Kinetics of the Addition of Methyl, Propyl, and Acetonyl Radicals to

Ethylene and of the Abstraction of Hydrogen from Acetone by

Methyl and Propyl Radicals

by L. Endrenyi and D. J. Le Roy

Lash Miller Chemical Laboratories, University of Toronto, Toronto 5, Ontario, Canada
(Received September 22, 1966)

The photolysis of acetone in the presence of ethylene has been studied in the temperature range 403–503°K. By making a detailed quantitative analysis of the products, it has been possible to obtain kinetic parameters for the addition of methyl, propyl, and acetonyl radicals to ethylene as well as for the abstraction of hydrogen from acetone by methyl and propyl radicals.

Of the six basic types of reaction undergone by free radicals, abstraction, combination, disproportionation, decomposition, isomerization, and addition, the first four have received a considerable amount of attention, both theoretical and experimental.[1,2] Radical isomerizations have been observed on numerous occasions but, with the exception of some recent results from this laboratory on the isomerization of n-pentyl and 4-oxo-1-pentyl,[3] detailed kinetic data are lacking. This is unfortunate because such reactions would provide scope for interesting theoretical considerations. A somewhat similar situation obtains for radical addition reactions. Although a large body of information exists, because of the importance of this type of reaction in polymerization, there have been relatively few detailed studies of the kinetics of the addition of simple radicals to simple olefins.

It was evident from a number of earlier studies that methyl radicals could initiate the polymerization of ethylene, but it was difficult to distinguish the addition reaction

$$CH_3 + C_2H_4 = C_3H_7$$

from subsequent chain-propagating steps. This same difficulty applied to the work of Mandelcorn and Steacie,[4] when they used the rate of consumption of ethylene as a measure of the rate of the addition reaction. They also used a method based on the difference in the methyl radical balance when acetone was photolyzed in the

presence and in the absence of ethylene but did not take account of such a chain-terminating process as the combination of methyl with propyl radicals. Brinton[5] and also Hogg and Kebarle[6] used the pyrolysis of di-*t*-butyl peroxide as the source of methyl radicals for studying the kinetics of the addition of methyl radicals to ethylene and measured its rate in terms of the sum of the rates of the reactions consuming the propyl radicals produced. The method of propyl radical balance is undoubtedly the best for determining the rate of the addition reaction and was used in the present work. It involves analytical and interpretive difficulties because of the necessity for an essentially complete product analysis and mechanism.

In this paper, we present the results of a study of the kinetics of the addition of methyl radicals to ethylene utilizing the photolysis of acetone as the source of methyl radicals. By using gas chromatographic methods, we were able to follow in some detail most of

(1) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, 1, 107 (1961).

(2) S. W. Benson and W. B. De More, *Ann. Rev. Phys. Chem.*, 16, 397 (1965).

(3) L. Endrenyi and D. J. Le Roy, *J. Phys. Chem.*, 70, 4081 (1966).

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

(5) R. K. Brinton, *J. Chem. Phys.*, 29, 781 (1958). This paper contains a good discussion of earlier work.

(6) A. M. Hogg and P. Kebarle, *J. Am. Chem. Soc.*, 86, 4558 (1964). The procedure and interpretation were the same as Brinton's.[5]

the important processes occurring in the system and to determine kinetic parameters not only for this addition reaction but also for several other reactions, including the radical isomerization reactions referred to above[3] and the addition of propyl radicals to ethylene, a reaction which Brinton[5] believed to be of minor importance.

Experimental Section

The basic reagents, acetone and ethylene, were Fisher Certified reagent and Phillips research grade, respectively. Matheson Bone Dry reagent carbon dioxide and Matheson Alcohol-Free reagent isopropyl ether were used as reference substances in the quantitative gas chromatographic analysis of the products. None of the reagents showed detectable amounts of impurities.

The cylindrical quartz cell, 6.0 cm long, 5 cm in diameter, was completely filled by a parallel beam from a 250-w British Thomson Houston mercury lamp. A No. 9700 Corning filter eliminated the shorter wavelengths and left 3130 A as the strongest single line absorbed by the acetone.

The products were separated into two fractions at $-120°$, using a Le Roy still.[7] The more volatile fraction, after measurement in the calibrated section of a Toepler pump, was separated into homogeneous aliquots. These were, in turn, swept into a modified Model 154C Perkin-Elmer vapor fractometer by a stream of helium. A 13-ft, 0.25-in. column containing 35–100 mesh activated silica gel was used for this fraction. The reference substance, carbon dioxide, was in some instances added to the reagents before reaction and in some instances was added to the volatile fraction after reaction. Elution temperatures of 0, 80, 115, and 130° were used for carbon monoxide and methane; ethane, ethylene, and carbon dioxide; propane; and propylene and butane, respectively. The specially constructed thermistor-type thermal conductivity detector was immersed in an ice–water bath. Base-line drift was minimized by placing a 10-ft column containing inert material between the analytical column and the detector; this was kept at 0°.

A more accurate determination of propane and propylene was obtained by passing certain aliquots of the more volatile fraction through a 4 in. long column containing 35–50 mesh alumina to remove the carbon dioxide and then through a 23-ft column containing bis-2-(2-methoxyethoxy)ethyl ether (23% by weight on 35–80 mesh Columpak P) at 0°. In these analyses, butane, which had been determined relative to carbon dioxide using the silica gel column, served as the reference substance. No evidence could be found for iso-

butane, cyclopropane, or acetylene; it was estimated that no more than 1.5×10^{-7} mole of these substances could have been produced.

Transfer of the less volatile fraction to the still and to the gas chromatographic sampling system was effected with a slow stream of helium. The reference substance for this fraction, isopropyl ether, was added after reaction. Separation was carried out at 120° using a 20-ft column containing tri-m-tolyl phosphate (31% by weight on 30–60 mesh firebrick). The reaction products were identified by their calibrated relative retentions[8] and retention indices.[9] The conclusions were supported by additional calibrations followed by reaction product analyses on a 10 ft long bis-2-(2-methoxyethoxy)ethyl ether column at 65°, and also on a 13-ft di(2-ethylhexyl) sebacate column at 120°. Further confirmation of the classifications was obtained by functional group tests. The chromatographic column effluent was absorbed in a slightly acidic methanol solution of 2,4-dinitrophenylhydrazine. Appearance of a colored precipitate indicated the presence of carbonyl group(s).[10] The sensitivity of the test was greatly increased (to a detectability of less than 10^{-8} mole) by examining the visible spectrum of the alkalinified solution. Similarly, by passing the effluent through ethanol and observing the ultraviolet spectrum (near 224 mμ), it was shown that no α,β-unsaturated ketones or aldehydes were present in detectable amounts among the reaction products. Particularly significant was the absence of 3-penten-2-one (methyl propenyl ketone), which would have been produced by the isomerization[11] of 4-penten-2-one (methyl allyl ketone), a suspected reaction product.

The quantative analysis of every product was based on its calibrated relative molar response (*i.e.*, relative to the known amounts of carbon dioxide or isopropyl ether used).

Results

The experimental conditions and results are summarized in Table I. Most of the features are explained in terms of the 16 reactions (eq 1–16) illustrated in Figure 1. A few additional reactions will be referred to in the text.

(7) D. J. Le Roy, *Can. J. Res.*, **B28**, 492 (1950).

(8) D. Ambrose, E. Bayer, P. Chovin, A. I. M. Keulemans, E. Kováts, and F. H. Storss, *Pure Appl. Chem.*, **8**, 553 (1964).

(9) E. Kováts, *Helv. Chim. Acta*, **41**, 1915 (1958); A. Wehrli and E. Kováts, *ibid.*, **42**, 2709 (1959); L. S. Ettre, *Anal. Chem.*, **36** (7), 31A (1964).

(10) L. Dubois and J. L. Monkman in "Gas Chromatography," H. J. Noebels, R. F. Wall, and N. Brenner, Ed., Academic Press Inc., New York, N. Y., 1961, p 237; J. T. Walsh and C. Merritt, Jr., *Anal. Chem.*, **32**, 1378 (1960).

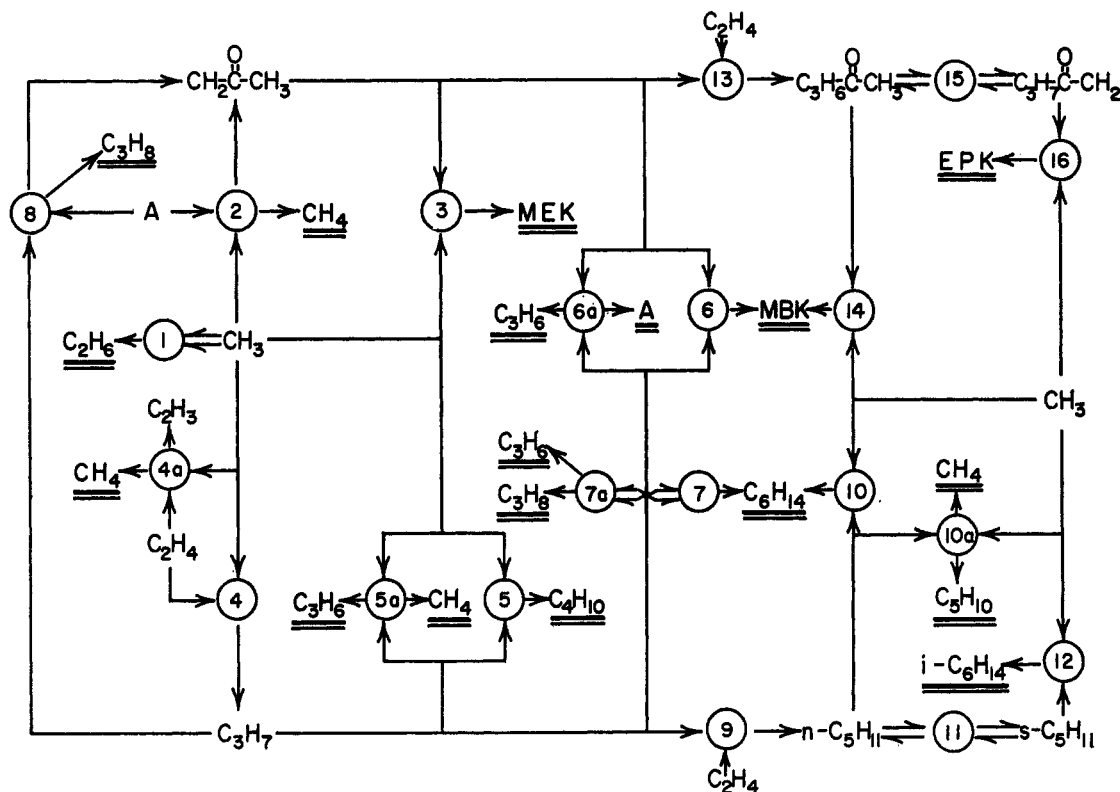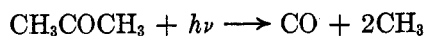(11) M. Gaudemar, *Bull. Soc. Chim. France*, 974 (1962).

Figure 1. Reaction mechanism for the photolysis of acetone in the presence of ethylene.

It has been well established[12] that in the photolysis of acetone alone, under the conditions used in the present experiments (130 to 230°), the initial step

$$CH_3COCH_3 + h\nu \longrightarrow CO + 2CH_3$$

is followed by reactions 1, 2, and 3. Diacetonyl has been observed in some cases, but not in the present experiments; in any event, it would not affect our calculated rates.

The propane and methyl propyl ketone (MPK) formed in experiments 35, 36, and 37 are believed to arise from the photolysis of the methyl ethyl ketone (MEK) formed in reaction 3. The ethyl radicals produced in this way would be expected to undergo the reactions

$$C_2H_5 + CH_3 = C_3H_8 \tag{17}$$

$$C_2H_5 + CH_2COCH_3 = MPK \tag{18}$$
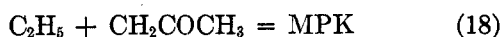
Ethyl radicals produced by the photolysis of MEK would also be expected to attack acetone. The ethane and acetonyl radicals so formed could not be distinguished from the products of reactions 1 and 2; however, the amounts so formed would be quite negligible. The methyl isopropyl ketone (MiPK)

formed in experiments 35, 36, and 37 is undoubtedly a secondary product resulting from the sequence

$$R + MEK = RH + CH_3COCHCH_3 \tag{19}$$

$$CH_3COCHCH_3 + CH_3 = MiPK \tag{20}$$
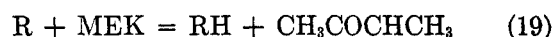
where R is any free radical, but most likely CH_3, since it is the radical present in highest concentration.

In the presence of ethylene (runs 25–31) several new products arise: butane, methyl butyl ketone (MBK), ethyl propyl ketone (EPK), propylene, and n-hexane with smaller amounts of pentane, pentene, and isohexane (2-methylpentane). At the same time the rate of production of propane is greatly enhanced; no dramatic change occurs in the rate of production of the other products formed in the presence of acetone alone. We believe that these facts can be explained in terms of the mechanism shown in Figure 1.

The Reaction $CH_3 + CH_3COCH_3 = CH_4 + CH_2-COCH_3$ (2). In the usual manner, we write

$$\frac{k_2}{k_1^{1/2}} = \frac{R_2}{R_1^{1/2}} \frac{1}{\langle (CH_3COCH_3) \rangle} \tag{i}$$

(12) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

Table I: Experimental Results

No.	T, °K	t, sec	$(CH_3COCH_3)_0$[a]	$\langle(CH_3COCH_3)\rangle$	$(C_2H_4)_0$	$\langle(C_2H_4)\rangle$	(CO_2)	CO[b]	CH_4	C_2H_6	C_3H_8	C_3H_6	C_4H_{10}
25	502.5	519.0	3.60	3.53	0.300	0.275	…	158.1	105.4	41.9	13.4	6.70	19.4
26	502.9	360.0	3.60	3.54	0.240	0.223	0.192	204.5	124.6	63.8	12.5	5.14	22.4
30	479.8	530.0	3.60	3.53	0.240	0.222	0.192	177.2	92.2	79.7	8.64	2.75	22.1
27	457.5	900.0	3.60	3.49	0.240	0.219	0.192	176.5	61.3	94.2	4.40	1.39	20.5
31	438.5	1250.0	3.60	3.49	0.240	0.221	0.192	142.0	38.8	91.8	2.45	0.82	15.6
28	420.2	1800.0	3.60	3.44	0.240	0.221	0.192	156.5	26.7	115.0	1.81	(0.66)	13.8
29	403.3	2200.0	3.60	3.43	0.240	0.225	0.192	135.1	16.2	112.7	0.92	0.37	9.33
35	502.7	1500.0	3.60	3.38	…	…	…	164.1	135.1	61.5	1.32	…	…
36	438.0	2500.0	3.60	3.38	…	…	…	137.4	39.6	102.2	1.35	…	…
38	403.4	3000.0	3.60	3.40	…	…	…	117.1	15.7	103.6	0.686	…	…

No.	C_6H_{12}	C_6H_{10}	i-C_5H_{12}	C_5H_{10}	MEK	MiPK	MPK	EPK	MBK
25	0.16	0.03	1.49	3.10	36.6	0.69	2.60	8.27	10.77
26	0.09	0.06	1.27	2.62	47.5	…	2.47	9.89	11.29
30	0.12	0.06	0.702	2.35	42.9	0.51	1.37	6.58	8.27
27	0.029	0.016	0.401	1.97	34.1	0.35	1.18	4.38	5.07
31	0.021	0.021	0.203	1.31	23.8	0.46	0.58	2.38	3.21
28	0.018	0.012	0.097	0.833	17.6	0.24	0.80	1.01	1.72
29	0.007	…	0.077	0.427	11.6	0.15	1.04	0.37	1.00
35	…	…	…	…	66.4	2.3	1.26	…	…
36	…	…	…	…	28.9	0.94	0.38	…	…
38	…	…	…	…	12.3	0.23	0.063	…	…

[a] Reagent concentrations are expressed in mole $cm^{-3} \times 10^6$. [b] Products are expressed in terms of their rates of formation in mole $cm^{-3} sec^{-1} \times 10^{12}$.

To a first approximation, $R_2 = R_f[CH_4]$, but corrections will be made for the small amounts of methane formed in (5a), (10a), (4a), and the secondary reaction between CH_3 and MEK according to reaction 19. Since ethyl radicals are only produced by the secondary photolysis of MEK and their cross disproportionation/combination ratio with methyl is of the order of 0.05,[2] we neglect methane formation by the process

$$CH_3 + C_2H_5 = CH_4 + C_2H_4$$

Published values of k_{5a}/k_5 range from 0.025 to 0.095.[2] We have chosen to use the value 0.04, so that $R_{5a} = 0.04 R_f[C_4H_{10}]$.

The rate of production of methane by reaction 10a, and in the corresponding reaction with sec-C_5H_{11} radicals, which is not shown in Figure 1, is quite small and will simply be equated to $R_f[C_5H_{10}]$.

The rate of formation of methane by reaction 4a has been estimated from the relation

$$R_{4a} = \frac{k_{4a}}{k_1^{1/2}} R_f[C_2H_6]^{1/2}(C_2H_4) \tag{ii}$$

where

$$\frac{k_{4a}}{k_1^{1/2}} = 10^{4.5} \exp\left(-\frac{11,100}{RT}\right) (cm^3 \ mole^{-1} \ sec^{-1})^{1/2} \ [13]$$

Actually, Trotman-Dickenson and Steacie[13] obtained a value of 10.0 kcal mole^{-1} for $E_{4a} - \frac{1}{2}E_1$, but later experiments showed that they had underestimated the activation energy for deuterium abstraction from acetone-d_6 by about 1.1 kcal mole^{-1}.[14-16]

To calculate the rate of formation of methane by the reaction of CH_3 with MEK according to reaction 19, it will be sufficient to equate it to the rate of formation of MiPK, $R_f[MiPK]$. Thus, if we assume the same rate constant for the abstraction of H from MEK by all radicals, then the fraction $(CH_3)/\sum(R)$ of the $CH_3CHCOCH_3$ radicals formed by reaction 19 will be associated with methane formation. The same fraction of $CH_3CHCOCH_3$ radicals will form MiPK by methyl radical addition.

The calculated rates of formation of CH_4 by reactions 5a and 4a are given in Table II; $R_{10a} = R_f[C_5H_{10}]$ is given in Table I. It is evident that these correction terms are relatively small compared to $R_f[CH_4]$. The Arrhenius plot for $k_2/k_1^{1/2}$ is shown in Figure 2; the kinetic parameters are shown in Table III.

The Reaction $C_3H_7 + A = C_3H_8 + CH_2COCH_3$ (8). Kinetic data for this reaction have not been reported previously. While the accuracy of the results is influenced by the production of propane by other reactions, we believe that this can be allowed for and that the data for reaction 8 are reasonably accurate.
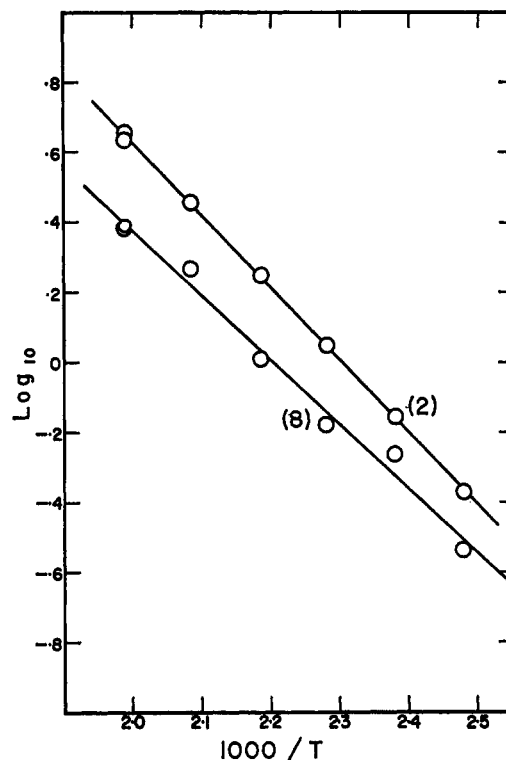

Figure 2. Abstraction of hydrogen from acetone by methyl (2) and n-propyl radicals (8). Arrhenius plots for $k_2/k_1^{1/2}$ and $k_8/k_7^{1/2}$.

The relative rate constant $k_8/k_7^{1/2}$ is given by the expression

$$\frac{k_8}{k_7^{1/2}} = \frac{R_8}{R_7^{1/2}} \frac{1}{\langle(CH_3COCH_3)\rangle} \tag{iii}$$

To obtain R_8 we subtract from $R_f[C_3H_8]$ the rates of all other propane-forming reactions. Of these, the most important are (7a) and (17).

The rate of reaction 7 is given by the expression

$$R_7 = k_7(C_3H_7)^2 = \frac{k_7 k_1}{k_5^2} \frac{R_f[C_4H_{10}]^2}{R_f[C_2H_6]} \tag{iv}$$

There appears to be general agreement that $k_7 k_1/k_5^2 = \frac{1}{4}$.[1,2]

Several values of the ratio k_{7a}/k_7 have been published;[1,2] the most recent values range from 0.14 to 0.17. We have chosen 0.155 as a "best value." Thus

$$R_{7a} = 0.0388 \frac{R_f[C_4H_{10}]^2}{R_f[C_2H_6]} \tag{v}$$

(13) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 169 (1951).

(14) E. Whittle and E. W. R. Steacie, *ibid.*, **21**, 993 (1953).

(15) J. R. McNesby and A. S. Gordon, *J. Am. Chem. Soc.*, **76**, 823, 1416 (1954).

(16) M. H. J. Wijnen, *J. Chem. Phys.*, **22**, 1074 (1954).

Table II: Calculated Rates[a]

T, °K	R_{5a}	R_{4a}	R_7	R_{7a}	R_{17}	R_8	R_6	R_{22}	R_4
502.5	0.78	0.91	2.25	0.35	0.21	12.84	3.90	2.59	50.87
502.9	0.90	0.91	1.965	0.31	0.21	11.98	3.84	2.46	50.48
479.8	0.88	0.60	1.53	0.24	0.31	8.09	2.74	1.36	41.58
457.5	0.82	0.37	1.115	0.17	0.46	3.77	1.71	1.17	32.53
438.5	0.62	0.21	0.663	0.10	0.47	1.88	0.93	0.58	22.35
420.2	0.55	0.14	0.414	0.06	0.54	1.21	0.49	0.80	18.50
403.3	0.37	0.08	0.193	0.03	0.45	0.44	0.22	1.04	12.26

[a] All rates are expressed in mole cm^{-3} sec$^{-1} \times 10^{13}$.

Table III: Relative Rate Constants and Corresponding Arrhenius Parameters

T, °K	$k_2/k_1^{1/2}$ [a]	$k_8/k_7^{1/2}$	$k_4/k_1^{1/2}$	$k_{18}k_1^{1/2}/k_1$	$k_9/k_7^{1/2}$
502.5	4.507	2.43	28.58	30.82	14.87
502.9	4.315	2.41	28.34	36.87	13.93
479.8	2.862	1.85	20.98	26.01	10.41
457.5	1.763	1.023	15.30	18.72	8.56
438.5	1.120	0.662	10.55	14.03	6.78
420.2	0.697	0.547	7.80	9.46	4.86
403.3	0.428	0.292	5.13	6.47	4.13
Log A[b]	4.75 ± 0.04	4.05 ± 0.2	4.43 ± 0.07	4.41 ± 0.15	3.38 ± 0.1
E[c]	9.43 ± 0.07	8.4 ± 0.4	6.84 ± 0.14	6.6 ± 0.3	5.1 ± 0.2

[a] In (cm^3 mole^{-1} sec^{-1})$^{1/2}$. [b] "A" = $A_2/A_1^{1/2}$, etc. [c] In kcal mole^{-1}.

Calculated values of R_7 and R_{7a} are given in Table II.

The rate of formation of propane by reaction 17 could easily be allowed for if all of the MPK came from reaction 18. Thus

$$\frac{R_{17}}{R_t[\text{MPK}]} = \frac{k_{17}(\text{CH}_3)}{k_{18}(\text{CH}_2\text{COCH}_3)} = \frac{k_{17}k_3}{k_{18}k_1}\frac{R_t[\text{C}_2\text{H}_6]}{R_t[\text{MEK}]} \quad \text{(vi)}$$

This relation does hold for the runs with acetone alone; here it was found that

$$R_t[\text{C}_3\text{H}_8] = R_{17} = \frac{R_t[\text{C}_2\text{H}_6]}{R_t[\text{MEK}]}R_t[\text{MPK}] \quad \text{(vii)}$$

with an average deviation of about 10%, indicating

$$\frac{k_{17}k_3}{k_{18}k_4} \approx 1$$

It is evident, however, that in the presence of ethylene, MPK must also be formed by a reaction other than (18); in spite of the lower conversions of acetone, considerably more MPK is formed. A possible explanation for this will be offered when we consider the kinetics of reaction 4.

To a sufficiently good approximation, the rate of formation of C_2H_5 by the photolysis of MEK will be proportional to (MEK) and equal to $\alpha\langle(\text{MEK})\rangle$, say.

In a run of t sec duration, $\langle(\text{MEK})\rangle = \frac{1}{2}R_t[\text{MEK}]t$ and hence the rate of formation of (C_2H_5) will be equal to $\frac{1}{2}\alpha R_t[\text{MEK}]t$.

Most of the ethyl radicals will be consumed by reactions with other radicals. Thus, equating the rates of formation and consumption of C_2H_5

$$\frac{1}{2}\alpha R_t[\text{MEK}]t = (\text{C}_2\text{H}_5)\sum_i k_i(\text{X}_i)$$

or

$$R_{17} = \frac{k_{17}(\text{CH}_3)}{\sum k_i(\text{X}_i)} \times \frac{1}{2}\alpha R_t[\text{MEK}]t \quad \text{(viii)}$$

where (X_i) is the concentration of the ith radical and k_i is the rate constant for its reaction with C_2H_5. Assuming, for this purpose only, the equality of k_{17} and the k_i's

$$R_{17} = \frac{1}{2}\alpha f_{\text{CH}_3}R_t[\text{MEK}]t \quad \text{(ix)}$$

where f_{CH_3} is the ratio of the CH_3 concentration to the total concentration of radicals. To obtain the latter sum, we evaluated (CH_3) from the expression

$$(\text{CH}_3) = \left\{\frac{R_t[\text{C}_2\text{H}_6]}{k_1}\right\}^{1/2}$$

using Shepp's value of 2.2×10^{13} cm^3 mole^{-1} sec^{-1} for k_1,[17] and calculated the concentrations of the other radicals from their rates of combination with methyl.[18] The value assumed for α was obtained from the experiments with acetone alone, since in these experiments $R_{17} = R_f[\mathrm{C_3H_8}]$. The average value of α was $3.8_7 \times 10^{-5}$ sec^{-1}, with an average deviation from the mean of 6%.

Values of R_{17} and of R_8 are given in Table II. Values of $k_8/k_7^{1/2}$ and the corresponding kinetic parameters are given in Table III; the Arrhenius plot is shown in Figure 2.

The Reaction $CH_3 + C_2H_4 = C_3H_7$ (4). The rate of formation of propyl radicals by (4) will be equal to their rate of consumption. On the basis of the mechanism outlined in Figure 1, we will therefore write

$$R_4 = k_4(\mathrm{CH_3})(\mathrm{C_2H_4}) = \frac{k_4}{k_1^{1/2}}R_f[\mathrm{C_2H_6}]^{1/2}(\mathrm{C_2H_4})$$

$$= R_f[\mathrm{C_4H_{10}}] + R_{5a} + R_6 + R_{6a} + 2R_7 +$$
$$2R_{7a} + R_8 + R_9 + R_{22} \quad (\mathrm{x})$$

Reaction 21 has been included as one of the modes of consumption of $\mathrm{C_3H_7}$.

$$\mathrm{CH_3CO} + \mathrm{C_3H_7} = \mathrm{MPK} \quad (21)$$
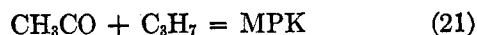
As mentioned previously, the rate of formation of MPK is appreciably enhanced in the presence of ethylene. In the absence of ethylene, the MPK was adequately accounted for by the combination with $\mathrm{CH_2COCH_3}$ of ethyl radicals formed by the secondary photolysis of MEK. There is strong evidence that the most important primary process in the photolysis of MEK is the reaction

$$\mathrm{MEK} + h\nu = \mathrm{CH_3CO} + \mathrm{C_2H_5}[19] \quad (22)$$

Combination with $\mathrm{C_3H_7}$ of $\mathrm{CH_3CO}$ formed in this reaction would seem to be reasonable because of the relatively high $\mathrm{C_3H_7}$ concentration.

On this assumption, R_{22} can be evaluated from the relation

$$R_{22} = R_f[\mathrm{MPK}] - R_{18} \quad (\mathrm{xi})$$

The value of R_{18} can be calculated from relation vi

$$\frac{R_{18}}{R_{17}} = \frac{k_{18}(\mathrm{C_2H_5})(\mathrm{CH_2COCH_3})}{k_{17}(\mathrm{C_2H_5})(\mathrm{CH_3})}$$

or

$$R_{18} = R_{17}\frac{k_{18}k_1}{k_{17}k_3}\frac{R_f[\mathrm{MEK}]}{R_f[\mathrm{C_2H_6}]} \quad (\mathrm{xii})$$

For the purpose of this correction, we can equate k_{18} with k_3. The value of k_1/k_{17} is given by the expression

$$\frac{k_1}{k_{17}} = \frac{(k_1k_{23})^{1/2}}{k_{17}}\left(\frac{k_1}{k_{23}}\right)^{1/2} \quad (\mathrm{xiii})$$

where k_{23} refers to the reaction

$$2\mathrm{C_2H_5} = \mathrm{C_4H_{10}} \quad (23)$$

Combining the relation

$$\frac{(k_1k_{23})^{1/2}}{k_{17}} = \frac{1^{1,2}}{2}$$

with Shepp's value for k_1[17] and the value $k_{23} = 1.6 \times 10^{13}$ cm^3 mole^{-1} sec^{-1} at the mean temperature of $450°$K.[20] We calculate that $k_1/k_{17} = 0.59$. Values of R_{22} are given in Table II; they are very close to the values of $R_f[\mathrm{MPK}]$.

Values of R_{5a}, R_7, R_{7a}, and R_8 have already been calculated and are listed in Table II.

The value of R_6 can be obtained from the expression

$$R_6 = k_6(\mathrm{C_3H_7})(\mathrm{CH_2COCH_3})$$

$$= \frac{k_6k_1}{k_5k_3}\frac{R_f[\mathrm{C_4H_{10}}]R_f[\mathrm{MEK}]}{R_f[\mathrm{C_2H_6}]} \quad (\mathrm{xiv})$$

If we accept the values $k_1k_7/k_5^2 = 1/4,[1,2]$ $k_1 = 10^{13.34},[1,17]$ and $k_7 = 10^{14},[1]$ and assume $k_6 \approx k_3$, it follows that

$$\frac{k_6k_1}{k_5k_3} = \frac{k_1}{k_5} = 0.23$$

The values of R_6 calculated in this way are given in Table II.

While reaction 6a has been included in the reaction scheme, we have no way of estimating its rate. We assume that this is considerably smaller than R_6 and omit its contribution from the propyl radical balance.

On the basis of the reaction scheme shown in Figure 1, R_9 would be equal to $R_f[i\text{-}\mathrm{C_6H_{14}}] + R_{10} + R_{10a}$. However, both $n\text{-}\mathrm{C_5H_{11}}$ and $sec\text{-}\mathrm{C_5H_{11}}$ would undoubtedly be consumed by reactions with other substances as well as $\mathrm{CH_3}$, although reaction with $\mathrm{CH_3}$ would be of greatest importance. To allow for these other reactions, we can write the following equation

(17) A. Shepp, *J. Chem. Phys.*, **24**, 939 (1956).

(18) For this purpose, a common steric factor of 0.3 was assumed. Collision diameters for $\mathrm{CH_3}$ (3.50 A) and $\mathrm{CH_2COCH_3}$ (4.95 A) were taken from T. L. Hill, *ibid.*, **17**, 1125 (1949); those for the higher alkyl radicals were assumed to be equal to the values for the corresponding hydrocarbons and taken from J. S. Rowlinson, *Quart. Rev.* (London), **8**, 168 (1954): 4.30 A for $\mathrm{C_2H_6}$, 4.75 A for $\mathrm{C_3H_7}$, and 5.50 A for $n\text{-}\mathrm{C_5H_{11}}$ and $sec\text{-}\mathrm{C_5H_{11}}$; a value of 5.70 A was used for $\mathrm{C_3H_6COCH_3}$ and $\mathrm{C_3H_7COCH_3}$.

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

(20) A. Shepp and K. O. Kutschke, *J. Chem. Phys.*, **26**, 1020 (1957); K. J. Ivin and E. W. R. Steacie, *Proc. Roy. Soc.* (London), **A208**, 25 (1951).

to represent the consumption of n-C_5H_{11} and sec-C_5H_{11} (not including their isomerization)

$$R_9 = k_{10}(CH_3)\left[1 + \sum_i \frac{k_{n,y_i}}{k_{10}} \frac{(y_i)}{(CH_3)}\right] \quad (n\text{-}C_5H_{11}) +$$

$$k_{12}(CH_3)\left[1 + \sum_i \frac{k_{s,y_i}}{k_{12}} \frac{(y_i)}{(CH_3)}\right] \quad (sec\text{-}C_5H_{11}) \quad (xv)$$

where k_{n,y_i} is the rate constant for the reaction of n-C_5H_{11} with the species y_i and k_{s,y_i} is the rate constant for the reaction of sec-C_5H_{11} with the species y_i. The analogous equation for the consumption of C_3H_7 is

$$R_4 = k_4(CH_3)\left[1 + \sum_i \frac{k_{p,y_i}}{k_4} \frac{(y_i)}{(CH_3)}\right] \quad (C_3H_7) \quad (xvi)$$

If C_3H_7, n-C_5H_{11}, and sec-C_5H_{11} are sufficiently *similar*, then

$$\frac{k_{p,y_i}}{k_4} \approx \frac{k_{n,y_i}}{k_{10}} \approx \frac{k_{s,y_i}}{k_{12}} \quad (\text{for all } i^{21}) \qquad (xvii)$$

Assuming the ACR relation to hold

$$\frac{R_9}{R_4} = \frac{k_{10}(CH_3)(n\text{-}C_5H_{11}) + k_{12}(CH_3)(sec\text{-}C_5H_{11})}{k_{10}(CH_3)(C_3H_7)}$$

$$= \frac{R_{10} + R_t[i\text{-}C_6H_{14}]}{R_t[C_4H_{10}]}$$

$$= \frac{R_t[C_6H_{14}] - R_7 + R_t[i\text{-}C_6H_{14}]}{R_t[C_4H_{10}]} \qquad (xviii)$$

Equation x may therefore be rewritten in the form

$$\frac{k_4}{k_1^{1/2}} = \frac{R_t[C_4H_{10}] + R_{5a} + R_6 + 2R_7 + 2R_{7a} + R_8 + R_{22}}{\left\{1 - \dfrac{R_t[C_6H_{14}] - R_7 + R_t[i\text{-}C_6H_{14}]}{R_t[C_4H_{10}]}\right\} \times R_t[C_2H_6]^{1/2}\langle(C_2H_4)\rangle}$$

$$(xix)$$

Values of $k_4/k_1^{1/2}$ are given in Table III and are plotted in Arrhenius form in Figure 3.

The Reaction $CH_2COCH_3 + C_2H_4 = C_3H_6COCH_3$ (13). Although MBK (by reaction 14) and EPK were the only products which could be attributed to the C_3H_6-$COCH_3$ radicals formed in (13), it is reasonable to assume that both $C_3H_6COCH_3$ and $C_3H_7COCH_2$ reacted with other substances y_i, in addition to CH_3 radicals. We therefore apply the ACR method,[21] assuming CH_2COCH_3, $C_3H_6COCH_3$, and $C_3H_7COCH_2$ to be *similar*, and obtain the relation

$$\frac{R_{13}}{R_2 + R_8} = \frac{R_{14} + R_t[EPK]}{R_t[MEK]} \qquad (xx)$$

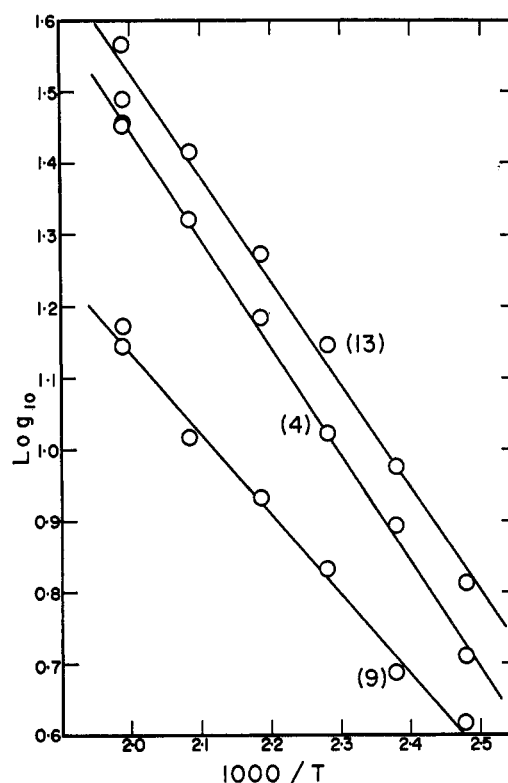
Figure 3. Addition of methyl (4), n-propyl (9), and acetonyl (13) to ethylene. Arrhenius plots for $k_4/k_1^{1/2}$, $k_9/k_7^{1/2}$, and $k_{13}k_1^{1/2}/k_3$.

Now

$$R_{13} = k_{13}(CH_2COCH_3)(C_2H_4)$$

$$= \frac{k_{13}k_1^{1/2}}{k_3} \frac{R_t[MEK](C_2H_4)}{R_t[C_2H_6]^{1/2}} \qquad (xxi)$$

and

$$R_{14} = R_t[MBK] - R_6 \qquad (xxii)$$

Values of R_6 are given in Table II. Values of $k_{13}k_1^{1/2}/k_3$ are given in Table III and are plotted in Arrhenius form in Figure 3.

The Reaction $C_3H_7 + C_2H_4 = n$-C_5H_{11} (9). The relation between R_9 and R_4 is given in eq xviii. Also

$$R_9 = k_9(C_3H_7)(C_2H_4)$$

$$= k_9 R_7^{1/2}(C_2H_4)/k_7^{1/2} \qquad (xxiii)$$

(21) This relation, which we have chosen to call the ACR relation (approximation for corresponding reactions), may be expressed in general form $k_{xj,yi}/k_{xj,z}$ and is a constant for all j and i. It is obvious that the members of the x_j series must be *similar* for the relation to hold with any accuracy. Also, if reactions of identical species are concerned, allowance must be made for the symmetry number.

We have, therefore, calculated $k_9/k_7^{1/2}$ from the relation

$$\frac{k_9}{k_7^{1/2}} = \frac{R_f[C_6H_{14}] - R_7 + R_f[i\text{-}C_6H_{14}]}{R_f[C_4H_{10}]R_7^{1/2}\langle(C_2H_4)\rangle}R_4 \quad \text{(xxiv)}$$

Values of this are given in Table III and are plotted in Arrhenius form in Figure 3.

Discussion

Measurements of $k_2/k_1^{1/2}$ have been made by numerous workers. Their results, together with the present ones, are summarized in Table IV. In contrast to this well-studied reaction, there are no previous data on the corresponding abstraction of hydrogen from acetone by propyl radicals. As can be seen from Table III, E_8 is approximately 1 kcal mole^{-1} less than E_2. No explanation for this can be offered. On the basis of enthalpy data for CH_3, CH_4, n-C_3H_7, and C_3H_8,[19] reaction 8 is about 4 kcal mole^{-1} more endothermic than reaction 2, although absence of enthalpy data[22] for the acetonyl radical makes it difficult to predict whether reaction 8 is itself either endothermic or exothermic. It is worth noting that the lower value of E_8 in comparison with E_2 is similar to the relative behavior of methyl and n-propyl radicals in the abstraction of the aldehydic hydrogen from the corresponding aldehydes.[1]

The results for the addition of methyl radicals to ethylene are remarkably, and undoubtedly fortuitously, close to those of Mandelcorn and Steacie[4] ($E_4 = 7.0 \pm 1.5$ kcal mole^{-1}). Our values of $k_4/k_1^{1/2}$ lie between those of Brinton[5] and those of Hogg and Kebarle.[6] The latter workers used exactly the same experimental conditions and interpretation of results as Brinton but used gas chromatographic methods of analysis instead of low-temperature distillation followed by mass spectrographic analysis. Brinton obtained 6.41 and 8.66 kcal mole^{-1} for log $A_4/A_1^{1/2}$ and E_4, respectively, while Hogg and Kebarle obtained 5.85 and 7.82 kcal mole^{-1}.

Brinton[5] used the thermal decomposition of di-t-butyl peroxide as the source of methyl radicals and a temperature range of 397 to 432°K. In contrast to the present work, he equated R_4 to $R_f[C_4H_{10}] + R_{5a} + R_7 + R_{7a}$ (cf. eq x), but made an allowance for reaction 9 by extrapolating the observed data to zero ethylene concentration on the assumption that reaction 9 would become less important at low ethylene pressures. While this is undoubtedly true, we have chosen to use a constant pressure of ethylene and to take account of reaction 9. We have discussed the case for this reaction above, but in general terms, it would be most un-

Table IV: Kinetic Parameters for the Reaction $CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3$

	Temp range, °K	Log $(A_2/A_1^{1/2})^a$	$E_2 - E_1/2^b$
Cher and Hollingsworth[c]	386–573	4.89	9.87
Shannon and Harrison[d]	415–499	4.69	9.25
Thynne and Grey[e]	395–526	4.66	9.53
Mandelcorn and Steacie[f]	378–561	4.73	9.48
Pritchard, Pritchard, and Trotman-Dickenson[g]	403–428	5.02	9.5
Whittle and Steacie[h]	408–573	?	9.7
Majury and Steacie[i]	405–564	4.77	9.53
Jaquiss, Roberts, and Szwarc[j]	400–448	4.66	9.5
Gomer and Kistiakowsky[k]	398, 448	4.75	9.5
Nicholson[l]	393–?	4.80	9.6
Trotman-Dickenson and Steacie[m]	394–573	4.82	9.72
Endrenyi and Le Roy[n]	403–503	4.75	9.43

[a] $A_2/A_1^{1/2}$ in cm$^{3/2}$ mole$^{-1/2}$ sec$^{-1/2}$. [b] Activation energies are expressed in kcal mole^{-1}. [c] M. Cher and C. S. Hollingsworth, *Anal. Chem.*, **38**, 353 (1966). [d] T. W. Shannon and A. G. Harrison, *Can. J. Chem.*, **41**, 2455 (1963). [e] J. C. J. Thynne and P. Gray, *Trans. Faraday Soc.*, **58**, 2403 (1962). [f] L. Mandelcorn and E. W. R. Steacie, *Can. J. Chem.*, **32**, 79 (1954). [g] G. O. Pritchard, H. O. Pritchard, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1425 (1954). [h] E. Whittle and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 993 (1953). [i] T. G. Majury and E. W. R. Steacie, *Can. J. Chem.*, **30**, 800 (1952); *Discussions Faraday Soc.*, **14**, 45 (1953). [j] M. T. Jaquiss, J. S. Roberts, and M. Szwarc, *J. Am. Chem. Soc.*, **74**, 6005 (1952). [k] R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951). [l] A. J. C. Nicholson, *J. Am. Chem. Soc.*, **73**, 3981 (1951). [m] A. F. Trotman-Dickenson and E. W. R. Steacie, *ibid.*, **72**, 2310 (1950); *J. Chem. Phys.*, **18**, 1097 (1950). [n] This work.

likely for it not to occur when there is good experimental evidence for the addition of acetonyl radicals to ethylene. Neither Brinton[5] nor Hogg and Kebarle[6] obtained any evidence for isohexane, which accounts for an appreciable fraction of the C_6 fraction, as shown in Table I. Reaction 8 would, of course, be of little importance in the di-t-butyl peroxide system since acetone is only a product of the reaction; reaction 21 would not have to be taken into account.

The only previously published study of the addition of propyl radicals to ethylene is that of Kerr and Trotman-Dickenson,[23] who used the photolysis of n-

(22) A referee has pointed out that S. W. Benson (*J. Chem. Educ.*, **42**, 502 (1965)) has estimated $\Delta H°_f$ for the acetyl radical to be -11 ± 2 kcal mole^{-1}. This corresponds to $DH°(CH_3COCH_2\text{-H}) = 85 \pm 2$ kcal mole^{-1}, about 13 kcal mole^{-1} less than $DH°(CH_3CH_2\text{-}CH_2\text{-H})$.

(23) J. A. Kerr and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **55**, 572 (1959).

butyraldehyde as the source of n-propyl radicals. They found $\log A_9 = 10.9$ (assuming $A_7 = 10^{14}$ cm^3 mole^{-1} sec^{-1}) and $E_9 = 6.5$ kcal mole^{-1}, in comparison with $\log A_9 = 10.4$ (with the same assumption) and $E_9 = 5.1$ kcal mole^{-1} from the present experiments. Their value of $k_9/k_7^{1/2}$ was obtained from the relation

$$\frac{k_9}{k_7^{1/2}} = \frac{R_t[\text{pentyl products}]}{R_t[\text{C}_6\text{H}_{14}]^{1/2}(\text{C}_2\text{H}_4)} \qquad \text{(xxv)}$$

The products resulting from the pentyl radicals formed in (9) were assumed to be n-pentane, by abstraction

of hydrogen from the n-butyraldehyde, and n-heptane, resulting from the n-heptyl radicals formed by the addition of the pentyl radicals to ethylene.

No previous results have been reported for the addition of acetonyl radicals to ethylene. However, it is interesting to note that E_{13} differs very little from E_4. Furthermore, since $k_3/k_1^{1/2} \approx k_1^{1/2}$, the results of Table III indicate that $A_{13} \approx A_4$.

Micellar Properties of a Series of Sodium Dodecylpolyoxyethylene

Sulfates from Hydrodynamic Data

by Fumikatsu Tokiwa and Kenji Ohki

Research Laboratories, Kao Soap Company, Wakayama-shi, Japan *(Received September 22, 1966)*

Sedimentation, diffusion, viscosity, and density measurements have been made of the micellar solutions of sodium dodecyl sulfate and a series of sodium dodecylpolyoxyethylene sulfates, $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_n\text{OSO}_3\text{Na}$, with oxyethylene units from 1 to 10. From these hydrodynamic data it is concluded that the micelles are small and spherical irrespective of the polyoxyethylene chain length and highly hydrated in dilute solutions. The Scheraga-Mandelkern β value, calculated from experimental data, was compared with the theoretical value as an aid in estimating the shape of the micelles. Hydration was discussed in terms of the frictional ratios and intrinsic viscosities. For the surfactants with $n \geq 3$ there is a linear relationship between the hydration of the polyoxyethylene chain and the chain length.

Introduction

A relatively large number of studies have been reported of nonionic polyoxyethylated surfactants on their micellar properties in solutions in relation to the length of polyoxyethylene chain.[1-7] On the other hand, investigations of polyoxyethylated surfactants having an ionic head at the end of the molecule have scarcely been made[8] in spite of their wide applicability

in industry, probably because of some difficulties in obtaining pure materials. It is, however, interesting

(1) L. M. Kushner and W. D. Hubbard, *J. Phys. Chem.*, **58**, 1163 (1954).

(2) C. W. Dwiggins, Jr., R. J. Bolen, and H. N. Dunning, *ibid.*, **64**, 1175 (1960).

(3) F. Tokiwa and T. Isemura, *Bull. Chem. Soc. Japan*, **35**, 1737 (1962).