Be III were used to evaluate the derivatives for the first two states, but data on He I and Li II only were used for the other states. Table II shows data and calculated quantities. From Table II, it is evident that, as the electron becomes more excited, the ratio, $|E_n^1/E_e^1|$ approaches $Z/(n-1)$.

The Photochemistry of Gaseous Acetone

by Henry Shaw and Sidney Toby

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The photochemistry of acetone was reinvestigated in the temperature range 121–298° and the pressure range 0.1–220 torr. The quantum yield of carbon monoxide production was independent of pressure over the large pressure range studied. Data were obtained giving the variation of quantum yields of methane, ethane, methyl ethyl ketone, 2,5-hexanedione, and a number of minor products as a function of pressure and temperature, and a mechanism is proposed which accounts for the major products. The behavior of methane formation at low pressures suggests that intramolecular formation of methane is important under some conditions. The quantum yield for acetone disappearance was unity at low pressures but increased rapidly at pressures of acetone greater than 10 torr. After taking energy-transfer considerations into account, excellent agreement was obtained with published values of $k_2/k_a^{1/2}$ for the reactions $CH_3 + A \xrightarrow{2} CH_4 + CH_3COCH_2$ and $2CH_3 \xrightarrow{a} C_2H_6^*$. By correcting literature values of k_a, the high-pressure limit was found to be $k_{a\infty} = (2.0 \pm 0.15)10^9T^{1/2}$ l. mol^{-1} sec^{-1}. This yields $k_2 = (3.3 \pm 1.5)10^8 \exp[(-9440 \pm 350)/RT]$ l. mol^{-1} sec^{-1}.

Introduction

The photolysis of gaseous acetone (A) has been extensively studied because it is one of the principle sources of quantitative data on the kinetics of methyl radical reactions. The mechanism was postulated by Dorfman and Noyes[1] and may be written

$$A + h\nu \longrightarrow CH_3 + CH_3CO$$

$$CH_3CO\ (+ A) \xrightarrow{1} CH_3 + CO\ (+ A)$$

$$CH_3 + A \xrightarrow{2} CH_4 + CH_3COCH_2$$

$$CH_3 + CH_3COCH_2 \xrightarrow{3} C_2H_5COCH_3$$

$$2CH_3 \underset{b}{\overset{a}{\rightleftharpoons}} C_2H_6^*$$

$$C_2H_6^* + A \xrightarrow{c} C_2H_6 + A$$

Reactions a, b, and c were shown to be important at low pressures by Dodd and Steacie,[2] and the asterisk indicates vibrationally excited ethane. More recently, Darwent, Allard, Hartman, and Lange[3] determined that reaction 2 was not sufficient to account for all of the methane produced in the photolysis of acetone above 200°. They speculated on the additional abstraction reaction

$$CH_3 + CH_3COCH_2 \xrightarrow{4} CH_4 + CH_2COCH_2$$

but they did not obtain any direct evidence for this reaction.

Henderson and Steacie[4] also observed more methane than would be predicted from reaction 2 only. They attributed this methane to a reaction of methyl radicals with excited acetone. They presented strong evidence to show that the source of this additional methane was not due to methyl radicals abstracting from ethane. Ausloos and Steacie[5] clearly demonstrated that at 27° additional methane was produced from the reaction

$$CH_3 + CH_3CO \xrightarrow{5} CH_4 + CH_2CO$$

They observed ketene in their product gases and found a product dependency on the square root of the incident intensity. O'Neal and Benson[6] demonstrated that the acetyl radical is sufficiently long lived to react with hydrogen iodide at temperatures above 200°.

The photolysis of gaseous acetone at low pressures is

(1) L. M. Dorfman and W. A. Noyes, Jr., *J. Chem. Phys.*, **16**, 557 (1948).

(2) R. E. Dodd and E. W. R. Steacie, *Proc. Roy. Soc.* (London), **A223**, 283 (1954).

(3) B. deB. Darwent, M. J. Allard, M. F. Hartman, and L. J. Lange, *J. Phys. Chem.*, **64**, 1847 (1960).

(4) J. F. Henderson and E. W. R. Steacie, *Can. J. Chem.*, **38**, 2161 (1960).

(5) P. Ausloos and E. W. R. Steacie, *ibid.*, **33**, 47 (1955).

(6) E. O'Neal and S. W. Benson, *J. Chem. Phys.*, **36**, 2196 (1962).

Table I: Quantum Yields of Products at 121°[a]

10^4[A], mol l.$^{-1}$	Photolysis time, sec × 10^{-3}	Φ_M	Φ_E	$10^2\Phi_{70}$	$10^2\Phi_{MEK}$	$10^2\Phi_{86}$	$10^3\Phi_{98}$	$10^3\Phi_{112}$	Φ_{114}	10^9R_{CO}, mol/l. sec^{-1}	$\frac{1}{2}\Phi_M + \Phi_E^{1/2}$	$\Phi_E^{1/2} + \Phi_{114}^{1/2}$	$\Phi_E + \frac{1}{2}\Phi_M + \frac{1}{2}\Phi_{MEK}$
89.3	1.00	0.976	0.478							4.78	1.18		
74.6	1.10	0.887	0.525							4.70	1.16		
58.1	1.25	0.792	0.596							4.17	1.17		
42.5	1.50	0.687	0.658							3.54	1.15		
33.0	1.80	0.553	0.648							3.17	1.08		
24.6	2.20	0.526	0.749							2.48	1.12		
17.2	2.30	0.399	0.781							1.88	1.08		
7.97	2.50	0.301	0.890							0.916	1.09		
2.08	3.50	0.184	1.02							0.274	1.10		
1.14	5.00	0.147	1.07							0.146	1.10		
0.574	7.50	0.102	0.993	1.1	5.4	0.7	2	6	...	0.074	1.05	1.00	1.07
0.38	10.0	0.10	1.1	1.3	4.8	0.8	4	5	...	0.043	1.10	1.05	1.17
0.23	12.0	0.097	1.1	1.1	4.0	0.9	2	4	...	0.033	1.10	1.05	1.17
0.11	18.5	0.11	1.2	1.5	3.2	1.4	2	2	...	0.014	1.15	1.10	1.27
0.083	22.0	0.11	1.3	2.0	3.3	1.8	2	4	...	0.0094	1.20	1.14	1.37
0.040	25.0	0.17	1.3	4.2	3.0	4.6	7	8	...	0.0046	1.22	1.14	1.40

[a] Blanks indicate that no analysis was performed and dots indicate that no product was detected.

of interest as an energy-transfer system[2,7] and can be used to provide data to test unimolecular rate theory.[8] Since methane is an important product even at low pressures, it is necessary to evaluate quantitatively all sources of methane additional to step 2. It is then possible to correlate much previous work on the acetone photolysis and obtain more accurate Arrhenius parameters. For these rate data to be obtained on an absolute basis, the rate of dimerization of methyl radicals should be accurately known. By taking energy-transfer considerations into account, it has been possible to correlate much of the published work on this reaction.

Experimental Section

A conventional high-vacuum apparatus, with greaseless valves in the photolysis and product fractionation sections, was used. The cylindrical, quartz photolysis cell, volume 558 cm^3, was thermostated in a modified convection oven within ±0.5° up to 300°.

The beam from an Osram HBO-75W high-pressure mercury arc, made parallel with a quartz lens, completely filled the photolysis cell. A mirror at the back of the cell increased light intensity and uniformity. The 3130-Å region was isolated with a solution filter,[9] and the potassium biphthalate solution was changed whenever the light output decreased by a few per cent.[10] Light intensity was varied with neutral density filters. In some experiments a less monochromatic but more intense beam was obtained using a Kimax plate with a Corning 7-54 filter. When corrected for intensity differences, both solution and glass filters gave the same results.

Spectroquality (Matheson Coleman and Bell) acetone was distilled from a Linde 5A[11] molecular sieve and then was distilled from bulb to bulb.

Products were fractionated at low temperature. Carbon monoxide, methane (M), and ethane (E) were analyzed gas chromatographically using a silica gel column at 25°. The less volatile products were analyzed using a mass spectrometer. Conversions were kept below 5%, except for the four lowest pressure runs at 298°.

Results

Results are summarized in Tables I–III. Products giving mass spectrometric parent peaks of 70, 86, 98, 112, and 114 were not unambiguously identified, but comparisons with API spectra indicated that the peaks were due to methyl vinyl ketone, biacetyl, mesityl oxide, 2,5-hexenedione, and 2,5-hexanedione, respectively. Analysis for the heavier products were not accurate, since these products were present as a very small fraction of the unreacted acetone.

A dark reaction was carried out for 15 hr at 298° with 200 torr of acetone. The rate was less than 0.01% of the corresponding photoreaction.

The quantum yield for carbon monoxide production, Φ_{CO}, was assumed unity at 216°.[12] Φ_{CO} at the other temperatures were determined using the Beer–Lambert law for slab geometry.[13] The absorption coefficients at

(7) G. B. Kistiakowsky and E. K. Roberts, *J. Chem. Phys.*, **21**, 1637 (1953).

(8) H. Shaw, J. H. Menczel, and S. Toby, *J. Phys. Chem.*, **71**, 4180 (1967).

(9) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941.

(10) M. Venogapalan, G. O. Pritchard, and G. H. Miller, *Nature*, **200**, 563 (1963).

(11) K. S. Howard and F. P. Pike, *J. Phys. Chem.*, **63**, 311 (1959).

(12) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966.

(13) H. Shaw and S. Toby, *J. Chem. Educ.*, **43**, 408 (1966).

Table II: Quantum Yields of Products at 216°[a]

10^4[A], mol $l.^{-1}$	Photolysis time, sec $\times 10^{-3}$	Φ_M	$10^2\Phi_E$	$10^2\Phi_{70}$	Φ_{MEK}	$10^2\Phi_{86}$	$10^3\Phi_{98}$	$10^2\Phi_{112}$	Φ_{114}	10^9R_{CO}, mol/l. sec^{-1}	$\frac{1}{2}\Phi_M + \Phi_E^{1/2}$	$\Phi_E^{1/2} + \Phi_{114}^{1/2}$	$\Phi_E + \frac{1}{2}\Phi_M + \frac{1}{2}\Phi_{MEK}$
72.3	1.25	1.74	4.29	...	0.64	...	...	180	0.82	6.36	1.08	1.12	1.23
60.8	1.50	1.67	4.63	...	0.53	...	...	73	0.73	6.09	1.04	1.06	1.14
40.2	2.50	1.56	7.04	...	0.53	...	...	41	0.41	5.15	1.04	0.90	1.11
30.3	2.60	1.53	9.30	...	0.47	...	...	110	(3.2)	4.20	1.07		1.09
20.4	2.80	1.40	12.1	...	0.51	...	...	20	0.73	3.29	1.05	1.20	1.07
12.4	1.10	1.30	15.1	...	0.68	...	...	79	Trace	2.00	1.04	0.39	1.14
7.53	6.00	1.20	16.2							0.838	1.00	0.40	
3.53	2.00	1.10	27.9	...	0.35	...	...	...	...	0.655	1.03	0.53	1.00
1.27	3.10	0.869	34.5	...	0.29	...	...	...	...	0.252	1.02	0.59	0.92
0.646	3.60	0.774	42.8	1.8	0.24	1.6	4	0.8	...	0.131	1.03	0.65	0.93
0.412	4.00	0.761	48.9	2.6	0.21	1.4	4	0.9	...	0.079	1.08	0.70	0.98
0.24	6.10	0.73	50	1.6	0.16	0.7	2	0.4	...	0.047	1.07	0.71	0.95
0.12	11.0	0.72	51	1.6	0.10	0.9	2	0.4	...	0.023	1.07	0.71	0.92
0.065	20.0	0.77	36	2.4	0.043	1.8	4	0.5	...	0.011	0.98	0.60	0.70
0.029	30.0	0.93	49	2.8	0.063	2.5	4	0.5	...	0.005	1.16	0.70	1.00

[a] Blanks indicate that no analysis was performed and dots indicate that no product was detected.

Table III: Quantum Yields of Products at 298°[a]

10^4[A], mol $l.^{-1}$	Photolysis time, sec $\times 10^{-3}$	Φ_M	$10^2\Phi_E$	$10^2\Phi_{70}$	Φ_{MEK}	$10^2\Phi_{86}$	$10^3\Phi_{98}$	$10^2\Phi_{112}$	Φ_{114}	10^9R_{CO}, mol/l. sec^{-1}	$\frac{1}{2}\Phi_M + \Phi_E^{1/2}$	$\Phi_E^{1/2} + \Phi_{114}^{1/2}$	$\Phi_E + \frac{1}{2}\Phi_M + \frac{1}{2}\Phi_{MEK}$
59.7	0.50	1.94	0.316	...	...	...	Trace	Trace	(...)	5.01	0.92		0.86
56.3	0.75	1.92	0.369							4.27	1.02		
51.6	1.60	1.95	0.501	...	0.21	...	...	63	0.6	6.10	1.04	0.84	1.08
42.3	1.20	1.90	0.501	...	....	...	Trace	Trace	(...)	4.20	1.02		0.95
36.9	2.30	1.88	0.651	...	0.21	...	...	31	1.0	5.26	1.02	1.08	1.05
29.4	1.50	1.83	0.416							2.36	0.97		
26.0	2.40	1.87	0.879	...	0.18	...	...	33	2.1	4.24	1.02	1.5	1.04
20.3	2.50	1.88	1.16	...	0.16	...	...	30	1.2	3.57	1.05	1.21	1.03
13.9	1.50	1.94	1.03							2.04	1.07		
11.9	3.33	1.76	1.80	...	0.25	...	...	15	1.3	2.41	1.01	1.27	1.01
8.77	4.00	1.73	1.35							1.41	0.98		
6.17	4.50	1.71	1.97	...	0.20	...	...	34	0.7	1.02	0.99	0.98	0.97
3.39	6.00	1.59	2.85	...	0.14	...	...	...	...	0.627	0.96	0.17	0.89
1.85	7.50	1.62	3.79	...	0.14	...	...	...	...	0.344	1.00	0.19	0.92
1.23	10.0	1.50	5.43	...	0.14	...	...	...	...	0.248	0.98	0.23	0.87
0.891	13.3	1.48	6.52	...	0.13	...	...	...	...	0.175	1.00	0.26	0.87
0.441	18.0	1.43	8.42	...	0.11	...	....	...	...	0.090	1.00	0.29	0.85
0.280	18.0	1.69	5.60	1.4	0.03	1.2	3	0.4	...	0.0215	1.08	0.24	0.92
0.24	13.0	1.4	12	1.4	0.11	0.6	1	0.2	...	0.054	1.05	0.35	0.87
0.19	14.0	1.4	12	1.3	0.08	0.6	1	0.2	...	0.043	1.05	0.35	0.86
0.093	66.0	1.1	5.8	1.0	0.015	0.8	1	0.2	....	0.012	0.79	0.24	0.61
0.076	61.0	1.4	5.7	1.4	0.014	1.1	4	0.2	....	0.0074	0.94	0.24	0.76
0.051	76.0	1.2	6.0	2.0	0.007	....	....	1.4	....	0.007	0.84	0.24	0.66
0.031	60.0	1.1	4.3	2.0	0.012	2.4	2	0.4	....	0.0033	0.76	0.21	0.59

[a] Blanks indicate that no analysis was performed and dots indicate that no product was detected.

the temperatures of this study were determined from the data of Caldwell and Hoare.[14] Φ_{CO} was 0.86 at 121° and 1.0 at 298°. Plots were made for the rate of carbon monoxide production (R_{CO}), calculated from the Beer–Lambert law, as a function of acetone concentration. These plots gave excellent agreement with experimental values of R_{CO}, except that at the highest pressures of this study the experimental values of R_{CO} were consistently slightly lower than the calculated values.

A reaction mechanism which accounts for the major products is

$$A + h\nu \longrightarrow {}^1A_n$$

(14) J. Caldwell and D. E. Hoare, *J. Amer. Chem. Soc.*, **84**, 3987 (1962).

$$^1A_n + A \xrightarrow{7} {}^3A_n + A$$

$$^3A_n \xrightarrow{8} 2CH_3 + CO$$

$$^3A_n + A \xrightarrow{9} {}^3A_0 + A$$

$$^3A_0 + A \xrightarrow{10} 2CH_3 + CO + A$$

$$^1A_n + A \xrightarrow{11} {}^1A_0 + A$$

$$^1A_0 \xrightarrow{12} {}^3A_n$$

$$CH_3 + A \xrightarrow{2} CH_4 + CH_2COCH_3$$

$$CH_3 + CH_2COCH_3 \xrightarrow{3} C_2H_5COCH_3$$

$$2CH_3 \underset{b}{\overset{a}{\rightleftharpoons}} C_2H_6^*$$

$$C_2H_6^* + A \xrightarrow{c} C_2H_6 + A$$

$$2CH_3COCH_2 \xrightarrow{13} (CH_3COCH_2)_2$$

The superscripts refer to the lowest excited singlet and the triplet state; the subscripts refer to thermal (0) and higher-than-thermal (n) vibrational levels of the electronically excited states. Making the usual steady-state assumption for the transient species and assuming[15,16] that $k_3/k_a^{1/2}k_{13}^{1/2} = 2$, we have for the high-pressure region the following relationships for the major products

$$\Phi_E^{1/2} + \Phi_{114}^{1/2} = 1 \quad (1)$$

$$^1/_2\Phi_M + {}^1/_2\Phi_{MEK} + \Phi_E = 1 \quad (2)$$

$$^1/_2\Phi_M + \Phi_E^{1/2} = 1 \quad (3)$$

The experimental values for equations 1–3 are shown in Tables I–III. Good agreement in the high-pressure region is seen and the few scattered values are clearly due to our inaccurate analyses for Φ_{114}.

At constant incident intensity, as [A] increases most of the methyls disappear by reactions 2 and 3, whereas at low values of [A] reactions a–c become more important. The limiting low- and high-pressure quantum yields would then be given by

$$\Phi_M^0 = 0; \quad \Phi_E^0 = 1; \quad \Phi_{MEK}^0 = 0; \quad \Phi_{114}^0 = 0; \quad -\Phi_A^0 = 1 \quad (4)$$

$$\Phi_M^\infty + \Phi_{MEK}^\infty = 2; \quad \Phi_E^\infty = 0; \quad \Phi_{114}^\infty = 1; \quad -\Phi_A^\infty = 3 \quad (5)$$

The quantum yields of methane, ethane, methyl ethyl ketone formation and acetone disappearance are given in Figures 1–4 as a function of acetone concentration. The correlation between anticipated and actual values will be discussed shortly.

High-Pressure Rate Constants. The mechanism leads to the previously obtained[2,7] relation

$$\frac{R_M}{R_E^{1/2}[A]} = \frac{k_2}{k_a^{1/2}}\left(1 + \frac{k_b}{k_c[A]}\right)^{1/2} \quad (6)$$

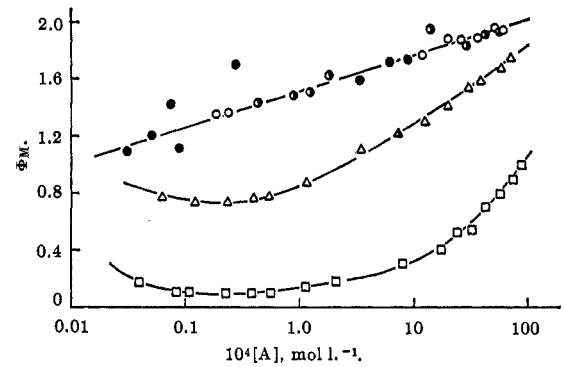

Figure 1. Plot of the quantum yield of methane formation against the acetone concentration: □, 121° ($I_0 = 1.75 \times 10^{-10}$ einstein cm^{-2} sec^{-1}); ▲, 216° ($I_0 = 1.35 \times 10^{-10}$ einstein cm^{-2} sec^{-1}); △, 216° ($I_0 = 1.75 \times 10^{-10}$ einstein cm^{-2} sec^{-1}); ●, 298° ($I_0 = 0.66 \times 10^{-10}$ einstein cm^{-2} sec^{-1}); ◐, 298° ($I_0 = 1.35 \times 10^{-10}$ einstein cm^{-2} sec^{-1}); ○, 298° ($I_0 = 1.75 \times 10^{-10}$ einstein cm^{-2} sec^{-1}).

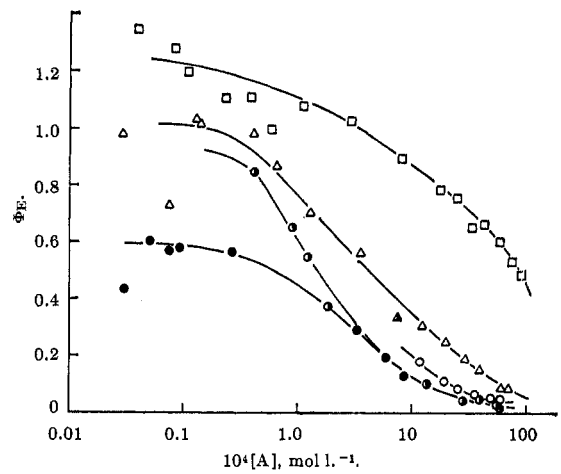

Figure 2. Plot of the quantum yield of ethane formation against acetone concentration: $2\Phi_E$, 216°; $10\Phi_E$, 298°. Symbols the same as in Figure 1.

A Lindemann–Hinshelwood plot of our data as well as that of various literature sources gave us the values of $k_2/k_a^{1/2}$ as [A] → ∞. Figure 5 is the Arrhenius plot for a large body of data from different laboratories. It shows excellent agreement and yields for the high pressure limits

$$E_2 - {}^1/_2E_a = 9.44 \pm 0.35 \text{ kcal mol}^{-1}$$

$$\log (A_2/A_a^{1/2}) = 3.17 \pm 0.17$$

(units of A factors are l. mol^{-1} sec^{-1}; probable errors are given.)

The Methyl Combination Rate Constant. The absolute value of k_2 requires a knowledge of k_a. The latter constant has been measured by a large number of investigators under a variety of conditions, but there has

(15) R. K. Brinton, *J. Amer. Chem. Soc.*, **83**, 1541 (1961).

(16) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 105 (1961).

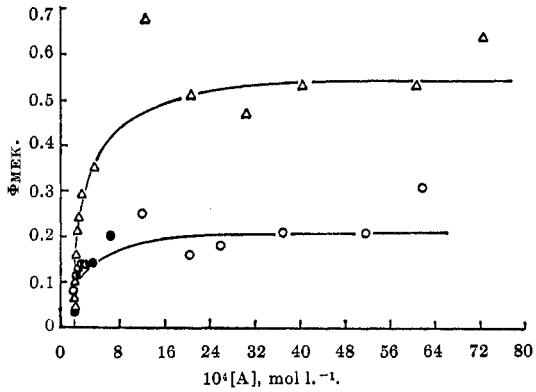

Figure 3. Plot of the quantum yield of methyl ethyl ketone formation against the acetone concentration. Symbols the same as in Figure 1.

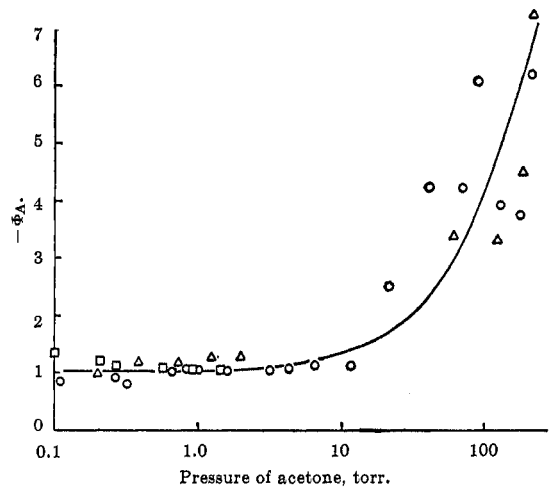

Figure 4. Plot of the quantum yield of acetone disappearance against the acetone pressure. Symbols the same as in Figure 1.

been no systematic attempt to correct all the data for energy-transfer effects. We have obtained the infinite-pressure value of k_a for all published data. The Lindemann mechanism is, of course, a poor approximation at lower pressures and our corrections were made using the data of Setser and Rabinovitch,[17] which were calculated from RRKM unimolecular rate theory. The values are given in Table IV and are plotted in Figure 6 as a function of temperature.

There is considerable scatter, but a better fit is obtained with a $T^{1/2}$ dependence.

Assuming no activation energy for the high-pressure rate constant the best value is

$$k_a = (2.0 \pm 0.15) \times 10^9 T^{1/2} \text{ l. mol}^{-1} \text{ sec}^{-1}$$

Hence

$$k_2 = (3.3 \pm 1.5) \times 10^8 e^{(-9440 \pm 350)/RT} \text{ l. mol}^{-1} \text{ sec}^{-1}$$

Discussion

High-Pressure Mechanism. The high-pressure quantum yields predicted by eq 5 are well obeyed by our data. At higher pressures than used in this study $\Phi_M^\infty \rightarrow 2$. We have not shown a plot of Φ_{114}, since our values are rather scattered, but the trend in Tables I–III is clear. The quantum yield for acetone disappearance shown in Figure 4 is based on a carbon balance and, therefore, includes the yield of 2,5-hexene-

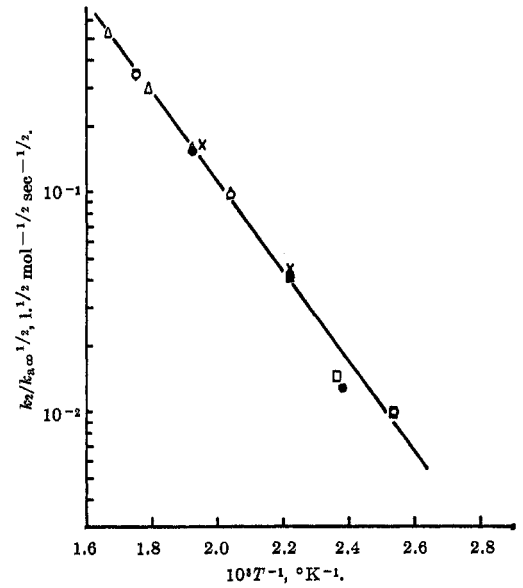

Figure 5. Arrhenius plot of $k_2/k_{a\infty}^{1/2}$: ●, A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **18**, 1097 (1950); □, R. H. Linnell and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **73**, 3986 (1951); ×, Kistiakowsky and Roberts;[7] △, Darwent, *et al.*;[3] △, Brinton;[15] ○, this work.

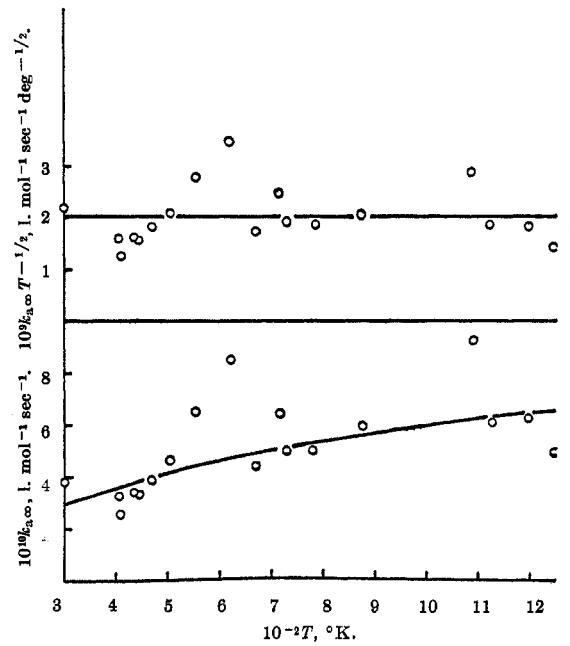

Figure 6. Plot of the methyl dimerization rate constant against the temperature.

(17) D. W. Setser and B. S. Rabinovitch, *J. Chem. Phys.*, **40**, 2427 (1964).

dione. This product was not included in the mechanism because of a large uncertainty in its origin, and if it is omitted from the carbon balance, then $-\Phi_A$ at high pressures is closer to 3, the expected value. The liquid product of a dark reaction contained this unsaturated product. Majer and Simons[18] observed 2,5-hexenedione in the photolysis of halogenated ketones and assumed that it was produced by the reactions

$$2CH_3COCH_2 \xrightarrow{14} CH_3COCH: + A$$

$$2CH_3COCH: \xrightarrow{15} CH_3COCH{=}CHCOCH_3$$

Brinton[15] photolyzed acetone in the range 300–475° and found no 2,5-hexenedione. The other products found in this study were in general agreement with Brinton's findings, although it is clear that ethylene is only formed in appreciable amounts above 300°.[15,19]

Low-Pressure Mechanism. The low-pressure quantum yields predicted by eq 4 correlate well with the experimental results, with the exception of $\Phi_M°$ which is nonzero and may be unity (Figure 1). In addition, $\Phi_E°$ at 121° appears to be somewhat greater than unity, although, as seen in Figure 2, the points at pressures less than 0.3 torr are rather scattered.

The existence of an additional methane-forming step at low pressures is strongly suggested by a plot of $R_M/R_E^{1/2}$ against [A]. This is shown in Figure 7, where a positive intercept not predicted by eq 6 is found, in agreement with previous work.[3] We cannot reconcile previous suggestions[3-5] for the source of the extra methane with our data, and we postulate an additional primary step

$$^1A_n \xrightarrow{6} CH_4 + CH_2CO$$

Equation 6 then becomes

$$\frac{R_M}{R_E^{1/2}} = \frac{k_6 I_a}{(k_6 + k_7[A] + k_{11}[A])R_E^{1/2}} + \frac{k_2[A]}{k_a^{1/2}}\left(1 + \frac{k_b}{k_c[A]}\right)^{1/2} \quad (7)$$

At *sufficiently low pressures*, we may write

$$R_E = \frac{k_a k_c[A][CH_3]^2}{k_b} = \frac{I_a(k_7 + k_{11})[A]}{k_6 + k_7[A] + k_{11}[A]}$$

where steps 2 and 3 can be neglected in the steady-state equation of methyl radicals. Substitution into eq 7 gives the intercept, λ, in Figure 7 as

$$\lambda = \frac{k_6 I_a^{1/2}}{[(k_6 + k_7[A] + k_{11}[A])(k_7 + k_{11})[A]]^{1/2}} \simeq \left(\frac{k_6 I_0 \epsilon}{k_7 + k_{11}}\right)^{1/2}$$

which accounts for the finding of Darwent, *et al.*, that the intercept varies with the square root of the incident intensity.

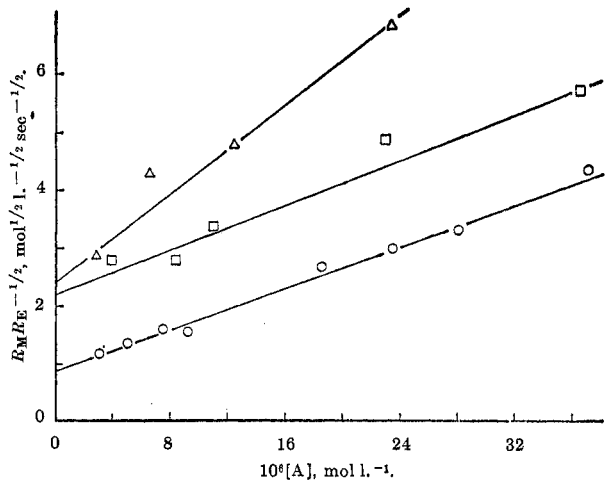

Figure 7. Plot of $R_M/R_E^{1/2}$ against the acetone concentration at low pressures. Symbols the same as in Figure 1. Ordinate is multiplied by 10^7, 10^6, and 10^5 at 121, 216, and 298°, respectively.

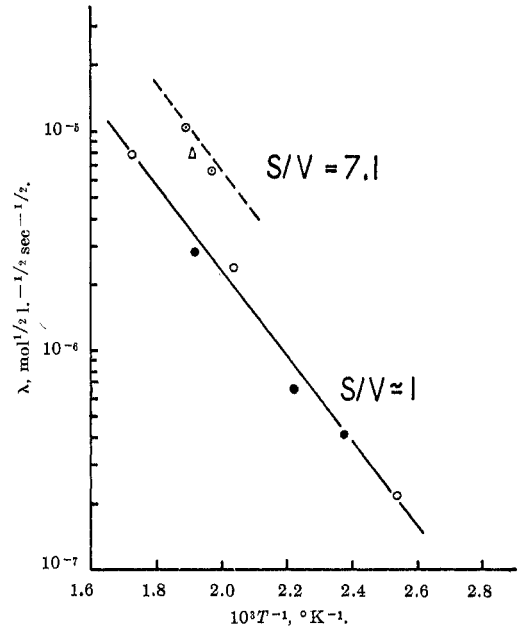

Figure 8. Arrhenius plot of λ (defined in text): ●, Dodd and Steacie[2] (s/v = 1.1 cm^{-1}); △, Dodd and Steacie[2] (s/v = 7.1 cm^{-1}); ⊙, Ausloos and Steacie[5] (s/v = 7.1 cm^{-1}); ○, this work (s/v = 0.9 cm^{-1}).

Figure 8 shows an Arrhenius plot for λ using data presented here and the data of Dodd and Steacie[2] and Ausloos and Steacie.[5] The slope corresponds to an activation energy of 9.4 kcal mol^{-1} and an apparent surface effect is seen. We believe this effect is spurious, since an Arrhenius plot of k_6 (assuming collision numbers for k_7 and k_{11}) shows considerable scatter but no surface effect, suggesting that packing the reaction vessel may have changed the effective incident intensity. Al-

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though the occurrence of heterogeneous effects affords a possible explanation for the intercepts in Figure 7, we believe an intramolecular process is more likely.

The fate of the ketene produced in reaction 6 is uncertain. We found traces of ketene in some of the mass spectrographic analyses, but this molecule is very reactive and may have been consumed in a CO-forming polymerization reaction.[20] The primary photochemical reactions proposed here are similar to those previously considered[21] with the addition of reaction 6, a molecular elimination reaction, important at low pressures.

The production of molecular entities in photochemical reactions has been observed in the photochemistry of acetaldehyde where methane is produced presumably from an excited singlet state.[12] Also, in the photoxidation of acetone, methane is produced in the presence of oxygen,[20,22] suggesting an intramolecular process.

Φ_{CO} was unity at the higher temperatures of this study; at 121° the quantum yield was 0.86 in agreement with Cundall and Davies[23a] and Pearson.[23b]

The Rate Constants. Step 6 is unimportant at high pressures and at the intensities employed in our work and has little effect on Figure 5. The third-body effect is, however, important in obtaining the high-pressure[24] value $k_2^2/k_{a\infty}$. It is important to note that the assumption that $E_a = 0$ is only valid at high pressures, for at low pressures E_a will have an apparently negative value.[25]

The high-pressure correction to convert k_a to $k_{a\infty}$ varied considerably, as shown in Table IV. The values of $k_{a\infty}/k_a$ ranged from near unity at low temperatures to more than 20 at the highest temperatures. In the case of the mass spectrometric determinations the helium carrier gas was assumed to be $^1/_{15}$th as efficient as acetone in stabilizing excited ethane.

The scatter of the data is too great to decide whether or not the simple collision theory $T^{1/2}$ dependence is a better fit than a Gorin model[26] which leads to a $T^{1/6}$ dependence.

It is interesting to note that using simple collision theory with a collision diameter $\sigma(CH_3) \simeq 3.8$ Å $= \sigma(CH_4)$,[27] assuming that σ is not a function of temperature[28] and that there is an electronic steric factor of 0.25, we obtain a value for the dimerization rate constant of $k_{a\infty}T^{-1/2} = 1.8 \times 10^9$. The value obtained in averaging all 18 determinations in Table IV is $k_{a\infty}T^{-1/2} = 2.0 \times 10^9$.

Acknowledgments. We are grateful to the National Science Foundation for its support of this work. We thank the Colgate-Palmolive Research Center for the mass spectrometric analyses. We are indebted to a referee for helpful criticism.

Table IV: Observed (k_a) and Corrected ($k_{a\infty}$) Rate Constants for Dimerization of Methyl Radicals

Footnote	Temp, °K	$10^{10}k_a$, l. mol^{-1} sec^{-1}	$10^{10}k_{a\infty}$ l. mol^{-1} sec^{-1}
a	298	3.81	3.81
b	403	2.40	3.23
c	407	2.30	2.56
d	434	1.36	3.40
b	443	2.00	3.33
d	466	1.17	3.90
d	502	1.16	4.64
d	551	0.973	6.49
d	617	0.853	8.53
e	669	0.673	4.49
d	713	0.646	6.46
e	726	0.753	5.02
e	779	0.753	5.02
d	872	0.590	5.90
d	1087	0.462	9.24
e	1123	0.302	6.03
f	1198	0.311	6.23
f	1248	0.248	4.96

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