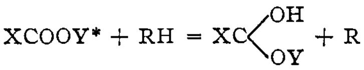
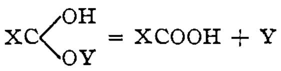
It is conceivable that this process might occur in two steps



$$XCOOY^* + RH = XC(OH)(OY) + R$$



$$XC(OH)(OY) = XCOOH + Y$$

Such a mechanism may be expected to depend on the ease of abstraction of a hydrogen atom from the solvent molecule and would also account for the increase of the YH yields with increase of solvent concentration and increase in temperature. If every Y radical abstracts a hydrogen atom from the surrounding molecules, one YH molecule may be expected to be formed for every excited ester molecule reacting by process VII. The data of Tables I, II, III and IV indicate, however, that the YH yield is always too small compared with the number of molecules deactivated by the solvent. The occurrence of a recombination process such as

$$Y + R = YR$$

may account for this discrepancy. In the photolysis of methyl *n*-butyrate–ethyl alcohol mixtures, the CH_4 yield does not change at high dilution while the C_2H_4 yield is still decreasing. The explanation of these points is not obvious.

In connection with this work it may be mentioned that in the photolysis acetone–hydrocarbon mixtures an alcohol was formed,[2,3] while the quantum yield of the volatile products was less than for the undiluted ketone.[4] A process analogous to VII may account for these results

$$CH_3COCH_3^* + RH = (CH_3)_2COH + R \quad (VIII)$$

followed by

$$(CH_3)_2COH + R = (CH_3)_2COHR$$

It is likely that processes VII and VIII also occur in the gas phase at high pressures and intensities.[8]

Acknowledgment.—The author is indebted to Professor W. A. Noyes, Jr., for advice and encouragement.

(8) ADDED IN PROOF.—Recently G. K. Osler and R. A. Marcus, *J. Chem. Phys.*, **27**, 472 (1957), suggested a process such as VIII in the flash photolysis of acetone in the presence of butane.

ROCHESTER 20, NEW YORK

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

A Kinetic Study of the Thermodynamic Properties of the Acetyl Free Radical[1]

BY JACK G. CALVERT AND JERRY T. GRUVER

RECEIVED SEPTEMBER 6, 1957

Azomethane is photolyzed at 3660 Å. in the presence of acetaldehyde or carbon monoxide in gas phase experiments at several temperatures and reactant concentrations. Product rate data lead to estimates of the rate constants for the acetyl free radical decomposition reaction, $CH_3CO \rightarrow CH_3 + CO$ (1), and the formation reaction, $CH_3 + CO \rightarrow CH_3CO$ (2). From these data the approximate thermodynamic functions of reaction (1) are estimated. These results and suitable published enthalpy values give the heat of formation of the acetyl free radical $\cong -3.0$ kcal./mole, and the bond dissociation energies, $D_{CH_3CO\text{-}CH_3} \cong 82$, $D_{CH_3CO\text{-}H} \cong 89$, $D_{CH_3CO\text{-}COCH_3} \cong 72$ kcal./mole.

Quantitative information is needed concerning the acetyl free radical reactions of decomposition (1) and formation (2)

$$CH_3CO \longrightarrow CH_3 + CO \qquad (1)$$

$$CH_3 + CO \longrightarrow CH_3CO \qquad (2)$$

to establish the thermodynamic properties of the acetyl free radical and to obtain realistic estimates of the bond strengths in the ketones and aldehydes. Published information related to (1) and (2) is very limited and of questionable reliability. The data pertinate to reaction 1 have been re-evaluated recently.[2] It was concluded that the majority of the information favored a "low" activation energy ($E_1 \cong 12 \pm 2$ kcal./mole), but a clear choice between this and an alternative "high" value ($E_1 \cong 17 \pm 1$ kcal./mole) was not possible.

The available information concerning reaction 2 is even less satisfactory. Faltings[3] has given indirect evidence that this reaction may occur at room temperature. He reports that acetone was detected among the products of the Schumann ultraviolet photodecomposition of ethane in the presence of added carbon monoxide. However, Porter and Benson[4] were unable to detect the occurrence of (2) at 150°; C^{14}-containing acetone was not found in the products of di-*t*-butyl peroxide thermal decomposition in the presence of $C^{14}O$. They concluded that $k_2 \leqslant 3 \times 10^9$ cc./mole-sec. at 150°.

In the work reported here the rate constants for the reactions 1 and 2 are estimated from rate data derived in azomethane photolyses in the presence of added acetaldehyde and carbon monoxide.

Experimental

Apparatus.—The photolysis system consisted of a cylindrical quartz photolysis cell (420-cc. volume), a quartz spiral manometer, an all glass in-line circulating pump and a trap. This system was isolated by modified Veeco metal valves. In most of the experiments the photolysis cell was suspended in a large aluminum block oven regulated to ±1°. In three experiments at 0° the oven was removed and the cell was surrounded with an ice-bath. A collimated beam of filtered 3660 Å. light almost completely filled the cell; it was generated from a Hanovia Type A (S-500) burner operated on a regulated a.c. power supply, and filtered with a Corning 5840 filter in combination with a 0.8 cm. thickness of plate glass. The relative energies of the various wave lengths present in the "3660 Å." filtered beam were: 4045 Å., 0.23; 3906 Å., 0.53; 3660 Å., 100.00; 3340 Å., 1.04; 3130 Å., 0.05.

Materials.—Azomethane was prepared and purified by

---

[1] This study was aided by a research grant from the Department of Health, Education, and Welfare, Public Health Service, National Institutes of Health, Bethesda 14, Md.

(2) J. G. Calvert, *J. Phys. Chem.*, **61**, 1206 (1957).

(3) K. Faltings, *Ber.*, **72B**, 1207 (1939).

(4) G. B. Porter and S. W. Benson, THIS JOURNAL, **75**, 2773 (1953).

the method of Renaud and Leitch.[5] No detectable contamination of the azomethane product could be found mass spectrometrically. The vapor pressure of the product at −78° was 6.1 mm. Acetaldehyde was taken from a volatile fraction of Eastman White Label product. Carbon monoxide reagent gas was purchased from the Air Reduction Co., and was used without further purification; it contained the impurities (mole %): CO_2, 0.25; H_2, 0.05; A, 0.035%. The standard reference samples of methane and ethane were Phillips research grade.

Product Analysis.—The duration of each run was sufficiently short so that less than 2% of the original reactants underwent change. Thus rates measured should correspond closely to the initial rates of product formation. Following the $(CH_3)_2N_2$–CH_3CHO mixture photolyses the products of the reaction were separated into three fractions for convenience in analysis. First the CH_4, CO and N_2 were removed with a Toepler pump with the reactants and condensable products in the trap at liquid nitrogen temperature. A second fraction, C_2H_6, was removed in the same fashion with the trap temperature maintained in the range −140 to −160° by means of a simple Ward still. The first two fractions were analyzed separately using a General Electric analytical mass spectrometer. The third fraction, remaining products together with the large excess of the reactants, was distilled from the photolysis system and analyzed in its entirety by vapor–liquid partition chromatography.

After the photolysis of $(CH_3)_2N_2$–CO mixtures, the reactants and products were circulated for one hour through the in-line trap which was cooled to liquid nitrogen temperature. The excess reactant CO and the non-condensable products CH_4 and N_2 were discarded by pumping on the system for 1.5 min. The ethane and the condensable product fractions were then removed and analyzed as before.

The chromatographic column was constructed of 5 mm. i.d. Pyrex glass tubing, 4 m. in total length. It was packed with C-22 firebrick (Johns-Manville) on which was placed a liquid phase (40% by weight) of polyethylene glycol-400 (Carbide and Carbon). The column was suspended in a 50 mm. i.d. glass tube wrapped with heating tape and surrounded with a Magnesite jacket. A thermal conductivity cell bridge was used as detector. With the column temperature of 70° and a helium flow rate of 28 ml./min., the elution times and resolution of the peaks of the various reactants and products were found to be satisfactory for quantitative analysis of the acetone and most of the other products. The expected products, methylethyldi-imine and ketene could not be separated nor detected with this system. With the conditions chosen for column operation the approximate elution times of the various compounds in min. were: $(CH_3)_2N_2$, 6; CH_3CHO, 21; $(CH_3)_2CO$, 41; $(CH_3)_2NN(CH_3)_2$, 56; $(CH_3)_2NN(H)CH_3$, 71; $(CH_3CO)_2$, 110. The column was calibrated using measured pure samples of the known products mixed with the appropriate large excess of the reactants used in the photochemical experiments. The tetramethylhydrazine and trimethylhydrazine products were trapped on elution from the column and identified by mass spectrometry. The rates of formation of the hydrazines are not reported here but will be discussed in detail in a later publication dealing with the methyl addition reaction in azomethane photolysis.

Product Rate Data.—The results of the $(CH_3)_2N_2$–CH_3CHO and $(CH_3)_2N_2$–CO mixture photolyses are summarized in Tables I and II, respectively. Run I of Table I is a photolysis of pure azomethane. The rate ratio, $R_{CH_4}/R_{C_2H_6}^{1/2}[(CH_3)_2N_2] = 0.0528$ (cc./mole-sec.)$^{1/2}$, is considerably lower than that reported for this temperature by Jones and Steacie[6] (0.0678). However, their data showed a definite curvature in the Arrhenius plot at the low temperatures. Our value is in reasonable agreement with the linear extrapolation of the Arrhenius plot of the high temperature data. The agreement was taken as reasonable evidence that the analytical techniques and the photochemical equipment were operating satisfactorily.

The product rates shown in Tables I and II have been determined by direct product analysis with the exception of the rate of biacetyl formation, R_{Ac_2}. This rate was determined directly in run 8 of Table II ($R_{Ac_2} = 8.6_6 \times 10^{-12}$ moles/cc.-sec.) where the length of the run and the pressure of carbon monoxide favored a measurable yield of biacetyl. From the measured rate data the function $R_{Ac_2}^{1/2}R_{C_2H_6}^{1/2}/R_{Me_2CO} = 0.45_4$; this measured function is in close agreement with the ratio of the collision theory Z-factors, $Z_5^{1/2}Z_7^{1/2}/Z_4 = 0.46_5$ (independent of the values assumed for σ_{CH_3} and σ_{CH_3CO}). Noyes and Dorfman have estimated indirectly from acetone photolysis data that $k_5^{1/2}k_7^{1/2}/k_4 \cong 0.9$.[7] Although there is considerable difference between this and the present estimate, other results of Noyes and Dorfman are entirely consistent with the conclusion which our results support; namely, the relative rates of simple radical association reactions are approximately equal to the ratio of the collision theory Z-factors. The biacetyl peaks from the chromatogram of the usual runs in the present work were so small that accurate estimates of R_{Ac_2} were not possible. Hence it was deemed expedient to estimate the value of this rate from the measured values R_{Me_2CO} and $R_{C_2H_6}$ using the theoretical function which was verified experimentally in run 8. All of the R_{Ac_2} data of Table II have been calculated in this fashion.

Discussion

The Acetyl Radical Decomposition Reaction, $CH_3CO \rightarrow CH_3 + CO$ (1).—It has been well demonstrated that the selective photolysis of azomethane at 3660 Å. in the presence of acetaldehyde will sensitize the thermal decomposition of the acetaldehyde.[8] The probable reactions in this system leading to the products ethane, carbon monoxide and acetone are

$$(CH_3)_2N_2 + h\nu \longrightarrow 2CH_3 + N_2 \qquad (I)$$

$$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO \qquad (3)$$

$$CH_3CO \longrightarrow CH_3 + CO \qquad (1)$$

$$CH_3CO + CH_3 \longrightarrow CH_3COCH_3 \qquad (4)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad (5)$$

Ausloos and Steacie have successfully estimated the rate constant ratio $k_3/k_5^{1/2}$ using the azomethane–acetaldehyde system.[9] Product analysis was not complete enough in the previous studies to derive information about the rate of reaction 1.

In the present study the selective photolysis of azomethane was used to generate acetyl radicals by the sequence of reactions I and 3. The rates of the decomposition reaction 1 and the radical combination reactions 4 and 5 were measured by following the rates of the final products carbon monoxide, acetone and ethane, respectively. These rate data are summarized in Table I.

The choice of mechanism is not unambiguous, but there is considerable evidence which favors the homogeneous mechanism chosen. It will be instructive to review some of this evidence briefly. Azomethane is the only significant light absorber in the present system; acetaldehyde, acetone, carbon monoxide, methane, ethane, nitrogen and the substituted hydrazines are all transparent at 3660 Å. The expected products, biacetyl and ketene, which are potential absorbers of 3660 A., absorb negligibly at the low concentrations at which they are present here. Then this system should generate only thermally equilibrated acetyl free radicals. The interpretation of the results should be free from the usual complication encountered in the photochemical production of acetyl free radicals; there is some uncertainty in the photochemical system about the fraction of the acetyl radicals which

---

(5) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

(6) M. H. Jones and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 1018 (1953).

(7) W. A. Noyes, Jr., and L. M. Dorfman, *ibid.*, **16**, 788 (1948).

(8) F. E. Blacet and A. Taurog, THIS JOURNAL, **61**, 3024 (1939).

(9) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 31 (1955).

TABLE I

RATE DATA FROM PHOTOLYSES OF AZOMETHANE–ACETALDEHYDE MIXTURES AT 3660 Å.

Run no.	Temp., °C.	$P_{\mathrm{Me_2N_2}}$, mm.	P_{AcH}, mm.	Rates of products, moles/cc.-sec. × 10^{12} $R_{\mathrm{N_2}}$	$R_{\mathrm{CH_4}}$	R_{CO}	$R_{\mathrm{C_2H_6}}$	$R_{\mathrm{Me_2CO}}$	$\frac{R_{\mathrm{CO}}R_{\mathrm{C_2H_4}}^{1/2} \times 10^6}{R_{\mathrm{Me_2CO}}}$
1	23.0	25.5	0.0	2.65	0.0649	0.00	0.793	0.00	....
2	22.0	36.8	20.0	6.47	1.56	.0259	3.71	.24	0.0208
3	22.7	40.0	30.0	4.92	3.02	.0616	2.89	.531	.0197
4	30.3	32.5	62.7	5.73	6.25	.0641	2.99	.534	.0208
5	40.5	30.2	30.8	5.36	4.92	.133	3.93	.513	.0513
6	52.5	41.7	25.8	6.06	4.15	.482	2.22	.300	.239
7	71.4	41.8	28.3	..	2.54	1.87	2.06	.283	.948
8	71.5	41.4	59.3	6.03	12.0	2.75	1.87	.406	.926
9	79.3	40.3	29.5	5.89	8.27	2.36	1.46	.283	1.01
10	101.5	14.2	29.2	2.11	4.21	3.12	0.316	.150	1.17
11	102.5	31.1	32.7	3.42	4.69	3.31	0.558	.149	1.66
12	115.7	44.1	30.6	7.95	10.4	6.90	1.01	.132	5.25
13	127.1	42.8	31.6	..	13.8	10.8	1.13	.133	8.63

TABLE II

RATE DATA FROM PHOTOLYSES OF AZOMETHANE–CARBON MONOXIDE MIXTURES AT 3660 Å.

Run no.	Temp., °C.	$P_{\mathrm{Me_2N_2}}$, mm.	P_{CO}, mm.	Rates, moles/cc.-sec. × 10^{12} $R_{\mathrm{C_2H_6}}$	$R_{\mathrm{Me_2CO}}$	R_1	$R_{\mathrm{Ac_2}}$	R_2	$\frac{R_2 \times 10^2}{R_{\mathrm{C_2H_6}}^{1/2}[\mathrm{CO}]}$
1	0.0	44.7	51.2	3.36	0.138	0.0022	0.0012	0.143	2.60
2	.0	44.8	112.9	3.39	.342	.0054	.0074	.362	2.96
3	.0	45.3	143.9	2.70	.329	.0058	.0087	.352	2.54
4	21.4	43.1	197.8	2.78	.636	.068	.0314	.767	4.26
5	21.4	41.8	99.1	4.43	.365	.031	.0065	.409	3.61
6	22.3	41.7	389.1	1.28	.599	.101	.0686	.837	3.51
7	23.9	45.6	75.0	4.51	.351	.036	.0059	.399	4.64
8	24.3	43.6	340.3	1.223	.716	.143	.0905	1.04	5.12
9	32.3	41.8	46.5	3.83	.182	.033	.0019	0.219	4.59
10	38.9	43.3	81.5	3.79	.389	.129	.0086	.535	6.56
11	39.3	42.1	49.3	4.18	.217	.071	.0024	.293	5.68
12	47.9	43.8	43.7	4.49	.210	.118	.0021	.332	7.17
13	48.5	86.9	124.3	3.15	.499	.348	.0171	.881	8.01
14	55.1	44.0	56.2	3.60	.214	.213	.0027	.432	8.29
15	58.1	44.2	82.2	2.52	.251	.361	.0054	.623	9.86

are excited in the primary photochemical act and undergo rapid decomposition as the radicals are formed. It seems likely then that carbon monoxide is formed only in reaction 1. The experimental evidence proves that ethane is not formed from azomethane in a primary process,[6,10] and it is likely that reaction 5 is its only source. By analogy with the evidence for (5) it is suggested that a homogeneous reaction 4 leads to acetone formation.

If the suggested mechanism is operative then the rate function 6 should be a constant at a given temperature, independent of the concentration of the reactants azomethane and acetaldehyde.

$$R_{\mathrm{CO}}R_{\mathrm{C_2H_6}}^{1/2}/R_{\mathrm{Me_2CO}} = k_1k_5^{1/2}/k_4 \qquad (6)$$

Within the rather large experimental error this is seen to be the case in runs at 22° (2, 3 of Table I) and 71° (7, 8 of Table I). The methyl and acetyl combination reactions 4 and 5 are in the pressure region where bimolecular kinetics hold.[11] Since the rate function 6 is pressure independent, reaction 1 must be in the region of first-order kinetics. An Arrhenius plot of the rate function 6 is given in Fig. 1. The points shown as triangles were calculated by the authors from the kinetic data of Volman and Brinton.[12] They studied the thermal decomposition of acetaldehyde sensitized by di-*t*-butyl peroxide. The method of treatment of their data has been described previously.[2] The consistency of the rate functions calculated from the results of the very different experiments lends support to the choice of homogeneous reaction mechanism suggested here. The least squares treatment of all of the data from the present work gives

$$k_1k_5^{1/2}/k_4 = 1.8_3 \times 10^3\, e^{-13.5/RT}(\text{cc./mole-sec.})^{1/2}$$

Thus $E_1 + E_5/2 - E_4 = 13.5$ kcal./mole, and since $E_4 \cong E_5 \cong 0$, $E_1 \cong 13.5$ kcal./mole. This result is in excellent agreement with the recent work of Volman and Graven[13] from which it was estimated $E_1 \cong 13.5 \pm 2$ kcal./mole. The data clearly confirm the choice of the "low" value for E_1.[2]

An estimate of k_1 can be derived from the present work. Taking $k_5 = 2.2 \times 10^{13}$ (cc./mole-sec.)[14] and assuming that $k_4 = k_5Z_4/Z_5$ ($Z_4 = 11.3 \times 10^{12} \cdot T^{1/2}$, $Z_5 = 5.82 \times 10^{12}T^{1/2}$), we estimate

$$k_1 \cong 1.66 \times 10^{10}\, e^{-13.5/RT}\ \text{sec.}^{-1}$$

This is in fair agreement with a recent estimate[2] based on all the published data related to reaction 1, $k_1 \cong 1.6 \times 10^9 e^{-12\pm 2/RT}$ sec.$^{-1}$; the estimate was

---

(10) G. R. Hoey and K. O. Kutschke, THIS JOURNAL, **33**, 496 (1955).

(11) (a) G. B. Kistiakowsky and E. K. Roberts, *J. Chem. Phys.*, **21**, 1637 (1953); (b) R. E. Dodd and E. W. R. Steacie, *Proc. Roy. Soc.* (*London*), **A223**, 283 (1954).

(12) D. H. Volman and R. K. Brinton, *J. Chem. Phys.*, **20**, 1764 (1952).

(13) D. H. Volman and W. M. Graven, *ibid.*, **20**, 919 (1952).

(14) A. Shepp, *ibid.*, **24**, 939 (1956).

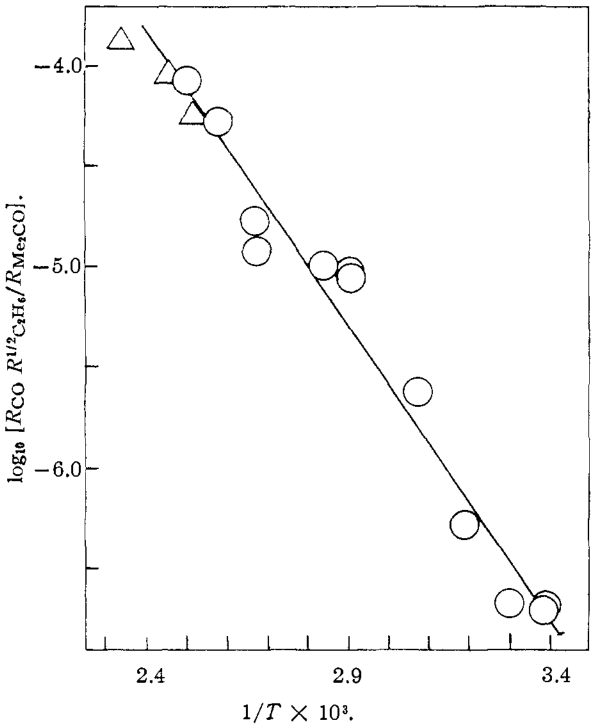


Fig. 1.—An Arrhenius plot of the rate function theoretically equal to $k_1k_5^{1/2}/k_4$. The circles are from data obtained in the present study of the selective photolysis of azomethane in acetaldehyde mixtures. The triangles are calculated by the authors from data of Volman and Brinton.[12]

based on data from seven independent investigations using a variety of photochemical and thermal studies. An unwarranted weight may have been given to some of the scattered and unreliable data from the different sources. Using the single most complete set of data obtained by Anderson and Rollefson[15] to estimate the rate constant ratio $k_1/k_7^{1/2}$ as has been described,[2] and taking k_7 = 1.8×10^{13}, we estimated that $k_1 \cong 1.25 \times 10^{10} \cdot e^{-13.4/RT}$ sec.$^{-1}$ which is in excellent agreement with the present estimate. It is interesting that the experimental pre-exponential factor for k_1 is about 10^3 lower than that expected for "normal" first-order reactions. It is highly unlikely that this difference is the result of experimental error. However, a realistic theoretical justification for the unexpected low probability of the reaction 1 is not obvious to the authors.

The Formation Reaction of the Acetyl Free Radical, $CH_3 + CO \rightarrow CH_3CO$ (2).—In the second phase of this work methyl radicals from azomethane photodecomposition were allowed to react in part with an added excess of carbon monoxide by reaction 2. That this reaction occurred is evidenced by the formation of acetone and biacetyl in the experiments summarized in Table II. An inherent difficulty in the measurement of the rate of reaction 2 lies in the multitude of reaction paths which the initial transient product, CH_3CO, may take in forming the final stable products which can be found by analysis. Several possible reactions of the acetyl radical should be considered for the present system

$$CH_3 + CO \longrightarrow CH_3CO \tag{2}$$

$$CH_3CO \longrightarrow CH_3 + CO \tag{1}$$

$$CH_3CO + CH_3 \longrightarrow CH_3COCH_3 \tag{4}$$

$$CH_3CO + CH_3 \longrightarrow CH_4 + CH_2CO \tag{4'}$$

$$2CH_3CO \longrightarrow (CH_3CO)_2 \tag{7}$$

$$2CH_3CO \longrightarrow CH_3CHO + CH_2CO \tag{7'}$$

$$CH_3CO + (CH_3)_2N_2 \longrightarrow CH_3CHO + CH_2N_2CH_3 \tag{8}$$

$$CH_3CO + (CH_3)_2N_2 \longrightarrow CH_3CO(CH_3)N_2CH_3 \tag{9}$$

As the temperature increases the fraction of the acetyl radicals which decompose by (1) will increase rapidly, and the sum of the rates of the final products other than CO (since this is a reactant, it is indistinguishable as a product) formed from the acetyl radical will be considerably lower than the actual rate of reaction 2. The rates of acetone and ethane formation have been measured in these experiments and their relation to the rate of reaction 1 has been established experimentally. Thus the rate of acetyl reaction by (1) can be calculated for each experiment: $R_1 = (R_{Me_2CO}/R_{C_2H_6}{}^{1/2})\ 1.83 \times 10^3 e^{-13.5/RT}$ moles/cc.-sec. Values of R_1 calculated in this fashion are listed in Table II. As expected R_1 is unimportant in the runs at the lowest temperatures but it is a dominant mode of reaction at the highest temperature. The rates of reactions 4 and 7 can be determined directly. The amount of acetaldehyde in the products was below the detection limit in these runs, so the possible reactions 7′ and 8 must not be important in this system. The expected ultimate product of reaction 9, acetyltrimethylhydrazine, was not observed in this work, although the exact elution time of such a compound is uncertain. In a subsequent publication it will be shown that the methyl addition to the azomethane molecule

$$(CH_3)_2N_2 + CH_3 \longrightarrow (CH_3)_2N_2CH_3 \tag{10}$$

is relatively unimportant up to 60°, the highest temperature used in this phase of the study. The addition of acetyl to the butadiene molecule has a significantly higher activation energy (5.4 kcal./mole)[13] than the corresponding methyl radical reaction (2.5 kcal./mole),[16] and the analogous addition reactions 9 and 10 may show a similar difference. We conclude from these considerations that reaction 9 is probably unimportant in this system, and in the treatment of these results it has been neglected. A direct measure of reaction 4′ was not possible in this study. However, it can be inferred from the data of Ausloos and Steacie[17] that k_4' is small compared to the rate constant for radical combination reactions ($k_4' \leqq 0.1\ k_5$), so the neglect of reaction 4′ should not affect the present results significantly. With these assumptions we derive the rate function 11

$$R_2/R_{C_2H_6}{}^{1/2}[CO] = k_2/k_5{}^{1/2} \cong (R_{Me_2CO} + 2R_{Ac_2} + R_1)/R_{C_2H_6}{}^{1/2}[CO] \tag{11}$$

The various rate terms and the values of the rate function 11 are summarized in Table II. The col-

---

[15] H. W. Anderson and G. K. Rollefson, THIS JOURNAL, **63**, 816 (1941); H. W. Anderson, Ph.D. Thesis, 1941, Univ. Calif., Berkeley.

[16] L. Mandelcorn and E. W. R. Steacie, *Can. J. Chem.*, **32**, 474 (1954).

[17] P. Ausloos and E. W. R. Steacie, *ibid.*, **33**, 39 (1955).

umn headed "R_2" is derived from the relation $R_2 = R_{\mathrm{Me_2CO}} + 2R_{\mathrm{Ac_2}} + R_1$. If the mechanism choice is correct the function 11 should be a constant at a given temperature, independent of the concentrations of the azomethane and the carbon monoxide. This is seen to be the case within the experimental error for experiments at 0° (runs 1, 2, 3 of Table II); 21° (4, 5, 6); 24° (7, 8); and 39° (10, 11).

An Arrhenius plot of the function 11 is shown in Fig. 2. The least squares treatment of these data gives

$$k_2/k_5^{1/2} = 3.01 \times 10^1 e^{-3.8_4/RT} \text{ (cc./mole-sec.)}^{1/2}$$

Taking $k_5 = 2.2 \times 10^{13}$ we estimate

$$k_2 \cong 1.41 \times 10^8 e^{-3.8_4/RT} \text{(cc./mole-sec.)}$$

It is interesting to test the compatibility of the experimental rate functions derived for k_1 and k_2. It may be calculated very approximately that $\Delta S^0_{298.2}$ for reaction (1) $\cong$ 8.45 e.u. taking the standard state as 1 mole/cc.[18] Since $\Delta S^0 = R \ln(A_1/A_2)$, where A_1 and A_2 are the pre-exponential factors of the reactions 1 and 2, respectively, we estimate from theory that $A_1/A_2 \cong 70$. The experimental value derived in this work is: $A_1/A_2 \cong 1.66 \times 10^{10}/1.41 \times 10^8 = 118$. Of course there is considerable uncertainty in the theoretical estimate of ΔS^0. Furthermore it should be noted that an error of only 0.3 kcal./mole in the difference of the experimental activation energies, $E_1 - E_2$, would cause the observed difference in the theoretical and experimental ratios of A_1/A_2. In view of these facts the agreement is considered sufficiently close to establish the internal consistency of the present rate constant estimates.

The Thermodynamic Properties of the Acetyl Free Radical.—The information obtained in this work can be used to derive approximate values for the thermodynamic functions of reaction 1 at temperatures near 25°.

$$CH_3CO \longrightarrow CH_3 + CO \qquad (1)$$

The data suggest $\Delta H_1 = E_1 - E_2 \cong 9.7$ kcal./mole; $\Delta F^0_1 = -RT \ln(k_1/k_2) \cong 9.7 - 0.00948T$ kcal./mole; and $\Delta S^0_1 = (\Delta H^0_1 - \Delta F^0_1)/T \cong 9.4_8$ e.u., taking the standard state as 1 mole/cc. From these results and accepted thermal data[19] the enthalpy of formation of the acetyl free radical $\cong$ -3.0 kcal./mole. The data definitely favor the "high" bond strengths for ketones and aldehydes suggested by Calvert.[2] For example, we estimate $D_{\mathrm{CH_3CO-CH_3}} \cong 82$; $D_{\mathrm{CH_3CO-H}} \cong 89$; $D_{\mathrm{CH_3CO-COCH_3}} \cong 72$ kcal./mole. These estimates of bond dissociation energies are significantly higher than the "currently accepted" values derived from studies of the thermal decomposition of acetone using the toluene carrier technique; for example, it is accepted commonly that $D_{\mathrm{CH_3-COCH_3}} \cong 72$ kcal./mole.[20]

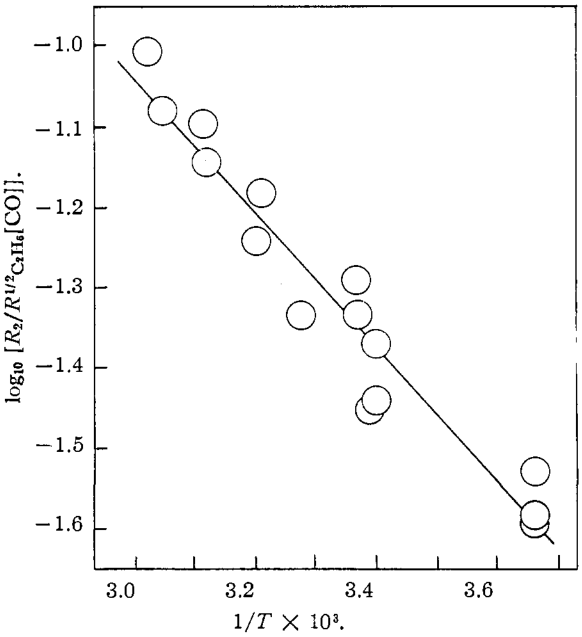


Fig. 2.—An Arrhenius plot of the rate function theoretically equal to $k_2/k_5^{1/2}$. The data were obtained in the photolysis of azomethane in the presence of carbon monoxide.

If one assumes that $D_{\mathrm{CHO-H}} \cong D_{\mathrm{CH_3CO-H}}$ then some approximate energy relations involving the formyl radical reaction 12 can be derived.

$$CHO + M \longrightarrow CO + H + M \qquad (12)$$

Thus we estimate $\Delta H_{12} \cong 16.5$ kcal./mole. This is in fair agreement with estimates based on kinetic data from the aldehydes ($E_{12} \cong 15$ kcal./mole).[2] It is incompatible with recent theoretical and experimental estimates which conclude that $E_{12} \cong$ 26–30 kcal./mole.[21]

COLUMBUS, OHIO

---

[18] We have used Bryant's calculated value of $S^0_{298.2}$ for $CH_3(g) \cong 46.11$ e.u. (W. M. D. Bryant, *J. Polymer Sci.*, **6**, 359 (1951)), the literature value $S^0_{298.2}$ for $CO(g) = 48.30$ e.u., and have estimated $S^0_{298.2}$ for $CH_3CO(g) \cong 64.8_8$ e.u. by taking the literature value for $CH_3CHO(g)$ corrected for the additional electronic contribution (1.38 e.u.) of the doublet ground state. Values of S^0 in this footnote all refer to a standard state of 1 atm. pressure.

[19] $D_{\mathrm{CH_3-H}} = 103$ kcal./mole; enthalpies of formation (kcal./mole) used: $CH_4(g)$, −17.9; $CO(g)$, −26.4; $H(g)$, 52.0; $CH_2O(g)$, −27.7; $CH_3CHO(g)$, −39.8; $CH_3COCH_3(g)$, −51.8; $CH_3COCOCH_3(g)$, −77.8.

[20] (a) D. Clark and H. O. Pritchard, *J. Chem. Soc.*, 2136 (1956); (b) A. H. Sehon and M. Szwarc, *Ann. Revs. Phys. Chem.*, **8**, 439 (1957).

[21] (a) L. Schoen, "Fifth Symposium (International) on Combustion," Reinhold Publ. Corp., New York, N. Y., 1955, p. 786; (b) F. H. Dorman and A. S. Buchanan, *Australian J. Chem.*, **9**, 34 (1956); (c) R. Klein and L. J. Schoen, *J. Chem. Phys.*, **24**, 1094 (1956); (d) R. I. Reed, *Trans. Faraday Soc.*, **52**, 1195 (1956); (e) J. C. D. Brand and R. I. Reed, *J. Chem. Soc.*, 2386 (1957).