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Reactions of Free Methylene: Photolysis of Ketene in Presence of Other Gases[1,2]

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Photolysis of ketene at constant concentration in the temperature range 27 to 412° was used as a constant rate source of free methylene radicals. Detailed analyses of the products from both pure ketene and ketene with added gases are reported. Studies with added H_2 and D_2 indicate that reactions of the type $CH_2 + H_2 \rightarrow CH_4$ (15) and $CH_2 + D_2 \rightarrow CH_2D_2$ (16) proceed even at room temperature with the activation energy small but definitely not zero; $r_{15}/r_{16} \simeq 1.5$ for equal concentrations of H_2 and D_2 at room temperature. Photolysis of mixtures containing acetone cannot be interpreted in support of a reaction between unexcited CH_2 and CH_3 to yield C_2H_2. A redetermination of the relative reaction rates of $CH_3 + (CH_3)_2CO \rightarrow CH_4 + CH_3COCH_3$ (35) and $CH_3 + CH_3 \rightarrow C_2H_6$ (13) as a function of temperature yields $E_{35} - {}^1/_2E_{13} = 9.8 \pm 0.4$ kcal.; $a_{35}/a_{13}{}^1/_2 = 1.1 \times 10^{-7}$. From studies with CD_4, evidence is offered in support of the one-step reaction $CH_2 + CD_4 \rightarrow CH_2D_2 + CD_2$ (21). In such work ethanes are produced at room temperature by some reaction other than 13. Comparison of various yields and consideration of the reaction $CH_2 + CH_2CO \rightarrow C_2H_4 + CO$ (5) gives $E_{21} - E_5 = 0.9$ kcal. and $a_5/a_{21} = 1.4$. Excited methylene plays no significant role in photolysis of ketene. In general, the results suggest that, under the conditions of the Wiener–Burton electric discharge through methane, the effective kinetic temperature was low.

1. Introduction

In a study of effects of electric discharge through methane at atmospheric pressure, Wiener and Burton[3] found that CH_2 was the dominant free radical present and that a major portion of the important reactions involved that free radical. Typical reactions described were a one-step addition to molecular hydrogen (also described previously by Bawn and Milstead[4]), a metathetical reaction with methane involving shift of a pair of hydrogen atoms in a single step, and a complicated reaction with free methyl, resulting in a presumed unstable free ethyl radical. The temperature of the discharge region itself was not known but a rather primitive calculation indicated that the few molecules in the region around an excited free methyl radical could not have attained a temperature greater than 1100°K.

The work herein reported was undertaken to elucidate the reactions of free CH_2 radicals and, thus, if possible, to shed more light on the mechanism of electric discharge reactions.

2. Experimental

2.1. **Materials.**—Ketene was prepared according to a modification of the Fisher–Maclean–Snizer procedure[5] (Peytral method[6]). Acetic anhydride (Eimer and Amend, "TP") was distilled in a column equivalent to 20 theoretical plates and the middle fraction boiling at 139.6° was collected. The pure anhydride was then boiled in a current of dry oxygen-free nitrogen at a pressure slightly greater than atmospheric. The distillate was passed into the upper end of an annular reaction vessel mounted vertically and made of Pyrex glass having an outer diameter of 20 mm. and an inner one of 12 mm. This pyrolysis chamber was similar to that of Fisher, *et al.*,[5] except that Pyrex glass was used instead of quartz and that the temperature was maintained at 400 to 410°. The reaction vessel was surrounded by a manually controlled electric furnace and the temperature as recorded by a thermocouple varied ±5° in the region of the vessel within the furnace. The current of nitrogen helped to keep the residence time in the pyrolysis chamber small. The vapors were swept directly into a short vertical condenser packed with glass helices and cooled to −45° by melting chlorobenzene and maintained at this temperature by addition of solid carbon dioxide. The condensate, comprising virtually all the acetic acid and unreacted anhydride, flowed into a large trap cooled to −80° where it was frozen out and thus removed. Since the reverse reaction between acetic acid and ketene to form acetic anhydride is rather rapid,[5] the contact time of gas and liquid was kept as small as possible by use of very short lengths of path. The effluent gases then flowed through a trap cooled in liquid nitrogen; the ketene condensed therein and the nitrogen gas and other non-condensables were allowed to es-

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[1] Contribution from the Radiation Project of the University of Notre Dame, supported in part under Atomic Energy Commission contract AT(11-1)-38 and Navy equipment loan contract Nonr-06900.

[2] Part I of this paper was presented before the Division of Physical and Inorganic Chemistry, national meeting of the American Chemical Society, Cincinnati, Ohio, April 6, 1955.

[3] H. Wiener and M. Burton, THIS JOURNAL, **75**, 5815 (1953).

[4] C. E. H. Bawn and J. Milstead, *Trans. Faraday Soc.*, **35**, 889 (1939).

[5] G. J. Fisher, A. F. Maclean and A. W. Snizer, *J. Org. Chem.*, **18**, 1055 (1953).

[6] E. Peytral, *Compt. rend.*, **193**, 1199 (1931).

cape through a mercury bubbler. The trap containing ketene was isolated from the rest of the apparatus and dissolved gases were removed by a series of successive melting, freezing and pumping processes. In the final purification, the ketene was allowed to distil under its own vapor pressure at −118° (ethyl bromide mush) into two successive traps cooled to −140° (14% *trans*-dichloroethylene + 20% chloroform + 21% trichloroethylene + 45% ethyl bromide) and liquid nitrogen temperature, respectively. The distillation was repeated with the ketene which had collected in the trap at −140°.

The purity of the ketene was established by analysis using a Consolidated Analytical Model 21-103A mass spectrometer with an ionizing potential of 70 volts. Non-occurrence of 27 and 44 peaks showed absence of ethylene and carbon dioxide, respectively. A small peak at 43 represented a contribution of the C^{13} isotope. Non-occurrence of higher peaks showed absence of diketene, acetone, acetic acid, acetic anhydride, C_3 and higher hydrocarbons. Vanishingly small peaks were observed from 30 to 39 inclusive.[7] A very small peak of mass 16 was not due to methane, for the ketene was completely absorbed by potassium hydroxide leaving no residual gases as determined by a microgas buret.

Deuterium (Stuart Oxygen Company) and hydrogen (Matheson, "Research grade, Electrolytic") were passed slowly through traps cooled in liquid nitrogen before use. Mass spectrometric analysis showed them to be essentially pure.

Acetone (reagent grade) was distilled through a Todd fractionation still of about 25 theoretical plates. The middle fraction of about 200 ml. was collected (take-off ratio 1:40 over a 30-hour period) and dried with a mixture of anhydrous cupric sulfate and anhydrous magnesium sulfate. By repeated processes of freezing, pumping and melting, dissolved air was removed. The acetone was allowed to boil at reduced pressure and the middle-third fraction collected and stored. Mass spectrometric analysis was used to check the purity of the material.

Impure methane-d_4 (Tracerlab, Inc.) was condensed in liquid nitrogen and fractionated, yielding material consisting of 99.22% methane-d_4 and 0.77% methane-d_3, established mass spectrometrically.

2.2. **Light Source.**—A Hanovia "L" mercury burner operating at 135 v., 2.8 amp. and 400° was used as the source of illumination. The lamp gives a high intensity band spectrum characteristic of the high pressure quartz mercury arc. The photochemically important lines from this lamp extend from the short ultraviolet at 1849 Å. to the long ultraviolet at 4045 Å., except that the resonance lines are reversed and not present. The lamp was mounted horizontally in a T shaped metal housing provided with adequate ventilation. The light escaped horizontally through the leg of the T, a cylinder about 4.5 cm. in diameter and 8 cm. in length. Optical alignment of the cylinder, the aperture (and its shutter) and the window of the reaction vessel tended to give a fairly well collimated beam of light falling on the latter. The lamp was turned on 20 minutes prior to an exposure. The lamp intensity (as measured by a photocell) did not vary over ±5% during the entire course of the investigation.

2.3. **Reaction System.**—The reaction vessel was made of quartz and was cylindrical in shape, 12.5 cm. long and 2.4 cm. i.d. The light entered through a plane fused-quartz window (with sharp optical cut-off at 2100 Å.) sealed to one end while the other end was joined *via* a 3.0 mm. quartz tube, graded seal and a Pyrex tube to the rest of the apparatus. The reaction vessel was mounted horizontally within an aluminum block furnace provided with a shutter and a window of two quartz plates slightly separated from each other. The whole furnace was surrounded by a brass cylinder for protection from drafts. The furnace was heated electrically and temperature was controlled by a Brown pyrometer regulator. Temperatures were measured with an iron–constantan thermocouple. The temperature gradient over the length of the reaction vessel was about 1° at 412°. The light filled the whole of the reaction vessel. The reaction volume was 58.88 ml. and that of the dead space was 0.62 ml.

2.4. **Procedure.**—The various gases were admitted individually into a mixing vessel whose volume was accurately known. Pressures were read on a wide-bore mercury manometer. Mixing was effected by the repeated raising and lowering of mercury in the mixing vessel. The mixture was then forced into the reaction vessel, now illuminated (shutter open prior to the introduction of gas) and maintained at the desired temperature. The process of transfer took about 5 seconds. After photolysis for precisely 15 minutes, the shutter was closed, the mixture withdrawn into a Saunders–Taylor type of apparatus[8] and the total amount of gas measured.

After each run the reaction vessel was removed, cleaned in hot concentrated nitric acid, rinsed several times with distilled water and dried at 120°. It was then reattached to the apparatus (geometric reproducibility being maintained), the temperature of the furnace raised to 450°, and the cell pumped to a high vacuum overnight.

2.4.1. **Part I. Hydrogen or Deuterium Added.**—Preliminary runs performed in the temperature range 27 to 412° showed there was no thermal reaction of the ketene and of ketene–deuterium mixtures except for very slight polymerization of the ketene at higher temperatures.[9] Since it was thought that mercury vapor in the system might cause sensitization during a photolysis, a number of mixtures of hydrogen and deuterium, made according to the same procedure employed in the ketene runs, were exposed to radiation at various temperatures. No observable HD was formed; the result showed that mercury photosensitization did not occur to any measurable extent.

2.4.2. **Part II. Acetone Added.**—In preliminary work, pure acetone was photolyzed over the temperature range 27 to 412° in runs of precisely 15 minutes. In the mixture experiments, ketene and acetone, at equal concentrations, were similarly treated.

For establishment of any thermal dark-reaction effects, mixtures of acetone and ketene were introduced into the reaction vessel and allowed to remain for 15 minutes. At the lower temperatures there was no measurable reaction; at 412°, a very small amount of CH_4 was formed from the thermal decomposition of acetone and there was very slight polymerization of ketene.

2.4.3. **Part III. Methane-d_4 Added.**—The procedure was routine; it involved no special features.

2.5. **Analysis.**—All analyses were mass spectrometric. A small portion from each sample volatile at −78° was analyzed directly with a Consolidated Analytical Model 21-103A mass spectrometer with ionizing potential at 70 v. For assistance in interpretation of patterns, the remainder of each sample was fractionated into portions volatile at −195, −140, −120, −78° and room temperature; the individual patterns were then analyzed. Analyses were performed immediately after completion of the runs.

The mass spectrometer was calibrated with pure samples of CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, butane, isobutane and butylenes. Acrolein, diketene, diacetal, acetonylacetone and acetylacetone, which were obtained commercially, were distilled at low pressure and, after suitable condensation, were likewise employed for spectrometer calibration. Analysis for the deuterated methanes and deuterated ethylenes was based on results of Dibeler and Mohler[10] and of Dibeler, Mohler and de Hemptinne,[11] who used a similar mass spectrometer. Spectra for the deuterated ethanes were calculated according to the method of Schissler, Thompson and Turkevich.[12] In Part III, due to lack of precise knowledge of sensitivities and over-all approximations, the yields for the various ethanes are in error to the extent of about 30%. Also in Part III, since CD_4 is in such excess compared to the yields of the other methanes and since differences between large peak heights were utilized in analysis, the values for the other methanes are accurate only to about 15%. For other compounds conventional procedures were employed.[13]

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[7] *Cf.* F. A. Long and L. A. Friedman, This Journal, **75**, 2837 (1953).

[8] K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, **9**, 616 (1941).

[9] *Cf.* A. N. Strachan and W. A. Noyes, Jr., This Journal, **76**, 3258 (1954), for observations up to 175°. They report a slow polymerization, negligible during their runs.

[10] V. H. Dibeler and F. L. Mohler, *J. Research Natl. Bur. Standards*, **45**, 441 (1950), and a private communication March 10, 1954.

[11] V. H. Dibeler, F. L. Mohler and M. de Hemptinne, *ibid.*, **53**, 107 (1954).

[12] D. O. Schissler, S. O. Thompson and J. Turkevich, *Disc. Faraday Soc.*, **10**, 46 (1951).

[13] Mass Spectral Data: American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa.

3. Results

In this work, only the gaseous products were measured. Polymer, such as described by other authors, was produced—particularly at the higher temperatures. It was cleaned out of the reaction vessel without measurement, after each run. In all experiments at higher temperatures, acrolein ($CH_2{=}CHCHO$) was produced in trace quantities.[14]

3.1. Effect of Temperature in Photolysis of Ketene.—The results obtained in this background portion of the work are summarized in Table I in which the initial concentrations of ketene are in the ratio 0.5:1:2. They are in substantial agreement with those of Knox, Norrish and Porter.[15] Yield of CO for a given light energy input is more than doubled in the range 27 to 412°, while that of C_2H_4 goes up by a factor of roughly 1.8. At lower temperature CO_2 is absent; at higher temperature it is formed to almost one fourth the extent of CO. Acetylene is formed at 27° with very small yield; at 412° the C_2H_2 yield has increased by a factor of the order of 10 but is very far below the CO_2 yield. Methane like C_2H_2 is formed at 27° and its yield increases by about the same factor; the yield is always low. Some ethane is produced at low temperature but the yield drops as the temperature is raised. The yield of ketonic compounds and higher hydrocarbons increases with increasing temperature.

TABLE I

ANALYSIS OF GASEOUS PRODUCTS FROM PHOTOLYSIS OF PURE KETENE

Initial concentrations are in units of 10^{-7} mole/ml.; yields are in units of 10^{-8} mole ml.$^{-1}$.

$[CH_2CO]_0$			Temp., °C.				
			27	99	200	298	412
(a)	19.37	CO	14.01	16.82	21.07	28.32	37.21
		C_2H_4	6.36	7.87	8.81	10.18	12.84
		CO_2	0	0.40	1.00	2.08	6.73
		C_2H_2	0.03	0.10	0.32	0.53	0.87
		C_2H_6	0.29	0.20	0.12	0.09	0.07
		CH_4	0.18	0.28	0.49	0.88	1.63
		Ketonic compd. and higher hydrocarbons	0.6	1.2	1.8	2.4	3.8
(b)	38.74	CO	20.11	24.01	31.06	41.14	53.07
		C_2H_4	9.20	10.81	12.48	14.32	16.06
		CO_2	0	0.51	2.14	4.98	13.45
		C_2H_2	0.080	0.171	0.392	0.695	1.000
		C_2H_6	0.410	0.276	0.212	0.152	0.098
		CH_4	0.23	0.422	0.841	1.330	2.420
		Ketonic compd. and higher hydrocarbons	0.9	1.6	2.7	4.3	8.3
(c)	77.48	CO	29.93	34.99	40.82		78.70
		C_2H_4	14.19	15.28	16.65		18.65
		CO_2	0	0.61	2.30		20.51
		C_2H_4	0.76	1.21	1.82		4.08
		C_2H_6	0.71	0.41	0.30		0.18
		CH_4	0.34	0.62	1.48		5.69
		Ketonic compd. and higher hydrocarbons			Not measured		

3.2. Ketene, Hydrogen and Deuterium.—Table IIa shows the effect of temperature in the photolysis of ketene in the presence of H_2 and D_2. The total initial concentration of the latter two equaled that of the ketene. As compared with the results in the absence of these added gases (*cf.* Table Ib) over-all decomposition is increased with substantially increased CO and C_2H_6 and decreased CO_2 production. The C_2H_4 yield appears to be somewhat smaller. The trends with temperature are, however, as in the absence of added H_2 and D_2.

Interesting points are the production of $C_2H_4D_2$ (but no C_2H_5D), CH_4 and CH_2D_2 even at 27°. Both the latter were expected from the results of Wiener and Burton but the production at 27° is especially interesting. On the other hand, CH_3D is found first at 99° and, in increasing yield, at higher temperatures. Notably, HD production is first observed at 298°. Yield of ketonic compounds and higher hydrocarbons is substantially cut below that found in the absence of H_2 or D_2.

3.3 Ketene and Deuterium.—Table IIb, c, d summarizes the results for the photolysis of ketene in the presence of deuterium. It is noteworthy that the CO and C_2H_4 yields in Tables IIb and IId are similar to those shown in Table IIa. Their distinctive feature is that $C_2H_4D_2$ is formed in relatively large amount (decreasing slightly as the temperature is raised) but that C_2H_6 is not formed at all. Increased D_2 concentration favors increased production of $C_2H_4D_2$ and also of CH_2D_2; it has but modest effect on CH_3D yield. The yield of CH_4 is reduced substantially below the little shown in Tables Ia and b, respectively (*i.e.*, in the absence of hydrogen or deuterium); interestingly, CH_4 production is observed first at 99°. The yield of CH_4 at 412° is substantially the same for all experiments in which H_2 was initially absent; however, there seems to be a slight depressant effect of D_2 concentration on CH_4 yield even at that temperature.

The yields of ketonic compounds and higher hydrocarbons are notably reduced by the presence of either hydrogen or deuterium; the effect seems to be very roughly a function of the concentration of the added gases.

3.4. Photolysis of Acetone.—Table III summarizes results on the photolysis of acetone. They are in substantial agreement with results based on less detailed product analysis reported by the Steacie and Noyes schools. Features of particular interest are formation of ethylene at 99° and of ketene at 298°. Recently Ausloos and Steacie[16] reported ketene production at 27° on prolonged irradiation but our runs apparently were too short to produce such a result.

The fraction not volatile at −78° was too complicated for precise analysis. However, a room temperature (27°) photolysis definitely yielded detectable amounts of acetaldehyde and biacetyl in that fraction. These two substances could not be identified in the products of the photolysis at 99° and higher. Acetonylacetone, diacetone and methyl ethyl ketone were produced in quantities that increased with rise in temperature from 99 to 412°. The values reported for methyl ethyl ketone in Table III are accurate to within 25%. The rate of production of acetonylacetone plus diacetone was of the same order as that of methyl ethyl ketone.

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(14) *Cf.* G. B. Kistiakowsky and N. W. Rosenberg, THIS JOURNAL, **72**, 321 (1950).

(15) K. Knox, R. G. W. Norrish and G. Porter, *J. Chem. Soc.*, 1477 (1952).

(16) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 47 (1955).

TABLE II

ANALYSIS OF GASEOUS PRODUCTS FROM PHOTOLYSIS OF KETENE MIXTURES

Initial concentrations and yields are in same units as in Table I.

$[CH_2CO]_0$	$[H_2]_0$	$[D_2]_0$	Temp., °C.	27	99	200	298	412
(a) 38.74	19.37	19.37	CO	29.61	32.11	42.03	58.44	91.46
			C_2H_4	8.82	9.85	11.11	13.06	14.97
			CO_2	0	0.22	1.61	3.63	9.44
			C_2H_2	0	.04	0.10	0.17	0.31
			C_2H_6	1.13	.96	0.88	0.78	0.68
			$C_2H_4D_2$	0.79	.73	0.69	0.63	0.60
			CH_2D_2	0.08	.20	0.45	0.80	1.44
			CH_3D	0	.06	0.45	2.04	4.80
			CH_4	0.12	.44	1.31	4.81	11.93
			HD	0	0	0	0.15	4.00
			Ketonic compd. and higher hydrocarbons	0	0.2	0.5	2.2	4.7
(b) 38.74		38.74	CO	28.84	31.21	39.06	49.52	89.20
			C_2H_4	8.85	9.85	11.60	13.10	15.06
			CO_2	0	0.25	1.51	3.07	9.12
			C_2H_2	0	0.04	0.11	0.20	0.31
			$C_2H_4D_2$	1.62	1.43	1.24	1.05	0.93
			CH_2D_2	0.31	0.40	0.92	2.13	3.96
			CH_3D	0	0.05	0.31	1.42	4.73
			CH_4	0	0.04	0.37	1.02	2.04
			Ketonic compd. and higher hydrocarbons	0	0.2	0.5	2.3	4.7
(c) 19.37		38.74	CO	17.81	20.92	25.10	35.25	57.31
			C_2H_4	5.45	5.90	6.25	7.12	8.04
			CO_2	0	0.18	0.53	1.20	3.60
			$C_2H_4D_2$	1.56	1.39	1.20	0.96	0.86
			CH_2D_2	0.22	0.85	1.82	3.27	5.31
			CH_3D	0.01	0.04	0.34	1.08	3.84
			CH_4	0	0.03	0.20	0.54	1.05
			Ketonic compd. and higher hydrocarbons	Not measured				
(d) 38.74		77.48	CO	28.80	32.30	40.18		92.00
			C_2H_4	8.80	9.22	9.85		11.91
			CO_2	0	0.21	1.10		8.51
			C_2H_2	0	0	0.05		0.10
			$C_2H_4D_2$	2.31	2.22	2.03		1.76
			CH_2D_2	1.50	1.90	3.11		9.36
			CH_3D	0	0.06	0.40		5.11
			CH_4	0	0.04	0.32		1.52
			Ketonic compd. and higher hydrocarbons	0	0	0.5		4.6

TABLE III

RATES OF PRODUCT YIELD IN PHOTOLYSIS OF PURE ACETONE

Initial concentration 116.61 × 10^{16} molecules ml.$^{-1}$ in each case[a]; 15-minute exposures. Rates[b] of production of products in units of 10^{10} molecules ml.$^{-1}$ sec.$^{-1}$.

	Temp., °C.				
	27	99	200	298	412
CO	372	5390	7130	9750	12280
CH_4	5.4	166.7	2790	9200	21360
C_2H_6	744	5490	5000	1620	509
C_2H_4	0	40	256	502	810
CO_2	0	0	0	31.4	378
CH_2CO	0	0	0	20.3	601
$CH_3COC_2H_5$	0	10	150	300	500
r^c	0.170	1.93	33.9	196	812

[a] This concentration is 19.37 × 10^{-7} mole/ml.; *cf.* Table Ia. [b] At 27 and 99° (very small fractional decomposition) the rates are essentially the initial rates; at higher temperatures they are only approximately so—they are the average rates over 15 minutes. [c] $r = r_{CH_4}/r_{C_2H_6}{}^{1/2}((CH_3)_2CO)$ in units of 10^{-13} molecule$^{-1/2}$ sec.$^{-1}$ ml.$^{1/2}$.

Table III includes values of $r_{CH_4}/r_{C_2H_6}{}^{1/2}((CH_3)_2CO)$. The logarithm of this quantity is a linear function of $1/T$. The activation energy difference and frequency factor ratio for the reactions

$$CH_3 + (CH_3)_2CO \longrightarrow CH_4 + CH_3COCH_2 \quad (35)$$
$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad (13)$$

calculated by the method of least squares yields $E_{35} - {}^1/_2E_{13} = 9.8 \pm 0.4$ kcal., $a_{35}/a_{13}{}^{1/2} = 1.1 \times 10^{-7}$. The results may be compared with the Trotman-Dickenson and Steacie[17] values of 9.7 kcal. and 9.1×10^{-8} and the Nicholson[18,19] values of 9.6 kcal. and 8.2×10^{-8}. The results of photolysis at 27° were not used in this calculation since the production of CH_4 at low temperature probably involves other factors.

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(17) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **18**, 1097 (1950).

(18) A. J. C. Nicholson, THIS JOURNAL, **73**, 3981 (1951).

(19) In the course of this work we also examined the photolysis of acetone in the presence of D_2 in the temperature range 151 to 299°, in which case the reaction $CH_3 + D_2 \rightarrow CH_3D + D$ (38) must also be considered. We obtained $E_{38} - E_{35} = 2.3 \pm 0.5$ kcal. and $a_{38}/a_{35} = 1.7 \pm 0.4$, which values in turn thus yielded $E_{38} - {}^1/_2E_{13} = 12.1 \pm 0.6$ kcal. and $a_{38}/a_{13}{}^{1/2} = 1.8 \times 10^{-7}$; *cf.* 11.8 kcal. given by E. Whittle and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 993 (1953).

3.5. Photolysis of Ketene–Acetone Mixtures.—Table IV shows results of photolysis of ketene-acetone mixtures at various temperatures in the initial ratio 1:1. The initial concentrations were identical with those for acetone in Table III and for ketene in Table Ia. A feature of interest is the considerable yield of methyl ethyl ketone. The yields of acetylacetone and diacetone are not very different from those in the case of pure acetone photolysis, *i.e.*, very much less than that of methyl ethyl ketone in the mixtures.

3.6. Ketene and Methane-d_4.—Results of all experiments are summarized in Table V.[20] They may be best understood by reference to Table Ib.

TABLE IV

RATES OF PRODUCT YIELD IN PHOTOLYSIS OF KETENE–ACETONE MIXTURES[a]

Initial concentrations 116.61 × 10^{16} molecules ml.$^{-1}$ each; 15-minute exposures. Rates of production are in units of 10^{10} molecules ml.$^{-1}$ sec.$^{-1}$. Rates naively calculated on the assumption of no interaction between ketene and acetone or their products are given in italics.[b] The ratios (ρ) of the observed to naively expected rates are given in parentheses.

	Temp., °C. 27	99	200	298	412
CO	6920	12250	16260	21630	28610
	8850	*15000*	*19100*	*25800*	*33400*
	(0.78)	(0.82)	(0.85)	(0.84)	(0.86)
C_2H_4	3150	4050	4930	5760	7580
	3870	*4820*	*5580*	*6630*	*8520*
	(0.81)	(0.84)	(0.88)	(0.87)	(0.89)
CO_2	0	11.0	156	610	2010
	0	*243*	*608*	*1290*	*4420*
		(0.05)	(0.26)	(0.47)	(0.45)
C_2H_2	0	10.1	30.1	100	201
	18	*61*	*195*	*322*	*529*
	(0)	(0.17)	(0.16)	(0.31)	(0.38)
C_2H_6	766	3080	3280	1420	494
	830	*4950*	*4470*	*1480*	*490*
	(0.92)	(0.62)	(0.73)	(0.96)	(1.01)
CH_4	83.5	267	1844	6800	15900
	114	*317*	*2750*	*8630*	*19800*
	(0.73)	(0.84)	(0.67)	(0.79)	(0.80)
C_3H_8	0	39.9	289	1320	2540
	0	*0*	*0*	*0*	*13.2*
$CH_3COC_2H_5$	800	1018	1562	2260	3111
	0	*8.8*	*130*	*260*	*440*
		(116)	(12)	(8.7)	(7.1)

[a] *Cf.* footnotes *a* and *b* of Table IV. [b] The naive calculation involves among other assumptions the one that quantum yields are in each case independent of wave length and that the rate of formation of each of the products is proportional to the first power of the intensity. Thus the italicized values are useful only for orientation. For a more thorough investigation of this system the optical absorption of the mixture should be studied as a function of wave length and compared with the absorption expected on the basis of a no-interaction assumption. It should also be mentioned, as Professor W. A. Noyes, Jr., has pointed out to us, that the naive calculation of rates which involves also the assumption of slowly varying extinction coefficients may be considerably vitiated by the possible existence of line absorption in the absorption spectrum of acetone.

An outstanding feature is that, although C_2H_4 and CH_2CD_2 are produced during photolysis of ketene in presence of CD_4, no other mixed ethylene is produced under conditions of the study up to 412°. Absence of CH_4 from the products at room temperature is also noteworthy.

Another interesting point is that, although CH_2D_2 is produced in considerable amount at 27°, no other mixed methane is produced. This result may be compared with the fact that, at the same temperature, C_2H_6, $C_2H_4D_2$ and $C_2H_2D_4$ are produced in detectable amounts.

At the lower temperatures, the CO yield from photolysis of ketene is unaffected by presence of CD_4 even though the latter compound must surely participate in the formation of deuterated products.

4. Discussion

4.1. Photolysis of Ketene.—The major items which must be explained in the photolysis of ketene are the facts that for λ 2700 Å. the quantum yield of CO is *ca.* 2 at room temperature (decreasing at longer wave lengths) while the ratio of yields CO/C_2H_4 is *ca.* 2.2[9,13,21–24] and that higher hydrocarbons as well as compounds containing a carbonyl group are produced. Reactions necessary to explain such results have been reviewed most recently by Strachan and Noyes[9] and by Kistiakowsky and Rosenberg.[14] For convenience we write the major reactions as

$$CH_2CO + h\nu \longrightarrow CH_2CO^* \qquad (1)$$

$$CH_2CO^* \longrightarrow CH_2 + CO \qquad (2)$$

$$CH_2CO^* \longrightarrow CH_2' + CO \qquad (3)^{25}$$

$$CH_2' + CH_2CO \longrightarrow -CH_2{\cdot}CH_2{\cdot}\overset{|}{C}O \text{ or } -CH_2{\cdot}CO{\cdot}CH_2- \qquad (4)$$

$$CH_2 + CH_2CO \longrightarrow C_2H_4 + CO \qquad (5)$$

$$C_2H_4 + CH_2' \longrightarrow -CH_2{\cdot}CH_2{\cdot}CH_2- \qquad (6)$$

$$M + (CH_2)_2{\cdot}CO' \longrightarrow M + C_2H_4 + CO \qquad (7)$$

$$M + -(CH_2)_3- \longrightarrow M + C_3H_6 \qquad (8)$$

$$(CH_2)_2CO + CH_2CO \longrightarrow CO + \underset{\text{biradical}}{(CH_2)_3CO} \qquad (9)$$

$$(CH_2)_2CO + CH_2CO \longrightarrow C_2H_4 + CO + CH_2CO \qquad (10)$$

Apart from the work of Knox, Norrish and Porter,[5] there has been no detailed consideration of the mechanism of ketene photolysis at higher temperature. In their work certain reactions must be considered which can occur only at the extremely high free radical concentrations characteristic of flash photolysis.[26] They show free methyl produced by the reaction

$$2CH_2 \longrightarrow CH_3 + CH \qquad (11)$$

but it is highly improbable that in our work any significant quantity of free methyl can be formed by such a two-radical reaction. It is consistent with our results to conclude, however, that some free methyl is always produced under the conditions we employ for photolysis of pure ketene. We suggest that the reaction

$$CH_2 + CH_2CO \longrightarrow CH_3 + CHCO \qquad (12)$$

occurs to a small extent even at low temperature.

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[20] *Cf.* M. Vanpee and F. Grard, *Ann. mines Belg.*, **49**, 37 (1950), who studied the photolysis of ketene in the presence of CH_4.

[21] R. G. W. Norrish, H. G. Crone and O. D. Saltmarsh, *J. Chem. Soc.*, 1533 (1933); THIS JOURNAL, **56**, 1644 (1934).

[22] W. F. Ross and G. B. Kistiakowsky, *ibid.*, **56**, 1112 (1934).

[23] M. Vanpee and F. Grard, *Bull. soc. chim. Belg.*, **60**, 208 (1951).

[24] G. B. Kistiakowsky and W. L. Marshall, THIS JOURNAL, **74**, 88 (1952).

[25] In this series of reactions the superscript ′ is used particularly to distinguish the biradical from the unpromoted form of CH_2. In subsequent discussion (*cf.* section 4.6.3) we do not maintain this distinction.

[26] *Cf.* G. Porter, *Proc. Roy. Soc.* (*London*), **A200**, 284 (1950); *Disc. Faraday Soc.*, **9**, 60 (1950).

Table V

Photolysis of Ketene–Methane-d_4 Mixtures

Analysis of products volatile at −78°. 15 minute exposure. Initial concentration of ketene 38.74 × 10^{-7} mole ml.$^{-1}$. Yields are in units of 10^{-8} mole ml.$^{-1}$.

Temp., °C.	27°			99°	200°			298°	412°		
$(CD_4)_0$ 10^{-7} mole ml.$^{-1}$	19.37	38.74	77.48	38.74	19.37	38.74	77.48	38.74	19.37	38.74	77.48
CO	20.10	20.09	20.15	24.20	30.91	30.73	30.40	38.26	50.73	48.61	43.10
C_2H_4	8.63	8.08	7.23	9.00	11.20	10.20	8.72	11.27	14.06	12.27	9.52
CH_2CD_2	0.60	1.15	2.05	1.55	1.01	1.81	3.30	2.05	1.34	2.26	3.39
CH_2D_2	0.72	1.36	2.44	1.97	1.55	2.80	5.05	3.92	3.32	5.74	8.28
CH_3D	0	0	0	0.02	0.09	0.11	0.14	0.33	0.94	1.02	1.18
CH_4	0	0	0	0.08	0.26	0.20	0.16	0.59	2.51	1.52	1.08
CD_3H	0	0	0	0	0.03	0.07	0.12	0.21	0.68	0.75	1.24
C_2H_6	0.38	0.36	0.32	0.22	0.19	0.15	0.10	0.10	0.09	0.06	0.04
C_2H_5D	0	0	0	0.01	0.03	0.03	0.03	0.04	0.03	0.05	0.05
$C_2H_4D_2$	0.03	0.05	0.09	0.07	0.06	0.10	0.14	0.11	0.08	0.09	0.09
$C_2H_3D_3$	0	0	0	0	0.01	0.02	0.03	0.03	0.04	0.04	0.05
$C_2H_2D_4$	0.01	0.01	0.03	0.03	0.04	0.06	0.08	0.09	0.11	0.17	0.24
C_2HD_5	0	0	0	0	0.01	0.02	0.03	0.03	0.04	0.05	0.08
C_2D_6	0	0	0	0	0.01	0.03	0.05	0.09	0.11	0.16	0.27
CO_2	0	0	0	0.2	2.0	1.0	0.8	1.5	9.2	7.4	5.4

Accordingly, ethane production could result from

$$2CH_3 \longrightarrow C_2H_6 \qquad (13)$$

Decrease in yield of ethane at higher temperature could result from increased probability of competitive processes such as

$$CH_3 + CH_2CO \longrightarrow CH_4 + CHCO \qquad (14)$$

However, the kinetics are different from the usual case of a simple competition between reactions 13 and 14; if $\Delta(CH_4)$ and $\Delta(C_2H_6)$ are yields of methane and ethane, respectively, the plot of log $[\Delta(CH_4)/\Delta(C_2H_6)^{1/2}]$ *vs.* $1/T$ is not a straight line nor is the quantity $\Delta(CH_4)/\Delta(C_2H_6)^{1/2} \times [CH_2CO]$ constant at constant temperature. The significance of the relationships is discussed in section 4.4.

A variety of suggestions can be offered regarding the mechanism of formation of CO_2, but, in view of the lack of corroborative evidence, such speculation is not particularly fruitful at this time. Production of higher hydrocarbons can be explained in terms of reaction 6 and its consequences. The source of acetylene is not evident from the results on ketene alone; it is notable that the yield increases with temperature but is not of major importance even at 412° in spite of the fact that free CH_2 must be formed in significant amounts at all concentrations. The implication of this result is that if, in the work of Weiner and Burton on electric discharge in methane,[3] acetylene is produced by reaction between two free CH_2 radicals, the temperature required for the process must be much greater than 400°; they do not advance such a mechanism.

4.2. Reactions of Free Methylene with Hydrogen and Deuterium.—Photolysis of ketene in presence of hydrogen was first studied by Rosenblum.[27] Our interpretation is assisted by the use of deuterium as tracer; it is essentially different from that of Rosenblum.

Plots of the data from Table I show that in the photolysis of pure ketene, irrespective of its concentration, methane is formed even at 27° and that the yield increases rapidly with temperature. On the other hand, plots of the data from Table II show that, in those experiments where D_2 was present, no CH_4 was formed at 27°. Such plots clearly show that these differences are real, and well beyond the limits of experimental error. A reasonable interpretation is that in pure ketene CH_4 is formed from some species that is removed by deuterium. Also, as Table II shows, CH_3D is not formed at 27° in the presence of deuterium even though CH_2D_2 is formed. The observation that at 27°, in the presence of hydrogen or deuterium, the yield of C_2H_4 (which is presumably formed from CH_2) is less than that for pure ketene adds support to this interpretation of the results. Finally, in the photolysis of ketene in the presence of hydrogen and deuterium in concentration ratio 2:1:1, the yield of CH_4 at 27° is 1.5 times the yield of CH_2D_2 and no CH_3D is formed. In agreement with Wiener and Burton[3] and with Bawn and Milstead,[4] but contrary to Rosenblum,[27] we suggest the competing reactions

$$CH_2 + H_2 \longrightarrow CH_4 \qquad (15)$$

$$CH_2 + D_2 \longrightarrow CH_2D_2 \qquad (16)$$

It is improbable that CH_3D formation, which occurs only above room temperature, involves as one of the steps such two-radical processes as

$$CH_2 + D \longrightarrow CH_2D \qquad (17)$$

or

$$CH_3 + D \longrightarrow CH_3D \qquad (18)$$

An interpretation more reasonable than the assumption of reactions 17 or 18, is that either the highly endothermal reaction

$$CH_2 + D_2 \longrightarrow CH_2D + D \qquad (19a)$$

or the reaction

$$CH_3 + D_2 \longrightarrow CH_3D + D \qquad (20a)$$

(with activation energy $E_{20a} \sim 11.7$ kcal.[28]) is involved. However, CH_3D is absent from the prod-

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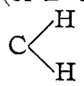
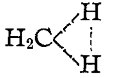
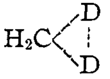
[27] C. Rosenblum, This Journal, **60**, 2819 (1938); **63**, 3322 (1941).

[28] *Cf.* T. J. Majury and E. W. R. Steacie, *Disc. Faraday Soc.*, **14**, 45 (1953).

ucts at 27°. Consequently, neither 19a nor 20a nor the analogous reactions involving H_2

$$CH_2 + H_2 \longrightarrow CH_3 + H \qquad (19b)$$
$$CH_3 + H_2 \longrightarrow CH_4 + H \qquad (20b)$$

contribute to the total methane yield at that temperature.

On the basis of simple collision theory, the ratio of the frequency factors of reactions 15 and 16 should be $(2 \times {}^{16}/_{18})^{1/2} = 1.33$, if the steric factors of the two reactions are identical.[29] The measured ratio of yields of CH_4 and CH_2D_2 at 27° in this case is 1.5, so that the conclusion is that within the limits of error the activation energy E_{15} is less than E_{16} by no more than 70 cal. The zero point energies of the reactants in reaction 15 are 1.8 kcal. greater than those of the reactants in reaction 16. The implication then is that the differences of the zero-point energies of the activated complexes for the two reactions are also nearly 1.8 kcal. This conclusion may be examined in terms of the fact that the activated complex contains more vibrational degrees of freedom than do the reactants.[30] From the fundamental frequencies[31] of CH_4 and CH_2D_2 the zero point energies of the products are calculated to be $E_0(CH_4) = 26.3$ kcal. and $E_0(CH_2D_2) = 23.4$ kcal. If the products had the same zero point energies as the activated complexes, the conclusion would be that E_{15} is greater than E_{16} by 1.1 kcal. However, a more reasonable estimate should consider that many of the frequencies characteristic of the methane molecule are not fully excited in the activated complex; on the other hand, the conversion of an H–H (or D–D) vibration into an in-plane bending of the  bonds involves a small decrease of energy. The result is that the difference of zero point energies of the activated complexes of reactions 15 and 16 is near 1.8 kcal.; *i.e.*, either the activated complex for these reactions is more nearly like the reactants than like the products or the changes which occur in the formation of the activated complex compensate each other in such a way that the zero-point energies of the complexes  and  differ about as much as the zero point energies of $CH_2 + H_2$ and $CH_2 + D_2$.

In the same set of experiments (Table IIa), the yields of CH_3D and CH_4 rise more sharply than that of CH_2D_2 with increase in temperature; this result reflects the fact that at higher temperatures, reactions such as 19a, 19b, 20a and 20b contribute with increasing importance to the yields of CH_3D and CH_4, respectively. This last point is important in regard to the results of Wiener and Burton.[3] It would appear from their work that, under the conditions of their experiments, no reaction of the general types of 19 or 20 occurs. Nevertheless, they find CH_2D_2 in electric discharge through methane–deuterium mixtures although CH_3D is not produced. A reasonable inference is that reaction 16, presumed by them, occurs under conditions of electric discharge at relatively low temperatures, that no high temperature reaction (*i.e.*, 19 or 20) can occur, and that therefore, from the kinetic viewpoint, the region of an electric discharge is an essentially low temperature region.

Part of the CH_3D and CH_4 may come also from another series of reactions suggested by the work of Weiner and Burton[3] (*cf.* section 4.6 for further confirmation), namely

$$CH_2 + CH_2D_2 \longrightarrow CH_3D + CHD \qquad (21a)$$
$$CH_2 + CH_3D \longrightarrow CH_4 + CHD \qquad (21b)$$

Absence of C_2H_3D (formed by possible interaction of CHD and CH_2CO; *cf.* reaction 5) indicates that the contribution of these processes is low relative to that of reactions 19 and 20.

At all temperatures the yield of ethylene greatly exceeds that of the mixed methane CH_2D_2 even when the deuterium concentration is twice that of ketene. The implication is that other reactions of free CH_2 (*e.g.*, 4, 5, 6) have even a lower activation energy than reaction 16; *i.e.*, while E_{16} is small, it does not approach zero.

Acetylene yield decreases in the presence of hydrogen or deuterium; the importance of reactions 15 and 16 suggests that removal of free CH_2 is responsible. The similar effect on the higher hydrocarbon and ketonic compounds yield is probably traceable to the same cause. Acetylene is formed only when CH_4 is produced. If the CH_4 is formed exclusively *via* reaction 15 (*cf.* Table IIa for a temperature of 27°), acetylene is absent nevertheless. Removal of CH_2 *via* reaction 15 prevents formation of acetylene and also prevents occurrence of reaction 14. A reasonable inference is that the entire acetylene yield is via reaction 14, *e.g.*, by the reaction

$$2CHCO \longrightarrow C_2H_2 + 2CO \qquad (22)$$

At relatively high D_2 concentration, reactions 14 and 22 (or other reactions of CHCO) are entirely, or almost entirely, prevented even at the highest temperatures.

The fact that, in photolysis of ketene in the presence of hydrogen and deuterium, yield of HD becomes detectable first at 298° suggests that exchange reactions such as

$$H + D_2 \longrightarrow HD + D \qquad (23a)$$
$$D + H_2 \longrightarrow HD + H \qquad (23b)$$

compete unfavorably with other reactions by which H or D atoms (formed by reactions of type 19 and 20) may disappear, *e.g.*, simple addition reactions of the atoms to an unsaturated link.[32]

Apparently, the back reaction

$$CH_2 + CO \longrightarrow CH_2CO \qquad (24)$$

tends (to a small degree) to limit the quantum yield of decomposition in the photolysis of ketene.[24] Consequently, presence of hydrogen or deuterium

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(29) *Cf.* A. Farkas and L. Farkas, *Proc. Roy. Soc. (London)*, **A152**, 124 (1935).

(30) *Cf.* J. Hirschfelder, H. Eyring and B. Topley, *J. Chem. Phys.*, **4**, 170 (1936); A. Wheeler, B. Topley and H. Eyring, *ibid.*, **4**, 178 (1936), who have made detailed calculations of the amount of such an effect in 3- and 4-atom reactions, respectively.

(31) *Cf.* G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 309.

(32) Suggestive traces of partially deuterated compounds were formed in the fraction labelled ketonic compounds and higher hydrocarbons.

and reactions like 15 or 16 tend to increase CO production slightly, but the effect is greater than can be expected on this basis. The increase in yield of CO under these conditions still requires explanation.

4.3. Production of Ethanes in Ketene Photolysis (Part I).—In absence of hydrogen or deuterium, C_2H_6 yield drops to very low values at 412°. In presence of deuterium (but no hydrogen), $C_2H_4D_2$ yield is high while C_2H_6 is not produced. No other mixed ethane was ever found.

Any explanation of this result should be consistent with the findings of Wiener and Burton,[3] who report no $C_2H_4D_2$ resultant from electric discharge through a mixture of methane and deuterium; under the same condition free CH_2 is stated to be the dominant free radical present. One possible explanation of the results of this work is simply the reaction of deuterium with the free radical produced in reaction 4; *i.e.*

$$D_2 + (CH_2)_2CO \longrightarrow C_2H_4D_2 + CO \tag{25}$$

in a single step as written. The yield of $C_2H_4D_2$ actually decreases with temperature and is not linearly dependent on the deuterium concentration. Perhaps, the explanation may lie in increased probability of the competitive reaction 16 with increased temperature; this view is consistent with the suggestion in section 4.2 that, while E_{16} is small, it is nevertheless greater than E_4, E_5 and E_6. The effect of deuterium concentration on the yields of ethylene (*e.g.*, *via* reactions 5 or 7) and of the higher molecular weight compounds (*via* reactions 8 and 9) is consistent with this suggestion.

In the photolysis of pure ketene, ethane production occurs at low temperature and rapidly decreases as the temperature rises. No hydrogen is produced. If deuterium is initially present, CH_2D_2 and $C_2H_4D_2$ are both produced at low temperature but neither the other mixed ethanes nor CH_3D and CHD_3 are produced. The yield of $C_2H_4D_2$ decreases slowly as the temperature is raised. If both hydrogen and deuterium are initially present, C_2H_6 and $C_2H_4D_2$ are both formed at room temperature. The inferences from these results follow.

a.—CH_2 is involved in production of C_2H_6. If the CH_2 is removed, as by reaction 16, no C_2H_6 can be formed irrespective of the temperature.

b.—Formation of ethane at any temperature *cannot* be by a reaction like

$$CH_2 + CH_4 \longrightarrow C_2H_6 \tag{26a}$$

because, if it were, other mixed ethanes would be formed at higher temperature, in the presence of excess deuterium, *via* reactions like

$$CH_2 + CH_3D \longrightarrow C_2H_5D \tag{26b}$$

The CH_3D itself is produced by reaction (21a) and the CHD disappears by the reaction

$$CHD + D_2(\text{or } H_2) \longrightarrow \text{methane} \tag{27}$$

before it can enter into any other reaction.

c.—Nevertheless H_2 and D_2, if present, do enter into the formation of C_2H_6 and $C_2H_4D_2$. The reaction cannot involve intermediate formation of acetaldehyde by reaction such as

$$CH_2CO^* + H_2 \longrightarrow CH_3{\cdot}CHO \tag{28a}$$

$$CH_2CO^* + D_2 \longrightarrow CH_2D{\cdot}CDO \tag{28b}$$

for the photolysis of a mixture of those intermediates could yield other mixed ethanes.

4.4. Ratio of Methane and Ethane Yields in Pure Ketene.—In the absence of hydrogen or deuterium the significant reactions in terms of which the initial yields of CH_4 and C_2H_6 may be explained are

$$CH_2CO \xrightarrow{h\nu} CH_2 + CO \qquad (I)^{33}$$

$$CH_2 + CH_2CO \longrightarrow CH_3 + CHCO \tag{12}$$

$$CH_2 + CH_2CO \longrightarrow C_2H_4 + CO \tag{5}$$

$$CH_3 + CH_2CO \longrightarrow CH_4 + CHCO \tag{14}$$

$$2CH_3 \longrightarrow C_2H_6 \tag{13}$$

$$CH_2 + CH_2CO \longrightarrow \text{-}(CH_2)_2CO\text{-} \tag{4}$$

$$CH_2 + \text{-}(CH_2)_2CO\text{-} \longrightarrow C_2H_6 + \text{residue} \tag{29}$$

$$CH_2 + \text{-}(CH_2)_2CO\text{-} \longrightarrow \text{Polymer} \tag{30}$$

$$CH_2 + \text{-}(CH_2)_nCO\text{-} \longrightarrow \text{Polymer} \tag{30_n}$$

Reaction 29 is included as a possibility, the contribution from which may be best assessed by an examination of the results of the kinetic analysis. Reaction 6 as well as a number of other possible reactions of CH_2, which are in no way involved in production of CH_4 or C_2H_6, are not specifically included in the above scheme. We designate the sum of the rates of such reactions plus those of the polymerization reactions (30–30_n) by the symbol Σ. The steady-state concentrations of the free radicals CH_2, CH_3 and $-(CH_2)_2CO-$ are represented by M, (Me) and R, respectively, the concentration of ketene by K and the incident light intensity by I. We define ϕ by the relationship

$$\phi = \frac{k_{29}\,MR + \Sigma}{K}$$

The method of steady-state calculations then yields the results

$$M = k_1 I/(k_{12} + k_5 + 2k_4 + \phi) \tag{1}$$

$$(Me) = \frac{-k_{14}K + \sqrt{(k_{14}K)^2 + 4k_{12}k_{13}M{\cdot}K}}{2k_{13}} \tag{2}$$

$$R = \frac{k_4}{k_{29} + k_{30}}\,K \tag{3}$$

In the value of ϕ, all terms for polymerization reactions above that corresponding to k_{30} itself can be neglected in the initial stages of the reaction; the value of R is given on that basis.

The initial rates are given by

$$d(CH_4)/dt = k_{14}(Me)K \tag{4}$$

$$d(C_2H_6)/dt = {}^1/_2 k_{13}(Me)^2 + k_{29}MR \tag{5}$$

Initially, the ratio of yields $\Delta(CH_4)/\Delta(C_2H_6)$ is the same as the ratio of rates. If we note that in equation *2* the term $4k_{12}k_{13}MK$ is very small compared with $(k_{14}K)^2$ and employ the approximation $(1 + 2a)^{1/2} \simeq 1 + a$, it follows that

$$Me \simeq k_{12}M/k_{14} \tag{6}$$

and that

$$\Delta(CH_4)/\Delta(C_2H_6) \propto (k_{29} + k_{30})k_{12}/k_4k_{29} \tag{7}$$

Figure 1 shows a plot of log $[\Delta(CH_4)/\Delta(C_2H_6)]$ as a function of $1/T$. Marked curvature at the higher temperatures is to be attributed to the fact that in some of those experiments nearly 20% of the ketene was decomposed, while at the lower temperatures the decomposition amounted to only 2–3%. Thus,

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[33] Reaction I is an over-all reaction including reactions 1, 2 and 3.

the values of $\Delta(CH_4)/\Delta(C_2H_6)$ at the lower temperatures fairly well represent the ratio of initial yields, while at the higher temperatures they do not. The slight departure from a straight-line relationship at the lower temperatures may result from the fact that the ratio of rate constants includes a sum, $k_{29} + k_{30}$; a linear relationship between the logarithm of that quantity and $1/T$ would not be expected. This interpretation is consistent with the conclusion that, in view of the degree of rearrangement involved in reaction 29, $k_{29} << k_{30}$. Thus, the ordinate in Fig. 1 approximately represents log $k_{30}k_{12}/k_4k_{29}$ and the slope of the straight line reveals that $E_{30} + E_{12} - E_4 - E_{29} \simeq 3.5$ kcal.

4.5. Photolysis of Ketene–Acetone Mixtures.—The outstanding feature of the results summarized in Table IV is that in most cases the rates of product yield are lower than those naively estimated on the basis of a concept of no interaction between the reactants, their various products, or both. The obvious conclusion from the "decreased rates" is that there is a real interaction. However, in the cases of propane and methyl ethyl ketone production, the rates are considerably above the naively expected values.

4.5.1. Yield of C_2H_2—The yield of C_2H_2 in the mixture is definitely less than that which would be expected on the basis of no interaction of the reactants or products. The important photolytic reactions include 1, 2 and

$$(CH_3)_2CO + h\nu \longrightarrow (CH_3)_2CO^* \qquad (31)$$

$$(CH_3)_2CO^* \longrightarrow CH_3 + CH_3CO \qquad (32)$$

$$CH_3CO \longrightarrow CH_3 + CO \qquad (33)$$

At the higher temperatures, reaction 33 plays an increasingly important role.[34] The decrease in yield of C_2H_2 thus indicates that, at the steady-state concentrations existent under the conditions of the photolysis, reaction between free CH_2 and free CH_3 makes no significant contribution to acetylene yield, such as suggested by Wiener and Burton.[3] This result does not rule out the possibility of similar reaction involving electronically excited radicals under the high concentration conditions attainable in an electric discharge but it certainly does not support the view of interaction between unexcited radicals.

4.5.2. Yields of Other Products.—At 27° all the C_2H_4 and nearly all the CO originates from ketene; nearly all the C_2H_6 from acetone. At that same temperature, the ratio of the observed rates to the rates expected on the "no-interaction" assumption are nearly the same for C_2H_4 and CO, somewhat higher for C_2H_6. Apparently, the factor responsible for the small decrease in $r_{C_2H_6}$ is not responsible for the decrease in $r_{C_2H_4}$ or r_{CO}. A simple explanation for the value of $\rho(C_2H_6)$ so near unity is that the major effect of ketene on the acetone photolysis is a simple pressure effect, namely, a deactivation process

$$(CH_3)_2CO^* + CH_2CO \longrightarrow (CH_3)_2CO + CH_2CO \quad (34)$$

On the other hand, the effect of acetone on the ketene photolysis at 27° is rather marked. If the result could be accepted without reservations (*cf.* Table IV, footnote *b*), it might reflect a possible deactivation effect on ketene.

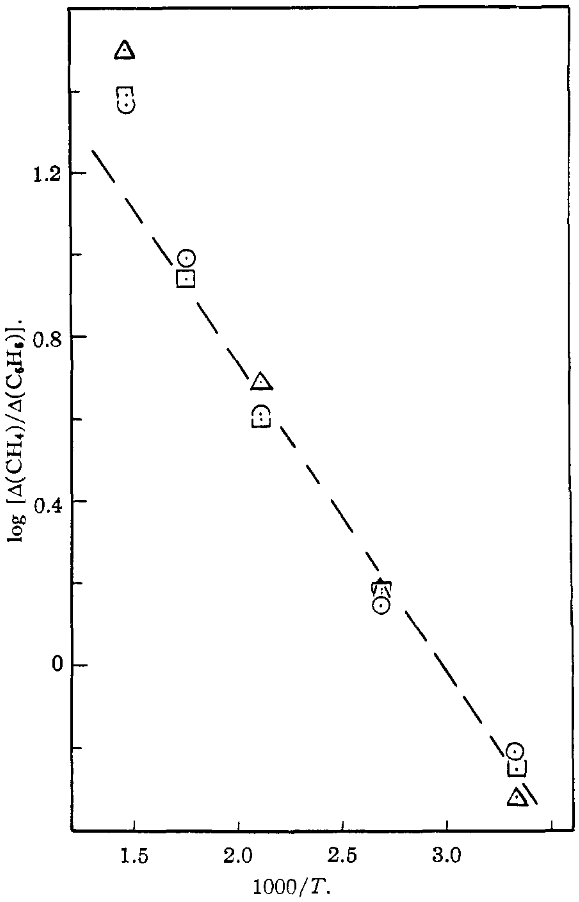

Fig. 1.—Photolysis of pure ketene, 15 min. exposure; ⊙, 19.37; ⊡, 38.74; ◬, 77.48; (units of 10^{-7} mole/ml. initially).

Judging from yields for the pure compounds at 27 and 99°, the big contributor to the CH_4 yield is the ketene itself (a factor of 23 at 27°, 1.2 at 99°), but at higher temperatures acetone becomes the major contributor (a factor ranging from 8 at 200° to 19 at 412°). Except at 99°, CH_4 yield is more affected by the interaction of ketene and acetone, than is C_2H_6 (*cf.* Table IV). Free CH_3 may yield CH_4 by reaction with acetone

$$CH_3 + (CH_3)_2CO \longrightarrow CH_4 + CH_3COCH_2 \quad (35)$$

or by a reaction like 14 with ketene or excited ketene. Competing reactions which involve removal of CH_3 in addition processes (*e.g.*, to give CH_3CH_2CO or CH_3COCH_2 by reaction with CH_2CO) might account for low yields of CH_4 but the calculated values do not have sufficient validity to warrant further speculation.

Carbon dioxide undoubtedly comes from the ketene.

4.6. Photolysis of Ketene in Presence of Methane-d_4.—An adequate explanation of the results may be given in terms of steps already discussed; *i.e.*, reaction I and

$$CH_2 + CD_4 \longrightarrow CH_2D_2 + CD_2 \qquad (21)^3$$

as well as a number of reactions involving either

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[34] D. S. Herr and W. A. Noyes, Jr., THIS JOURNAL, **62**, 2052 (1940).

CH_2 or CD_2, namely, 4 and a counterpart 4a, and similarly 5 and 5a, 12 and 12a, 30 and 30a

$$CH_2 + CD_4 \longrightarrow CH_2D + CD_3 \quad (36)$$

and 36a, reaction 14 (as well as three other reactions involving deuterated methyl groups) and

$$CH_3 + CD_4 \longrightarrow CH_3D + CD_3 \quad (37)$$

$$CH_2D + CD_4 \longrightarrow CH_2D_2 + CD_3 \quad (37a)$$

Superficially, it is apparent that CO is produced both by reaction 2 and by the sum of steps 5 and 5a, which involve reactions of CH_2 or CD_2 with ketene. Since CD_2 is created at the expense of CH_2 (reaction 21), the yield of CO is not affected by introduction of CD_4 into the mixture at lower temperatures. This point is quantitatively examined in section 4.6.1.

In section 4.6.1 it is shown that interpretation of the results on the basis of the suggested mechanism yields $E_{21} - E_5 = 0.9$ kcal. and $a_5/a_{21} = 1.4$. These differences account for the low yields of CH_2CD_2 relative to those of C_2H_4. Formation of other mixed ethylenes, *e.g.*, CH_2CHD, depends on the occurrence of an intermediate step such as

$$CD_2 + CH_2D_2 \longrightarrow CHD_3 + CHD \quad (36b)$$

Since CH_2D_2 is itself formed in relatively low concentration by reaction 21, occurrence of reactions such as 36b plays no important role and ensuant production of other mixed ethylenes must be insignificant.

The same argument as that given in the previous paragraph accounts for the absence of mixed methanes other than CH_2D_2 at room temperature. At higher temperatures formation of other mixed methanes becomes important because the H or D atom extraction reactions yield a variety of methyl radicals which, in turn, produce a variety of mixed methanes by still other atom extraction reactions.

Presence only of the "even" mixed ethanes in the ethane yield at 27° again suggests that, in photolysis of ketene, ethane is produced by reaction other than combination of methyl radicals, *e.g.*, reaction 29. According to the mechanism here suggested, atom extraction reactions yield no significant amount of free methyl radicals (*e.g.*, CH_2D) at room temperature because reactions such as 36 are too endothermal. A point worthy of particular emphasis is the complete absence of CH_4 production at room temperature although C_2H_6 is found. Since it may reasonably be assumed that $k_{14} \nless k_{12}$, the inference is that $r_{12} << r_{21}$. The implication is that reaction 13 does not contribute significantly to ethane yield at room temperature and that ethane is produced at that temperature mainly by reaction 29 (which, as has already been noted, is probably very slow in comparison with reaction 30).

4.6.1. Yields of Ethylenes.—Rate constants k_5 and k_{5a} should differ only by the small amount corresponding to change in collision frequency (*cf.* section 4.2). Since the ratio $(m_{CD_2}/m_{CH_2})^{1/2}$ is only 1.07, it follows that the difference between k_5 and k_{5a} is within limits of experimental error of this work. Similar remarks may be made about pairs of rate constants like k_4, k_{4a}; k_{12}, k_{12a}; etc.

For very small conversion of ketene to products the yields of the various products per unit time are approximately equal to the rates of their production; *i.e.*, $\Delta C_2H_4/t \simeq r(C_2H_4)$. Employing conventional steady-state methods and the additional approximations $k_4 \sim k_{4a}$, $k_5 \sim k_{5a}$, $k_{12} \sim k_{12a}$ and $k_{36} \sim k_{36a}$ it follows that

$$\frac{\Delta C_2H_4}{\Delta CH_2CD_2} \simeq \frac{(CH_2CO)}{(CD_4)} \times \frac{2k_4 + k_5 + k_{12}}{k_{21}} + \frac{k_{36}}{k_{21}} \quad (8)$$

where the quantities in parentheses are the initial concentrations.

Plots of the data in Table V show that $\Delta C_2H_4/\Delta CH_2CD_2$ is indeed a linear function of $(CH_2CO)/(CD_4)$ at each temperature, as required by equation *8*. Establishment of the intercept is difficult. However, k_{36}/k_{21} does not appear to exceed 0.3 even at 412°. At 27 and 200° the relationship extrapolates closely to zero; *i.e.*, $k_{36} << k_{21}$ at room temperature. Slopes obtained from such plots and the ratios of yields at 99 and 298°, where $(CH_2CO) = (CD_4)$, and where we suggest that $k_{36}/k_{21} \simeq 0.1$ at 298°, give values

	27°	99°	200°	298°	412°
$(2k_4 + k_5 + k_{12})/k_{21}$	7.10	5.80	5.60	5.40	5.25

It may be shown (using approximations like those already described) that for pure ketene

$$\frac{\Delta CO}{\Delta C_2H_4} \simeq 2 + \frac{2k_4 + k_{12}}{k_5} = 1 + \frac{2k_4 + k_5 + k_{12}}{k_5} \quad (9)$$

Values obtained from Table I for the concentrations employed in these experiments are

	27°	99°	200°	298°	412°
$(2k_4 + k_5 + k_{12})/k_5$	1.18	1.29	1.49	1.87	2.30

Hence, we have the values

	27°	99°	200°	298°	412°
k_5/k_{21}	6.02	4.51	3.76	2.88	2.28

Plot of log k_5/k_{21} as a function of $1/T$ yields an approximate straight line and shows that $E_{21} - E_5 \simeq 0.9$ kcal. and that $a_5/a_{21} \simeq 1.4$; in such plot the 412° value is ignored because in the pure ketene photolysis from which the datum was taken, about 20% of the initial ketene (as indicated by production of CO, CO_2 and the higher compounds) had disappeared.

Employing approximations like those already described, it may be shown that for mixtures employed in this work

$$\frac{\Delta CO}{\Delta \text{ethylenes}} = 2 + \frac{2k_4 + k_{12} + k_{36}(CD_4)/(CH_2CO)}{k_5} \quad (10)$$

For pure ketene, this ratio reduces to equation *9*. Comparison of the ratios taken from Table V (at three different values of $(CD_4)/(CH_2CO)$) with those taken from Table I indicates that addition of CD_4 is without significant effect.

Temp., °C.	$\frac{\Delta CO}{\Delta \text{ethylenes}}$	$\frac{\Delta CO}{\Delta C_2H_4}$
27	2.18, 2.18, 2.17	2.18
99	2.29	2.29
200	2.53, 2.56, 2.53	2.49
298	2.87	2.87
412	3.30, 3.35, 3.34	3.30

Evidently k_{36} is very small in comparison with either k_4 or k_{12}. We may summarize the information gained from this work about reaction 36 by the statement

$$k_{36} \ll k_4, k_{12}, k_{21}$$

4.6.2. Yields of Methane.—Employing approximations similar to those already described it may be shown that

$$\frac{\Delta C_2H_4}{\Delta CH_2D_2} \simeq \frac{k_5}{k_{21}} \frac{(CH_2CO)}{(CD_4)} \qquad (11)$$

Values of $[\Delta C_2H_4 \times (CD_4)]/[\Delta CH_2D_2 \times (CH_2CO)]$, equal in each case to k_5/k_{21}, may be calculated directly from Table I; they are

Temp., °C.	k_5/k_{21}
27	5.99, 5.94, 5.92
99	4.56
200	3.61, 3.64, 3.46
298	2.88
412	2.11, 2.14, 2.30

The usual $1/T$ plot (omitting the 412° values) yields values for $E_5 - E_{21}$ and a_{21}/a_5 the same as those given in section 4.6.1.

Another interesting point relates to the relative yields of CH_2D_2 and CH_2CD_2. If we assume that significantly all CH_2D_2 is formed by reaction 21 even at the highest temperatures, it follows (employing the usual approximations) that

$$\frac{\Delta CH_2D_2}{\Delta CH_2CD_2} = \frac{2k_4 + k_5 + k_{12}}{k_5} \qquad (12)$$

Values for the right-hand term are derived from the data of Table I in section 4.6.1. Comparisons of the two sets of values give

	Left-hand term	Right-hand term
27°	1.18	1.18
99°	1.29	1.27
200°	1.49	1.53
298°	1.87	1.91
412°	2.30	2.55

Too much credence must not be given to the 412° values, (a) because too much ketene has decomposed, and (b) because other reactions for production of mixed methanes become increasingly important. Otherwise, the data reveal a high degree of internal consistency.

4.6.3. Excitation of Methylene.—In some previous work on ketene (*cf.* section 4.1), distinction has been made between methylene radicals produced in excited and unexcited condition. In the treatment of sections 4.6.2 and 4.6.3 rate constants for reactions involving CD_2 have been treated as being practically the same as those involving CH_2 with generally self-consistent results. Three different conclusions are admissible. Either we may write that in the steady-state $(CH_2)/(CH_2') = (CD_2)/(CD_2')$ or that $(CH_2') = (CD_2') = 0$ or that there are no perceptible differences in the rate constants for reactions involving CH_2, CH_2', CD_2 or CD_2'. If the latter view is accepted, there would appear to be no reason for hypothesizing the existence of excited methylene radicals in photolysis of ketene.

The view that in the steady-state $(CH_2)/(CH_2') = (CD_2)/(CD_2')$ entails some consideration of the nature of the excited radicals and the manner of the formation of CD_2'. The simplest concept is that CH_2' is triplet; for maintenance of equality of ratios it is required in reaction 21 not only that multiplicity be conserved (which would be normally expected) but also that the rate constants k_{21} and k_{21}' for the reactions of CH_2 and CH_2' be the same. Thus, once again whatever view we adopt we require that, if the excited radicals exist in this case, they behave the same as the unexcited.

Without specific evidence to the contrary, it appears most satisfactory to conclude that $(CH_2') = 0$ in the photolysis of ketene.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Diffusion Kinetics: The Photolysis of Azo-bis-isobutyronitrile[1]

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The photolysis of 2,2'-azo-bis-isobutyronitrile in benzene solution with iodine as scavenger gives evidence of diffusion controlled combination of isobutyronitrile radicals. The thermal decomposition does not exhibit this effect.

It has been shown by Lewis and Matheson[3] that 2,2'-azo-bis-isobutyronitrile (AIBN) is an efficient photosensitizer and thermal initiator of free radical polymerization. The thermal decomposition gives a quantitative yield of nitrogen and a somewhat smaller yield of tetramethylsuccinonitrile.[3,4] The rate of decomposition is nearly the same in a variety of solvent types.[3,5,6] The rate of thermal decomposition, measured by nitrogen evolved, is unimolecular[3,5] and is uninfluenced by addition of tetrachloroquinone[3] or diphenylpicrylhydrazyl.[6] We also find no change in rate upon adding iodine, in the presence of which the iodoisobutyronitrile is known to form.[7] The efficiency of iodine as scavenger in this case is much less than unity[8] at *ca.* 10^{-3} mole/l.

After considering the facts available at the time this work was started it was anticipated that photolysis and/or thermal decomposition of AIBN in solution in the presence of appropriate concentrations of iodine as free radical scavenger might pro-

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