, and 3) which either decompose or become equilibrated through collisions. Since the value of \(D(H\text{-CHO})\) is not established, not even a qualitative estimate of the "carry over energy" can be given. Since the first excited electronic state of the hydrogen atom is energetically unattainable in this circumstance (i.e., \(E > 10.0\) e.v.), it can only carry off energy as translation. It is probable that some of the excess energy is carried off by the HCO fragment in the form of vibrational excitation.

The reasoning for this is as follows. For bond rupture to occur, one of the normal modes must essentially become the reaction coordinate. For

\[
\text{CH}_2\text{O} + h\nu \rightarrow \text{H} + \text{CHO}
\]

this mode is presumed to be \(\nu_5\). Now a normal vibration imparts no net momentum to the molecule. However, when \(\nu_5\) is transformed to the reaction coordinate a change takes place. As the bond is stretched past the critical coordinate the motion becomes aperiodic and the excess energy accumulated in that mode over that necessary
to cause bond rupture appears as translational energy. Since momen-
tum must be conserved, the H atom, by virtue of its greater velocity,
will carry off a proportionately greater amount of this kinetic
energy.

There are, however, normal modes of the excited molecule which
take no direct part in the decomposition except to serve as energy
sinks. Such modes are only slightly perturbed as the molecule as-
sumes the configuration of the transition state. These "adiabatic
modes" contain the excess energy that has not accumulated in the
breaking bond. Now when E(photon) = D(H-COH), these modes must be
very close to their normal thermal levels at the moment of dis-
sociation since the greatest part of the energy of excitation is
necessary to cause bond rupture. However, when E(photon) > D(H-COH),
it is neither necessary nor likely that these modes are all in their
thermal levels. Thus these modes act as energy reservoirs and retain
the excess energy as vibrational excitation. Since the formyl radi-
cal is the only fragment with vibrational modes, any of the excess
energy remaining as vibrational energy must be associated with this
radical.

Thus at shorter wave-lengths, the life-time of this photolytical-
ly formed radical should decrease. Lossing (12) found that at 2537Å
(Hg sensitized) a significant portion of the formyl radicals formed
decomposed so rapidly that the process was effectively

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

[I-a]
At longer wave-lengths, where the "carry over energy" is less, the equilibration reaction, [2], competes more favorably with decomposition and the effect of "hot" radicals is correspondingly reduced. Thus the rate constants $k_1$ and $k_2$ are not true rate constants but should be described as proportionality factors which are dependent on $\lambda$, $T$, and $P$. By performing the experiments at various wave-lengths under similar conditions of temperature and pressure it was hoped that a measure of the carry over energy would be obtained. Since the thermal chain should be similar in all these experiments, only differences would be photolytic in origin. Thus the increase in the normalized free radical quantum yield* of $H_2$ or CO should mirror the number of formyls which were decomposing as a result of "carry over energy." However, the occurrence of another intermolecular [III] primary process sufficiently complicates the expression for $\phi_{H_2}$, $\phi_{CO}$ and $\phi_{CO}/\phi_{H_2}$ that this type of comparison has little validity.

The data for formaldehyde-$d_2$ show a maximum quantum yield at 265 $\mu\text{A}$. Presumably, the deutero compound does not undergo photoreduction at these temperatures. However, it may well be that reactions leading to a deuterium excess are masking the effect. While several explanations could be offered for the apparent maximum, there is little data to work with and hence little value in presenting unsupported speculation.

It has not proved possible to evaluate the effect of "hot" radicals from our data.

* Since both $\phi_I$ and $\phi_{II}$ are changing with wave-length it is necessary to normalize the free radical quantum yields for comparison, (i.e., $\phi_{CO}/\phi_{II}$).
Pressure effects

Several workers have noted an acceleration of the formaldehyde decomposition rate when "inert gases" were added (13, 14). A similar effect was noted in this work. Usually the effect is ascribed to

$$\text{HCHO} + \text{M} \rightarrow \text{H} + \text{CO} + \text{M} \quad [4]$$

This reaction is presumed to be in the second order region under most experimental conditions (15). However, in the low temperature photolysis of formaldehyde, the effects of pressure can take other forms. Since the thermal chain is short, any change in the efficiency of the primary processes will be noted. Thus we might expect deactivation of the excited molecules or a change in the relative importance of the primary processes with additional pressure. These pressure effects will be operative in addition to the enhancement of formyl decomposition.

Only a few experiments were performed with added "inert" gas (i.e. neopentane) (experiments 20, 34, 35). However, an enhancement of both $\phi_{\text{H}_2}$ and $\phi_{\text{CO}}$ was noted. In both the experiments at $P_{\text{CH}_2\text{O}} = 79.0$ mm Hg and $P_{\text{CH}_2\text{O}} = 161.0$ mm Hg the increase was greater for $\phi_{\text{CO}}$ than for $\phi_{\text{H}_2}$. The difference in the change was considerably greater at higher formaldehyde pressure. Also it appeared that a plateau was reached such that additional inert gas had little effect (compare F-34 and F-35). Here again several explanations could be made; but with only three experiments such speculation is unwarranted. Suffice to say that the acceleration effect of added gases may be more complicated than merely an acceleration of formyl decomposition.
Considerable emphasis has been placed on the fact that HD is a product when mixtures of formaldehyde and formaldehyde-d\textsubscript{2} are photolyzed at 3660\textdegree A (16-18). This is taken as evidence that D(H-COH) \approx 78-82 kcal/mole. These experiments were carried out using high formaldehyde pressures at temperatures greater than 150\textdegree C. These conditions favor

$$\text{CH}_2\text{O}^* + \text{CH}_2\text{O} \rightarrow \text{CH}_3\text{O} + \text{HCO}$$  \hspace{1cm} [\text{III}]

as a primary process. Since at 300\textdegree C a large fraction of the formyl radicals decompose, the source of H and D atoms is not necessarily the unimolecular process

$$\text{CH}_2\text{O}^* \rightarrow \text{H} + \text{CHO}$$  \hspace{1cm} [\text{I}]

Kutschke found a large H\textsubscript{2}-CO imbalance in his experiments at 3660\textdegree A and it is possible that [\text{III}] was responsible for the observed HD. Hence the formation of HD at 3660\textdegree A cannot be taken as proof that D(H-COH) \approx 78-82 kcal/mole.

**Inhibited Photolyses**

**Choice of scavenger**

The main portion of this work was concerned with evaluating the relative importance of the primary processes as a function of wave-length. It was thought at the start that only two primary processes were operative and by determining the importance of one, the other could be approximated. However, the discovery of a third
process has complicated the interpretation of our results. As shown in the mechanism presented in the previous section, only one primary process yields $H_2$ by a non-free radical route. It was our intent to suppress the free radical reactions by a suitable scavenger and use the hydrogen formed as a measure of the concerted primary process. Thus a scavenger which would effectively suppress free radical hydrogen formation and yet perturb the system as little as possible was desired.

The three traditional scavenging agents; oxygen, nitric oxide, and iodine were all considered and rejected for several reasons. The reactions of $H$ atoms with NO and $O_2$ are not well understood. Presumably $H_2O$ is the final fate of the hydrogen, but the intermediate processes are subject to considerable uncertainty. Also, all three appear to exert a strong deactivating effect on certain excited states. Both $O_2$ and NO are paramagnetic and have an affinity for triplet species (19). Martin and Sutton's as well as Pitts and Blacet's work with iodine inhibition indicated that $I_2$ also is quite effective in deactivating excited molecules (20,21). Since the nature of the state which gives rise to the concerted process was not known, it seemed unwise to use any material which would perturb the course of the photolysis to a rather large and unknown extent. However, olefins were known to be good free radical traps and do not exert a particularly strong deactivating effect on excited molecules. They do, however, suffer from the disadvantage that a relatively large amount must be added to insure complete suppression of the free radical reactions.
Propylene was chosen as the scavenger for this study because it was readily available and a fair amount of data concerning its scavenging ability was available. That propylene removes H atoms effectively has been reported by Melville and Robb (22). Recently, Rebbert and Ausloos reported that olefins do exert some deactivating effect on triplet species (23). However, for propylene that effect was extremely weak. These conclusions were based on emission quenching studies using acetone. It is probable that emission yields are more sensitive to quenching effects than are decomposition yields. That propylene did not exhibit any unusual quenching effect will be shown later in the Discussion. It was then necessary to show that the scavenging agent was effective under our experimental conditions.

Intensity dependence

To establish that propylene was an effective scavenger and that in its presence the hydrogen produced was a valid measure of the concerted process was the object of several series of experiments. If the hydrogen formed in the inhibited experiments came only from the concerted primary process, then \( \Phi_{II} \) (observed) as calculated from the hydrogen quantum yield should be independent of absorbed intensity. That this is true is shown by Figure 6. In this series of experiments at 3130 Å, the cell temperature was held constant (129.0 ± 1.0°C) and two different initial pressures of the aldehyde used. That the limiting value of the hydrogen quantum yield is the same for both series even though \( I_a \) and \( P_{CH_2O} \) were changed by a factor of more than two indicated that propylene is effective in suppressing all but intramolecular hydrogen formation. In the remaining work aldehyde
Figure 6: $\phi_H$ as a function of $\frac{P_{C_3H_6}}{P_{CH_2O}}$
pressures of 80-120 mm Hg were used both as a matter of convenience and to assure a low steady state concentration of radicals.

Additional proof that the observed value of $\phi_{II}$ is not intensity dependent is found by comparing experiments F-27 and F-47. In these two experiments all conditions were the same except the incident intensity was changed by a factor of two. The two values of $\phi_{II}$ obtained are the same within experimental error.

**Temperature dependence**

McQuigg and Calvert (24) found that the ratio $\phi_{II}/\phi_I$ was independent of temperature in the range 60-100°C. It was of interest to examine the temperature dependence of $\phi_{II}$ under our conditions. Figure 7 shows the results of two series of experiments at 3130Å using the same pressure of formaldehyde but different temperatures. The two limiting values are the same within experimental error. Thus it would appear $\phi_{II}$ is not a function of temperature in the range 91-129°C. These experiments again indicate the efficiency of propylene in removing atomic hydrogen since higher temperatures should enhance abstraction reactions.

Several other checks were performed to show that the hydrogen observed came only from the concerted process. One possibility for stray hydrogen is

$$H + C_3H_6 \rightarrow H_2 + C_3H_5 \quad [15]$$

To test the importance of this reaction, formaldehyde-d$_2$ was photolyzed in the presence of propylene at 2654 and 3130Å, and the HD/D$_2$ ratio of the product hydrogen determined by mass spectrometry. Within
Figure 7. \( \phi_{H_2} \) as a function of \( \frac{P_{C_3H_6}}{P_{CH_2O}} \).
experimental error, 0.2%, the HD/D₂ ratio was the same as that found for the uninhibited photolyses. Thus reaction [15] is not important under our conditions.

To further test the ability of propylene as a scavenger, a different and presumably more efficient olefin (isobutylene) was substituted for two experiments; one using H₂CO and one with D₂CO (see experiments F-75 and F-81-D). Within experimental error, the quantum yields obtained were the same as for an equivalent pressure of propylene. Thus the nature of the olefin did not appear to have a pronounced effect on the results. This argues against any significant deactivating effect of the olefin since Rebbert and Ausloos' results indicate that a definite increase in deactivating ability should be observed with increased branching of the olefin. However, in fairness to their work, it should be pointed out that for unconjugated olefins the net deactivating effect is very small even at their temperatures (25°C) and may have escaped detection in our work.

As a final test, a mixture of formaldehyde and formaldehyde-d₂ was photolyzed with added propylene and the HD/D₂ and HD/H₂ ratio determined (see experiment F-82-D).

The sample yielded an HD/D₂ ratio of 0.08. From previous photolyses of CD₂O, the HD/D₂ ratio for "pure" deuteroformaldehyde was found to be 0.04. Thus the effective change was 0.04. By assuming that all the H₂ and D₂ came from the concerted process, it was possible to estimate the absolute amount of H₂ and D₂ in the sample. By further assuming that all HD was produced by
\[ D + H_2CO \rightarrow HD + HCO \]  \[ H + D_2CO \rightarrow HD + DCO, \]

and that the activation energy was the same for both reactions, it was then possible to set upper limits on the amount of spurious products (i.e. free radical in origin). A limit of 5% was found for CD_2O and 8% for CH_2O. The difference in the two limits arises from the assumption of a 1 kcal/mole difference between

\[ H + H_2CO \rightarrow H_2 + HCO \]
\[ D + D_2CO \rightarrow D_2 + DCO. \]

These limits represent a systematic error which tends to give artificially high values for the quantum yield of the concerted process. The error limits set here are upper limits and the rest of the data suggest that they are rather high. Also, the pressure effect studies showed there is a systematic error which tends to lower the observed quantum yields due to the deactivating effect of the added gases. It is probable that the two effects cancel each other to a large extent. While the absolute magnitude of the quantum yield of the concerted process may be subject to some uncertainty at a given wave-length, the trend of this function with wave-length is real.

The following mechanism includes some of the many reactions which could be occurring in the inhibited photolyses.

\[ H_2CO + h\nu. \rightarrow H_2CO^* \]  \[ [Ia] \]
\[ H_2CO^* \rightarrow H + HCO^* \]  \[ [I] \]
\[ H_2CO^* \rightarrow H_2 + CO \]  \[ [II] \]
When propylene is present in the photolysis mixture, the quantum yield of CO is greatly enhanced. Comparison of experiments F-18 and F-20 prove that the effect cannot be attributed solely to pressure effects. As seen by comparison of Figures 8 and 9 with Figures 6 and 7, the maximum CO quantum yield was obtained at roughly the same propylene/formaldehyde ratio as that which caused maximum hydrogen suppression. Also, addition of more olefin than necessary
Figure 8: $\phi_{CO}$ as a function of $P_{C_3H_6}/P_{CH_2O}$
Figure 9. $\phi_{CO}$ as a function of $P_{C_3H_6}/P_{CH_2O}$.
to completely suppress the free radical hydrogen lowered the CO quantum yield (compare Figure 7 with Figure 8). Thus whatever step or series of steps is responsible for the high $\phi_{CO}$ must be subject to deactivation. An isotope effect must also be included since the enhancement was much greater for CH$_2$O than for CD$_2$O (compare experiments F-26 and F-56-D). Since some of the formyl radicals surely add to the olefin, it is probable that the actual enhancement is greater than that observed. Unfortunately, no sequence of reactions which meets all the constraints of the data suggests itself at present.

Another point of puzzlement is the CO quantum yield for CD$_2$O-C$_3$H$_6$ mixtures. At 3340Å it appears that the majority of the formyls formed must be rather long lived and add to the olefin. At 3130Å the quantum yield of CO was virtually unchanged on addition of propylene. However, at 2654 and 2537Å, an enhancement similar to that found for CH$_2$O was observed. While a complete explanation cannot be offered for the high CO yields several observations can be made to help explain the phenomenon.

It is probable that "carry over energy" is an important factor. If the formyl radical is nearly thermally equilibrated there is a better chance it will add to the olefin than decompose thermally. This is presumably why the CO yield for CD$_2$O-C$_3$H$_6$ is so low at 3340Å.

When H or D atoms add to olefins, the resulting radical is nearly 40 kcal/mole "hot." Thus the C$_3$H$_7$ formed will be very reactive. However, the majority of the excess energy must be rapidly dissipated since repeated searches for CH$_4$, an expected
fracture product of hot C\textsubscript{3}H\textsubscript{7}, showed none was present. As stated earlier, the exact set of reactions which will fit all the data is not evident. Since the CO quantum yield is not necessary for evaluation of the concerted process, little harm is done by our failure to derive a detailed mechanism from the inhibited experiments. There is always the danger that some unknown step may yield spurious hydrogen, but this does not appear likely.

A comment should be made on the method of estimating $\phi_{\Pi}$. Propylene has one rather serious drawback as a scavenger; namely, that large amounts must be used to insure complete removal of the free radicals. Consequently some collisional deactivation of the excited species and energy transfer from the excited triplet might be important. Considerable care must be used in finding a limiting value for $\phi_{\Pi}$ since the addition of an excess of the olefin will cause a lowering of the hydrogen quantum yield; but, the effect is one of deactivation and not more effective scavenging. Thus it was necessary to find that pressure of olefin which provided essentially complete scavenging while holding deactivation to a minimum. An example may help to better illustrate the problem.

An olefin pressure of 155.5 mm Hg was used for experiment F-30. The hydrogen quantum yield for this experiment was 0.44. A hydrogen quantum yield of 0.48 was obtained with an olefin pressure of 103.1 mm Hg using the same aldehyde pressure (experiment F-27). An experiment, F-31, was then performed using 102.0 mm Hg of propylene and 53.0 mm Hg of neopentane, an "inert" gas. The hydrogen quantum yield was 0.45. Thus much of lowering effect of the additional propylene...
in experiment F-30 was due to deactivation of the excited aldehyde. Since an experiment, F-26, in which 51.0 mm Hg of propylene were used, resulted in a quantum yield of 0.50, it was possible to bracket the best value between 0.48 and 0.47. Thus all the limiting values reported are compromise values. Fortunately, a fair amount of latitude was available, so that some excess olefin could be tolerated without seriously affecting the observed values.

**Pressure effects**

The effect of pressure on the inhibited photolyses was of interest for two reasons. First, the sensitivity of the concerted process to collisional deactivation would provide a clue as to the life-time and energetics of the state giving rise to this process. Second, the pressure sensitivity would provide an estimate of the accuracy of the limiting hydrogen yields since rather large amounts of scavenger were added. The "inert" gas used in these experiments was neopentane. Since all the hydrogens in this molecule are primary, abstraction should not be an interfering reaction at the low temperature used. The procedure used was to find the pressure of propylene that gave complete scavenging and then add neopentane in various pressure increments. Two series of experiments at 3130° were done, one at 129°C and the other at 91°C.

Figures 10 and 11 show the results of these studies at 129 and 91°C respectively. Some scatter is evident in the data at 129°C. However, this is not surprising in view of the fact that M is actually three species; each with a somewhat different ability to
Figure 10—Effect of pressure on the concerted process.
Figure 11. Effect of pressure on the concerted process.
deactivate the excited species. The data taken at 91°C show less scatter and confirm the presumed linear relationship, $1/\gamma_{H_2} = k[M] + b$.

The slopes obtained from a least squares treatment are $1.050 \times 10^{-3}$ (mm Hg)$^{-1}$ and $1.682 \times 10^{-3}$ (mm Hg)$^{-1}$ for 129 and 91°C respectively. The intercepts, which are a measure of the concerted process at zero pressure, correspond to $\theta_{II}$ values of 0.51 and 0.53 for the two temperatures. Since the difference is well within experimental error, we have additional proof of the temperature independence of the concerted process at 3130°C. The small value of the slope function indicates that the life-time of the excited species is short relative to the time between collisions.

These conclusions are based on a steady state treatment of the following general mechanism.

\[ \text{H}_2\text{CO} \left( ^1\text{A}_1 \right) + h\nu \rightarrow \text{H}_2\text{CO} \left( ^1\text{A}_2 \right) \quad \text{I}_a \]

\[ \text{H}_2\text{CO} \left( ^1\text{A}_2 \right) \rightarrow \text{H}_2 + \text{CO} \quad \text{[a]} \]

\[ \text{H}_2\text{CO} \left( ^1\text{A}_2 \right) + M \rightarrow \text{H}_2\text{CO} \left( ^1\text{A}_2 \right) + M \quad \text{[b]} \]

\[ \text{H}_2\text{CO} \left( ^1\text{A}_2 \right) \rightarrow \text{H}_2\text{CO} \left( ^3\text{A}_2 \right) \quad \text{[c]} \]

Standard spectroscopic term symbols are used with the addition of a letter superscript to denote various degrees of vibrational excitation. Reaction [b] denotes deactivation of the excited molecule such that it can no longer undergo decomposition to $\text{H}_2$ and CO by the intramolecular mechanism. Step [c] represents the intersystem crossing to the triplet manifold.

Now hydrogen is the observed product and it can only arise
through step [a] since the propylene will suppress its formation from any free radical source. Thus we have
\[
d[H_2]/dt = k_a[H_2CO (^1A_2)]^a,
\]
and in the steady state
\[
[H_2CO (^1A_2)]_{ss} = I_a/[k_a + k_b[M] + k_c].
\]
This results in
\[
\frac{1}{\phi_{H_2}} = \frac{k_a + k_c}{k_a} + \frac{k_b [M]}{k_a}.
\]
This type of relation was observed for our system.

Since no emission is observed at 3130Å under our conditions (25), and internal conversion is unlikely to be important for such a simple molecule, [a] and [c] represent the only reactions of the \[^1A_2\] molecules as [M] approaches zero. In the limit we have
\[
\frac{1}{\phi_{H_2}} = \frac{k_a + k_c}{k_a}; [M] = 0
\]
Since no fate other than [a] or [c] is allowed the excited molecules, the ratio
\[
k_a/k_a + k_c; [m] = 0,
\]
represents that fraction of the excited molecules that decompose by the concerted mechanism in the low pressure limit.

The foregoing mechanism is surely over-simplified. Decomposition via the concerted process may occur from several vibrational
levels and deactivation is almost surely a multi-step process. The mechanism was introduced at this point only to suggest a possible explanation for the observed pressure effects. The validity of the separate steps will be discussed in detail later.

**Energy transfer**

One of the major points of interest concerning the photo-chemistry of formaldehyde is the nature of the excited states involved. Effectively all the formaldehyde molecules that absorb light in the 3500-2500Å region are excited to the $^1A_2$ state. The oscillator strength for the direct singlet-triplet transition is so low as to preclude any significant contribution. However, polyatomic molecules can undergo a radiationless transition to a close lying (in the sense of energy) triplet state. In many cases it is thought that this state also gives rise to dissociation. Thus we wished to determine the nature and importance of triplet participation in our system.

Biacetyl has been used frequently as a triplet energy transfer agent (26). While the detailed mechanism of the energy transfer process is not established, there seems to be general agreement on the basic ideas involved. Essentially

\[
\begin{align*}
3F_n + B &\rightarrow F + 3B_m \quad [29] \\
3B_m + M &\rightarrow 3B_o + M \quad [30] \\
3B_o &\rightarrow B + h\nu \quad [31] \\
3B_n &\rightarrow \text{dissociation} \quad [32]
\end{align*}
\]
As used here $^3F_h$ denotes a vibrationally excited triplet formaldehyde molecule and $^3B_m$ a vibrationally excited triplet biacetyl molecule. The symbol $^3B_o$ denotes a vibrationally equilibrated triplet biacetyl while F and B refer to the aldehyde and biacetyl in their ground states. In all cases the triplet species is electronically excited.

The mechanism implies that an excited triplet formaldehyde molecule transfer its energy on collision to a ground state biacetyl molecule. The excited biacetyl can then be vibrationally deactivated or dissociate. If deactivated, the molecule may emit radiation and return to the ground state.

If triplet formaldehyde was giving rise to dissociation, the addition of biacetyl should cause a noticeable decrease in the quantum yield of formaldehyde decomposition. Biacetyl yields CO but not $H_2$ on decomposition (27). Thus, the quantum yield of hydrogen would provide an ideal indicator of any change in the primary quantum efficiency. The experiments were performed using formaldehyde–d$_2$ for several reasons. First, the amount of CH$_3$D found would serve as additional proof of energy transfer and also allow an estimate of

$$\text{CH}_3 + \text{D}_2\text{CO} \rightarrow \text{CH}_3\text{D} + \text{DCOe} \quad [33]$$

Second, at the low temperatures used the deuterio radicals are sufficiently less reactive that interfering abstractions and chain processes are greatly reduced. Finally, deuterio compounds generally have a longer excited life-time than the corresponding protonated compounds and thereby increased opportunity for energy transfer (28).

One must exercise caution in interpreting energy transfer
experiments of this type. If the excited state is very short lived due to rapid dissociation, the biacetyl may not provide an effective transfer media and no effect will be observed even though a triplet may be involved.

Figure 12 shows the results of these experiments. These experiments were performed at 109°C using formaldehyde pressures of 72-82 mm Hg. Surprisingly even at 15 mm Hg biacetyl pressure complete suppression of triplet dissociation is not achieved. This could be accounted for either because biacetyl is an inefficient energy acceptor or because the life-time of the triplet state relative to dissociation is quite short. Recent work on the formaldehyde sensitized emission of biacetyl done in this laboratory favors the latter explanation (29). Thus it appears that a triplet state is important and does give rise to dissociation.

A least squares treatment of the data results in a slope of $2.34 \times 10^{-2} (\text{mm Hg})^{-1}$. This is presumably the ratio of the formaldehyde dissociation rate constant to that of energy transfer. However, the observed variable $\Phi_{D_2}$ is tied to secondary reactions and thus equating the slope to the above rate constant ratio may not be justified. However, since virtually no HD was found in the products it is probable that the secondary reactions were not greatly altered by the presence of biacetyl.

An attempt was made to calculate a sensitized decomposition quantum yield for biacetyl. It was assumed that all the CH$_3$D found came from reaction [33]. It was further assumed that

$$2 \text{DCO} \rightarrow \text{CO} + \text{CD}_2\text{O} \quad [5a]$$
Figure 12. Effect of biacetyl on the photolysis of CD$_2$O at 3130A°.
was the major fate of the formyl radicals formed by methyl sensitized decomposition of formaldehyde. These assumptions plus a knowledge of the drop in the CO quantum yield of formaldehyde in the presence of biacetyl (assumed equal to the drop in the D₂ quantum yield) allowed estimation of the CO resulting from sensitized decomposition of biacetyl. Values of $\phi_{CO}$ were found to range from about 2.0 at 4 mm Hg biacetyl to about 1.3 at 15 mm Hg biacetyl pressure. This effect may be real, but more likely our assumptions are not valid and the change is only a reflection of some other process not considered.

Prior to the above series of experiments, a mixture of CD₂O, C₃H₆, and 1 mm Hg biacetyl was photolyzed at 3130 Å (see experiment F-58-D). Since the limiting value of the deuterium quantum yield was known for this wave-length, any change in the yield with the addition of biacetyl should reflect deactivation of the excited state giving rise to molecular deuterium. The experimental results showed no change in $\phi_{D₂}$ within experimental error. Unfortunately, the inefficiency of energy transfer from formaldehyde was not fully appreciated at that time. Thus the experiment cannot be taken as definitive proof that the singlet state gives rise to the concerted process.

Wave-length dependence of the concerted process

Figure 13 shows the results of the inhibited photolyses of both CH₂O and CD₂O. The points at 3340 Å are taken from one experiment each and are subsequently subject to greater error. The remaining points are averages of three or more experiments. A least
Figure 13. $\phi_\Pi$ as a function of $\tilde{\nu}$ for CH$_2$O and CD$_2$O.
squares treatment indicates slopes of $5.141 \times 10^{-5}$ cm$^{-1}$ and $6.868 \times 10^{-5}$ cm$^{-1}$ for CH$_2$O and CD$_2$O respectively. The intercepts have no physical meaning in this case.

To a first approximation the concerted process is linear with wave-number or energy. The linearity is likely due to the similar experimental conditions used throughout this work. However, it seems safe to say that the importance of the concerted process increases monotonically with wave-number over the wave-length region investigated. Thus it appears that formaldehyde decomposition shows the same wave-length dependence as the other small aliphatic aldehydes.

**Isotope effect**

Since decomposition via the concerted process involves a symmetric C-H stretching frequency, an isotope effect is expected. The isotope effect for the rupture of C-H and C-D bonds is largely a reflection of the difference in zero point energy of the two modes giving rise to decomposition. While the activated complex rate theory is not strictly applicable to photochemical primary processes, it is still instructional to consider how the isotope effect enters into the absolute rate constant. If we treat only the ratio of the two rate constants, $k_H/k_D$, and neglect all contributions to the partition function except that due to the vibrational mode which effectively becomes the reaction coordinate,* we have

* This is not nearly so gross an approximation as it might seem. For a complete discussion of the problems involved, see reference 30.
\[ k_{H}/k_{D} = \frac{\sinh(\hbar \nu_{H}/2kT)}{\sinh (\hbar \nu_{D}/2kT)} \]

For large values of \( \nu \), the above expression can be approximated by

\[ k_{H}/k_{D} \approx \exp \left[ (\hbar c/2kT)(\nu_{3}^{H} - \nu_{3}^{D}) \right] \]

Now as \( T \) becomes greater the isotope effect is correspondingly reduced. The term \( kT \) is a measure of the internal energy of the molecule at the temperature \( T(\degree K) \). Now for photochemical decomposition we might define \( T \) as a "vibrational temperature" which would, for this expression, be a measure of the energy accumulated in the mode \( \nu_{3} \). Now as \( E \) (photon) increases, the vibrational excitation of the absorbing molecules is increased and hence the effective vibrational temperature is raised also. Thus we would expect the isotope effect to be reduced at shorter wave-lengths; and, this is observed.

**Primary Processes**

It is now possible to describe in a semi-quantitative way the primary processes involved in the photolysis of formaldehyde.

\[ \text{H}_2\text{CO} \left( ^1A_1 \right) + h\nu \rightarrow \text{H}_2\text{CO} \left( ^1A_2^n \right) \quad \text{(Ia)} \]

\[ \text{H}_2\text{CO} \left( ^1A_2^m \right) \rightarrow \text{H}_2 + \text{CO} \quad \text{(a)} \]

\[ \text{H}_2\text{CO} \left( ^1A_2^m \right) + M \rightarrow \text{H}_2\text{CO} \left( ^1A_2^m \right) \quad \text{(b)} \]

\[ \text{H}_2\text{CO} \left( ^1A_2^m \right) \rightarrow \text{H}_2\text{CO} \left( ^3A_2^P \right) \quad \text{(c)} \]

\[ \text{H}_2\text{CO} \left( ^3A_2^P \right) \rightarrow \text{H} + \text{HCO} \left( ^2A_1^* \right) \quad \text{(d)} \]
The usual spectroscopic term symbols are used with the addition of a letter superscript to denote various degrees of vibrational excitation.

It is worthwhile to discuss the individual steps in detail. As stated earlier, in the absorption region studied virtually all the formaldehyde molecules which absorb light are excited to the $^1A_2$ state with greater or lesser vibrational energy.

If we accept the spin conservation constraint, then the concerted process, \[a\] can only arise from the excited singlet state due to the energetics involved. If triplet formaldehyde yields $H_2$ and CO in a concerted process, one of the following must be true.

\[
\begin{align*}
\text{[a]} & \quad H_2CO \; ^3A_p^+ + H_2CO \rightarrow CH_3O + HCO \\
\text{[f]} & \quad H_2CO \; ^1A_2^- + M \rightarrow H_2CO \; ^1A_2^- + M \\
\text{[g]} & \quad H_2CO \; ^1A_2^- \rightarrow H + HCO \; ^2A^+ \\
\end{align*}
\]

From thermodynamic considerations process \[h\] requires at least 306.3 kcal/mole and process \[i\] about 156.6 kcal/mole. Since even at 2537 Å, $E(\text{photon}) = 113$ kcal/einstein, such energies were not available in this study.

The behavior of the concerted process with increasing photon energy is consistent with an excited singlet mechanism. As the energy of the photon increased above the minimum necessary for electronic excitation, the vibrational modes are the effective
energy sinks. Thus a molecule excited by 2537\textsuperscript{0} radiation possesses considerably more vibrational energy than one excited by 3340\textsuperscript{0} radiation even though the electronic state is the same. We know that $v_4$ and $v_2$ are the principle modes excited on absorption of a photon. However, rapid redistribution of this vibrational energy to other modes is possible due to anharmonic effects. The time lag for redistribution of this energy to the modes which give rise to decomposition makes possible the competition of other processes (i.e. deactivation) with the decomposition of the excited species. Unimolecular rate theory is based on the concept of a critical oscillator coordinate\textsuperscript{*} which must be attained before decomposition can occur. Now as the energy content of the molecule rises, the probability that the necessary energy will accumulate in the correct mode for decomposition becomes greater. As a consequence the time lag between photon absorption and decomposition becomes shorter and the other processes compete less effectively. Hence, decomposition which arises from the first formed vibrationally excited molecule becomes more probable as $E(\text{photon})$ is increased. The concerted process shows this type of behavior.

Though not definitive, the biacetyl-propylene experiment also indicates that a triplet state is not involved in the concerted process.

That the deactivation steps, [b] and [f], must be included was clearly shown by the experiments using added neopentane.
Qualitatively it was shown that intromolecular decomposition must be rather fast even at 3130Å. We would expect that collisional deactivation would become less important at shorter wave-lengths.

Steps such as [c] are subject to considerable uncertainty. Contrary to what we have postulated, it is often assumed that the cross-over from the singlet to the triplet state occurs only from the lower vibrational levels of the singlet state. The basis for this argument is essentially that since fluorescence is usually observed only from the lower vibrational levels that equilibration (vibrational) of the excited state is very rapid relative to the radiative life-time of the excited singlet. Even though "intersystem crossing" is a nonradiative process, it is assumed that the time lag between excitation and cross-over is comparable to the radiative life-time of the singlet. Thus the molecule would be vibrationally equilibrated before crossing to the triplet state. Since in most systems it would be impossible to prove a step such as [c], it has not been included in most primary process mechanisms.

Since "intersystem crossing" is a non-radiative transition, the selection rules for this process are not well defined. It appears that a spin dependent perturbation is necessary to allow uncoupling of the spin and orbital angular momentum. The restrictions on this process are not clear.

Formaldehyde is one of the few polyatomic molecules for which the configurations of the excited singlet and the triplet states are known and are similar (see Table 1). Also, the two excited states are very similar in energy. Thus from a naive viewpoint
we should expect that the interconversion of singlet-triplet should be easier since no great changes in molecular geometry or energy are required.

The persistence of the free radical process even at 2537Å is difficult to explain without step [c]. Presumably deactivation is the other major process competing with decomposition and crossover. However, deactivation of the excited species to the point where the concerted process cannot occur has been shown to be a very inefficient process even at 3130Å, and would be expected to be less so at 2537Å. Added proof for the necessity of step [c] is supplied by the experiments of Lossing (31) using mercury sensitization. If we assume spin is conserved during the energy exchange process, it follows that

$$Hg\left( ^{3}P_{3/2} \right) + CH_{2}O\left( ^{1}A_{1} \right) \rightarrow CH_{2}O\left( ^{3}A_{2}^{n} \right) + Hg\left( ^{1}S_{0} \right) \quad \text{[j]}$$

is the energy transfer process. The fact that the concerted process did contribute to the decomposition of the aldehyde suggests

$$3_{P_{n}} \rightarrow 1_{P_{m}} \quad \text{[k]}$$

in which the excited singlet can still undergo concerted decomposition. If crossover of the vibrationally excited triplet were not possible, presumably all the molecules which did not dissociate would be deactivated and eventually return to the ground state. It could be argued that an excited ground state (vibrationally) was responsible for the concerted process.
It could also be argued that the intramolecular dissociation originated from the upper vibrational levels of the ground state in the direct photolysis. Parmeter (32) investigated the photolysis of glyoxal and found a negative temperature coefficient for the process producing molecular hydrogen. He argued that this suggested an excited ground state was responsible for the process. However, that argument alone is inconclusive since vibrationally excited species will show a negative temperature coefficient for decomposition if its life-time is long enough to permit many collisions and it contains many more vibrational quanta than its collision partners. Thus the temperature coefficient does not characterize the electronic state of vibrationally excited molecules. If no temperature effect is observed, as for formaldehyde, one can say that the state giving rise to the process is very short-lived and hence suffers few collisions before dissociating. In Parmenter's work, however, there are more convincing arguments put forward for a ground state dissociation.

Unfortunately our data do not allow us to rule out completely a ground state concerted dissociation. However, it is very hard to rationalize the wave-length dependence of the concerted process on this basis. It is also improbable that the state involved for the concerted process in Lossing's work is different than that for the direct photolysis. However, neither of the foregoing hypotheses can be ruled out on the basis of our data alone.

As stated earlier, it could be argued that deactivation is responsible for the small amount of free radical process that occurs
at the shorter wave-lengths. Thus the vibrationally excited singlet would be degraded to thermal levels by collision and then crossover to the triplet state from which the free radical process occurs. If we demand that "intersystem crossing" take place in this manner, it is difficult indeed to rationalize the results of Lossing without assuming a violation of the spin rule during energy transfer. Thus

\[
\text{Hg}^{(3P/2)} + \text{CH}_2\text{O}^{(1A^0)} \rightarrow \text{CH}_2\text{O}^{(3A^\pi)} + \text{Hg}^{(1S_0)} [4] \\
\rightarrow \text{CH}_2\text{O}^{(1A^m)} + \text{Hg}^{(1S_0)} [1]
\]

would be necessary. While heavy atoms do sometimes violate the spin selection rule for absorptive transitions, there appears to be considerable evidence to indicate spin is conserved in the energy transfer process (33).

Lossing performed a similar series of experiments using acet-aldehyde (34). However, he found no evidence for

\[
\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO} [34]
\]
as a mode of decomposition. This was in marked contrast to the results of the direct photolysis studies which showed that under these conditions the intramolecular process was an important one at 2537 Å. Now Mulliken has estimated that the first triplet state of methane is at least 140 kcal/mole above the ground state (35). Thus for similar energetic reasons as given for formaldehyde, the triplet state of acetaldehyde cannot give rise to the concerted split. This conclusion is further validated by the work of Parminter and Noyes (36). Thus for the concerted process to be
operative for acetaldehyde under Lossing's conditions, a triplet-singlet cross-over was necessary. If the spin selection rules were violated in the energy transfer process, we should have expected some singlet acetaldehyde to be formed and subsequently give rise to intramolecular decomposition. That this was not observed argues against violation of the spin conservation rule during energy transfer.

Unfortunately the configuration and energy for the triplet state of acetaldehyde are not known. On the basis of our previous arguments the triplet may be sufficiently different from the singlet that "intersystem crossing" is slower than for formaldehyde.

Reaction [e] is postulated to originate from the triplet for several reasons. The quantum yield of the concerted process at 3130Å was essentially unchanged by a two-fold variation in the pressure of formaldehyde. Thus if reactions [a] and [e] were in competition for the excited singlet species, a drop in the quantum yield of the concerted process should have been observed with increasing formaldehyde pressure.

Also, from a naive consideration, the triplet is longer lived than the singlet and hence a bimolecular process could compete more favorably with the unimolecular decomposition due to the increased number of collisions.

Finally, one can argue from analogy with various ketones. It appears likely that a triplet state is involved in the photoreduction of ketones (37). Since the mechanism of excitation is the same for
unconjugated aldehydes and ketones, it is reasonable to assume that a triplet is also involved for the aldehydes.

The last step \([g]\) is included as a possibility which can neither be proven nor disproven by our data. Parmenter and Noyes (38) included such a step in their mechanism for the primary processes of the photolysis of acetaldehyde. It was needed to account for the yield of free radical process at shorter wave-length. However, as stated earlier, reaction \([c]\) is favored by the data for formaldehyde. Nevertheless, step \([g]\) cannot be ruled out as a possibility and is therefore included.

Thus far nothing has been said about the relative energetics for the free radical and intramolecular primary processes. Since at least two different electronic states are involved, and one state precedes the other, it is impossible from our data to determine which mode of decomposition is energetically favored. This is a general problem in applying various rate theories to photochemical systems. Since so little information is available regarding the transition states of molecules undergoing decomposition, the usual approach has been, if possible, to consider two competitive processes. If both processes occur from the same state, then the expression for the ratio of the rate constants is greatly simplified due to cancellation of similar terms.

Unfortunately, this approach is seldom applicable to photodecomposition. The formaldehyde system is an excellent example of the problems involved. Thus, it is not proper to consider the two modes of decomposition as competitive as they are actually
consecutive. In other words, we are not justified in just considering energetics, but must also consider timing as well. For formaldehyde this involves knowledge of the rate of "intersystem crossing." This is also true of many other systems in photochemistry. Unfortunately these rates are not known.

Until rate constants for "intersystem crossing" are known it is doubtful that quantitative predictions can be made from rate theory about the relative importance of primary processes occurring from different states.

The only process truly competitive with decomposition is deactivation. Very little is known about the transition state involved in deactivation. As a consequence, predictions as to relative rates of decomposition vs. deactivation cannot be made with any certainty using current rate theory.
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