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THE REACTIONS OF METHYLENE RADICALS WITH ACETALDEHYDE AND PROPIONALDEHYDE[1]

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ABSTRACT

The reactions of methylene radicals with acetaldehyde and propionaldehyde have been studied over the temperature range 48–118 °C and over a range of pressures of aldehyde and carbon dioxide. From acetaldehyde, the main products were carbon monoxide, methane, ethane, and acetone, with small amounts of ethylene at low pressures of acetaldehyde. With carbon dioxide present, small amounts of propylene oxide were formed, but propionaldehyde was not observed. The main products from the reaction with propionaldehyde were carbon monoxide, methane, ethane, and ethylene, with small amounts of methyl ethyl ketone, butene oxide, and isobutyraldehyde. The relation of the results to the relative rates and mode of attack of methylene on the various bonds is discussed.

INTRODUCTION

The reactions of methylene radicals with hydrocarbons have been studied in some detail and a general pattern of reactivity has emerged (1). Methylene appears to be one of the most reactive radicals known and one of the most indiscriminate in its attack upon the various types of hydrocarbon bonds. Less is known about its reactivity with other types of bonds. Reactions with oxygen-containing compounds, for example, have not been extensively studied. In the gas-phase reaction of methylene with isopropyl ether (2) no evidence was found for attack of methylene on the C—O bond. The products appeared to be formed solely by abstraction of hydrogen and insertion into the various C—H bonds. The relative rate of attack on these bonds was similar to that found by Frey (3) and Knox and Trotman-Dickenson (4). This result confirmed the similar conclusion reached by von Franzen and Fikentsher (5) and Doering, Knox, and Jones (6) from a study of the reaction of methylene with aliphatic ethers and tetrahydrofuran in solution. The reaction of methylene with methanol vapor (7) produced, among other products, dimethyl ether, and it was suggested that this was formed by an insertion reaction into the OH bond. However, the possibility of its formation by radical combination reactions could not be ruled out.

The reactivity with carbonyl bonds as compared to C—H bonds is not well known. That methylene does react with carbonyl bonds has been shown by a study of the reaction with carbon monoxide (8) and carbon dioxide (9). With the former, ketene is the product, while with the latter the main product is carbon monoxide, probably initially accompanied by formaldehyde. To obtain more information on the reactivity of methylene towards carbonyl bonds, the aldehydes were chosen as reactants, since they contain three types of bonds: paraffinic C—H bonds, the labile aldehydic C—H bond, and the carbonyl bond. It was hoped that the relative rate and mode of attack of methylene on these various bonds might be measured. The photolysis of ketene was used as a source of methylene radicals.

EXPERIMENTAL

Materials

Acetaldehyde was obtained from Eastman Kodak Company. It was stored as a liquid at 0 °C and was degassed at −78 °C before use. Traces of ethane were thus removed, but a small amount of acetone remained

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[1] *Presented at the 47th Canadian Chemical Conference, Kingston, June, 1964.*

as an impurity. Correction for this became large only when very high pressures of acetaldehyde were used. The same treatment was given propionaldehyde, also obtained from Eastman Kodak Company, except that it was stored at room temperature. A trace of acetaldehyde was the main impurity observed in the propionaldehyde.

Ketene was prepared by the method described by Fisher, MacLean, and Schnizer (10) with slight modifications. Nitrogen was used as a carrier gas, and one trap kept at about −40 °C served to separate most of the acetic acid and unreacted acetic anhydride from the ketone. The ketene was then degassed at −196 °C and distilled at −120 °C (*n*-propanol bath). Ethylene could not be detected by gas chromatographic analysis of a sample of the size used in most experiments. It was stored at room temperature and low pressure ($<$ 3 cm) as suggested by Frey (11) and was found to be quite stable for periods of several months.

Carbon dioxide was a Matheson Co. product and was thoroughly degassed before use.

Apparatus

The lamp used for photolysis was a Hanovia S500 medium pressure mercury arc. A filter solution of 2,7-dimethyl-diaza-(3,6)-cycloheptadiene-(1,6)-perchlorate[2] cut off light of wavelength $< 3\,500$ Å. A 500 cc flask, through which water flowed continuously, was placed between the lamp and filter solution and served to collimate the light roughly and to absorb much of the heat generated by the lamp.

Two reaction vessels were used, both of about 250 cc volume. The first was a spherical flask with a central cold-finger for condensing reactants, and without external heating. The second was a cylinder of diameter approximately 5 cm and was fitted inside a steel tube wound with nichrome wire. Reactants were condensed into a small U tube. In some experiments with the cylindrical vessel the reactants were allowed to stand overnight before photolysis and no change in the behavior of the system was observed. These experiments are, however, not sensitive to slight changes in homogeneity of the reactant mixtures.

The pressure in the reaction vessel was measured with a small glass diaphragm gauge used as a null-point indicator. The sensitivity was ±0.5 mm. The volume of the gauge and connecting tubing was not more than 2 or 3 cc.

Analysis

The condensable products of the reaction were fractionated through a series of four traps. The first, at −115 °C, retained most of the acetaldehyde and any higher-boiling products. This was analyzed by gas chromatography on a polypropylene glycol column, 20 ft long, at 25 °C. Acetaldehyde, propionaldehyde, acetone, and propylene oxide were well separated. The same column at 50 °C was found to separate propionaldehyde and the corresponding isomers of butyraldehyde. The second trap was a LeRoy still maintained at −196 °C and the final two traps were held at −210 °C. Except when carbon dioxide was present, the contents of these three traps were analyzed together on a 6 ft silica gel column held at 30 °C. Ethane, carbon dioxide, and ethylene were separated under these conditions. When large amounts of carbon dioxide were present, the C_2 hydrocarbons were distilled from the LeRoy still at about −162 °C.

The noncondensable gases were collected in a Toepler pump – gas burette following the traps and were analyzed by combustion in a copper oxide furnace at about 325 °C.

RESULTS AND DISCUSSION

The complexities and experimental difficulties inherent in the present system did not allow the quantitative determination of rate constants, but only a qualitative interpretation of the modes of attack of methylene on the various bonds in aldehydes. To minimize absorption of light by the aldehyde, light of wavelengths $> 3\,500$ Å was used to dissociate ketene, and in this region the primary quantum yield for dissociation is strongly pressure dependent. Pressure effects on the reaction products were therefore obscured. Furthermore, at high pressures of aldehyde where the quantum yield for dissociation of ketene was very small, direct photolysis of the aldehyde became appreciable, especially at high temperatures where the chain length is long.

Acetaldehyde

Following the general pattern of reactivity of methylene, the possible reactions with acetaldehyde may be outlined as follows

$$[I_0] \qquad CH_2CO + h\nu \rightarrow CH_2 + CO$$

$$[a] \qquad CH_2 + CH_2CO \rightarrow C_2H_4 + CO$$

$$[1] \qquad CH_2 + CH_3CHO \rightarrow [CH_3COCH_3]^*$$

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[2] *The author thanks Dr. K. O. Kutschke of the National Research Council for a sample of this compound.*

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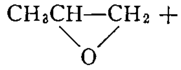
[S1] $[CH_3COCH_3]^* + M \rightarrow CH_3COCH_3 + M$

[S2] 
$\rightarrow \underset{O}{CH_3CH{-}CH_2} + M$

[S3] $\rightarrow CH_3CH_2CHO + M$

[D1] $[CH_3COCH_3]^* \rightarrow CH_3 + CH_3CO$

[D2] $\rightarrow CO + 2CH_3$

[D3] $\rightarrow CH_4 + CH_2CO$

[D4] $\rightarrow C_2H_6 + CO$

[2] $CH_2 + CH_3CHO \rightarrow CH_3 + CH_3CO$

[3] $CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$

[4] $CH_3 + CH_3 \rightarrow C_2H_6$

[5] $CH_3 + CH_3CO \rightarrow CH_3COCH_3$

[6] $2CH_3CO \rightarrow (CH_3CO)_2$

[7] $CH_3CO + M \rightarrow CH_3 + CO$

For simplicity the dissociation of ketene has been represented as a single reaction although, as already mentioned, pressure and temperature effects are important in the efficiency of this step. The designation of the excited molecule formed in reaction [1] is not intended to represent its actual structure, for which several possibilities exist, and which may, indeed, be different for each of the subsequent reactions.

The main products observed were carbon monoxide, methane, ethane, acetone, ethylene, and, under certain conditions, small amounts of propylene oxide. Propionaldehyde was not detected. The yields of products as a function of acetaldehyde pressure at two temperatures are shown in Figs. 1 and 2. At 45 °C the yield of carbon monoxide dropped sharply at first as the primary quantum yield for ketene dissociation decreased, but rose again at higher pressures as the direct photolysis of acetaldehyde became important. The products were similar to those obtained by direct photolysis of acetaldehyde and the main reaction of methylene appeared to be initiation of the chain decomposition of acetaldehyde. The yields of acetone were small and the variation with pressure not pronounced. It is most likely that it was formed mainly by combination of methyl and acetyl radicals rather than by the direct insertion of methylene. The ethylene yield was also small and even at equal pressures of ketene and acetaldehyde was less than the yield of ethane. Reaction of methylene with acetaldehyde thus appears at least as fast as with ketene.

At 118 °C the drop in quantum yield for ketene dissociation with pressure is not as sharp and the rate of decomposition of acetaldehyde much faster. Thus the yields of carbon monoxide and methane rose continuously with pressure. The yield of acetone relative to the yield of ethane has decreased, a result consistent with the suggestion that acetone was formed by combination of methyl and acetyl radicals. Again, no stabilization products were observed.

The decomposition of acetaldehyde may be initiated by reaction with an excited ketene molecule rather than by direct reaction with methylene radicals. However, the maximum energy absorbed by the ketene was 3 660 Å, equivalent to 78 kcal/mole, and this is barely sufficient to cause dissociation of acetaldehyde. Furthermore, the initial drop in carbon monoxide yield as acetaldehyde pressure was increased (Fig. 1) is difficult to explain unless deactivation of ketene occurs without decomposition of acetaldehyde. At 118 °C an energy transfer process may occur to some extent. It will be seen later that the results with propionaldehyde provide additional evidence that methylene radicals are the reactive species.

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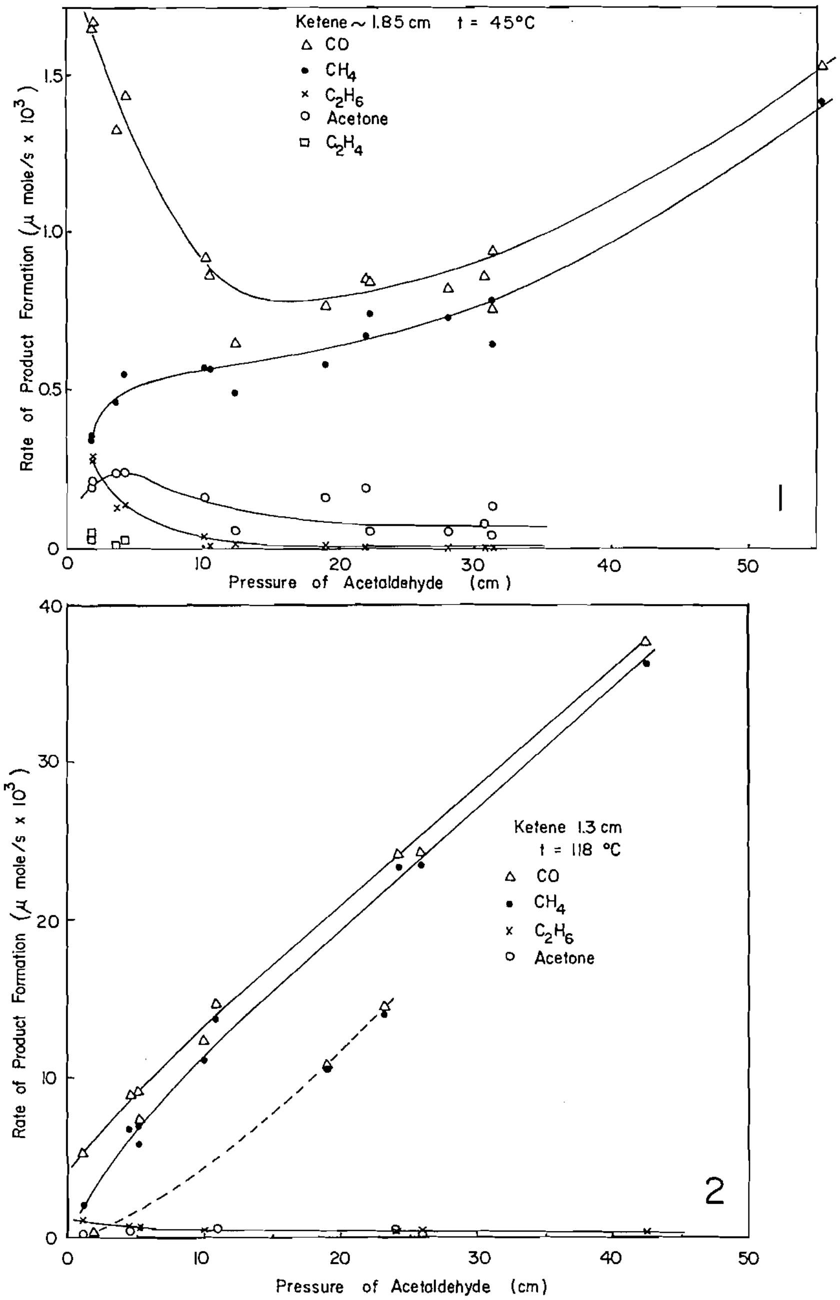

FIGS. 1 and 2. Rate of product formation from the photolysis of ketene in the presence of acetaldehyde. Dotted line shows rate of product formation from photolysis of acetaldehyde by itself.

The yield of methane divided by the square root of the yield of ethane is shown as a function of acetaldehyde pressure at the two temperatures in Figs. 3 and 4. In each case a linear relation was observed down to the lowest pressures used, showing that methane and ethane were formed from methyl radical reactions and not from a molecular decomposition of the excited molecule (reactions [D_3] and [D_4]). From the rate constants obtained

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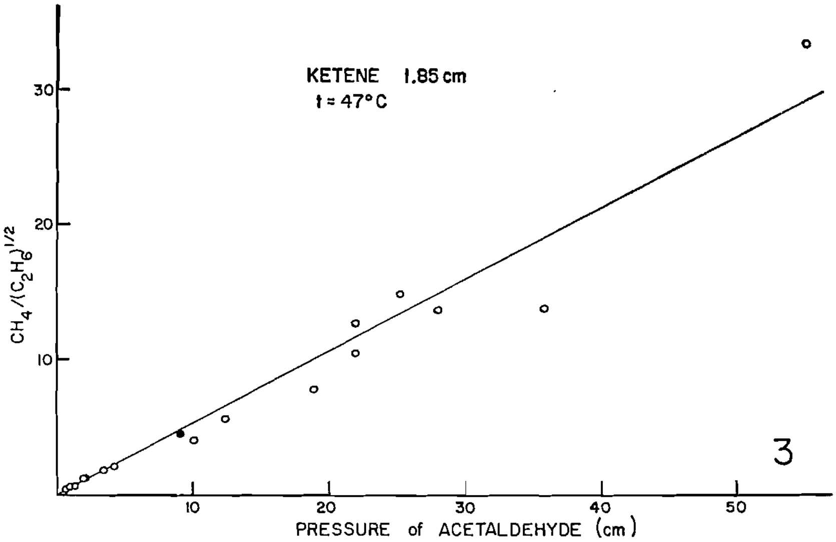

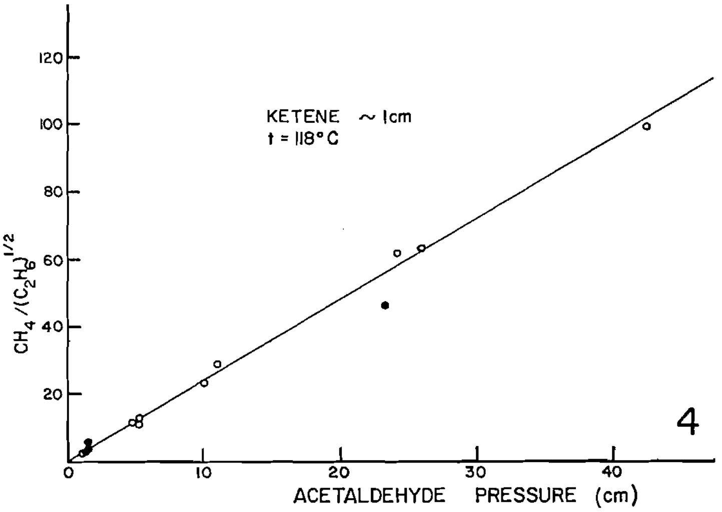

FIGS. 3 and 4. $CH_4/(C_2H_6)^{1/2}$ as a function of acetaldehyde pressure. Filled circles are results from photolysis of acetaldehyde by itself.

from these curves an activation energy of 6.2 kcal/mole was obtained for the abstraction of hydrogen from acetaldehyde. This is in satisfactory agreement with the accepted value of 7.5 kcal/mole (12).

In order to minimize the products from the chain decomposition of acetaldehyde and at the same time increase the pressure, carbon dioxide was added to small, constant amounts of ketene and acetaldehyde. The yields of products at three temperatures are shown in Figs. 5, 6, and 7. The very pronounced increase in yields of all products at 44 °C, before the expected decrease was observed, is not readily explained by any series of reactions and may be a phenomenon associated with the absorption of light in this complex system. Another possibility is that one of the effects of carbon dioxide is to

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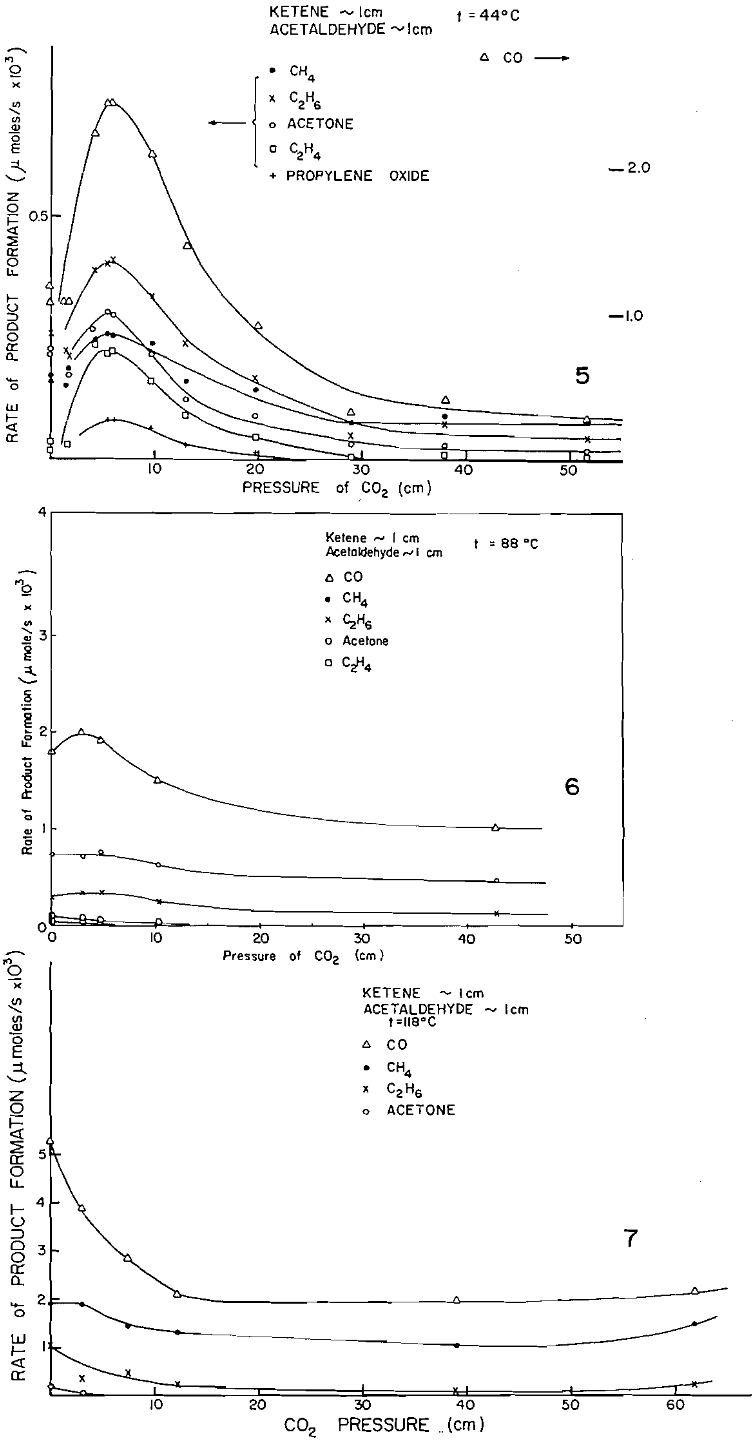

FIGS. 5, 6, and 7. Rate of product formation from the photolysis of ketene in the presence of acetaldehyde and carbon dioxide.

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increase the dissociation of ketene into methylene and carbon monoxide relative to the deactivation. The increase in yields of products may thus arise from an increased yield of methylene radicals. At higher pressures deactivation finally becomes faster than dissociation and product yields fall. Since a similar effect was not observed with acetaldehyde by itself, it must be assumed that carbon dioxide is more effective than acetaldehyde in promoting dissociation of ketene rather than deactivation. The effect diminished as the temperature was increased and as the dissociation of ketene was less affected by pressure.

At 44 °C propylene oxide was observed, but in very small yields. A comparison of the variation with pressure of the yield of stabilization product, propylene oxide, and the yield of dissociation product may be made if it is assumed that the yield of radicals from reactions [D_1] and [D_2] may be equated to the yield of termination products from reactions [4], [5], and [6]. Since the yield of biacetyl was not measured, it was estimated by assuming $k_4 = k_5 = k_6$, which gave a total yield of termination product = [ethane + acetone + ((acetone)^2/ethane)]. Plots of these products are shown in Fig. 8. The similar effect of pressure on each type of product is difficult to explain if the yield of propylene oxide is a measure of reaction [S_2] and the termination products are a measure of reactions [D_1] and [D_2]. However, if most of the radicals were formed by reaction [2], which is a true abstraction reaction, independent of pressure, and most of the excited propylene oxide was stabilized at fairly low pressures, then the variation in pressure of both types of products will simply reflect the variation in the quantum yield of ketene dissociation. The abstraction reaction may not have been observed in the reactions of methylene radicals with hydrocarbons because in this case its rate may be slower relative to the insertion reaction. With the aldehydes, abstraction of the labile aldehydic hydrogen atom may compete favorably with the insertion.

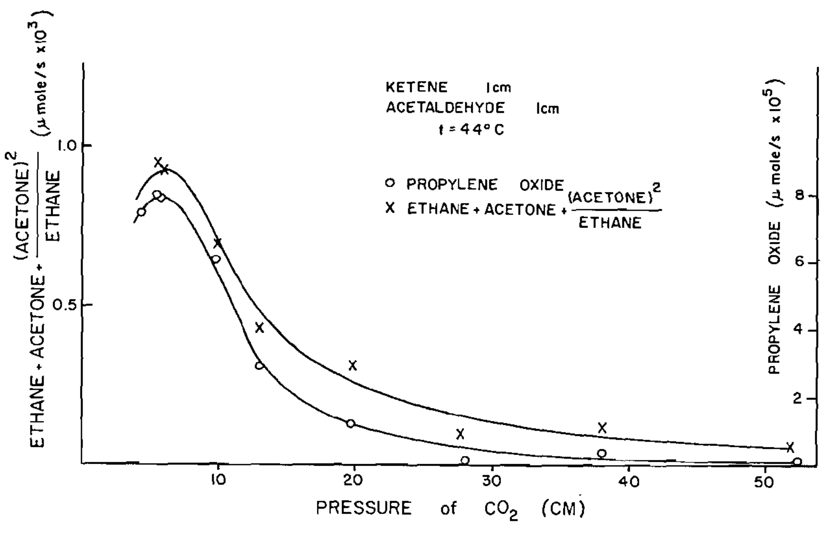

FIG. 8. Propylene oxide and radical yield as a function of carbon dioxide pressure.

An added effect of inert gas is to induce the singlet–triplet transition of the methylene radical, giving an increased concentration of triplet methylene radicals relative to singlet with rising pressure of carbon dioxide. If the triplet state radical were to react more readily by reaction [2] than the singlet, then the yield of radicals would not drop as sharply with pressure as expected on the basis of reactions [1], [S], and [D]. This effect may contribute to the similarity of the curves in Fig. 8, but it would be fortuitous if this alone caused the variations with pressure to be almost identical. These results, then, do not provide evidence for a difference in reactivity of singlet and triplet methylene by reaction [2].

Propylene oxide was not observed at 118 °C. From the results of Strachan and Noyes (13) it may be estimated that at this temperature the quantum yield of dissociation of ketene should be 2.5 times that at 45 °C. A yield of propylene oxide equivalent to 2.5 times that observed at 45 °C would have been easily measurable. Its absence again suggests the occurrence of an abstraction reaction which has a higher activation energy than the insertion and hence competes more favorably at the higher temperatures. The small change in temperature would not be expected to affect appreciably the amount of stabilization at any given pressure.

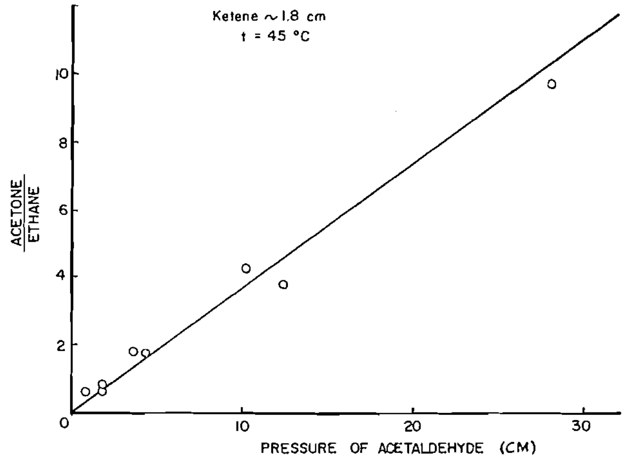

FIG. 9. Ratio of acetyl radical concentration to methyl radical concentration as a function of acetaldehyde pressure.

The ratio of acetone to ethane should be proportional to the ratio of concentration of acetyl radicals to that of methyl radicals. At 45 °C this ratio was found to be a linear function of the acetaldehyde pressure (Fig. 9). Thus for the series of experiments with constant acetaldehyde pressure the ratio would be expected to be unchanged by addition of carbon dioxide. In fact the ratio decreased with increasing total pressure (Fig. 10). This may be an indication of a pressure dependence of the decomposition of the acetyl radical.

Propionaldehyde

A series of reactions similar to those suggested for acetaldehyde would be expected to occur in the reaction of methylene with propionaldehyde. The possible stabilization products are methyl ethyl ketone, *n*-butyraldehyde, isobutyraldehyde, and α-butene oxide. Methyl, ethyl, and possibly propyl radicals may be formed by decomposition of the excited molecule, and these would initiate the chain decomposition of propionaldehyde. In accordance with this the main products observed were carbon monoxide, ethane, methane, ethylene, and small amounts of stabilization products. The results of the

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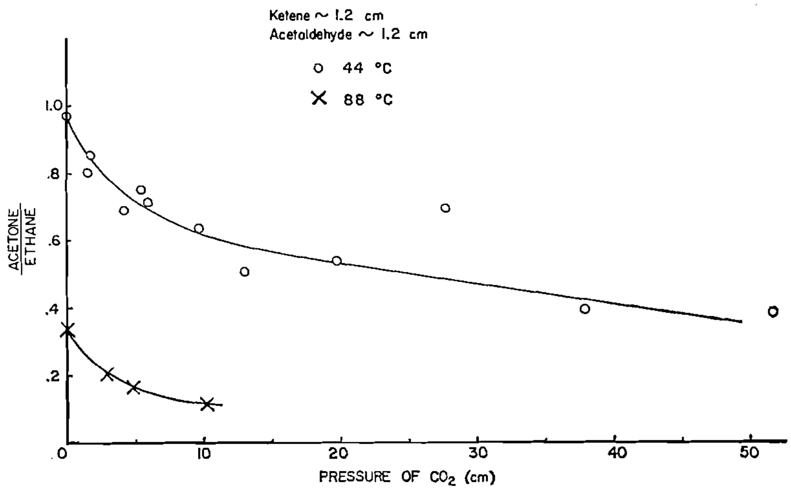


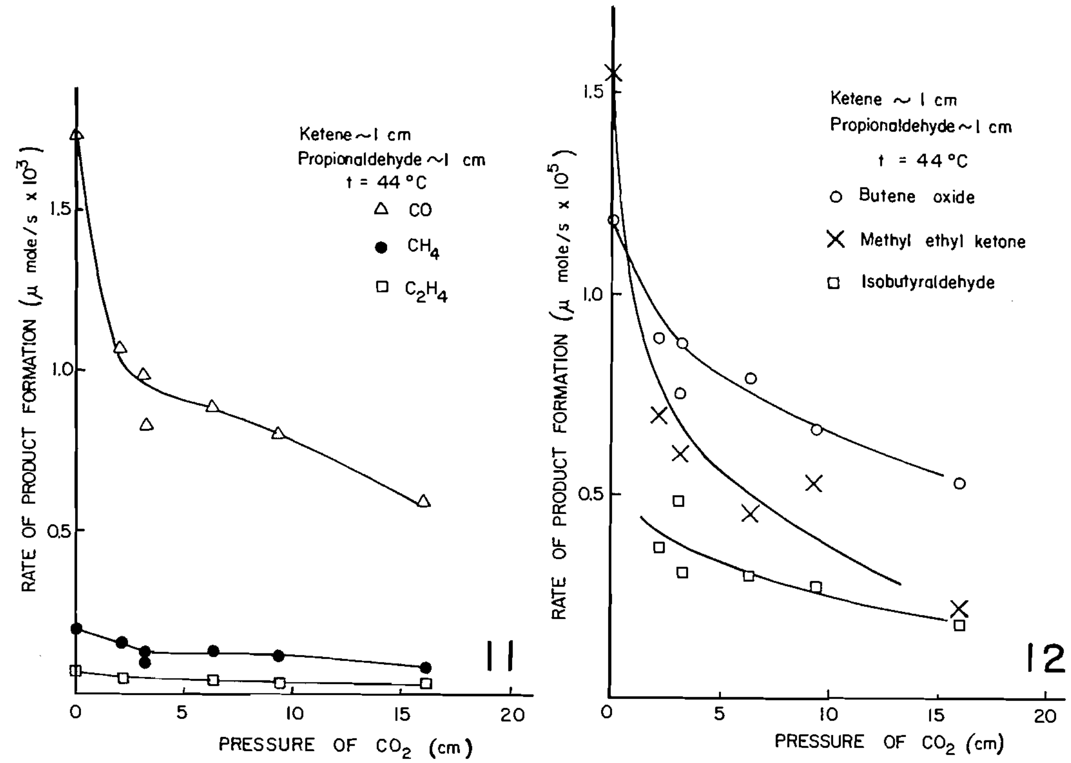
FIG. 10. Ratio of acetyl radical concentration to methyl radical concentration as a function of carbon dioxide pressure for constant acetaldehyde pressure.

photolysis of ketene in the presence of propionaldehyde and carbon dioxide at 85 °C are summarized in Table I. The yields of products at 45 °C as a function of carbon dioxide pressure are shown in Figs. 11 and 12. The yield of ethane was not plotted since it was similar at all pressures to that of methane. There is the suggestion of an inflection point in the variation of yields of the main products with carbon dioxide pressure, but the effect is much less than that observed with acetaldehyde. At 85 °C the yields of all products steadily decreased as the carbon dioxide pressure was increased. The presence of methane is good evidence that initiation of the decomposition of propionaldehyde occurs by reaction of free methylene radicals and not by energy transfer from an excited ketene molecule. Methane was not observed in the photolysis of propionaldehyde by itself.

The yields of stabilization products were still very small compared to those of the main products, carbon monoxide, methane, and ethane. *n*-Butyraldehyde was not observed under any conditions, but isobutyraldehyde was about one-third of the butene oxide. Again, methyl ethyl ketone may have been formed by stabilization or by termination.

The maximum ratio of propylene oxide to carbon monoxide found in the experiments with acetaldehyde was 0.32, but the maximum ratio of [isobutyraldehyde + butene oxide] to carbon monoxide from the reaction with propionaldehyde was 0.014. Stabilization would be expected to occur more readily with propionaldehyde than with acetaldehyde, and the apparently smaller relative yield of stabilization products may be the result of a longer chain length for decomposition of propionaldehyde than for acetaldehyde at the same temperature.

The sharp drop in yield of methyl ethyl ketone with rising pressure probably indicates that at low pressures it was formed largely by combination of radicals and not by stabilization. If the methyl ethyl ketone were formed by stabilization at higher pressures, the reactivity of the aldehydic C—H bond toward insertion of methylene is very similar to that of the secondary C—H bond. The epoxide is still the predominant stabilization product and it would thus appear that addition of methylene across the carbonyl bond is faster than insertion into a primary or secondary C—H bond.



FIGS. 11 and 12. Rate of product formation from the photolysis of ketene in the presence of propionaldehyde and carbon dioxide at 45 °C.

TABLE I

Rate of product formation from the photolysis of ketene in the presence of propionaldehyde and carbon dioxide at 85 °C

	Pressure (cm)				Rate of product formation (μmole/s × 10³)						
Expt.	Ketene	Propionaldehyde	CO_2	Time ($s \times 10^{-3}$)	CH_4	CO	C_2H_6	C_2H_4	Isobutyraldehyde	Butene oxide	Methyl ethyl ketone
1	1.02	1.08		10.9	.263	1.42	0.436	0.059	—	—	—
2	1.0	7.5		10.0	.135	1.02	1.13	—	—	—	—
3	1.0	3.8		12.0	.262	1.32	0.711	0.036	—	—	—
4	1.2	9.1		56.9	.147	1.10	0.882	—	—	—	—
5	1.1	1.1	55.5	59.0	.042	0.262	0.0525	0.0086	—	—	—
6	1.25	1.4	27.8	54.7	.0866	0.419	0.140	0.014	—	.0022	.0075
7	1.1	1.3	12.8	54.4	.114	0.570	0.163	0.0198	—	.0028	.0059
8	1.07	1.07	4.95	54.0	.152	0.786		0.031	.002	.056	.0080

It is of interest to compare the present results with those of Cvetanovic (14) on the reaction of oxygen atoms with olefins. In these two reactions the excited molecules formed by the addition of the diradical are isomeric, although the energy content is different in the two cases. The heat of formation of the complex formed by addition of oxygen atoms to propylene is about 64 kcal/mole, while that of the complex formed by the methylene reaction is about 51 kcal/mole[3] assuming no excess energy carried by the radicals. It

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[3] $\Delta H_f(CH_2)$ *taken as 90 kcal/mole.*

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might be expected, therefore, that relatively more stabilization of the excited molecule would be observed in the methylene reaction than in the oxygen atom reaction at a given pressure. The converse appears to be true. With propionaldehyde, taking methane as a measure of the dissociation and butene oxide and isobutyraldehyde as the stabilized products, the ratio of [butene oxide + isobutyraldehyde]/methane has the maximum value of 0.1 at a pressure of about 3 cm, whereas in the reaction of oxygen atoms with butene, yields of products were independent of pressure above 10 cm. However, if as suggested earlier, an abstraction reaction, independent of pressure, occurs simultaneously with the insertion reaction, the ratio given above does not represent the true ratio of stabilization to dissociation of the excited molecules formed by insertion. In fact, for these energy differences it is reasonable to assume, as already suggested, that in the addition of methylene to aldehydes stabilization may be complete at rather low pressures.

Another difference in the two sets of reactions is in the relative yields of the isomers of the stabilized molecule. These differences are most pronounced when the comparison is made with the reaction of ground state ^3P oxygen atoms with olefins. For example, with propylene, propylene oxide and propionaldehyde were formed in equal quantities, along with very small amounts of acetone, while the reaction of methylene radicals with acetaldehyde gave only propylene oxide and no propionaldehyde. Similarly, the stabilized products of the reaction of ^3P oxygen atoms with butene-1 were nearly equal yields of α-butene oxide and n-butyraldehyde, with small amounts of ketone. In the methylene radical reaction, the α-butene oxide predominated, and the aldehyde formed was isobutyraldehyde. In these systems methylene radicals were formed in the singlet state, and although some degradation to the triplet may have occurred in the presence of carbon dioxide, most of the radicals probably reacted in the singlet state. The difference in electronic state probably implies a fundamental difference in the mode of attack of the radical on the reactant and in the structure of the complex formed. For example, the addition of a ^3P oxygen atom to the double bond in an olefin forms a diradical complex, which, to form a stable molecule, may undergo migration of groups or may close the ring to form an epoxide. Excess energy may be lost before the structural changes occur. Insertion of singlet methylene, on the other hand, forms a singlet complex, which must lose energy by collisions to form a stable molecule. It is not surprising that the distribution of stabilized products is different from the two reactions.

In the reaction of ^1D oxygen atoms with butene-1 (15) the relative yield of α-butene oxide was increased to about three times that of n-butyraldehyde. The main stabilization product was thus the same for the reaction of ^1D oxygen atoms with butene-1 and the reaction of singlet methylene with propionaldehyde. However, the aldehyde from the oxygen atom reaction was exclusively n-butyraldehyde while from the methylene reaction only isobutyraldehyde was formed. This indicates there is still a difference in the mode of attack of the radicals even when both are in the singlet state and both therefore form singlet addition complexes. The oxygen atom attacks the molecule at one point only—the double bond—and subsequent products are formed by rearrangement or decomposition of the one excited molecule. Thus the excited α-butene oxide molecule initially formed may rearrange to n-butyraldehyde or methyl ethyl ketone (which was observed in small quantities), but not to isobutyraldehyde. Addition of methylene radicals, on the other hand, may occur at any bond in the molecule, usually with little discrimination. However, attack on a secondary C—H bond is usually faster than on a primary C—H bond and therefore isobutyraldehyde would be expected to predominate over n-butyraldehyde. Thus the differences between the oxygen atom reactions and the methylene radical

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reactions are for the most part the result of differences in the mode of attack of each on the reactant, rather than in the subsequent behavior of the isomeric complex.

Formaldehyde

At the beginning of this research a few experiments were done with formaldehyde as reactant. No conclusive evidence for stabilization products was observed and the main reaction of the methylene radicals appeared to be the initiation of the chain decomposition of formaldehyde. The main products were carbon monoxide, methane, and hydrogen in the approximate proportion, 70%, 20%, and 10%, respectively. Small amounts of acetaldehyde were observed but these may have been formed by radical combination. Ethylene oxide was not found.

TABLE II

Rate of product formation from the photolysis of ketene in the presence of carbon dioxide at 44 °C

	Pressure (cm)		Time	Rate of product formation (μmole/s $\times 10^3$)							
Expt.	Ketene	CO_2	($s \times 10^{-3}$)	CH_4	CO	C_2H_6	C_2H_4	CH_3-$COCH_3$	CH_3-CHO	Total product	CO/total product
1	1.1	39.2	68.7	.041	0.995	.040	.129	.0041	.008	0.659	1.51
2	1.0	50.0	72.1	.036	0.845	.0366	.111	.0029	.015	0.594	1.42
3	1.0	26.0	65.7	.0391	1.02	.0410	.155	.0033	.011	0.710	1.44
4	1.0	15.0	62.5	.034	1.18	.0474	.224	.0021	.005	0.841	1.40
5	1.0	5.7	58.5	.025	1.35	.0446	.276	.003	.007	0.904	1.49
6	1.0	6.0	26.0	.039	1.82	.084	.450	—	—	1.476	1.23

Carbon Dioxide

A few experiments were done with ketene and carbon dioxide, and these are summarized in Table II. Although the present conditions were somewhat different, the results are consistent with those found by Kistiakowsky and Sauer (9) and with their suggestion that the initial products are carbon monoxide and formaldehyde. The products formaldehyde and ethylene will be attacked more rapidly than carbon dioxide, and the minor products methane, ethane, acetaldehyde, and acetone probably arise by such secondary reactions. The number of moles of carbon monoxide which accompany each mole of minor product depends somewhat on an assumed mechanism. However, the simplest stoichiometry leads to the following. $CH_4 = 4CO$; $C_2H_6 = 5CO$; $CH_3CHO = 2CO$; $CH_3COCH_3 = 5CO$. The ratio of carbon monoxide to total products $[2C_2H_4 + 4CH_4 + 5C_2H_6 + 2CH_3CHO + 5CH_3COCH_3]$ is given in the table. The excess carbon monoxide indicates a loss of some product, which may be formaldehyde. However, the ratio increased with time of reaction (experiments 5 and 6) and extrapolated to one at zero time. This probably indicates the increasing formation of higher products which were not observed in the analysis. Loss of product as formaldehyde would be expected to be reduced at longer times of reaction, as formaldehyde is consumed by secondary reactions, so that this is not the main source of the discrepancy. Formaldehyde is probably converted to other products at very short times of reaction and has a low steady-state concentration in the reaction mixture.

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