All of these considerations make an addition reaction more probable. Although the addition of the bisulfite ion to the carbonyl groups is well known, we cannot conclude that this is the case in the present investigation, as no other proof is available for the existence of the carbonyl group as a part of the active site of the enzyme molecule.

## Summary

The bisulfite and the phenyl sulfinate ions inhibit reversibly the catalytic activity of urease, the inhibition being of first order in the concentration of the inhibitor. The inhibition reaction takes place only on those active sites which are not combined with urea. The heat of the reaction with the bisulfite is 9,200 cal./mole of the active sites and the standard entropy change is −21 e.u., which suggests that in this reaction bisulfite ion is added to the protein molecule. Sodium benzene sulfonate and sodium sulfate exert very much weaker inhibitory action. The oxidation–reduction potential of the sulfite–sulfate couple has no effect on the catalytic activity of crystalline urease.

CAMBRIDGE 38, MASSACHUSETTS

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[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# Photochemical Decomposition of Ketene. II

BY G. B. KISTIAKOWSKY* AND N. W. ROSENBERG†

The photochemical decomposition of ketene has been studied by several investigators.[1] Their work has definitely established that the decomposition of ketene into carbon monoxide and methylene occurs as a primary reaction. The secondary reactions of the methylene are less clearly understood. The final products of irradiation in pure ketene are carbon monoxide and ethylene in approximately 2:1 ratio; the quantum yield of this reaction is on the order of unity. It has been suggested that the formation of ethylene occurs by the attack of methylene on ketene; an alternative suggestion is that the ethylene is produced by the association of two methylene diradicals. In the presence of ethylene another reaction occurs, leading to the formation of a non-volatile polymer. Careful analytical studies by Rosenblum[1f] have shown that these ideas on the mechanism of the over-all reaction can only be approximately correct in view of the presence of appreciable quantities of higher volatile hydrocarbons.

The original purpose of the present investigation was the measurement of the rate of association of methylene diradicals. The data obtained in preliminary work indicated that the association did not occur under the conditions employed; therefore a study was made of the reactions of methylene under these conditions, *i. e.*, irradiation of ketene and ketene–ethylene mixtures at pressures of the order of 100 mm. The nature of these reactions has been largely clarified, although several aspects of the mechanism remain unsettled.

## Experimental Details

The reaction was studied in a static system utilizing radiation in the region 3000–3700 Å., largely that near 3100 Å. High radiation intensity and short illumination times avoided complications from dark reactions, notably the thermal polymerization of ketene. The progress of the reaction was studied manometrically and analytically; most runs were carried to less than five per cent. fractional decomposition.

The light source was of the type described by Taylor and Bates.[2] A low pressure mercury arc, it consisted essentially of two concentric quartz tubes. Through the central space was inserted the reaction cell, a 13-cm. length of 22-mm. o. d. Pyrex tubing with a wall thickness of 1.2 mm. and a volume of 40 cc. Water from a thermostat was forced through the annular space between the reaction cell and the inner lamp wall, maintaining the temperature of the reaction mixture constant to ±0.05°. This annular space also contained a 15-cm. length of aluminum tubing which could be moved back and forth, screening the reaction cell from radiation when desired. Capillary tubing led from the reaction cell to a wide-bore mercury manometer and to a capillary U-tube trap, from which, through a manifold, connections to reagent bulbs and to pumps were provided. The progress of the reaction was observed by measuring the change in the mercury level of the manometer by a microscope comparator; the reproducibility of the measurements was about 0.01 mm. A separate determination of the pressure of the condensible gases in the mixture was obtained by cooling the U-tube trap in liquid nitrogen and slowly pumping off the non-condensable fraction through it. After warming the residual gases, the pressure was measured by the microscope comparator. A Toepler pump permitted the withdrawal of samples for mass spectrographic analyses.

Ketene was prepared by the pyrolysis of acetone.[3] After passing through suitably cooled traps, it was condensed in the stillpot of a Podbielniak column 50 cm. long. Two fractionations of the sample with a stillhead temperature maintained constant at −78° by dry ice cooling resulted in a product containing no non-condensables (in liquid nitrogen) and less than 0.5% of impurities not absorbed in aqueous sodium hydroxide solution. Vapor density measurements indicated a molecular weight of 41.9 ± 0.1.

Ethylene, propylene and carbon dioxide were taken from high pressure cylinders and freed from non-condensable impurities by bulb-to-bulb distillation. A sample of

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[*] Harvard University Faculty 1930–.

[†] Harvard University Graduate School.

[1] (a) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1533 (1933); (b) Ross and Kistiakowsky, THIS JOURNAL, **56**, 1112 (1934); (c) Norrish, Crone and Saltmarsh, *ibid.*, **56**, 1644 (1934); (d) Pearson, Purcell and Saigh, *J. Chem. Soc.*, 409 (1938); (e) Burton, Davis, Gordon and Taylor, THIS JOURNAL, **63**, 1956 (1941); (f) Rosenblum, *ibid.*, **63**, 3322 (1941); (g) Norrish and Porter, *Disc. Far. Soc.*, **2**, 97 (1947).

[2] Bates and Taylor, THIS JOURNAL, **49**, 2438 (1927).

[3] Hurd, *ibid.*, **45**, 3095 (1923).

this purified ethylene, after mixing with an equal volume of ketene, and removal of the ketene by absorption in aqueous sodium hydroxide, was subjected to mass spectrographic analysis[4] which indicated the presence of 0.1% ketene and no other impurity. Evidently, the 0.5% impurity found in our ketene sample was ethylene, noted by previous investigators.[1d]

## Results and Interpretation

With the lamp operating at 600 watts (the standard operating condition), a pressure of 600 mm. of ketene was found to absorb almost completely the effective radiation. At this pressure in a Pyrex cell, the rate of ketene decomposition was 0.2 mm./sec., corresponding to $2 \times 10^{17}$ molecules/sec. The rate was higher by a factor of three in a quartz reaction cell, but complicating [illegible] reactions made necessary the removal of the 2537 Å. mercury resonance line, at the sacrifice of the higher light intensity, by the use of the Pyrex reaction cell. A heating of the gases even by the filtered radiation caused a thermal pressure rise, which necessitated the measurement of all pressures with the shutter drawn. Standard illumination periods of one hundred seconds, resulting in about four per cent. decomposition, were used, except in special cases.

The first objective of these experiments was the identification of the major reactions of methylene which, according to previously held views, may either recombine or react with ketene, as well as react with ethylene. The latter reaction is not accompanied by a pressure rise, with the result that as the ethylene/ketene ratio in the reaction cell is increased, the rate of pressure rise is lowered. Experiments were made with ethylene/ketene ratios as high as 4:1, insuring, as previous work has indicated, that the methylene formed in the decomposition of ketene would react almost exclusively with the large excess of ethylene. Under these conditions the pressure of the system remained constant on irradiation, indicating that little if any ethylene was being polymerized. Therefore we may write the reaction of methylene with ethylene formally as $CH_2 + C_2H_4 \rightarrow C_3H_6$. The reactions in the irradiation of ketene-ethylene mixtures may then be written

$$CH_2CO + h\nu \longrightarrow CH_2 + CO \qquad I_{abs} \qquad (1)$$
$$2CH_2 \longrightarrow C_2H_4 \qquad k_2 \qquad (2)$$
$$CH_2CO + CH_2 \longrightarrow C_2H_4 + CO \qquad k_3 \qquad (3)$$
$$CH_2 + C_2H_4 \longrightarrow C_3H_6 \qquad k_4 \qquad (4)$$

where the rate constants $k_2$, $k_3$ and $k_4$ may be functions of the concentrations and of the total pressure if three-body collisions are involved. They may also depend on the surface/volume ratio and the surface condition of the cell if wall reactions are taking place. For the presentation of our experimental results it is convenient to express the data in terms of the ratio $R$ of the rate of pressure change on irradiation of a given mixture of ethylene and ketene to the rate of pressure change in pure ketene at the same pressure as the ketene in the mixture. Small fractional decomposition insures that, in pure ketene, such small concentrations of ethylene are formed that reaction 4 is negligible.

With the usual steady state assumptions, and neglecting reaction 3, the following expression for the ratio $R$ is obtained

$$R = 1 - Z\sqrt{1 + \frac{2}{Z}}; \quad Z = \frac{k_4^2(C_2H_4)^2}{4k_2I_{abs}} \qquad (1)$$

Neglecting reaction 2, rather than reaction 3, leads to

$$R = 1\Big/\left(1 + \frac{k_4(C_2H_4)}{k_3(C_2H_2O)}\right) \qquad (2)$$

Thus the effect of light intensity offers a basis for rejecting one of the two reactions, 2 or 3; and the effect of total pressure at a fixed composition gives information as to the occurrence of three-body processes.

Figure 1 presents on a semi-logarithmic scale the actual observed rates of pressure change *vs.* total pressure for four different ethylene/ketene ratios. The dashed lines represent the lowering of the rate of pressure change as the ethylene/ketene ratio is increased at fixed ketene pressures, 20 and 100 mm. That the two lines are parallel demonstrates that the earlier defined ratio $R$ is independent of total pressure and is a function of the composition alone.

Figure 2 shows the value of $R$ as a function of the ethylene/ketene ratio at two different light intensities. The lower light intensity was ob-

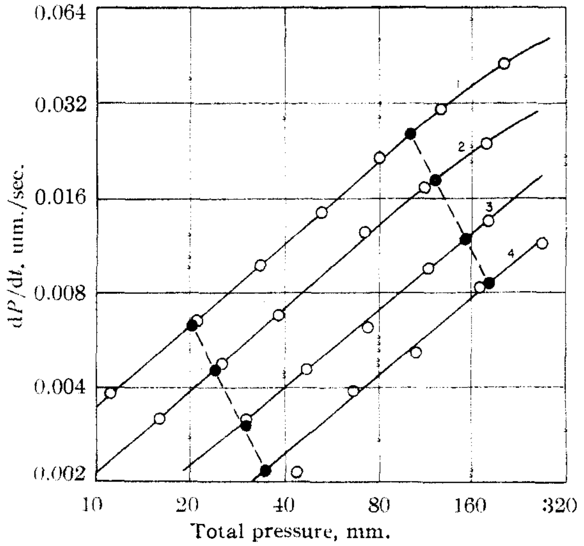

Fig. 1.—Rate of pressure change as a function of ketene and ethylene partial pressures. Curve 1 obtained in pure ketene; curve 2 with an ethylene/ketene ratio of 0.2; curve 3 with a ratio of 0.5 and curve 4 with a ratio 0.7. Black circles are rates interpolated for constant ketene pressures; *T*. 40°.

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[4] We are much indebted to the Shell Development Company, Emeryville, California, and to Dr. Otto Beeck, Dr. D. P. Stevenson, and others of the staff of the Company for carrying out for us a number of very detailed and exact analyses.

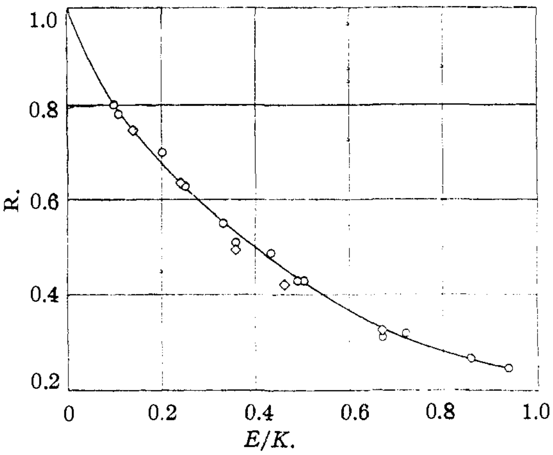

Fig. 2.—Effect of light intensity on rates of pressure change in several ethylene–ketene mixtures. Circles represent relative rates (R) in full light intensity as a function of the ethylene ketene ratio (*E*/*K*). Squares, rates with the light intensity reduced by a factor of four; *T*. 40°.

tained by inserting into the water jacket a tube made of Lectromesh foil[5] with 200 perforations/sq. cm. and transmitting 23% of incident radiation. It can be seen from Fig. 2 that a fourfold change in light intensity had no major effect on *R* as a function of the ethylene/ketene ratio.

The walls of the reaction cell were coated with a thin film of paraffin wax and the quantity *R* determined at an ethylene/ketene ratio of 0.32. Four determinations gave *R* values of 0.59, 0.56, 0.53, 0.58, compared with a value from Fig. 2 of 0.56. Evidently a hydrocarbon wall coating had no effect on the quantity *R*.

The reaction cell was packed with very thin Pyrex flakes, made by blowing out molten Pyrex bubbles. The surface–volume ratio was thereby increased at least by a factor of ten. Two determinations at an ethylene/ketene ratio of 0.85 gave values for *R* of 0.18 and 0.29, as compared with 0.26 for an unpacked tube from Fig. 2. The effect of increased surface/volume ratio is therefore unimportant.

Two determinations of *R* at a temperature of 85° were made at an ethylene/ketene ratio of 0.25, giving values of 0.56 and 0.54, compared with 0.63 from Fig. 2, obtained at 40°. An effect of temperature may exist but is at most slight.

The effect of an inert gas, carbon dioxide, was also determined. Maintaining a carbon dioxide/ketene ratio of 1.9, and varying the ketene pressure from 82 to 21 mm., identical rates of pressure change were obtained in four runs as in pure ketene at the same partial pressures. To an ethylene/ketene mixture with a ratio of 0.55 was added sufficient carbon dioxide to raise the pressure by 80%; an *R* value of 0.40 was obtained, identical to that obtained in the absence of carbon dioxide. Thus the addition of carbon dioxide had no effect on measured pressure changes.

All rates measured above were the average rates for the initial one hundred second irradiations (except that in the low intensity experiments, four hundred second illumination was used). Runs were made on which more frequent measurements were taken and to higher fractional decompositions, in which it was found that the measured rate of pressure rise decreased as the fractional decomposition increased, but extrapolation to the first instant of illumination gave substantially the same ratios *R* as were determined in the 100 sec. runs. Despite this it was felt that propylene formed in the initial stages of the reaction might significantly alter the course of the reaction. Therefore experiments were made with mixtures of propylene and ketene. Figure 3 shows that the dependence of *R* on the propylene/ketene ratio is similar to its dependence on the ethylene/ketene ratio. Therefore the formation of small quantities of propylene cannot significantly affect our results.

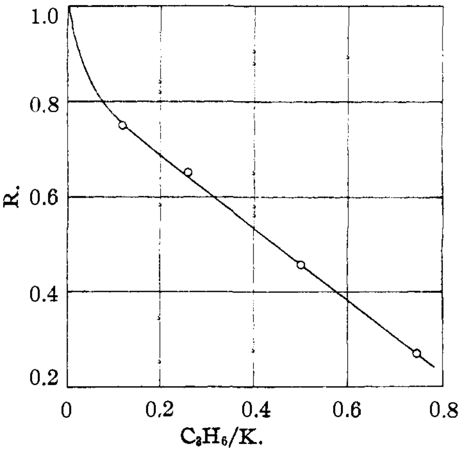

Fig. 3.—Relative rates of pressure rise (*R*) as a function of the propylene/ketene ratio ($C_3H_6$/K); *T*. 40°.

An important difference between the two mechanisms embodied in reactions 2 and 3 is that if reaction 2 predominates, the rate of carbon monoxide production should be independent of the ethylene/ketene ratio; if reaction 3 predominates, the rate of carbon monoxide production should decrease at higher ethylene/ketene ratios, approaching a limit of one half of the rate obtained in pure ketene. Rosenblum[1f] reported the absence of any effect of hydrocarbon/ketene ratio on the rate of carbon monoxide production. Our earlier experiments gave the same result. A more extensive investigation taking elaborate precautions to determine accurately the small amounts of non-condensable reaction products has, however, definitely established that the rate of carbon monoxide production does fall off with increasing ethylene/ketene ratios, although not to the extent predicted by considering only reactions 1, 2 and 4, and inserting data from Fig. 2. In pure ketene, the ratio of moles of carbon monoxide

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(5) Made by C. O. Jelliff Company, Southport, Connecticut.

formed to the mole number change (*i. e.*, moles of ethylene formed by reaction (3) is 2.19 ± 0.02; at an ethylene/ketene ratio of 0.4 this value drops to 1.94 ± 0.04; and when the ethylene/ketene ratio is 1.0, a value of 1.71 ± 0.04 is obtained.

The evidence of these experiments definitely rules out reaction 2, and we must conclude that methylene radicals do not undergo an association reaction but react with ketene or with ethylene under the conditions of our experiments. One of the writers is happy to offer his apologies to Professor Norrish for having once opposed this conclusion. Our data show further that reactions of methylene with ketene and with ethylene are both of the same order, *i. e.*, either both involve three-body collisions or both do not; and that wall effects do not influence the reaction to any major extent.

While in the presence of relatively high concentrations of ketene and low concentrations of methylene, the association reaction of methylene is negligible, under more favorable conditions the association reaction may become the dominant reaction. We believe that in the recent work of Norrish and Porter[1g] the decrease in methylene concentration with time was largely via association. Their calculated half-lives on the basis of first order disappearance vary by a factor of ten; but excellent agreement with a second-order reaction mechanism is obtained, especially from the second series of their data. The data from the first series scatter so badly that no choice of order can be made. For the following calculation we shall use the second order rate constant from the first series, however, because only for this series is sufficient background data presented in the paper.

Assuming that methylene radicals are quantitatively removed from the gas stream by the tellurium mirror[6] and using mirror removal times corresponding to distances up to 75 cm., we find for the recombination rate constant $2 \times 10^{-11}$ cc./molecule, sec. compared to a collision number of $2 \times 10^{-10}$ cc./molecule, sec. Thus ignoring the possibility of a second order wall reaction under the conditions of the Norrish experiment, methylene recombination without a three-body collision requirement apparently occurred in their work, *i. e.*, at a pressure of 1.5 mm. ketene. It may be noted that the Absolute Rate Theory[7] predicts a value of $2 \times 10^{-11}$ cc./molecule, sec. for the recombination of methyl radicals at 300°, if the transmission coefficient is taken as unity.

To evaluate the rate constant of the reaction of methylene with ketene we may tentatively assume that under the conditions of Norrish's work the quantity of methylene reacting via reaction 2 was at least a factor of four greater than that reacting via reaction 3, whereas under the conditions of the present work, the quantity of methylene reacting via reaction 3 was greater by at least a factor of four than that reacting via reaction 2. We therefore have the two inequalities

(Norrish and Porter) $k_2(\mathrm{CH_2})^2 > 4k_3(\mathrm{CH_2})(\mathrm{CH_2CO})$
This work $4k_2(\mathrm{CH_2})^2 < k_3(\mathrm{CH_2})(\mathrm{CH_2CO})$

In the Norrish work the ratio of methylene to ketene was of the order of $10^{-5}$, which, coupled with the above calculated $k_2$, leads to a $k_3 < 0.5 \times 10^{-16}$ cc./molecule, sec. At the lowest ketene concentration used in the present work, $I_{\mathrm{abs}}$ was $10^{14}$ molecules/cc. sec. Applying the steady state condition in ketene, $I_{\mathrm{abs}} = k_3(\mathrm{CH_2})(\mathrm{CH_2CO})$, gives $k_3 > 1.0 \times 10^{-16}$ cc./molecule, sec. We regard the slight inconsistency as well within the combined uncertainties of the calculations[6] and conclude that the absolute value of the rate constant $k_3$ for methylene–ketene reaction, is of the order of $10^{-16}$ cc./molecule, sec. This value is consistent with the observations of Pearson[1d] and Norrish[1g] on the longest lifetime of methylene radicals in the presence of ketene and at such low methylene concentrations that association was negligible.

The virtual temperature independence of the previously discussed ratio $R$ indicates that the activation energies of the reactions of methylene with ketene and with ethylene are nearly identical. The ratio of these rate constants ($k_4/k_3$), on the basis of equation 2 and Fig. 2, has the value 2.5. The same ratio is obtained for the rate constant of the reaction of propylene with methylene from Fig. 3. Thus not only the activation energies of these three reactions but also their frequency factors are almost identical. This is a rather surprising and somewhat improbable coincidence if the products of the elementary reactions are: ethylene and carbon monoxide in reaction 3; propylene in reaction 4; butene in the reaction with propylene, because the structures of the various critical complexes are quite different. Instead, the near identity of the rate constants suggests a very similar type of reaction to be occurring in all three cases. Such is the case if the first elementary step in all three cases is the formation of diradicals: $\dot{\mathrm{C}}\mathrm{H_2CH_2}\dot{\mathrm{C}}\mathrm{O}$, $\dot{\mathrm{C}}\mathrm{H_2CH_2}\dot{\mathrm{C}}\mathrm{H_2}$ and $\dot{\mathrm{C}}\mathrm{H_2CH_2}\dot{\mathrm{C}}\mathrm{HCH_3}$. The formation of these diradicals is also indicated by several observations, one of which is the imperfect agreement between predicted and observed effect of ethylene/ketene ratio on the rate of carbon monoxide production. A second is the inconstancy of the ratio of rate constants $k_4/k_3$, which varies experimentally from 2.3 at very low ethylene concentrations to 3.1 when the ethylene/ketene ratio is raised to 1.0. As will be shown, both these discrepancies can be quantitatively explained on the basis of diradical formation.

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(6) This assumption is made by Norrish in calculating the absolute concentration of methylene. An application of the diffusion equation indicates that under the conditions of the Norrish experiments an average methylene molecule traveled along the tube approximately 3 mm. between wall collisions. Thus unless reaction occurred on every collision the assumption is in error and the below-calculated rate constant is an upper limit to the true value.

(7) Glasstone, Laidler and Eyring, "Theory of Rate Processes," McGraw Hill Book Co., Inc., New York, N. Y., 1941, p. 260.

Glass bulbs containing irradiated mixtures, with ketene removed by absorption in sodium hydroxide, usually had the sharp odor characteristic of acrolein. The quantity of this material was quite small because the work of Rosenblum[1f] has shown that the decomposed ketene can be quantitatively accounted for by carbon monoxide and hydrocarbons formed. However, under exposure of ketene to the full radiation of the lamp, a copious deposit of brownish polymer was always obtained. Subjected twice to microanalysis, the composition was found to be $C_{2.6-3.3}H_{2.2-3.7}O$ which may be that of polymerized acrolein $C_3H_4O$, in view of the difficulties in recovering the material for analysis. The polymer was removed by treatment with warm aqueous alkali, whereupon it peeled from the wall as a film. In Pyrex cells also, a slight deposit of a colorless polymer under irradiation at higher fractional decompositions and higher ethylene/ketene ratios was noted (*cf.* also 1*f*). This polymer was unaffected by warm alkali, and it was necessary to submit it for analysis together with a large weight of the glass surface on which it formed. The composition found was $C_{3.7}H_{9.4}O$ (water adsorbed on the glass and not removed by previous heating is included in this analysis and the composition can be written as $CH_2(H_2O)_{0.27}$.)

The strongest evidence for rather complex secondary reactions is provided by mass spectrographic analyses on several irradiated samples, carried out by the staff of the Shell Development Company.[4] Table I summarizes the preparation and analyses of these samples. In sample no. 3 the analysis indicates more carbon in the hydrocarbon fraction than in the carbon monoxide fraction. This inconsistency is fully explained by the presence in the initial ketene of 0.5% ethylene impurity.

TABLE I

MASS SPECTROGRAPHIC DATA (VOLUME %)

| Sample no. → | | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| Initial ketene pressure, mm. | | 300 | 280 | 120 | 175 | 300 |
| Initial ethylene pressure, mm. | | 300 | 0 | 0 | 175 | 300 |
| Time of irradiation, sec. | | 0 | 360 | 250 | 1000 | 530 |
| Pressure rise, mm. | | | | 5.3 | | |
| Pressure of CO removed, mm. | | | 30 | Not removed | 50 | Not removed |
| Decomposition, % | | 0 | 10 | 10 | 30 | 10 |
| NaOH wash | | Yes | Yes | Yes | Yes | Yes |
| Drierite drying | | Yes | Yes | No | Yes | No |
| Mol. wt. | Constituent (mole %) | | | | | |
| 28 | $C_2H_4$ | 99.9 | 80 | 26 | 92.6 | 85.5 |
| 42 | $C_3H_6$ | | 11.8 | 5 | 6.4 | 3.8 |
| 56 | $C_4H_8$ | | 3.8 | 0.5 | 0.6 | 0.2 |
| 70 | $C_5H_{10}$ | | 0.4 | .1 | .2 | |
| 84 | $C_6H_{12}$ | | .02 | | | |
| 68 | $C_5H_8$ | | .1 | | .01 | .2 |
| 82 | $C_6H_{10}$ | | .02 | | | |
| 16 | $CH_4$ | | .04 | | .03 | .05 |
| 30 | $C_2H_6$ | | 1.5 | .7 | .02 | |
| 44 | $C_3H_8$ | | 2.2 | .3 | .13 | .1 |
| 58 | $C_4H_{10}$ | | 0.15 | | .15 | |
| 2 | $H_2$ | | | | | .02 |
| 28 | CO | | | 68 | | 9.5 |
| 40 | $C_3H_4$(?) | | | 1.5 | | |
| 46 | $C_2H_5OH$(?) | | | | | 0.1 |
| 56 | $C_3H_4O$(?) | | | 0.15 | | |
| 42 | $C_2H_2O$(?) | 0.1 | | | | 0.3 |
| | Corrected Hydrocarbon | | | | | |
| | $C_2H_4$ | | 80 | 79 | 93 | 96 |
| | $C_3H_6$ | | 9 | 9 | 6 | 4 |
| | $C_4H_8$ | | 5 | 2 | 0.6 | 0.2 |
| | $C_5H_{10}$ | | 0.5 | 0.5 | .2 | |
| | $C_6H_{12}$ | | 0.02 | | | |
| | $C_5H_8$ | | 0.1 | | .01 | 0.2 |
| | $C_6H_{10}$ | | 0.02 | | | |
| | $C_2H_6$ | | 2 | 3 | .02 | |
| | $C_3H_8$ | | 3 | 1 | .1 | 0.1 |
| | $C_4H_{10}$ | | 0.2 | 0.1 | | |
| | $C_3H_4$ | | | 6 | | |

Space considerations permit neither a discussion of these analyses in the detail their quality deserves nor a point by point justification of secondary reactions outlined below. Therefore only the major divergencies from the simple reaction mechanism previously discussed will be noted. Extrapolation to the initial instant of irradiation in pure ketene by means of the various rate constants shows the hydrocarbon fraction of the irradiation products to be about 80% ethylene, 10% propylene, and rapidly decreasing fractions of higher hydrocarbons, rather than 100% ethylene as previously postulated.[8] Irradiation of ethylene–ketene mixtures shows a smaller conversion of ethylene to propylene than predicted from the simple mechanism. Small amounts of higher volatile hydrocarbons are formed and from the hydrocarbon–carbon monoxide balance it is evident that some methylene has disappeared from the gas phase without formation of gaseous hydrocarbon. This fraction is initially quite small but rapidly grows as the percentage decomposition of ketene increases. Changes of total pressure have no effect on these findings.

A detailed mechanism which accounts for almost all observations made, but which of course is not thereby proven, is given below (* denotes diradical)

Major Reactions

1. $CH_2CO + h\nu \longrightarrow CH_2^* + CO$
2. $CH_2CO + CH_2^* \longrightarrow CH_2CH_2CO^*$
3. $C_2H_4 + CH_2^* \longrightarrow CH_2CH_2CH_2$
4. $M + (CH_2)_2CO^* \longrightarrow C_2H_4 + CO + M$
5. $M + (CH_2)_3^* \longrightarrow C_3H_6 + M$

Minor Reactions

6. $CH_2CO + (CH_2)_nCO^* \longrightarrow (CH_2)_{n+1}CO^* + CO$
7. $CH_2CO + (CH_2)_n^* \longrightarrow (CH_2)_{n+1}\,CO^*$
8. $C_2H_4 + (CH_2)_nCO^* \longrightarrow (CH_2)_{n+2}CO^*$
9. $C_2H_4 + (CH_2)_n^* \longrightarrow (CH_2)^*_{n+2}$
10. $M + (CH_2)_nCO^* \longrightarrow (CH_2)_n + CO$
11. $M + (CH_2)_n^* \longrightarrow (CH_2)_n$
12. $CH_2CH_2CO^* \longrightarrow CH_2{=}CHCHO$

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[8] This accounts in a semiquantitative fashion for the observed ratio of carbon monoxide to "ethylene" of 2.19 in decomposition of pure ketene.

To account for the results, M must represent both ethylene and ketene, so that it is necessary to postulate that the same reaction "partners" undergo two kinds of reaction, one of which, the rearrangement of the diradical into a stable molecule, is about ten times faster than the polymerization reaction. The above scheme does not explain why a non-volatile polymer is formed only at higher fractional decompositions.

Another puzzling aspect is the absence of lower cycloparaffins which would be expected, rather than the polymer, on the basis of reported behavior of polymethylene diradicals.

Notwithstanding these uncertainties, we believe that the formation of lower diradicals is well established by the experimental results. On the basis of this, a lower limit to the energy change in the reaction $CH_3 \rightarrow CH_2 + H$ can be established by the not unreasonable assumption that the energy change of the reaction $CH_3CH_2CH_3 \rightarrow \cdot CH_2CH_2CH_2\cdot + 2\ H$ is equal to twice the energy change[9] of the reaction $CH_3CH_3 \rightarrow CH_3CH_2 + H$. Coupling this assumption with the fact that the energy change in the reaction: $CH_2 + C_2H_4 \rightarrow CH_2CH_2CH_2$ cannot be more endothermic than the upper limit of the activation energy for the reaction (8 kcal./mole based on a rate constant of $10^{-16}$ cc./molecule sec.), we may set forth the equations

$$CH_2 + C_2H_4 \longrightarrow (CH_2)_3 \qquad \Delta E = E_{(CH_2)_3} - E_{CH_2} - E_{C_2H_4} < 8 \text{ kcal./mol.}$$

$$(CH_2)_3 + 2H \longrightarrow C_3H_8 \qquad \Delta E = E_{C_3H_8} - E_{(CH_2)_3} - 2E_H = 2 \times -100$$

$$CH_4 \longrightarrow CH_3 + H \qquad \Delta E = E_{CH_3} + E_H - E_{CH_4} = 102$$

$$CH_3 \longrightarrow CH_2 + H \qquad \Delta E_x = E_{CH_2} + E_H - E_{CH_3} = E_x$$

Summing:

$$E_x > 71 \text{ kcal./mole}$$

Thus the energy change of the dissociation of the second hydrogen atom from methane has a minimum value of 71 kcal./mole. Its true value is appreciably higher because the calculation implied that the trimethylene radical dissociates into ethylene and methylene without any activation energy. The present kinetic data, however, show that it has a reasonably long life and therefore the measured value of 8 kcal. is largely, if not wholly, a true activation energy. Thus the energy of formation of methylene by dissociation of a methyl radical is of the order of 80 kcal. or even higher, a value which is in reasonable agreement with Voge's theoretical estimate[10] of 90 kcal.

Determinations of quantum yield[1b] have given values below and near unity dependent on the wave length of the absorbed radiation, whereas the reaction of methylene with ketene should require a quantum yield of two. We are thus dealing, in the case of ketene, as pointed out by Norrish,[1c] with two alternative primary photochemical processes, only one of which yields free methylene radicals.

## Summary

An investigation has been carried out by manometric and analytical methods of the initial stages of decomposition of ketene, alone and in the presence of ethylene, propylene or carbon dioxide, under irradiation by the 3000–3700 Å. spectral region of a mercury arc. It has been definitely established that methylene diradicals, initially formed, react with ketene, ethylene and propylene, but do not undergo association reaction under the chosen experimental conditions. The absolute rate constants of these reactions, as well as that of the association reaction, have been deduced by combining the present data with those of a recent investigation of Norrish. From a more detailed investigation of the products of the reaction it is shown that the first elementary step, in the reaction of methylene with the three investigated compounds, is the formation of diradicals. The most probable secondary reactions of these diradicals are indicated. The energy change in the reaction $CH_3 \rightarrow CH_2 + H$ is estimated as 80 kcal.

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(9) Andersen, Kistiakowsky and Van Artsdalen, *J. Chem. Phys.*, **10**, 305 (1942).

(10) Voge, *ibid.*, **16**, 984 (1948).