less appear to be interruptions between CsI and $(CH_3)_4$-NI for the DMF-PC, CH_3OH-DMF, and CH_3OH-DMSO solvent pairs. The interruption for the CH_3-OH-PC solvent pair occurs between $(CH_3)_4NI$ and $(C_2H_5)_4NI$. At the present time it appears that no general statement can be made in terms of solvent structure to explain the $\Delta H_{tr}°$ data for the various solvent pairs.

We conclude that (1) the modified Born equation, satisfactory as it may be in describing free energies of solvation,[13,18] as it is now expressed is not suitable for predicting heats of transfer of cations even qualitatively, and (2) the large change observed in $\Delta H_{tr}°$ as one proceeds from Cs^+ to $(CH_3)_4N^+$ is not explained by the water structure alone but is the result of special interactions of the tetraalkylammonium ions with solvents in general.

Weeda and Somsen[17] have applied the van Eck theory[19] to enthalpies of transfer of alkali metal iodides and have found $\Delta H_{tr}°$ to be relatively constant, as predicted by the theory, for sodium, potassium, rubidium, and cesium iodides between water and formamide but not constant for the same salts upon transfer from water to N-methylformamide. Table IV shows that, in general, the van Eck theory is not consistent with $\Delta H_{tr}°$ data.

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(19) C. L. van P. van Eck, Thesis, University of Leiden, Leiden, The Netherlands, 1958.

The Pyrolysis of Biacetyl and the Third-Body Effect on the Combination of Methyl Radicals

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The kinetics of pyrolysis of biacetyl at 677–776°K and 0.6–45 torr have been investigated by the stirred-flow method. The decomposition (to carbon monoxide, methane, ketene, acetone, ethane, and 2,3-pentanedione) is shown to be a chain reaction initiated by reaction 1, propagated by reactions 3 and 8, and terminated mainly by reaction 6, which is strongly pressure dependent. The following kinetics data were obtained (k and A being in $cm^3 mol^{-1} sec^{-1}$)

		Order	k (at 730°K)	log A	E, kcal mol^{-1}
(1)	$(CH_3CO)_2 \rightarrow 2CH_3CO$	1	7.6×10^{-5}	16.0	67.2 ± 3.3
(3)	$CH_3 + (CH_3CO)_2 \rightarrow CH_4 + CH_2COCOCH_3$	2	1.2×10^9	11.8	9.1
(6)	$CH_3 + CH_3 (+M) \rightarrow C_2H_6 (+M)$	3	1.6×10^{20}	16.3	$\sim{-}13$
(8)	$CH_3 + (CH_3CO)_2 \rightarrow (CH_3)_2CO + CH_3CO$	2	2.6×10^8	10.3	6.3

Pressures of biacetyl, at which the second-order rate constant for reaction 6 is half its limiting high-pressure value, increase from 14 torr at 677°K to 30 torr at 776°K and are in satisfactory agreement with values calculated by previous authors on the basis of the RRKM theory assuming a "loose" activated complex and strong deactivating collisions. The presence of a trace of 2-hydroxy-2-methylbutan-3-one in the products is regarded as evidence that reaction 8 proceeds through formation of the radical $(CH_3)_2C(O{\cdot})COCH_3$. The heat of formation of the gaseous acetyl radical is estimated to be -5.1 ± 2.0 kcal mol^{-1} at 298°K.

Introduction

Much of the recent progress in understanding the kinetics of pyrolytic and free-radical reactions has been achieved from studies of the same elementary reactions in different reaction systems. Translation of an elementary reaction from one environment to another may bring into prominence in the second system kinetic features which are vestigial or absent in the first;

important examples of this are the occurrence of pressure dependence in recombinations[1–3] and the unimolecular decompositions[4–6] of radicals. The study of biacetyl reported here was carried out with a twofold pur-

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

(2) N. L. Arthur and T. N. Bell, *Chem. Commun.*, **9**, 166 (1965).

(3) L. F. Loucks, *Can. J. Chem.*, **45**, 2775 (1967).

pose: first, to examine the behavior of methyl and acetyl radicals in a somewhat different system from those hitherto investigated, and, second, to test the suitability of biacetyl as a pyrolytic source of methyl radicals for studies at higher temperatures than are available to less stable sources such as di-t-butyl peroxide and azomethane.

Rice and Walters[7,8] have established that the pyrolysis of biacetyl is a homogeneous first-order chain reaction at 650–740°K and about 200 torr, and Taylor[9] has applied the toluene-carrier technique to obtain Arrhenius parameters for the initial unimolecular fission of the molecule. A detailed kinetic analysis of the over-all reaction does not seem to have been carried out previously.

Experimental Section

The pyrolysis was carried out at 404–503° and 0.6–45 torr in a stirred-flow apparatus of the type described previously.[10–13] The pressure in the reactor was measured by a dibutyl phthalate manometer,[14] via a N_2 buffer. There was no carrier gas. Products and excess biacetyl passed successively through a trap at −78° and a Ward–LeRoy still at −175°. Products volatile at −175° passed to a calibrated volume and were analyzed by gas chromatography (±2% for each gas). A fraction, consisting solely of ketene (as determined by ir spectroscopy and gas chromatography), was distilled from the Ward still at −125° and was determined volumetrically (±2%). The liquid collected at −78° contained acetone and 2,3-pentanedione (pd) together with traces of 2-hydroxy-2-methylbutan-3-one (HMB) and an unidentified substance in a large excess of biacetyl. The liquid was weighed and analyzed by gas chromatography on a 3 ft × ¹/₈ in. Poropak Q column with a flame ionization detector (acetone to ±5%). This column, chosen after trying a number of others, gave fair resolution of 0.01–0.1% pd from the bulk of biacetyl, but the accuracy of determination was not better than ±10%. The presence of HMB was established by identical retention times with those of an authentic sample on Poropak Q and on Ucon 5% on Chromosorb G (80–100 M), respectively. The unknown trace product had a retention time on Poropak Q double that of 2-hydroxy-2-methylbutan-3-one; its mass spectrum (AEI, MS9) suggested 2-hydroxy-3-methoxy-2,3-dimethylbutane, but the small amount of product available prevented conclusive identification.
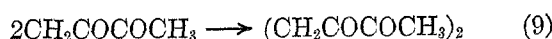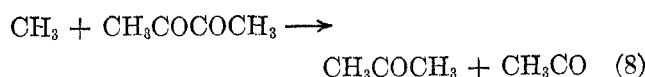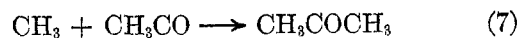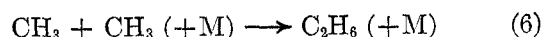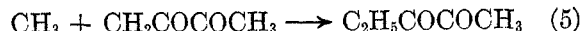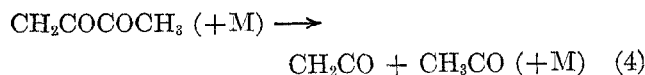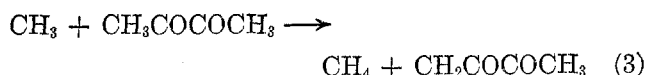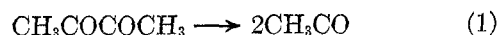
Biacetyl (BDH) was purified by preparative gas chromatography on Ucon (20%)–Chromosorb W (36–44 M) (24 ft × 0.5 in.). No impurity (⋝0.01%) could be detected in the purified product on an analytical column.

Results and Discussion

Products and Stoichiometry. The main products of pyrolysis (each greater than 5 mol % of the total) were found to be carbon monoxide, methane, ketene, and

acetone; minor products (<5, >0.3%) were ethane and 2,3-pentanedione. Traces (<0.3%) of ethylene, carbon dioxide, propane, 2-hydroxy-2-methylbutan-3-one, and possibly 2-hydroxy-3-methoxy-2,3-dimethylbutane were also found.

Primary kinetic data are given in Table I. The experiments identified by P in column 1 were carried out with a reactor containing 14 g of quartz wool; this increased the surface:volume ratio tenfold. Unless otherwise indicated, the following discussion refers to the unpacked reactor. Since the decomposition was not carried beyond 5% and frequently was <2%, the rates of disappearance of biacetyl and the formation of products could not be compared accurately. However, element balances H:C:O taken over the total products were always close to 3:2:1 (see Table II); it is therefore improbable that a major product was missed in the analysis. Stoichiometrically the products are accounted for by reactions 1–8 of the mechanism

$$CH_3COCOCH_3 \longrightarrow 2CH_3CO \tag{1}$$

$$CH_3CO \ (+M) \longrightarrow CH_3 + CO \ (+M) \tag{2}$$

$$CH_3 + CH_3COCOCH_3 \longrightarrow$$
$$CH_4 + CH_2COCOCH_3 \tag{3}$$

$$CH_2COCOCH_3 \ (+M) \longrightarrow$$
$$CH_2CO + CH_3CO \ (+M) \tag{4}$$

$$CH_3 + CH_2COCOCH_3 \longrightarrow C_2H_5COCOCH_3 \tag{5}$$

$$CH_3 + CH_3 \ (+M) \longrightarrow C_2H_6 \ (+M) \tag{6}$$

$$CH_3 + CH_3CO \longrightarrow CH_3COCH_3 \tag{7}$$

$$CH_3 + CH_3COCOCH_3 \longrightarrow$$
$$CH_3COCH_3 + CH_3CO \tag{8}$$

$$2CH_2COCOCH_3 \longrightarrow (CH_2COCOCH_3)_2 \tag{9}$$

which is essentially that proposed by Blacet and Bell[15,16]

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

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(6) M. F. R. Mulcahy and D. J. Williams, *Aust. J. Chem.*, **17**, 1291 (1964).

(7) F. O. Rice and W. D. Walters, *J. Chem. Phys.*, **7**, 1015 (1939).

(8) W. D. Walters, *J. Amer. Chem. Soc.*, **62**, 880 (1940).

(9) J. W. Taylor, Ph.D. Thesis, Manchester, 1953, quoted by A. F. Trotman-Dickenson, "Gas Kinetics," Butterworth and Co. Ltd., London, 1955, p 111.

(10) M. F. R. Mulcahy and D. J. Williams, *Aust. J. Chem.*, **14**, 534 (1961).

(11) J. de Graaf and H. Kwart, *J. Phys. Chem.*, **67**, 1458 (1963).

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(13) M. F. R. Mulcahy, B. G. Tucker, D. J. Williams, and J. R. Wilmshurst, *ibid.*, **20**, 1155 (1967).

(14) A. T. J. Hayward, *J. Sci. Instrum.*, **40**, 173 (1963).

(15) F. E. Blacet and W. E. Bell, *Discussions Faraday Soc.*, **14**, 70 (1953).

(16) W. E. Bell and F. E. Blacet, *J. Amer. Chem. Soc.*, **76**, 5332 (1954).

Table I: Kinetic Data for Pyrolysis of Biacetyl[a]

Experiment no.	Temp, °C	P, torr	$10^9 \times$ efflux of products (n_l), mol sec^{-1}						
			n_{CO}	n_m	n_e	n_k	n_{at}	n_{pd}	n_{en}
81	403.0	6.30	4.62	4.29	0.08	4.20	1.05		
82	403.2	32.0	37.6	29.9	0.18	28.0	7.79		
83	404.1	58.4	63.6	51.0	0.18	45.5	14.0	1.1	
84	404.9	21.4	27.0	20.7	0.17	20.3	7.86		
85	404.0	4.65	4.29	3.62	0.08	4.04	0.95		
86	404.5	31.7	28.7	22.3	0.12	20.2	5.53		
87	404.0	41.8	28.7	22.6	0.08	22.3	5.48		
88	404.1	13.3	13.9	11.3	0.11	10.7	2.49	0.2	
89	404.1	3.52	2.96	2.46	0.05	2.06	0.69		
90	443.0	3.30	18.8	14.6	0.66	12.5	3.81	0.2	
91	442.6	5.75	30.1	23.2	0.86	21.0	5.55	0.5	
92	443.0	13.8	93.1	72.0	1.85	63.0	16.5	1.0	
93	443.0	22.1	159	127	2.34	116	27.5	1.5	
95	440.0	44.0	209	165	1.72	149	38.0	5.3	
123	442.3	41.3	244	180	1.85	170	44.0	3.4	0.30
124	442.4	22.7	162	122	2.27	112	32.8	1.6	0.16
125	442.5	13.2	85.8	65.6	1.44	57.6	16.0	0.9	0.09
142P	443.0	13.8	48.6	30.1	0.35	25.5	11.5	5.45	0.06
143P	443.0	5.21	16.8	8.45	0.19	11.2	4.9	2.34	0.07
97	464.8	3.44	49.3	37.2	2.80	34.2	8.72	0.3	
98	464.1	3.18	36.9	26.9	2.15	24.2	5.50	1.1	
99	463.5	12.8	246	181	8.20	159	39.8	3.2	
100	463.5	24.5	465	343	11.9	329	75.4	4.0	
101	464.0	3.60	49.5	37.2	2.61	34.4	8.29	0.4	
126	463.2	13.4	271	201	9.65	186	42.2	1.3	0.33
127	463.7	16.4	332	249	9.93	229	52.4	1.8	0.45
112	478.0	5.45	162	119	9.70	110	24.5		
113	478.8	2.84	78.0	55.6	5.69	50.3	11.5	0.3	
114	478.7	13.1	485	345	22.5	333	72.1	1.9	
115	478.0	22.2	809	591	30.7	565	120	5.8	2.79
139P	478.3	23.9	512	332	8.82	284	67.7	67.2	0.93
140P	477.0	5.62	97.2	61.5	2.24	52.9	17.7	10.6	0.38
141P	478.4	13.8	306	182	5.71	159	49.8	40.5	0.91
116	488.3	0.64	24.0	17.9	1.59	13.7	4.10		0.19
117	489.1	2.83	108	72.5	7.18	65.7	14.7	0.8	0.56
118	489.2	5.34	243	162	15.2	154	32.5	1.7	0.76
128	989.6	32.2	2006	1481	91.7	1381	295	14	5.76
129	488.6	5.16	237	169	16.5	152	33.2		0.28
130	489.6	11.9	635	452	37.0	423	88.2	1.9	1.49
119	503.4	5.50	421	279	34.2	261	52.3	2.8	1.61
120	502.3	2.80	194	122	16.9	115	23.4	0.6	0.54
121	502.0	13.7	1186	788	77.0	743	150	8.7	3.83
122	503.5	0.60	48.4	32.6	5.78	25.8	7.51	0.5	
131	501.6	24.4	1851	1275	105	1175	240	11	12.5
132	503.4	27.0	2400	1623	135	1453	305	16	16.6
133	503.5	14.2	1370	889	96.8	839	170	5.6	8.05
134P	502.0	25.9	1591	983	47.0	769	....	108	7.73
135P	506.0	3.93	260	152	14.0	158	37.1	22.3	1.81
136P	501.0	14.8	970	566	36.2	485	127	108	4.19
137P	505.2	2.95	195	116	10.9	120	32.0	14.7	1.48
138P	501.5	22.8	1433	832	42.3	688	192	131	7.23

[a] m, methane; e, ethane; k, ketene; at, acetone; pd, 2,3-pentanedione; en, ethylene; P, packed reactor. The volume of the reactor (packed and unpacked) is 283 cm^3.

for the photolysis at 300–470°K. These reactions require the stoichiometric relations

$$n_{CO}/\Sigma_1 = 1 \qquad (I)$$

and

$$n_m/\Sigma_2 = 1 \qquad (II)$$

where $\Sigma_1 = n_m + n_{at} + 2n_e + n_{pd}$, $\Sigma_2 = n_k + n_{pd}$,

Table II: Stoichiometric Relations and Kinetic Parameters

Temp, °K	Pressure range, torr	Element balance C:O	H:O	n_{CO}/Σ_1	n_m/Σ_2	n_e/n_{pd} range	Order	$p_{1/2}$, torr	$10^{-20}k_6$, cm^6 mol^{-2} sec^{-1}
677	3.5–58.0	2.00 ± 0.03	3.05 ± 0.07	0.96 ± 0.08	1.05 ± 0.08	0.2–0.6	1.08 ± 0.02	13.5	3
716	3.3–44.0	2.00 ± 0.01	3.02 ± 0.09	1.00 ± 0.03	1.09 ± 0.03	0.4–3	1.09 ± 0.02	21	2
737	3.1–24.5	2.01 ± 0.07	3.03 ± 0.17	1.01 ± 0.04	1.08 ± 0.10	2–8	1.24 ± 0.02	24	1.7
751	2.8–22.2	1.99 ± 0.02	2.99 ± 0.09	1.00 ± 0.09	1.05 ± 0.03	5–20	1.15 ± 0.01	26.5	1.2
762	0.6–32.2	1.99 ± 0.03	2.96 ± 0.13	1.02 ± 0.05	1.11 ± 0.09	7–20	1.15 ± 0.02	29.5	1.0
776	0.6–24.4	1.97 ± 0.02	2.92 ± 0.08	1.04 ± 0.06	1.09 ± 0.12	9–25	1.04 ± 0.02	30	0.9

and n_i (in moles per second) is the rate of formation of product i (the meanings of the subscripts m, at, etc., are given in Table I). Evidence that reaction 9 can generally be neglected will be discussed later. The values given in Table II show that eq I is vindicated very well by the data. The experimental values of n_m/Σ_2 are 5–10% higher than required by eq II, probably because of a small degree of polymerization of the ketene.[17] (The small amounts of CO_2 and C_2H_4 found in the products probably arise from the pyrolysis of ketene,[18] but they are insufficient to account for the discrepancy.)

Kinetic Analysis. Reaction Order. The over-all rate of decomposition $-n_B$ was taken as half the total rate of appearance of O in the products. Plots of log $-n_B$ against log [B] gave straight lines, yielding the reaction orders given in Table II. The order is thus a little greater than 1 over the whole range of conditions. Neglecting the discrepancy from unity, the over-all first-order rate constant can be expressed approximately by

$$-n_B/(V[B]) = k_{ov} =$$

$$10^{11.4} \exp(-47,140/RT) \text{ sec}^{-1} \quad (III)$$

The Arrhenius plot is shown in Figure 1 (curve 1). In the "packed" reactor the order remained close to 1; the values of $(k_{ov})_P$ at 443, 478, and 503°, respectively, were 35, 27, and 18% less than the corresponding values of k_{ov}, showing that the surface exerts little effect on the over-all kinetics in the unpacked reactor.

Assuming that the above chain reaction scheme is basically correct, the reaction order considered in light of the principles of rate theory gives a preliminary guide to possible main terminating reactions. According to RRK theory, the pressure at which a unimolecular reaction such as reaction 1 begins to become second order decreases as $(E_1/SRT)^{S-1}$ increases,[19] where S is the number of active Kassel oscillators. The known behavior[6] of other molecules with about 12 atoms and similar values of E/SRT indicates that reaction 1 is probably substantially first order under the present experimental conditions. In this case first-order kinetics for the over-all decomposition require $\beta\mu$- or $\beta\beta$M-type termination reactions.[20] All $\beta\beta$M-
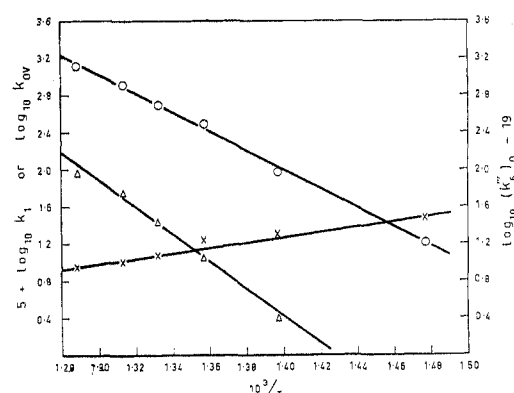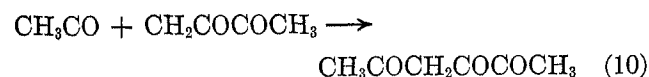

Figure 1. Arrhenius plots of k_1, k_{ov}, and $(k_6''')_0$: $\triangle$, log k_1; $\bigcirc$, log k_{ov}; $\times$, log $(k_6''')_0$.

type reactions can be eliminated on the grounds that S and $-\Delta H$ are too high, except reaction 6 and, possibly, the third-order version of reaction 7. Hence possible main terminating reactions at this stage are reactions 5, 6, 10, and perhaps 7.

$$CH_3CO + CH_2COCOCH_3 \longrightarrow$$

$$CH_3COCH_2COCOCH_3 \quad (10)$$

Origin of Acetone and the Role of the Acetyl Radical. The maximum rate of production of acetone by reaction 7 is given by

$$(n_{at})_7 = Vk_7[CH_3][CH_3CO] \quad (IV)$$

where V is the volume of the reactor and k_7 can be taken as approximately equal to the high-pressure limiting value of k_6. Assuming that ethane is formed exclusively by reaction 6, $[CH_3]$ for any experiment can be calculated from n_e and k_6 (the latter from ref 21 and data to be presented later); $[CH_3CO]$ can be derived from n_{CO} and the data relating to reaction 2 obtained by O'Neal and Benson.[4]

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

(18) W. B. Guenther and W. D. Walters, *ibid.*, **81**, 1310 (1959).

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

(20) K. J. Laidler and D. J. McKenney in "The Chemistry of the Ether Linkage," S. Patai, Ed., Interscience Publishers Ltd., London, 1967, p 169.

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

**Table III :**   Calculated Rates of Formation of $(CH_3)_2CO$ by Reaction 7 Compared with Experimental Rates

Experiment no.	$(n_{at})_7$, mol sec^{-1}	
	Calcd	Exptl
87	2×10^{-12}	5.5×10^{-9}
123	6×10^{-11}	4.4×10^{-8}
125	7×10^{-11}	1.6×10^{-8}
120	2.5×10^{-9}	2.3×10^{-8}
131	3×10^{-9}	2.4×10^{-7}

By extrapolating their results we estimate that the pressure at which the first-order constant $(k_2)_\infty$ falls to half its limiting high-pressure value is about 270 torr at 673°K and 430 torr at 773°K. Hence reaction 2 is effectively second order under the present conditions. Therefore

$$[CH_3CO] = n_{CO}/V(k_2)_0[M] \qquad (V)$$

where [M] is the total molecular concentration. The representative values of $(n_{at})_7$ given in Table III were calculated from the present data via eq IV and V using values of $(k_2)_0$ calculated from the Arrhenius parameters given by O'Neal and Benson.[4] First, they are notably less than the experimental values and another source of acetone must therefore be found. Second, they are much smaller than the experimental rates of formation of ethane (Table I); hence reaction 7 cannot be the main terminating reaction. Third, in general they are also smaller than n_{pd} (Table I); this means that, except for reaction 2, the acetyl radical plays an insignificant role in determining the kinetics, thereby eliminating reaction 10 as a possible terminating reaction.

Reaction 8, which occurs in the photolysis of biacetyl,[15,16] is the most likely source of acetone. If so, assuming the methane is produced by reaction 3, we should find $n_{at} \propto n_m$. Figure 2 shows that this is the case. An analogous reaction

$$CH_3 + CH_3CHO \longrightarrow CH_3COCH_3 + H \qquad (11)$$
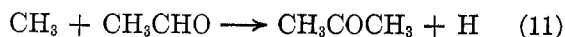
has been proposed to account for the formation of acetone in the pyrolysis of acetaldehyde.[22,23] The production of a trace of $(CH_3)_2C(OH)COCH_3$ by biacetyl suggests that reaction 8 occurs in two steps, as proposed earlier by Darwent[24]

$$CH_3\cdot + CH_3COCOCH_3 \longrightarrow CH_3\overset{\overset{\textstyle O}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}COCH_3 \longrightarrow$$

$$(CH_3)_2CO + \cdot COCH_3 \qquad (12)$$
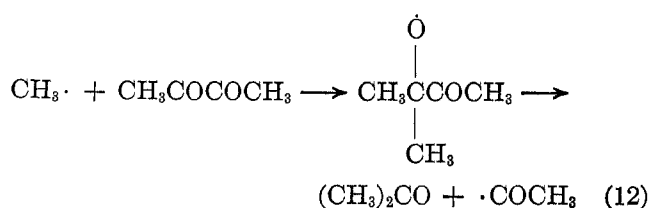
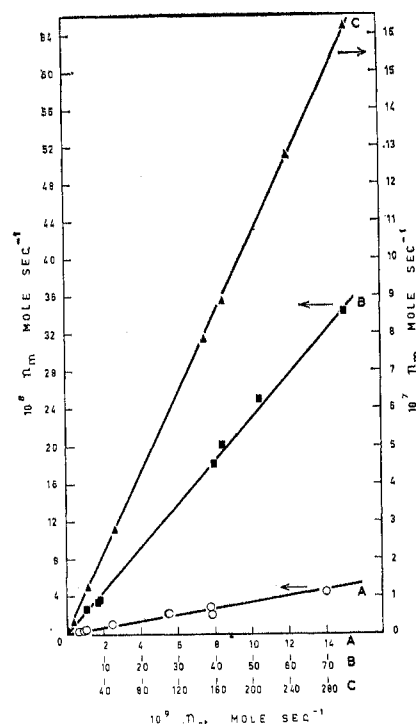the intermediate radicals being sufficiently long lived for a few of them to abstract a hydrogen from biacetyl.

Figure 2.   Typical plots of n_m against n_{at}: ▲, 776°K; ■, 737°K; O, 677°K.

Batt[25] has discussed evidence that reaction 11 also occurs by this mechanism.

Reactions 3, 4, 6, and 8.   The β-propagating reactions 3 and 8 are related kinetically by their common participant CH_3 to reaction 6, which, from its behavior at lower temperatures, is expected to be pressure dependent. Assuming a Lindemann–Hinshelwood mechanism

$$CH_3 + CH_3 \underset{-a}{\overset{a}{\rightleftharpoons}} C_2H_6{}^*$$

$$C_2H_6{}^* + M \overset{b}{\longrightarrow} C_2H_6 + M$$
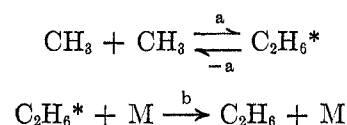
the following relation applies

$$\frac{n_\beta{}^2}{n_e[B]^2} = \frac{Vk_\beta{}^2}{k_a}\left\{1 + \frac{k_{-a}}{k_b}\frac{1}{[B]}\right\} = \frac{Vk_\beta{}^2}{k_6{}''} \qquad (VI)$$

where β refers either to reaction 3 or reaction 8, [B], the biacetyl concentration, is equated to [M], and $k_6{}''$ is the pressure-dependent bimolecular constant. That curves rather than straight lines are obtained by plotting $n_\beta{}^2/(n_e[B]^2)$ against $1/[B]$ (Figures 3 and 4) shows that the Lindemann–Hinshelwood mechanism should be replaced by one which takes account of the variation of the lifetime of $C_2H_6{}^*$ with its energy content, as found previously by Shaw, Menczel, and Toby[26] (see

(22) M. Eusuf and K. J. Laidler, *Can. J. Chem.*, **42**, 1851 (1964).

(23) K. J. Laidler and M. T. H. Lin, *Proc. Roy. Soc.*, **A297**, 365 (1967).

(24) B. deB Darwent, *Discussions Faraday Soc.*, **14**, 129 (1953).

(25) L. Batt, *J. Chem. Phys.*, **47**, 3674 (1967).

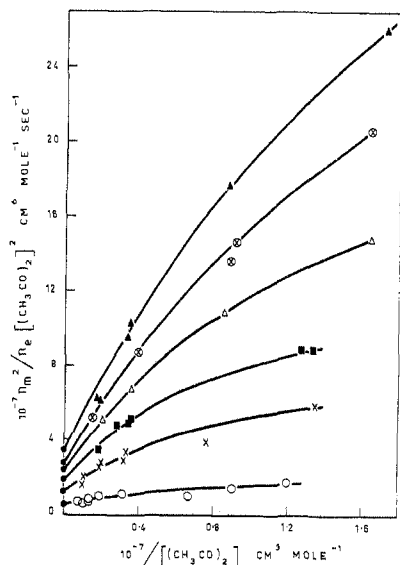(26) H. Shaw, J. H. Menczel, and S. Toby, *J. Phys. Chem.*, **71**, 4180 (1967).

Figure 3. Plots of $n_m{}^2/n_e[(CH_3CO)_2]^2$ against $1/[(CH_3CO)_2]^2$
▲, 776°K; ⊗, 762°K; △, 751°K; ■, 737°K; ✕, 716°K; ○,
677°K; ●, extrapolated from photolysis, R. Ausloos and
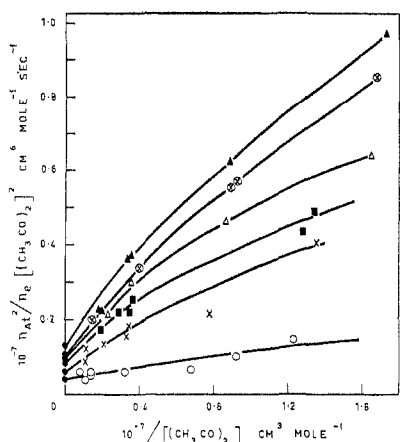E. W. R. Steacie, *Can. J. Chem.*, **33**, 39 (1955).

Figure 4. Plots of $n_{at}{}^2/n_e[(CH_3CO)_2]^2$ against $1/[(CH_3CO)_2]$:
▲, 776°K; ⊗, 762°K; △, 751°K; ■, 737°K; ✕, 716°K; ○,
677°K; ●, extrapolated from photolysis (Blacet and Bell[15]).

also ref 27 and 28). The points on the ordinates were
obtained by extrapolating, by means of Arrhenius
plots, values of $Vk_\beta{}^2/(k_6'')_\infty$ derived from photolytic
data[16,29] at 300–470°K and 20–50 torr, reaction 6 being
assumed to be at its high-pressure limit under these
conditions. The points are seen to be consistent with
the present data, as was verified by extrapolating
the latter to the ordinates without prior knowledge of
the photolysis data. These extrapolated values, when
combined with those derived from the photolysis, gave
9.1 and 6.3 kcal mol⁻¹ for E_3 and E_8, respectively,
which may be compared with 8.5[29] and 6.6[16] kcal mol⁻¹
based on the photolytic data alone.

Values of $p_{1/2}$, the pressure at which k_6'' has the
value $0.5(k_6'')_\infty$, interpolated from Figure 3 are given
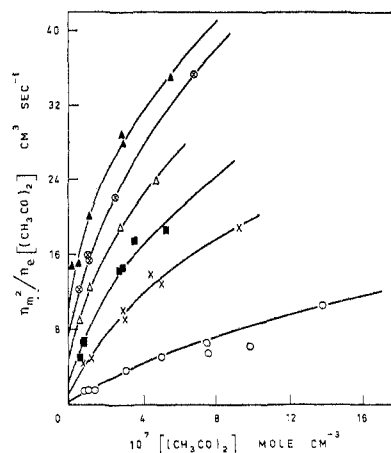in Table II. Values derived from the acetone–ethane

Figure 5. Plots of $n_m{}^2/n_e[(CH_3CO)_2]$ against $[(CH_3CO)_2]$:
○, 677°K; ✕, 716°K; ■, 737°K; △, 751°K; ⊗, 762°K;
▲, 776°K.

data (Figure 4), though expected to be of lower accu-
racy, were in fact all within ±10% of these. Further
reference to $p_{1/2}$ will be made later.

Plots according to eq VI emphasize the results ob-
tained at the high end of the pressure range. Re-
arrangement of eq VI to give

$$\frac{n_\beta{}^2}{n_e[B]} = \frac{Vk_\beta{}^2}{k_ak_b}\{k_{-a} + k_b[B]\} = \frac{Vk_\beta{}^2}{k_6'''} \qquad (VII)$$

produces the contrary effect (where k_6''' is the termolec-
ular constant).

Figure 5 shows $n_m{}^2/(n_e[B])$ as a function of [B].
Extrapolation to the ordinate yields $Vk_3{}^2/(k_6''')_0$, from
which, with the values of $Vk_3{}^3/(k_6'')_\infty$ determined above
and Shepp's value[30] of $(k_6'')_\infty$, the approximate values
of $(k_6''')_0$ given in Table II were derived. Similar
treatment of the acetone–ethane data gave values of
$(k_6''')_0$ within 15% of these. Although the absolute
values are subject to the uncertainties of the extrapola-
tions, there is little doubt that the inverse effect of tem-
perature on $(k_6''')_0$ is genuine. The best Arrhenius line
gives $E_6''' = -13$ kcal mol⁻¹ and log $A_6 = 16.3$ cm⁶
mol⁻² sec⁻¹ (see Figure 1). The results may also be
expressed by the relation $(k_6''')_0 = 10^{46.6}T^{-9.2}$ cm⁶ mol⁻²
sec⁻¹. The absolute values of $(k_6''')_0$ agree well
with the value $\geqslant 3 \times 10^{20}$ cm⁶ mol⁻² sec⁻¹ derived[31,32]
from the photolysis of acetone at 473°K.[1] Estimates
of −11.7 and −9.8 kcal mol⁻¹ made by Laidler, *et al.*,[33]
from photolytic data[1,17] are also compatible with the

(27) A. B. Trenwith, *Trans. Faraday Soc.*, **62**, 1538 (1966).

(28) M. C. Lin and M. H. Back, *Can. J. Chem.*, **44**, 2357 (1966).

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

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

(31) D. E. Hoare and A. D. Walsh, *Trans. Faraday Soc.*, **53**, 1102 (1957).

(32) E. K. Gill and K. J. Laidler, *Proc. Roy. Soc.*, **A250**, 121 (1959).

(33) See ref 20, p 195.

present figure for E_6'''. Further reference will be made to reaction 6 later.

An investigation of reaction 4 was attempted by means of the relation $n_k[CH_3]/n_{pd} = k_4'f([M])/k_5$ (where $f([M])$ is a function of $[M]$) but the results were inconclusive, probably because of insufficient precision in the determination of n_{pd} and the intervention of a surface effect in reaction 5 (as described later).

Initiation and Termination. Elimination of the acetyl radical from consideration leaves reactions 5 and 6 (the latter third order) as the only plausible termination reactions compatible with over-all first-order kinetics. From the values of n_e/n_{pd} listed in Table II it appears that reaction 5 is the main terminating reaction at 677°K but gives way to reaction 6 at higher temperature. Since the pressure in the great majority of the experiments above 677°K was less than $p_{1/2}$, it is legitimate to regard reaction 6 as substantially third order at these temperatures. The positive deviations from unity observed in the over-all order doubtless reflect the fact that the reaction is not actually at its third-order limit. Since the rates of termination and initiation must be equal (irrespective or order) the following relation should apply

$$Vk_1[B] = n_e + n_{pd} + n_x \qquad (VIII)$$

where x is the product of reaction 9.

The term n_x is added because $[CH_3]$ and $[CH_2COCOCH_3]$ were of comparable magnitudes in experiments at 677 and 716°K. Its magnitude, calculated from n_e and n_{pd} on the assumption that $(k_6'')_\infty/(k_3k_9)^{1/2} = 2$, was found to be negligible in all but a few experiments. Figure 6 shows that $n_e + n_{pd} + n_x$ is in fact linearly related to $[B]$. This vindicates the previous conclusion that reaction 1 is first order; furthermore, the fact that the lines pass through the origin shows that there is no appreciable contribution to the over-all reaction from an intramolecular decomposition. The Arrhenius plot of the slopes of the lines in Figure 6 shown in Figure 1 yields

$$k_1 = 10^{16.0} \exp[-(67200 \pm 3300)/RT] \ sec^{-1} \qquad (IX)$$

in good agreement with the values $A = 5 \times 10^{15} \ sec^{-1}$ and $E = 66.0 \ kcal \ mol^{-1}$ obtained by Taylor[9] by the toluene-carrier method. Absolute values of k_1 calculated from Taylor's parameters are within 20% of the present figures. The value of E_1 in eq IX may be used to obtain a second value for E_6'''. Since the chain length is of the order of 15–35 and reaction 6 is the dominant terminating reaction above 677°K, it follows that $E_{ov} \approx 1/2(E_1 - E_6''') + E_\beta$. An empirical value was found for E_β (namely, 7.5 kcal mol^{-1}) from a plot of $\log (k_3 + k_8)$ against $1/T$. Hence with $E_{ov} = 47.1$ kcal mol^{-1} and $E_7 = 67.2$ kcal mol^{-1}, we find $E_6''' = -12$ kcal mol^{-1}, comparing well with the value of -13 kcal mol^{-1} found from $(k_6''')_0$ directly.
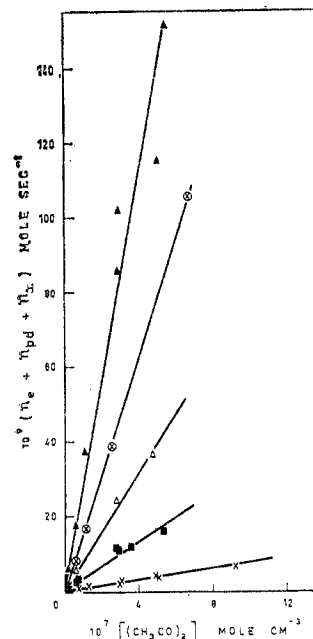

Figure 6. The total rate of formation of termination products as a function of $[(CH_3CO)_2]$: ▲, 776°K; ⊗, 762°K; △, 751°K; ■, 737°K; ×, 716°K.

Effect of Surface. Increasing the surface:volume ratio tenfold reduced the rates of formation of CO, CH_4, and CH_2CO by up to 50%, $(CH_3)_2CO$ by 25%, and C_2H_6 by up to 75% (see Table I). The rate of production of $CH_3CH_2COCOCH_3$, however, increased 10–15-fold. Formation of CO_2 and C_2H_4, which are probably decomposition products of CH_2CO, also increased notably. Table IV shows that n_m^2/n_e was unaffected apart from a small increase at low pressures, but n_{at}^2/n_e showed a distinct increase. The increase in n_{pd} is interesting because it suggests that reaction 5 occurs mainly at the surface. This would cause the stationary concentration of CH_3· to decrease in the packed vessel and thus lower the values of n_m, n_e, and n_{at}, as observed. The increase in n_{at}^2/n_e may also be indicative of surface catalysis of reaction 7. However, the constancy of n_m^2/n_e shows that reaction 6 is not appreciably catalyzed by the surface. Since surface catalysis of a radical combination presumably requires absorption of one or both radicals, it may be expected to increase with increasing molecular weight and polar character of the radicals.

Heat of Formation of the Acetyl Radical, $\Delta H_f°(CH_3CO)$. Recent determinations of $\Delta H_f°(CH_3CO)$ by several more-or-less indirect methods have given values ranging from -6.5[34] to -3 kcal mol^{-1},[35] and three "best values" have been derived from various com-

(34) E. Murad and M. G. Inghram, *J. Chem. Phys.*, **41**, 404 (1964).

(35) J. G. Calvert and J. T. Gruver, *J. Amer. Chem. Soc.*, **80**, 1313 (1958).

Table IV: Effect on Product Ratios of Increasing Surface:Volume by a Factor of 10 (the Volume of Packed and Unpacked Vessels Is 283 cm³)

Temp, °K	Pressure, torr	$10^5 n_m^2/n_e$, mol sec^{-1}		$10^7 n_{at}^2/n_e$, mol sec^{-1}		n_c/n_{pd}	
		Unpacked[a]	Packed	Unpacked[a]	Packed	Unpacked[a]	Packed
776	25.9	2.03	2.17	...	...	8.7	0.43
	22.8	1.68	1.68	5.88	8.74	9.9	0.32
	14.8	0.89	0.89	3.10	4.38	17.2	0.33
	3.9	0.14	0.16	0.51	0.99	12.2	0.63
	2.95	0.09	0.12	0.35	0.94	26.4	0.75
751	23.9	1.25	1.25	4.88	5.19	5.3	0.13
	13.8	0.57	0.62	2.16	4.34	11.9	0.14
	5.6	0.15	0.17	0.67	1.40	...	...
716	13.8	0.29	0.26	1.51	3.83	1.6	0.06
	5.2	0.07	0.06	0.43	1.29	1.6	0.08

[a] Interpolated.

binations of these, namely, -5.4 ± 0.8,[36] -4 ± 2,[37,38] and -4.3 kcal mol^{-1}.[39] Intrinsically the most reliable of the individual values seems to be that of -4.7 ± 0.7 kcal mol^{-1} found by Walsh and Benson,[36] though it rests on the assumption that $E = 0$ for the reaction $CH_3CO + I_2 \rightarrow CH_3COI + I$. The present work yields a value directly, if it is assumed only that fission of the biacetyl molecule occurs at the central C–C bond and that $E_{-1} = 0$. Thus

$$\Delta H_f{}^\circ(CH_3CO) = \frac{1}{2}\left\{ E_1 + \Delta H_f{}^\circ[(CH_3CO)_2(g)] + \Delta(H^\circ{}_{730} - H^\circ{}_{298}) \right\}$$

The value of $H^\circ{}_{730} - H^\circ{}_{298}$ for biacetyl was taken as equal to the value for n-butane[40] and that for the acetyl radical was calculated using a mean specific heat of 17 cal deg^{-1} mol^{-1} (after Walsh and Benson[36]). Hence with $\Delta H_f{}^\circ[(CH_3CO)_2(g)] = -78.10$[37] and $E_1 = 67.2 \pm 3.3$ kcal mol^{-1} we find $\Delta H_f{}^\circ(CH_3CO) = -5.1 \pm 2.0$ kcal mol^{-1}.

Combination of Methyl Radicals. The fact that both $(k_6''')_0$ and its negative temperature coefficient are notably larger than the corresponding values for combinations between simpler species is in accord with the RRK theory,[41] which predicts an increase in both quantities with increasing complexity of the combining species (as well as with increasing exothermicity of the combination). A semiquantitative correlation has been found[41,42] between the rates and $-\Delta H$ of reactions of the type

$$A + BC + M \longrightarrow ABC + M$$
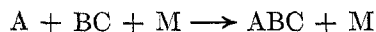
On this basis, $(k_6''')_0$ for such a reaction with $-\Delta H = -\Delta H_6 = 84$ kcal mol^{-1} and M a simple molecule would be 10^{16} to 10^{17} at 298°K. The major part of the difference between this value and $(k_6''')_0 \rightarrow 10^{22}$ at 298°K may be attributed to the greater complexity of the methyl radicals. (The greater efficiency of biacetyl

as third body is unlikely to involve more than a factor of 10^2; cf. ref 1.) Temperature coefficients for the triatomic combinations, as expressed by E, fall between -0.5 and -2 kcal mol^{-1}.[43] Although the considerably greater value of E_6 (-13 kcal mol^{-1}) may owe a little to the nature of the third body,[44] it seems likely that here again the complexity of the combined species is mainly responsible.[45–47] RRK theory leads to the relation

$$\log p_{1/2} = a + (S - {}^1/_2) \log T \qquad (X)$$

where a is almost independent of T. Figure 7 shows values of $\log p_{1/2}$ derived from several sources. Those at the five highest temperatures relate to the reverse of reaction 6, namely, the pyrolysis of ethane[27,28]; apart from the present results, and that of ref 48, the remainder were obtained from photolytic work. The present results are compatible with eq X and when extrapolated to lower temperatures agree well with the values obtained by Dodd and Steacie,[1,26] though the

(36) R. Walsh and S. W. Benson, *J. Phys. Chem.*, **70**, 3651 (1966).

(37) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(38) D. M. Golden, R. Walsh, and S. W. Benson, *J. Amer. Chem. Soc.*, **87**, 4053 (1965).

(39) J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley & Sons, New York, N. Y., 1966, p 820.

(40) National Bureau of Standards Circular C461, U. S. Government Printing Office, Washington, D. C., 1947.

(41) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 312.

(42) M. A. A. Clyne, D. J. McKenney, and B. A. Thrush, *Trans. Faraday Soc.*, **61**, 2701 (1965).

(43) T. C. Clark, M. A. A. Clyne, and D. H. Stedman, *ibid.*, **62**, 3354 (1966).

(44) G. Porter and J. A. Smith, *Proc. Roy. Soc.*, **A261**, 28 (1961).

(45) On the other hand, two independent sets of data yield[46] $E \approx$ 1 kcal mol^{-1} for the reaction $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$ (where M is $(CH_3)_2CO$ or $(CH_3N)_2$), whereas the value[47] for the about equally exothermic reaction $O + O_2 + CO_2 \rightarrow O_3 + CO_2$ is -1.5 kcal mol^{-1}.

(46) W. C. Sleppy and S. G. Calvert, *J. Amer. Chem. Soc.*, **81**, 769 (1959).

(47) M. F. R. Mulcahy and D. J. Williams, *Trans. Faraday Soc.*, **64**, 59 (1968).

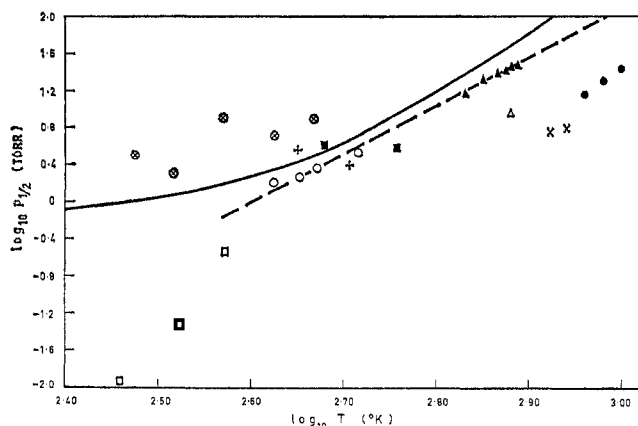(48) M. Krech and S. J. W. Price, *Can. J. Chem.*, **45**, 157 (1967).

Figure 7.   The dependence of log $p_{1/2}$ on log T:
----, log $p_{1/2}$ = (constant) + 5.2 log T; ———, log $p_{1/2}$,
RRKM absolute calculation (B. S. Rabinovitch and D. W.
Setser, *Advan. Photochem.*, **3**, 1 (1964); J. Grotewald, E. A.
Lissi, and M. G. Neumann, *J. Chem. Soc., A*, **2**, 375
(1968)). Third body: biacetyl, ▲; acetone: +, G. B.
Kistiakowsky and E. K. Roberts, *J. Chem. Phys.*, **21**, 1637
(1953); O, Dodd and Steacie;[1] azomethane–azoethane: □,
J. Grotewald, E. A. Lissi, and M. G. Neumann, *J. Chem.
Soc., A*, **2**, 375 (1968); ⊗, S. Toby and B. H. Weiss;
J. Phys. Chem., **68**, 2492 (1964); dimethyl ether: ■,
Loucks[3]; benzene: △, M. Krech and S. J. W. Price,
Can. J. Chem., **45**, 157 (1967); ethane: ✕, Lin and Back,[26]
●, Trenwith.[27]

agreement may be to some degree fortuitous. The
broken line has the slope corresponding to $S = 6$.
This is lower than, but according to RRK theory should
be equal to, the value derived from the temperature
coefficient of $(k_6''')_0$, namely, $S = 10$. Extrapolation
of the present values of $p_{1/2}$ to higher temperatures
leads to values 4–10 times greater than those derived
from ethane pyrolysis. Errors in the present deter-
minations of $p_{1/2}$ are more likely to cause the values to

be too low rather than too high. The results could be
reconciled by postulating a specifically high third-body
efficiency for ethane (due to a resonance effect).
However, experience with the recombination of I atoms[49]
and with the reaction

$$O_3 + M \longrightarrow O_2 + O + M$$
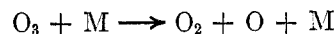
where M is O_3, CO_2, etc.,[50,51] suggests that such an effect,
if it exists,[52] may well be outweighed by that of the weaker
van der Waals' field of ethane compared with biacetyl.
Further evidence of a genuine discrepancy between the
present and the pyrolytic results comes from calcula-
tions of the absolute values of $p_{1/2}$ on the basis of the
RRKM theory.[53] These are shown as the unbroken
line in Figure 7 and were made[53,54] assuming a "loose"
activated complex (*i.e.*, tumbling methyls) and strong
deactivating collisions. The agreement with the present
values (and those of Dodd and Steacie[1]) is remarkably
good, the maximum difference between theory and ex-
periment being a factor of 1.6. This seems to dispose
of misgivings[54] concerning the validity of the loose acti-
vated complex model for the recombination, at least in
the range 430–800°K.

Acknowledgment. The authors are grateful to Dr.
J. R. Wilmshurst for advice on gas chromatographic
methods.

(49) M. I. Christie, *J. Amer. Chem. Soc.*, **84**, 4066 (1962).

(50) S. W. Benson and A. E. Axworthy, *J. Chem. Phys.*, **42**, 2614 (1965).

(51) F. Kaufman and J. R. Kelso, *ibid.*, **46**, 4541 (1967).

(52) J. W. Linnett and N. J. Selley, *Z. Phys. Chem.* (Frankfurt), **37**, 402 (1963).

(53) B. S. Rabinovich and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964).

(54) J. Grotewald, E. A. Lissi, and M. G. Neumann, *J. Chem. Soc., A*, **2**, 375 (1968).