only 10^{-15} sec., the efficiency of the forward process may be appreciably less than unity.

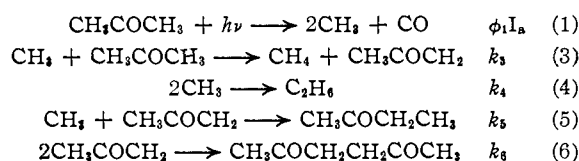[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA]

The High Temperature Photolysis of Acetone

By R. K. Brinton

The photolysis of acetone in the temperature range 200–475° has been investigated. Rates of formation of methane, ethane, ethylene, carbon monoxide, methyl ethyl ketone, ketene, methyl vinyl ketone and 2,5-hexanedione have been determined quantitatively. Methane formation is consistent with the mechanism $CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_3COCH_2$. However, the ratio $R_{CH_4}/R_{C_2H_6}{}^{1/2}(A)$ was found to be strongly dependent on acetone concentration (A) and light intensity, especially at higher temperatures which is contrary to evidence previously reported. The kinetics of another ethane reaction, $CH_3 + CH_3COCH_3 \rightarrow C_2H_6 + CO + CH_3$ is examined as an explanation for such a behavior. The production of ketene is in agreement with the decomposition of the acetonyl radical, $CH_3COCH_2 \rightarrow CH_2CO + CH_3$, whose activation energy is ca. 41 kcal. $(E_7 - {}^{1}/{}_{2}E_6)$. Possible reactions responsible for ethylene formation and their correspondence to kinetic data are discussed.
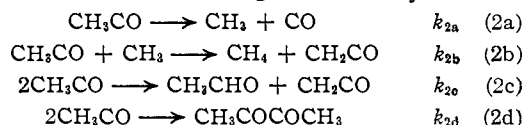
The photolysis of acetone at temperatures below 300° has been studied extensively[1] and in the range 100–300° may be explained satisfactorily by the mechanism.

$$CH_3COCH_3 + h\nu \longrightarrow 2CH_3 + CO \qquad \phi_1 I_a \quad (1)$$

$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_3COCH_2 \quad k_3 \quad (3)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad k_4 \quad (4)$$

$$CH_3 + CH_3COCH_2 \longrightarrow CH_3COCH_2CH_3 \quad k_5 \quad (5)$$

$$2CH_3COCH_2 \longrightarrow CH_3COCH_2CH_2COCH_3 \quad k_6 \quad (6)$$

Below 100° the simplified primary process 1 must be expanded to include the additional primary step

$$CH_3COCH_3 + h\nu \longrightarrow CH_3CO + CH_3 \qquad \phi_{1a} I_a \quad (1a)$$

and reactions involving the acetyl radical[2]

$$CH_3CO \longrightarrow CH_3 + CO \qquad k_{2a} \quad (2a)$$

$$CH_3CO + CH_3 \longrightarrow CH_4 + CH_2CO \qquad k_{2b} \quad (2b)$$

$$2CH_3CO \longrightarrow CH_3CHO + CH_2CO \qquad k_{2c} \quad (2c)$$

$$2CH_3CO \longrightarrow CH_3COCOCH_3 \qquad k_{2d} \quad (2d)$$

account for the biacetyl, ketene and acetaldehyde found in the low temperature photolysis. The relative abundance of (1) and (1a) is certainly wave length dependent[3] and perhaps temperature dependent, but above 100° the life of the acetyl radical formed by (1a) is short enough so that processes 1, 1a and 2a may be approximated quite well by (1) alone, and the reactions involving acetyl radical are no longer important.

Above 300° the photolysis is complicated by the production of ketene, probably formed by the decomposition of acetonyl radical, $CH_3COCH_2(Ac)$

$$CH_3COCH_2 \longrightarrow CH_3 + CH_2CO \qquad k_7 \quad (7)$$
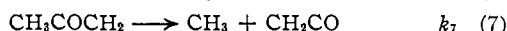
as well as ethylene whose mode of formation has not been satisfactorily explained. The investigations[4] of the photolysis above 300° are not ex-

tensive and are somewhat qualitative in nature. In the present study the rates of production of ketene (K), methyl ethyl ketone (MEK), 2,5-hexanedione (Ac₂), ethylene, methane and ethane have been determined quantitatively in order to test the validity of the total photolysis sequence, (1) through (7), in the temperature region above 300°. Of special interest is the kinetic treatment of reactions 5, 6 and 7 which have not been examined previously in a quantitative fashion.

Experimental

The photolyses were carried out in a 31 mm. diameter by 249 mm. long cylindrical fused silica cell (189 cm.³ volume) surrounded by a 290 cm. aluminum block furnace whose ends were covered by 2 mm. thick Vycor glass plates to minimize cooling of the cell windows. The temperature of the furnace was controlled to ±0.3° by a proportional amplifier heater control using a thermistor sensing element. In order to limit the percentage decomposition of the acetone to about 3% and yet obtain sufficient products for analysis, a one liter bulb and a 500 ml. toepler pump were included in the photolysis system (total system volume = 1572 cm.³). At intervals during the photolysis (5–7 times) the radiation was interrupted and the total acetone in the system collected in the 1 liter bulb by use of the toepler pump. After a mixing period the acetone was expanded into the cell and the irradiation resumed. The photolysis system and the vacuum system including gas burets and auxiliary apparatus for gas analysis was all glass with mercury check valves in all locations in contact with the products of the photolyses.

A B.T.H. ME/D 250 watt high pressure mercury arc operated on a stabilized a.c. source was used in all experiments. The Corning 9–53 Vycor plates used on the ends of the furnace, the self absorption of the lamp in the 2500 Å. region and the long wave length absorption limit of acetone restricted the effective wave length to λλ 2800–3300 Å. The light beam, which completely filled the cell in all experiments, was well collimated by use of quartz optics. Variation in the light intensity was accomplished by use of neutral density filters of chromel on fused silica plates.

The quantum yield determinations were made in the same system using acetone photolysis at 150° as an actinometer. A photolysis at the appropriate temperature was made directly preceding or following the actinometry. The amount of light absorption of the comparison experiment was made identical by adjusting the pressures so that equal percentage absorption was achieved. These percentage absorptions were previously determined by measurements with a 935 photocell and galvanometer measuring circuit. Pressures of the high temperature photolyses were always somewhat greater than the corresponding actinom-

(1) (a) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1954, pp. 330–340. (b) A. F. Trotman-Dickenson and E. W. R. Steacie, J. Chem. Phys., 18, 1097 (1950).

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

(3) D. S. Herr and W. A. Noyes, Jr., J. Am. Chem. Soc., 62, 2052 (1940).

(4) (a) R. C. Ferris and W. S. Haynes, ibid., 72, 893 (1950); (b) E. Whittle and E. W. R. Steacie, J. Chem. Phys., 21, 993 (1953); (c) L. Mandelcorn and E. W. R. Steacie, Can. J. Chem., 32, 331 (1954).

Table I

Rates of Production Formation of Acetone Photolysis

Run no.	1[e]	2[g]	3[e]	4[f]	5	6	7	8[f]	9	10
Temp., °C.	475	475	475	475	450	450	450	450	435	435
(A)[a]	1.070	1.070	1.062	1.048	1.093	1.110	1.110	1.110	1.138	1.118
R_{CH_4}[b]	1020	268	69.0	5.20	663	124.6	34.0	{0.74	695	535
R_{CO}	541	120	25.7	0.66	362	63.9	15.4		423	311
$R_{C_2H_4}$	61.0	22.8	7.70	0.235	14.1	7.12	3.37	{0.0214	16.4	12.1
$R_{C_2H_6}$	16.9	3.92	0.90	Tr.	24.8	1.71	0.269		26.6	15.9
R_K	317	134	38.5	4.25	83.6	39.0	16.6	0.253	118.5	86.2
$R_{MVK} + R_{MEK}$	...	...	...	...	...	...	...	...	171.8	100.2
R_{Ac_2}	...	...	...	...	...	...	...	...	268	134.0
$R_{CH_4}/R_{C_2H_6}^{1/2}(A)$[e]	...	...	...	...	...	...	...	...	118.6	112.0
$R_K/R_{Ac_2}^{1/2}$[d]	...	...	...	...	...	...	...	...	7.23	7.44

Run no.	11	12[g]	13	14	15	16	17	18	19	20
Temp., °C.	435	435	435	435	435	435	435	435	435	435
(A)[a]	1.224	1.133	1.133	0.568	2.30	1.130	1.149	2.28	1.118	2.26
R_{CH_4}[b]	591	540	548	318	394	315	234	172.7	118.0	98.0
R_{CO}	348	330	332	202	186.4	164.0	128.0	77.5	56.5	40.4
$R_{C_2H_4}$	15.0	19.5	14.9	6.00	10.7	5.95	8.60	9.17	5.49	4.98
$R_{C_2H_6}$	17.7	16.2	16.3	18.6	4.33	6.12	3.57	1.39	1.42	0.88
R_K	100.0	296	92.0	61.5	94.2	75.0	51.7	48.0	36.4	38.5
R_{MVK}	15.7	15.4	15.1	{89.6	{38.2	{49.4	{27.2	4.07	{11.7	{4.46
R_{MEK}	95.5	80.0	77.3					5.92		
R_{Ac_2}	123.5	115.6	119.8	100.9	96.4	76.5	48.5	26.3	23.4	17.4
$R_{CH_4}/R_{C_2H_6}^{1/2}(A)$[c]	125.1	118.0	119.6	130.0	82.6	112.3	108.0	63.2	87.8	46.3
$R_{MEK}/R_{C_2H_6}^{1/2}R_{Ac_2}^{1/2}$	2.05	1.84	1.75	...	...	...	...	0.98	...	...
$R_K/R_{Ac_2}^{1/2}$[d]	9.00	...	8.41	6.10	9.60	8.57	7.42	9.33	7.52	9.25

Run no.	21	22	23[h]	24	25[i]	26	27	28	29	30[j]
Temp., °C.	435	435	435	435	435	435	435	435	435	435
(A)[a]	0.566	1.108	2.04	2.04	2.06	1.138	1.141	1.139	1.160	1.224
R_{CH_4}[b]	71.0	59.4	17.10	16.32	0.46	12.80	13.70	12.20	6.26	{0.252
R_{CO}	32.5	32.2	8.90	7.95	.18	6.91	5.91	5.09	2.50	
$R_{C_2H_4}$	2.19	4.78	2.40	2.02	.053	1.56	1.35	1.37	0.656	.0054
$R_{C_2H_6}$	1.08	0.72	0.155	0.136	.012	0.156	0.130	0.119	0.052	.0069
R_K	23.6	19.2	12.6	6.89	7.55	4.22	4.10	3.88	2.87	.0223
R_{MVK}	{9.15	{3.85	0.194	0.181	0.000	{0.321	{0.307	0.131	{0.84	.000
R_{MEK}			.098	.089	.000			.108		.781
R_{Ac_2}	16.3	6.28	.635	.644	.000	0.541	0.730	.362	0.183	.644
$R_{CH_4}/R_{C_2H_6}^{1/2}(A)$[c]	120.5	63.5	18.5	18.3	...	28.5	33.5	31.1	23.8	...
$R_{MEK}/R_{C_2H_6}^{1/2}R_{Ac_2}^{1/2}$	...	...	0.310	0.299	...	...	...	0.525	...	...
$R_K/R_{Ac_2}^{1/2}$[d]	5.85	7.65	...	8.57	...	5.73	4.82	6.44	6.70	...

Run no.	31	32	33	34	35	36	37	38	39	40
Temp., °C.	400	400	400	400	400	400	400	400	400	400
(A)[a]	1.240	1.205	2.48	0.628	1.250	1.240	1.196	1.255	2.47	0.608
R_{CH_4}[b]	500	410	317	242	274	148.0	60.0	48.4	42.5	37.1
R_{CO}	327	281	185.9	185.0	180.2	95.5	34.7	28.2	22.8	21.8
$R_{C_2H_4}$	9.27	7.72	4.91	3.02	3.41	3.54	1.21	1.43	1.16	0.89
$R_{C_2H_6}$	31.1	19.9	5.43	22.8	11.5	4.33	0.78	0.48	0.32	0.71
R_K	21.6	18.0	19.2	11.9	20.2	5.34	6.60	5.36	5.84	4.50
$R_{MVK} + R_{MEK}$	128.5	97.4	45.8	88.0	68.6	25.9	6.80	5.81	3.03	5.95
R_{Ac_2}	134.0	102.1	122.0	83.9	106.0	46.6	13.8	14.0	13.8	11.21
$R_{CH_4}/R_{C_2H_6}^{1/2}(A)$[c]	72.2	76.4	54.8	80.5	64.6	57.3	57.2	55.4	30.4	72.2
$R_K/R_{Ac_2}^{1/2}$[d]	1.86	1.78	1.74	1.31	1.96	0.78	1.78	1.44	1.57	1.35

Run no.	41	42	43	44	45[k]	46	47	48	49	50
Temp., °C.	400	400	400	400	400	365	365	365	365	365
(A)[a]	1.204	1.166	1.164	1.159	1.187	1.355	0.610	2.70	1.289	1.320
R_{CH_4}[b]	29.2	23.8	22.0	22.5	22.9	284	190.5	25.6	66.4	11.73
R_{CO}	18.1	14.7	14.2	13.3	13.2	220	174.0	164.9	44.4	7.62
$R_{C_2H_4}$	1.19	1.03	1.01	0.90	0.97	2.60	1.42	2.26	1.050	0.219
$R_{C_2H_6}$	0.308	0.247	0.220	0.202	0.199	24.2	36.0	7.07	1.89	.114
R_K	3.01	3.54	2.49	2.50	2.10	...	...	2.98	1.13	.411

R_{MVK}	2.66	1.86	1.92	1.77	1.92	10.0	3.6	16.9	2.97	.378
R_{MEK}						81.5	86.4	32.7	9.75	.671
R_{Ac_2}	6.20	3.38	3.29	3.52	2.67	75.4	66.7	77.0	18.4	2.41
$R_{CH_4}/R_{C_2H_6}^{1/2}(A)^e$	43.5	40.5	38.6	41.3	40.5	42.5	52.0	37.0	37.5	26.4
$R_{MEK}/R_{C_2H_6}^{1/2}R_{Ac_2}^{1/2}$	...	...	...	...	...	...	...	1.52	1.65	1.29
$R_K/R_{Ac_2}^{1/2\,d}$	1.21	1.92	1.37	1.33	1.28	...	...	0.34	0.264	0.266

Run no.	51	52	53	54	55	56	57	58	59
Temp., °C.	305	305	305	305	305	305	305	250	200
$(A)^a$	1.399	0.705	2.80	1.399	1.418	0.675	2.79	1.535	1.685
$R_{CH_4}^b$	243	133.3	416	50.0	11.10	5.89	19.67	31.3	17.50
R_{CO}	292	189.5	374	35.3	6.15	3.65	9.73	29.6	28.4
$R_{C_2H_4}$	1.47	0.598	2.82	0.330	0.092	0.049	0.132	0.150	0.000
$R_{C_2H_6}$	84.2	79.3	70.6	3.48	.178	.174	.190	7.20	14.8
R_{MVK}	1.82	1.92	3.92	0.54	.176	.088	.278	0.168	0.000
R_{MEK}	113.0	79.0	154.0	13.55	1.15	.880	.145	12.7	10.2
R_{Ac_2}	44.6	19.4	85.2	12.8	2.43	1.35	4.45	5.54	1.28
$R_{CH_4}/R_{C_2H_6}^{1/2}(A)^e$	18.9	21.2	17.7	19.2	19.1	21.6	15.6	7.62	2.70
$R_{MEK}/R_{C_2H_6}^{1/2}R_{Ac_2}^{1/2}$	1.68	2.02	1.99	2.00	1.80	1.87	1.57	2.00	2.35

^{a} Mole cm.$^{-3}$ × 10^6. ^{b} All rates —mole cm.$^{-3}$ sec.$^{-1}$ × 10^{12}. ^{e} Mole$^{-1/2}$ cm.$^{3/2}$ sec.$^{-1/2}$. ^{d} Mole$^{1/2}$ cm.$^{-3/2}$ sec.$^{-1/2}$ × 10^6. ^{e} Corrected for dark reaction. ^{f} Dark reaction. ^{g} Added ketene equivalent to R_K of 233 in Run 12. ^{h} Added ketene equivalent to R_K of 7.75 in run 24. ^{i} Dark reaction added ketene equivalent to R_K of 7.70 in Run 24. ^{j} Dark reaction —MEK equivalent to R_{MEK} of 7.57 and Ac$_2$ equivalent to R_{Ac_2} of 8.15 added. ^{k} Products allowed to stand 8 hr. at 400°.

etry experiments. The Φ_{co} of acetone at 150° was taken as unity.[3]

Separation of the reaction products was made by a series of traps at various temperatures; the final two traps were Ward stills. Fractions volatile at -210, -185, -155 and $-95°$ measured in a gas buret, and a residue sample, whose size was calculated by the original acetone quantity corrected for the decomposition, were analyzed as follows:

Volatile at $-210°$: CH$_4$ and CO.—The mixture was heated in a CuO furnace at 220°. The products of this reaction, CO$_2$ and unreacted CH$_4$, were determined separately in a gas buret by condensing the CO$_2$ at $-185°$, measuring the CH$_4$ directly and finally measuring the CO$_2$ volatilized after the trap was warmed to $-80°$. It is significant that the volume of CH$_4$ + CO$_2$ measured after the CuO treatment always agreed within experimental error ($\pm 2\%$) with the original sample volume. This indicates that H$_2$ was not produced in any of the photolyses. In addition, mass spectrometric analysis of a number of the volatile at $-210°$ samples indicated that not more than a trace of H$_2$ could be present.

Volatile at $-185°$.—C$_2$H$_4$ and C$_2$H$_6$ present in this fraction were analyzed mass spectrometrically. Traces of propylene and small amounts of CO$_2$ were present in some samples.

Volatile at $-155°$.—This fraction, mainly ketene, was treated with acetic acid which removed the ketene quantitatively. The residue (ca. 10% of the ketene present) was pumped off the acetic acid at $-80°$ and measured in the gas buret. Analysis of this volatile portion was made by gas chromatography using a nonyl phthalate–firebrick column at 25° followed by a AgNO$_3$–benzyl cyanide–firebrick column at 0°. A typical analysis for this very small fraction was: propylene (81%), propane (7.1%), 1-butene (7.0%), isobutene (4.6%), trans-2-butene (0.7%).

Volatile at $-95°$.—This fraction was only collected until about 0.2% of original acetone was obtained. It was analyzed by gas chromatography with a AgNO$_3$–benzyl cyanide–firebrick column at 25°. The sample was about 99% acetone with traces of other compounds (not identified) present.

Residue Sample.—This sample was analyzed by gas chromatography. In the initial experiments the methyl ethyl ketone was determined on a nonyl phthalate–firebrick column at 100°. The peak used to measure methyl ethyl ketone later was determined by mass spectrometry to contain two components, methyl ethyl ketone and methyl vinyl ketone. Thus a large number of the photolyses have analyses for the sum of these two substances. Use of a Reoplex 400 (esterified polyethylene glycol)–firebrick column at 100° separated the two ketones, and the later experiments show individual analyses. The 2,5-hexanedione was determined on the Reoplex 400–firebrick column

at 175°. Methyl ethyl ketone, methyl vinyl ketone and 2,5-hexanedione were the only products found in appreciable concentration in the residue fraction. However, substances appreciably less volatile than 2,5-hexanedione would not have been found.

Attempts to determine the pyrolytic decomposition of acetone as well as the various products were made in several different ways. "Dark reactions" were made at 475, 450 and 435°. At 435° the production of pyrolytic product was negligible in 12 hr. time. At 450° the products found in the absence of light (Run 8) were small enough to be ignored. At 475° the dark reaction was appreciable and a rough correction in the photolyses product rates was made. Study of the photolysis above 475° is not warranted because of the rapid dark reaction.

Data on ketene decomposition[5] indicate that this product might well be unstable under conditions of the present experiments. Photolyses with added ketene at 435° both in the low (Run 23) and high (Run 12) intensity regions were conducted along with photolyses carried out in the normal manner (Run 13, Run 24). The companion experiments showed a very close correspondence in the rates of all products formed (see Table I). The only apparent difference was the rather small increase in C$_2$H$_4$ production in the photolyses with added ketene (10-20%). The amount of ketene added was much larger than the ketene normally produced in the photolyses, and about 8% and 15%, respectively, of the added ketene was lost during the course of the high and low intensity experiments (calculated on basis that a similar amount of ketene was produced in companion experiments). The dark reaction containing ketene added to acetone (Run 25) indicates that the rate of product formation of ketene pyrolysis is not important compared to the formation of photolysis products; ketene was almost quantitatively recovered (2% loss) in this trial. Another indication of the reliability of the ketene rate is shown at 400° by (Run 45) and a companion experiment (Run 44). The products of (Run 45) were allowed to stand for 8 hr. at 400° before analysis. The two ketene rates of 2.50 and 2.10 are in reasonable agreement.

Further investigations were made on the stability of methyl ethyl ketone and 2,5-hexanedione in the system. Acetone containing these two compounds was heated at 435° for 8 hr. (Run 30). Table I shows that there is evidently a small thermal decomposition of the diketone (ca. 20%) at this temperature. This is confirmed in the experiments previously mentioned (Run 45, Run 44) which show a decomposition of the same magnitude. The small increase in methyl ethyl ketone shown (Run 30) is probably

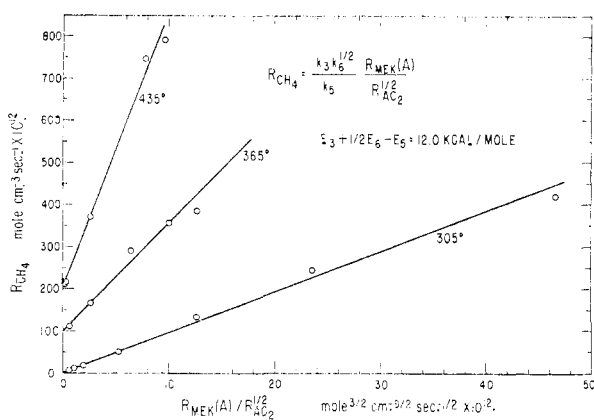(5) W. B. Gunther and W. D. Walters, J. Am. Chem. Soc., 81, 1310 (1959).

Fig. 1.—Plot of R_{CH_4} vs. $R_{MEK}(A)/R_{Ac_2}$. The 365 and 435° curves are displaced 100 and 200 units upward, respectively.

within the experimental accuracy of the analyses although the same trend is indicated in (Run 45).

The acetone used in all photolyses and in the preparation of synthetic standards for the residue fraction gas chromatographic analysis was Eastman Spectral grade. Ketene was prepared by the pyrolysis of acetic anhydride.[6] The only impurity that could be detected mass spectrometrically was approximately 3% CO_2.

Results and Discussion

The rates of formation of the photolysis products are listed in Table I. Three products appear in the high temperature photolyses which are not formed at lower temperatures; ethylene and methyl vinyl ketone could be detected at 250° and above, while ketene did not appear in detectable quantities below 305°. Also given in Table I are several calculated ratios of product rates which will be used in the following discussion. It is convenient to discuss the products of the photolysis in several separate sections.

C_2H_6 and CH_4 Formation.—The relationship of C_2H_6 and CH_4 produced in photolysis below 300° has been studied extensively.[1] At a single temperature the ratio $R_{CH_4}/R_{C_2H_6}^{1/2}(A)$ (where (A) represents acetone concentration and R_M the rate of production of substance M) is independent of light intensity, wave length and acetone *concentration* (except at low pressures[7]). Thus the formation of these two photolysis products is represented satisfactorily by reactions 3 and 4. Inspection of Table I shows that $R_{CH_4}/R_{C_2H_6}^{1/2}(A)$ above 300° is not constant at the various temperatures used in the present study. The deviation from constancy is greater the higher the temperature and the ratio is appreciably lower for low intensities and high pressures (R_{CO} may be taken as an estimate of the intensity. The validity of this approximation will be discussed later). It must be concluded that the productions of C_2H_6 and CH_4 are not represented adequately by the processes

(6) G. J. Fisher, D. F. McLean and A. W. Schnizer, J. Org. Chem., 18, 1055 (1953).

(7) R. E. Dodd and E. W. R. Steacie, Proc. Royal Soc. (London), A223, 283 (1954); G. B. Kistiakowsky and E. K. Roberts, J. Chem. Phys., 21, 1637 (1953). An increase in $R_{CH_4}/R_{C_2H_6}^{1/2}(A)$ at low acetone concentrations has been demonstrated to be due to the requirement of a third body in the combination of methyl radicals. At 247° Dodd and Steacie's results show this ratio to be about 25% higher at 25 mm. than at 100 mm.

3 and 4. An additional process favored at high intensities (radical–radical) to form CH_4 or one at low intensities (radical + acetone) to produce C_2H_6 are likely possibilities to explain the $R_{C_2H_6}/R_{C_2H_6}^{1/2}(A)$ behavior.

The first of these postulates may be tested by considering processes 3, 5 and 6. If these are the only reactions responsible for production of CH_4, MEK and Ac_2, respectively, this expression must hold.

$$R_{CH_4} = \frac{k_3 k_6^{1/2}}{k_5} \frac{R_{MEK}(A)}{R_{Ac_2}^{1/2}} \qquad I$$

Figure 1 shows the relationships of R_{CH_4} to $R_{MEK}(A)/R_{Ac_2}^{1/2}$ at 305, 365 and 435° for those photolyses having MEK analyses. The lines pass through the origin in each case as would be predicted and the fit of the individual points is quite reasonable considering the wide variation in experimental conditions and the many analyses involved in determining the functions. The Arrhenius curve for $k_3 k_6^{1/2}/k_5$ gives a good straight line through the three points and $E_3 + 1/2E_6 - E_5 = 12.0$ kcal./mole. This value is somewhat higher than the Trotman-Dickenson and Steacie[1b] value for $E_3 - 1/2E_4 = 9.7$ kcal./mole and probably represents a higher value for the individual value of E_3 although no data are available to evaluate the relative magnitude of $1/2E_4$ as compared to $E_5 - 1/2E_6$. Thus it may be concluded that 3, 5 and 6 represent the only processes producing CH_4, MEK and Ac_2 and the anomalous behavior of the $R_{CH_4}/R_{C_2H_6}^{1/2}(A)$ must be the result of an additional process producing ethane in the low intensity region.

A further confirmation of this conclusion is obtained by comparison of the rates of reactions 4, 5 and 6. Again if these were the only reactions forming C_2H_6, MEK and Ac_2, then

$$\frac{R_{MEK}}{R_{C_2H_6}^{1/2}R_{Ac_2}^{1/2}} = \frac{k_5}{k_4^{1/2}k_6^{1/2}} \qquad II$$

and its value might well be expected to be about 2 as predicted by collision theory for the self and cross combination of two radical types in the system. Table I indicates this to be the case at 200, 250 and 305°. However at the higher temperatures the values are much lower especially in the low intensity region. As R_{MEK} and R_{Ac_2} behave in a fashion consistent with (5) and (6) in expression I, it is clear that C_2H_6 must be produced by an additional process such as

$$CH_3 + CH_3COCH_3 \longrightarrow C_2H_6 + CO + CH_3 \quad k_8 \quad (8)$$
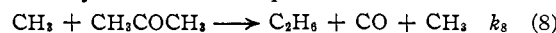
Under these conditions

$$\frac{R_{C_2H_6}(A)^2}{R_{CH_4}^2} = \frac{k_4}{k_3^2} + \frac{k_3 k_5}{k_3^2 k_6^{1/2}} \frac{R_{Ac_2}^{1/2}(A)}{R_{MEK}} \qquad III$$

These functions are plotted in Fig. 2 for the 435 and 365° data. The value of both $R_{CH_4}/R_{C_2H_6}^{1/2}(A)$ and $R_{MEK}/R_{C_2H_6}^{1/2}R_{Ac_2}^{1/2}$ at 305° do not show a consistent trend with intensity so that process 8 must be unimportant at that temperature. The points fit the lines quite well except for a single point on the 365° plot.

The intercepts of Fig. 2 give values of $k_3/k_4^{1/2}$ of 151 at 435° and 44.5 at 365°, $E_3 - 1/2E_4 = 15.6$ kcal./mole from these two values. Slopes from Fig. 2 show $E_8 + E_5 - 2E_3 + 1/2 k_6$ to be

— 8.6 kcal./mole. If the value of $E_3 + \frac{1}{2}E_6 - E_5 = 12.0$ from Fig. 1 is combined with this result, $E_8 - E_3 = 3.4$ kcal./mole.

A further confirmation of reaction 8 may be obtained by calculating $R_{C_2H_4}^{comb.}$, the C_2H_6 due to (4) alone, from the values of the intercepts of Fig. 2. The ratios $R_{MEK}/R_{C_2H_4}^{comb.} \cdot R_{Ac_2}^{1/2} = k_5/k_4^{1/2}k_6^{1/2}$ are shown in Table II. Also included are $R_{MEK}/R_{C_2H_6}^{1/2}R_{Ac_2}^{1/2}$ at the lower temperatures where the ratios may be assumed directly equal to $k_5/k_4^{1/2} \cdot k_6^{1/2}$. A weighted average of all results in Table II indicates $k_5/k_4^{1/2}k_6^{1/2} = 2.03 \pm 0.15$, a value corresponding closely to the theoretical value for radical combination.

TABLE II

Values of $k_5/k_4^{1/2}k_6^{1/2}$ at 365 and 435°

Run no.	$\dfrac{k_5}{k_4^{1/2}k_6^{1/2}}$	Run no.	$\dfrac{k_5}{k_4^{1/2}k_6^{1/2}}$	Run no.	$\dfrac{k_5}{k_4^{1/2}k_6^{1/2}}$
46	2.00	18	2.53	59	2.35 (200°)
47	1.52	11	2.45	58	2.00 (250°)
48	1.84	28	2.53		
49	1.99	13	2.20	305° Av.	1.84 ± 0.11
50	2.18	24	2.08		
	1.91 ± 0.18		2.36 ± 0.17		
	(365°)		(435°)		

Activation energies calculated from Fig. 2 must be accepted with certain reservations for the energy $E_3 - \frac{1}{2}E_4 = 15.6$ occupies a curving portion of the Arrhenius plot. This may be shown by combining the $k_3/k_4^{1/2}$ ratios given above with the values of $k_3/k_4^{1/2}$ at 305, 350 and 200° (for these lower temperatures the assumption that $R_{CH_4}/R_{C_2H_6}^{1/2}(A) = k_3/k_4^{1/2}$ was used). These data as well as the lines determined by Trotman-Dickenson and Steacie[1b] in the range 130–300° and Mandelcorn and Steacie[4c] in the range 271–439° are shown in Fig. 3. The curve of the present investigation between 200 and 305° $(E_3 - \frac{1}{2}E_4 = 10.1$ kcal./mole) agrees closely with that of Trotman-Dickenson and Steacie. However, there is a gradual increase of the slope above 300° which is not apparent in the Mandelcorn and Steacie curve. Deviations between the present work and the results of Mandelcorn and Steacie may be explained by differences in intensities used in the two studies. Their photolyses were all conducted at about the same intensity, approximately $\frac{1}{10}$ the highest intensities used in the present study. Thus the $R_{CH_4}/R_{C_2H_6}^{1/2}(A)$ values reported in Table I at $R_{CO} \cong 60$–80×10^{-12} mole cm.$^{-3}$ sec.$^{-1}$ should correspond to the experimental conditions used by Mandelcorn and Steacie. Use of $R_{CH_4}/R_{C_2H_6}^{1/2}$ (A) of about this intensity in the Arrhenius curve gives a straight line of similar slope to their curve. Although they ran two series of experiments, one with acetone at ca. 73 mm. and one at 37 mm., the R_{CO} for the lower concentration series was about one half that of the high concentration series. Thus the effect of lower concentration was compensated by lower intensity and the resultant $R_{CH_4}/R_{C_2H_6}^{1/2}(A)$ ratios fortuitously fit a single straight line Arrhenius curve.

There is considerable evidence[7] that reaction 4 shows at least a small pressure dependence in the pressure region (25–100 mm.) used in the present study. In addition it should be pointed out that
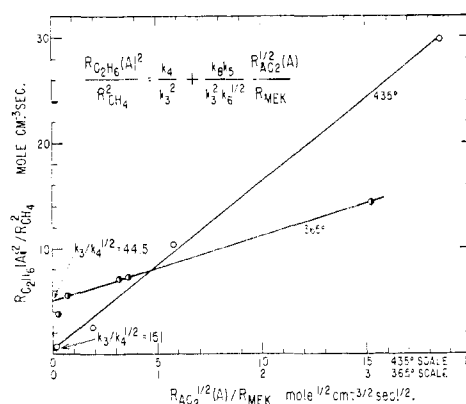
Fig. 2.—Plot of $R_{C_2H_6}(A)^2/R_{CH_4}^2$ vs. $R_{Ac_2}^{1/2}(A)/R_{MEK}$.

since the lifetime of the excited C_2H_6 molecule is shorter at higher temperatures, the pressure of gas necessary to eliminate the third body requirement will be higher at high temperature than at low. Thus the effect of acetone in the present investigation would be more pronounced than that observed by Dodd and Steacie.[7] Certainly such an effect is not sufficient to explain the large variation in $R_{CH_4}/R_{C_2H_6}^{1/2}(A)$ which was observed at the higher temperatures shown in Table I. However, the pressure dependent effect acts in the same general manner as a reaction such as (8). For this reason it is difficult to rule out a pressure dependency occurring simultaneously with reaction 8 and the fit of the data to curves in Fig. 2 is not exact enough to critically evaluate such a dual process. A possible explanation for at least part of the curvature in the Arrhenius plot in Fig. 3 may well be such a dependency.

Ketene Formation.—The occurrence of reaction 7, the decomposition of the acetonyl radical, was suggested by Rice and Herzfeld[8] to explain ketene formation in acetone pyrolysis. Ferris and Haynes[4a] detected ketene in acetone photolysis but made no quantitative study of its formation. The data of Table I furnish a test for validity of (7) since reactions 6 and 7 must conform to the expression

$$R_{Ket}/R_{Ac_2}^{1/2} = k_7/k_6^{1/2} \qquad \text{IV}$$

if these are the only processes producing ketene and 2,5-hexanedione. These ratios are shown in Table I at 435, 400 and 365° and are reasonably constant at each temperature. However, there is a small, but definite, increase with increase in pressure of acetone. Average values of $R_{Ket}/R_{Ac_2}^{1/2}$ at 435° are 9.06 ± 0.27 (90–100 mm.), 7.22 ± 0.85 (50 mm.) and 5.98 ± 0.13 (25 mm.); at 400° 1.66 ± 0.08 (100 mm.), 1.52 ± 0.31 (50 mm.) and 1.33 ± 0.02 (25 mm.); at 365° 0.34 (100 mm.) and 0.265 ± 0.001 (50 mm.). The logs of the 50 mm. values when plotted vs. $1/T$ give a good straight line and evaluate $E_7 - \frac{1}{2}E_6$ as 41 kcal./mole, a value rather close to that (48 kcal.) estimated by Rice and Herzfeld[8] for E_7 in the acetone pyrolysis. The variation in $k_7/k_6^{1/2}$ with pressure strongly suggests that the unimolecular decomposition of acetonyl radical is in the

(8) F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc., **56**, 274 (1934).

TABLE III
QUANTUM YIELDS OF CO AND CH₄ IN ACETONE PHOTOLYSIS

Temp., °C.	435	435	435	435	435	435	435	435	435	435
Acetone P (mm.)	100.0	100.0	100.0	50.0	50.0	50.0	50.0	50.0	24.0	25.0
$I_a{}^b$	384	8.87	2.92	237	112.9	108.6	3.15	2.38	135	3.54
ϕ_{CO}	1.07	2.31	2.26	1.27	1.50ᵃ	1.44	2.07	2.16	1.38	1.97
ϕ_{CH_4}	1.84	5.86	7.31	2.00	2.92ᵃ	2.68	6.62	6.69	2.08	4.71
Temp., °C.	400	400	400	400		365	365	365		300
Acetone P (mm.)	98.4	50.0	50.0	49.0		100.0	50.0	25.0		50.0
$I_a{}^b$	52.8	138.0	121.2	35.0		214	150.0	80.2		137.5
ϕ_{CO}	1.17	1.32	1.42ᵃ	1.19		1.34	1.29	1.39		1.26
ϕ_{CH_4}	2.18	1.82	2.20ᵃ	2.17		1.95	1.70	1.66		1.19

ᵃ Products allowed to stand 8 hr. at reaction temperature.   ᵇ Einstein cm.$^{-3}$ sec.$^{-1}$ × 10^{12}.

pressure dependent region just as probably is the case for the methyl radical combination (4). Such a dependency could of course be tested theoretically, at least, by addition of third body gases. However, the complication of large amounts of foreign gases in the analytical procedures would decrease their accuracy, and it is doubtful whether the small pressure dependence shown above could be checked with any certainty.
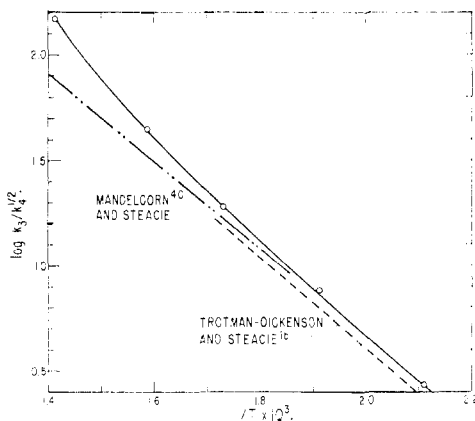

Fig. 3.—Plot of log $k_3/k_4{}^{1/2}$ vs. $1/T$.

Quantum Yield of CO. The Production of C₂H₄.—The quantum yields of CO and CH₄ at various temperatures, pressures and intensities are shown in Table III. At the highest intensities $\Phi_{CO} = 1.25$ and is essentially independent of temperature and pressure of acetone. Whether the 25% increase of Φ_{CO} over the 150° photolyses (Φ_{CO} taken as unity) used for intensity determinations represents a real change is difficult to ascertain. This magnitude is about the degree of accuracy of quantum yields determined in this manner. Very few determinations of the quantum yield of CO in acetone photolysis above 300° have been made. Leermakers[9] determined CO quantum yields up to 405° and his values of *ca.* 1.3 at that temperature agree very well with the present 400° results. However, the increase shown to values of $\Phi_{CO} = 2.1$ at low intensities is certainly significant at 435°. Such an increase indicates that CO is being formed by a process other than (1) or (1a). In addition a reaction of a radical with acetone is strongly suggested by the strong intensity dependence. Certainly process 8 quali-

(9) J. A. Leermakers, *J. Am. Chem. Soc.*, **56**, 1899 (1934).

fies as such a reaction, but the formation of ethane by this reaction is so small that it could not materially affect the CO yield. An attractive mechanism for CO formation is one which simultaneously accounts for C₂H₄ produced. It is seen from Table I that the production of this substance is most favored by the same conditions which raise the Φ_{CO}, *i.e.*, high temperature and low intensity. A possibility for such a mechanism is

$$CH_3COCH_2 + CH_3COCH_3 \longrightarrow$$
$$C_2H_4 + 2CO + CH_4 + CH_3 \quad k_9 \quad (9)$$
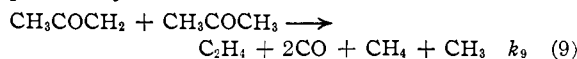
If this were the case, the ratio $R_{C_2H_4}/R_{Ac_2}(A)^{1/2}$ should be constant at a single temperature. Calculations from the data of Table I show this to be approximately true, but the correspondence isn't good enough to justify the definite establishment of (9) as the source of C₂H₄ formation. The behavior of $R_{C_2H_4}/R_{Ac_2}^{1/2}(A)$, especially at lower temperature strongly suggests that a radical-radical process may also contribute to the C₂H₄ yield. This type of reaction would of course be relatively more effective at lower temperatures where reaction 9 is slower. Such a reaction is possibly the disproportionation of methyl and acetonyl radicals

$$CH_3 + CH_3COCH_2 \longrightarrow C_2H_4 + CH_4 + CO \quad k_{10} \quad (10)$$

However, at the higher temperatures of this study this latter process must play a rather small part in the over-all C₂H₄ formation. CH₄ formed by (9) and (10) would tend to alter the conclusion reached earlier in the discussion that CH₄ is produced solely by reaction 3. However, the amount of CH₄ formed in equal amounts of C₂H₄ as required by (9) and (10) is small enough compared to the total CH₄ produced (*ca.* 10% in the most unfavorable cases) so that the curves of Fig. 1 would not be altered to any significant degree. Unless (9) and (10) are to be established on a more firm basis, the original conclusions as to CH₄ formation are adequate.

The data on MVK production in Table I are not extensive and, although this substance is most certainly a product of the photolysis, no mechanism can be suggested to explain its formation.