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Rate of Association of Methyl Radicals

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The recombination rate constant of methyl radicals has been redetermined by the intermittent illumination method as 3.7×10^{13} cc/mole sec at 165°, after a correction for the concurrent formation of methane. The recombination rate constant of deuterated methyl radicals has been found to have a substantially identical value. The dependence of these second-order rate constants on total pressure was studied over the range of 1- to 10-mm acetone pressure. Both rate constants were found to decrease identically with pressure. The form of their pressure dependence agrees with deductions from the "third-body" stabilization theory. It is shown that the absolute magnitude of the recombination rate constants, their near-identity and their identical decrease with pressure are all consistent with theoretical predictions, provided the methyl radicals form a loosely bound critical complex, in which they carry out essentially unhindered rotations. Recent literature data on the recombination of methyl radicals are reviewed, and it is shown that they are not in serious disagreement with the present measurements.

SEVERAL seemingly conflicting measurements have been reported in the recent literature on the rate of formation of ethane by the recombination of methyl radicals. Using the photochemical rotating sector technique with acetone and dimethyl mercury vapors at pressures of 10 to 50 mm and at 125 to 220°C, Gomer[1] obtained 4.5×10^{13} cc/mole sec for the recombination rate constant. Miller and Steacie[2] measured the ratio of the rate constants of the methyl radical recombination and their reaction with nitric oxide at a pressure of 4.5 mm of mercury dimethyl at room temperature; this result was used by Durham and Steacie[3] to calculate the rate constant of the recombination reaction as 1.1×10^{12} cc/mole sec by combining it with their measurements of the rate of the reaction of methyl radicals with nitric oxide (0.2 mm of dibutyl peroxide being the source of radicals). Lossing, Ingold, and Tickner[4,5] determined the recombination rate constant as 5.1×10^{12} cc/mole sec, by a mass spectrometric technique in the presence of 15 mm of helium and only a few microns pressure of organic vapors. The radicals were generated by thermal decomposition at 850–975°C. Ingold and Lossing,[6] refining this technique, reported that upon reducing the temperature to 160°, the recombination rate constant rose to about 1.3×10^{13} cc/mole sec. These values of the rate constant correspond to collision yields of 0.01 to 0.36 for an assumed cross section of 3.5A, but may be mutually consistent if the association rate constant is pressure and temperature dependent. A pressure dependence above *ca* 20 mm of acetone or dimethyl mercury is definitely ruled out by careful measurements of the ratio of the recombination and hydrogen abstraction reactions of methyl radicals carried out in the Noyes[7] and the Steacie[8] laboratories. Such dependence, however, may become significant at still lower pressures, and so account for the different collision yields mentioned above.

To shed further light on the mechanism of this reaction, the recombination rate of methyl radicals was compared in the present experiments to that of deuterated methyls. Furthermore, the pressure dependence of the recombination reactions was explored down to 1-mm total pressure.

The theory of the rotating sector as applied to the photolysis of acetone has been summarized elsewhere.[1] In brief, there are three important reactions involving methyl radicals in the photolysis of acetone,

$$(CH_3)_2CO+h\nu\rightarrow 2CH_3+CO, \tag{1}$$

$$2CH_3\rightarrow C_2H_6;\quad R(C_2H_6)=k_2[CH_3]^2, \tag{2}$$

$$CH_3+(CH_3)_2CO\rightarrow CH_4+CH_2COCH_3;\quad R(CH_4)=k_3[(CH_3)][(CH_3)_2CO]. \tag{3}$$

In the event that reaction (3) occurs to a much lesser extent than reaction (2), the recombination rate constant is given by

$$k_2=1/[4\tau^2R(C_2H_6)_s], \tag{4}$$

where τ is the mean life of the methyl free radicals, determined from the comparison of the rates of methane production under conditions of intermittent and steady illumination, while $R(C_2H_6)_s$ is the rate of ethane production with steady illumination. The theory, from which the equations relating the methane production to the radical lifetime and the duration of illumination are derived, has been worked out by Dickinson.[9]

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[3] R. W. Durham and E. W. R. Steacie, J. Chem. Phys. 20, 582 (1952).

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[5] Lossing, Ingold, and Tickner, Disc. Faraday Soc. 14, 34 (1953).

[6] K. U. Ingold and F. P. Lossing, J. Chem. Phys. 21, 308 (1953).

[7] W. A. Noyes and L. M. Dorfman, J. Chem. Phys. 16, 788 (1948).

[8] A. F. Trotman-Dickenson and E. W. R. Steacie, J. Chem. Phys. 18, 1097 (1950).

[9] W. A. Noyes and P. A. Leighton, *The Photochemistry of Gases* (Reinhold Publishing Corporation, New York, 1941), pp. 202–209.

TABLE I. Experiments with intermittent illumination of $(CH_3)_2CO$ at 30-mm pressure. Rates expressed as mole cc^{-1} sec^{-1}.

Run	Temp. °C	$R(C_2H_6)$	$R(CH_4)$	$R(CO)$	$\frac{R(CH_4)_i}{R(CH_4)_s}$	Sector speed (rpm)
1	165	$117.\times10^{-12}$	11.7×10^{-12}	$133.\times10^{-12}$		
2	165	30.2	4.05	34.5	0.344	218
3	165	25.6	4.34	30.1	0.381	218
4	165	109.	11.6	123.		
5	165	27.5	3.36	32.	0.286	55.6
6	165	28.3	3.58	31.8	0.303	89.6
7	165	113.	11.6	129.		
8	165	27.2	4.26	32.1	0.361	301
9	165	27.4	3.10	31.7	0.276	48.0
10	165	113.	11.4	129.		
11	165	26.4	4.70	32.4	0.419	582
12	165	30.6	4.31	36.0	0.359	287
13	165	128.	12.1	144.		
14	165	31.5	3.60	36.0	0.299	89.8
15	135	28.6	1.97	30.8	0.337	89.8
16	135	114.	5.89	122.		
17	135	29.0	2.22	31.4	0.372	287
18	135	28.6	2.80	31.8	0.469	940
19	135	113.	5.86	121.		
20	135	28.4	1.78	30.4	0.303	55.5
21	135	27.8	2.42	31.0	0.403	581
22	135	112.	5.91	121.		
23	135	28.2	2.84	31.6	0.476	581

In order to account for the pressure dependence of the recombination rate constant, a more detailed mechanism including deactivation by a third body is required,

$$2CH_3 \rightarrow C_2H_6^* \quad (k_a), \tag{5}$$

$$C_2H_6^* \rightarrow 2CH_3 \quad (k_b), \tag{6}$$

$$C_2H_6^* + M \rightarrow C_2H_6 + M\,(k_c). \tag{7}$$

If we apply the steady-state assumption to the energy-rich ethane molecules $C_2H_6^*$,

$$R(C_2H_6) = k_2[CH_3]^2 = \frac{k_a[M]}{k_b/k_c + [M]}[CH_3]^2. \tag{8}$$

In the present low-pressure experiments, it has been possible to determine only the ratio k_2/k_3^2, so that when acetone is assumed to be the third body,

$$\frac{k_2}{k_3^2} = \frac{k_a/k_3^2[(CH_3)_2CO]}{k_b/k_c + [(CH_3)_2CO]} = \frac{R(C_2H_6)}{R(CH_4)^2}[(CH_3)_2CO]^2 \tag{9}$$

and

$$\frac{k_3^2}{k_2} = \frac{k_3^2}{k_a} + \frac{k_3^2 k_b}{k_a k_c}\,\frac{1}{[(CH_3)_2CO]}. \tag{10}$$

It is assumed that k_3 is pressure independent, since it is associated with a metathetical reaction,

EXPERIMENTAL

The deuterated acetone was prepared by the method of Reitz;[10] 1.4 grams of Mallinckrodt analytical reagent acetone was refluxed with 2 grams of 99.8 percent D_2O obtained from the Stuart Oxygen Company with a few drops of concentrated H_2SO_4 added. The mixture was then passed twice over fresh Drierite by distillation at reduced pressure, the acetone being received at −195°. The refluxing and distillation was repeated four times, using 2 grams of fresh D_2O and a few drops of H_2SO_4 each time. According to the distribution ratio calculated by Reitz, D/H in acetone : D/H in water $= 0.8$, 95 percent of the hydrogen atoms of the original acetone should be replaced by deuterium. This means that 85 percent of the methyl radicals produced would be completely deuterated, and that practically all of the remainder would have only one normal hydrogen atom. The infrared spectrum of the deuterated acetone was compared with that of normal acetone, confirming the calculated extent of the deuteration reaction.

The deuterated acetone, as well as the normal acetone, were dried over Drierite and distilled once in vacuum at −78° and then thoroughly outgassed at −78° before each series of runs.

The CO_2 used as an inert gas in the low-pressure runs was obtained from the third quarter of a small piece of commercial dry ice which was allowed to evaporate in vacuum. The portion saved was distilled once at −115° and was outgassed before each use at −195°.

TABLE II. Experiments with intermittent illumination of $(CD_3)_2CO$ at 30-mm pressure. Rates expressed as mole cc^{-1} sec.$^{-1}$

Run	Temp. °C	$R(C_2D_6)$	$R(CD_4)$	$R(CO)$	$\frac{R(CD_4)_i}{R(CD_4)_s}$	Sector speed (rpm)
24	165	$116.\times10^{-12}$	2.72×10^{-12}	$119.\times10^{-12}$		
25	165	28.1	1.13	30.1	0.414	377
26	165	28.5	1.00	30.1	0.370	249
27	165	114.	2.71	118.		
28	165	28.7	0.834	30.1	0.309	89.6
29	165	28.7	1.24	30.8	0.461	961
30	165	115.	2.67	119.		
31	165	28.8	0.777	30.0	0.292	48.0
32	165	28.6	1.16	30.6	0.442	582
33	165	117.	2.64	122.		
34	165	28.9	0.900	30.7	0.341	154
35	165	29.6	0.825	31.1	0.313	89.8
36	165	115.	2.60	121.		
37	165	30.2	1.02	32.0	0.383	287
38	195	28.5	2.48	32.2	0.432	581
39	195	117.	5.77	126.		
40	195	25.8	1.79	28.4	0.329	89.8
41	195	28.1	2.64	32.1	0.479	940
42	195	118.	5.50	127.		
43	195	28.3	2.07	31.4	0.380	250

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[10] O. Reitz, Z. physik. Chem. **A179**, 119 (1937).

The experimental arrangement and methods used in the rotating sector experiments were the same as those developed by Gomer.[1] For the low-pressure runs, the cylindrical reaction flask was replaced by a spherical quartz flask, most of the experiments being made with one of 523 cc volume and a few with a 165-cc flask. These flasks were placed in a large furnace made from copper pipe and heated electrically through a Sola voltage regulator transformer. Several copper fins were placed in the open end of the furnace, between the flask and the mercury lamp, to reduce convection currents and improve temperature uniformity. Exploration with a thermocouple of the region of the furnace occupied by the flasks showed that the temperature was uniform to 0.5°.

The unfiltered output of a Cooper-Hewitt 110-volt dc mercury lamp was used as the light source. The lamp was stabilized by a large inductance, and its output was kept constant manually, using the photocell arrangement described by Gomer.[1] In two runs a Lectromesh screen interposed between the lamp and the reaction cell reduced the light intensity by a factor of nearly 10.

In the low-pressure runs with added CO_2, the acetone and CO_2 were measured separately, before being transferred to a mixing chamber incorporated in the vacuum system. After mixing, the gases were allowed to expand into the reaction cell. In the analysis of the reaction products it was necessary to eliminate some of the CO_2 carried over with the ethane. This was done by passing the mixture over KOH at −150°. A check on the accuracy of this separation was obtained by adding some CO_2 to the reaction mixture after the exposure of acetone alone; the error in the final result was less than 5 percent.

RESULTS AND DISCUSSION

The runs with the rotating sector were performed in series of three, the second of which was with steady illumination and provided a value for methane production to be compared with those of the first and third runs using intermittent illumination. The sector was cut so that the ratio of the dark period to the light period was 3:1. The exposure time in each series was so regulated as to obtain nearly equal quantities of methane in the three runs. The results of the rotating sector experiments are shown in Tables I and II and in Figs. 1 and 2. In order to correct for any variation in light intensity between the runs with steady and with intermittent illumination, the ratio of the rates of methane production with intermittent and steady illumination, $R(\mathrm{CH}_4)_i/R(\mathrm{CH}_4)_s$, was multiplied by the factor 1/0.99 $(R(\mathrm{CO})_s/4R(\mathrm{CO})_i)^{\frac{1}{2}}$, where 0.99 is the average value of $(R(\mathrm{CO})_s/4R(\mathrm{CO})_i)^{\frac{1}{2}}$ for all runs. This correction is applied because with steady illumination the rate of methane production is proportional to the square root of the absorbed light intensity, provided that the ratio of methane to ethane is small.

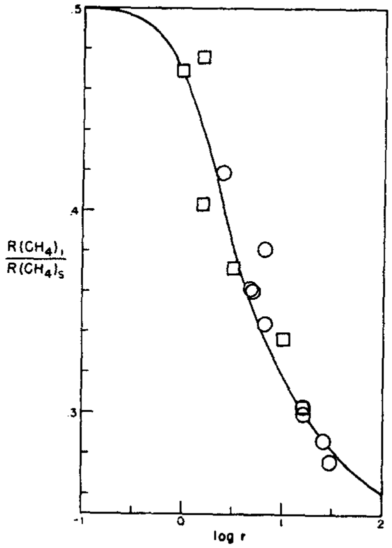

FIG. 1. The effect of flicker frequency upon the yield of methane from CH_3 radicals. ○ runs at 165° corresponding to $\tau=5.2$ msec. ☐ runs at 135° corresponding to $\tau=8.2$ msec. r=ratio of light period to the mean life τ of the radicals.

The lifetime of the methyl radicals was obtained from the best fit of the experimental data to the theoretical curve of Dickinson. The rate of ethane formation used in calculating the recombination rate constant is the average observed rate of formation with steady illumination.

A summary of the free radical lifetimes and recombination rate constants deduced from equations given above appears in Table III. The experimental error in the rate constants at 165° is about 15 percent, whereas at the other temperatures with fewer experimental points it is about 30 percent.

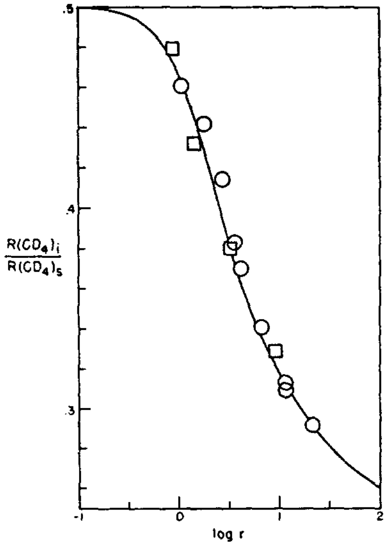

FIG. 2. The effect of flicker frequency upon the yield of methane from CD_3 radicals. ○ runs at 165° corresponding to $\tau=7.3$ msec. ☐ runs at 195° corresponding to $\tau=9.1$ msec.

Table III shows the rate constant for ordinary methyls at 165° to be much larger than the other values given. As shown by Table I this appears to be due to the breakdown of the assumptions made in deriving Dickinson's formula, namely, a negligible formation of methane. The effect of intermittent illumination has been worked out, therefore, for a kinetic mechanism more nearly representing the conditions encountered at 165°. Assuming that the only reactions involving methyl radicals are those given by Eqs. (1)–(3), it follows that during a light period:

$$\frac{d[\mathrm{CH_3}]}{dt}=2R(\mathrm{CO})-2k_2[\mathrm{CH_3}]^2-k_3[\mathrm{CH_3}][(\mathrm{CH_3})_2\mathrm{CO}] \quad (11)$$

and during a dark period:

$$-\frac{d[\mathrm{CH_3}]}{dt}=2k_2[\mathrm{CH_3}]^2+k_3[\mathrm{CH_3}][(\mathrm{CH_3})_2\mathrm{CO}]. \quad (12)$$

If we assume further that the acetone concentration remains constant, integrate these equations and solve them for the instantaneous methyl radical concentration, it is found that, during a light period,

$$[\mathrm{CH_3}]_l=-\frac{b}{4k_2}-\frac{Q}{4k_2}\frac{1+Ye^{Qt}}{1-Ye^{Qt}}, \quad (13)$$

and during a dark period,

$$[\mathrm{CH_3}]_d=\frac{b[\mathrm{CH_3}]_0'}{(b+c[\mathrm{CH_3}]_0')e^{bt}-c[\mathrm{CH_3}]_0'}, \quad (14)$$

where

$b=k_3[(\mathrm{CH_3})_2\mathrm{CO}]$,

$c=2k_2$,

$Q=[b^2+8cR(\mathrm{CO})]^{\frac{1}{2}}$,

$$Y=\frac{2c[\mathrm{CH_3}]_0+b-Q}{2c[\mathrm{CH_3}]_0+b+Q},$$

$[\mathrm{CH_3}]_0$ = methyl radical concentration at the beginning of a light period, and

$[\mathrm{CH_3}]_0'$ = methyl radical concentration at the beginning of a dark period.

TABLE III. Uncorrected association rate constants.

Radical	Temp.	Lifetime (msec)	k_2 cc/mole, sec
$\mathrm{CH_3}$	135	8.2	3.3×10^{13}
$\mathrm{CH_3}$	165	5.2	8.0×10^{13}
$\mathrm{CD_3}$	165	7.3	4.1×10^{13}
$\mathrm{CD_3}$	195	9.1	2.6×10^{13}

Equations (13) and (14) can be used to calculate the methyl radical concentration at the beginning of the light and dark periods by the method of successive approximations. At the sector speeds for which these calculations have been carried out, the methyl concentration at the end of a light period is the same as the methyl concentration with steady illumination within 1 percent. An integration of the expressions (13) and (14) for the instantaneous methyl radical concentration, over the light and the dark periods, respectively, gives the average methyl radical concentrations. During the light period,

$$\overline{[\mathrm{CH_3}]_l}=-\frac{b}{2c}+\frac{1}{2ct}\ln\frac{(e^{Qt}-Y)(1-Ye^{-Qt})}{(1-Y)^2} \quad (15)$$

and during the dark period,

$$\overline{[\mathrm{CH_3}]_d}=-\frac{b}{c}+\frac{1}{pct}\ln\frac{(b+c[\mathrm{CH_3}]_0')e^{pbt}-c[\mathrm{CH_3})_0'}{b}, \quad (16)$$

where $p=3$ is the ratio of the length of the dark period to the length of the light period. The average methyl radical concentration with intermittent illumination is given by

$$[\mathrm{CH_3}]_i=\frac{\overline{[\mathrm{CH_3}]_l}+p\overline{[\mathrm{CH_3}]_d}}{p+1}. \quad (17)$$

The average methyl radical concentration with steady illumination $[\mathrm{CH_3}]_s$ can be obtained from Eq. (13) by setting $t=\infty$.

A trial value of k_2 is then chosen, and from this k_3 is calculated, since the ratio $k_3/k_2^{\frac{1}{2}}$ is known from the runs with steady illumination. Then Eqs. (13)–(17) are used to calculate the ratio $[\mathrm{CH_3}]_i/[\mathrm{CH_3}]_s$, which should equal the experimental ratio $R(\mathrm{CH_4})_i/R(\mathrm{CH_4})_s$, since the average rate of methane production is proportional to the average methyl radical concentration, with either steady or intermittent illumination. New trial values of k_2 are tested until a value is found such that

$$([\mathrm{CH_3}]_i)/([\mathrm{CH_3}]_s)=[R(\mathrm{CH_4})_i]/[R(\mathrm{CH_4})_s]. \quad (18)$$

These calculations have been carried out for runs 12 and 13 with normal methyl radicals, and for runs 26 and 27 with deuterated methyl radicals. These runs were chosen for three reasons: (1) they fit well on the curves, (2) they occur near the inflection point of the curves, where the magnitude of the recombination rate constant has the greatest effect on the average methyl radical concentration with intermittent illumination, and (3) the runs have comparable experimental methane ratios. It was found that the recombination rate constant of normal methyl radicals at 165° must be reduced to 4.2×10^{13} cc/mole sec, corresponding to a mean lifetime of 6.7 msec, in order that Eq. (18) be satisfied. This is a reduction of 50 percent compared to the value obtained by using the formulas of Dickinson.

TABLE IV. The effect of total pressure on the recombination rate constant.

Run	Pressure acetone (mm)	CO_2 (mm)	Temp. °C	Exposure time (min)	$R(C_2H_6)$	$R(CH_4)$ mole/cc sec	$R(CO)$	k_2/k_3^2
44	10		215	8	17.4×10^{-12}	4.65×10^{-12}	22.1×10^{-12}	0.410
45	10		189	8	18.7	2.82	21.6	0.435
46	8		184	8	16.2	2.00	18.2	0.391
47	6		183	8	13.1	1.43	14.6	0.331
48	4		185	8	10.1	0.953	11.3	0.278
49	3		179	8	8.31	0.624	9.00	0.230
50	2		176	12	6.61	0.392	7.00	0.181
51	1		170	20	3.87	0.176	4.06	0.100
52	2		174	6	6.49	0.401	6.90	0.156
53	15		173	5	27.1	3.71	31.2	0.410
54	12		171	6	22.3	2.58	25.3	0.405
55	10		223	5	16.1	5.48	22.2	0.0292
56	8		232	6	13.2	4.81	18.3	0.0271
57	6		235	6	10.5	3.52	14.4	0.0253
58	4		237	6	8.06	2.27	10.5	0.0221
59	3		239	6	6.74	1.72	8.75	0.0193
60	2		238	8	5.46	1.18	6.67	0.0144
61	1		241	10	3.40	0.597	4.07	0.0096
62[a]	8		241	20	0.658	1.27	1.67	0.0264
63[a]	2		238	90	0.380	0.288	0.639	0.0168
64	1.5		239	8	4.37	0.837	5.26	0.0138
65	2		241	8	4.87	1.10	6.05	0.0162
66[b]	4		241	12	10.3	2.98	13.4	0.0187
67[b]	8		239	6	14.3	5.80	20.1	0.0256
68[b]	2		239	20	6.59	1.22	7.96	0.0166
69[b]	4		237	12	9.85	2.54	12.6	0.0216
70[b]	2		237	20	6.67	1.24	7.96	0.0155
71	6	9.9	241	6	10.2	3.88	14.2	0.0245
72	1	8.6	242	10	3.26	0.490	3.80	0.0142
73	1	38.	242	10	3.59	0.512	4.29	0.0143
74	1	37.	242	10	3.44	0.476	4.05	0.0159
75[c]	2	45.	242	8	4.54	1.12	5.97	0.0152
76	1	39.	244	10	3.27	0.478	4.02	0.0160
77	6	38.	241	6	9.20	3.61	13.5	0.0257
					Deuteroacetone			
78	6		237	10	12.5	1.23	13.6	0.260
79	2		237	15	5.89	0.351	6.25	0.168
80	10		237	6	17.3	2.18	19.6	0.321
81	1		238	20	3.88	0.193	4.09	0.095
82	4		238	10	9.41	0.731	10.2	0.257
83	1.5		239	18	4.99	0.260	5.32	0.156
84	1.1		240	20	4.15	0.210	4.40	0.113

[a] Light intensity reduced by Lectromesh screen.
[b] Reaction carried out in 165-cc cell.
[c] CO_2 added after exposure.

On the other hand, the rate constant for deuterated methyl radicals becomes 3.8×10^{13} cc/mole sec, thus changing by less than the experimental error from the value obtained directly from the Dickinson formulas. This small change is the result of the comparatively insignificant yield of methane from deuterated methyls at 165°. Accordingly it may be safely assumed that the other values of Table III would not be reduced by more than some 10 percent—within the estimated experimental error—after applying Eqs. (13)-(17). These laborious calculations were not carried out therefore. The corrected values of Table III show then that the recombination rate constants of the normal and deuterated methyl radicals are either identical, or that the former is greater by not more than some 30 percent.

The absolute rate theory predicts[11] a maximum value of 5×10^{13} cc/mole sec (correcting for the electronic multiplicity factor) for the recombination rate constant of normal methyls. The presently observed value, of about 3.7×10^{13}, agrees well with this prediction. The theory also requires that in order for the rate constant to be near the maximum value, the radicals must form a very loosely bound critical complex. In this case the ratio of the rate constants for the ordinary and the deuterated methyls must equal the square root of the inverse ratio of the masses of the radicals, i.d. $(6/5)^{\frac{1}{2}}=1.1$. The present experimental data are in excellent accord with this value; they show, therefore, very little hindrance of rotations of the methyl radicals in the critical complex.

For the elucidation of the pressure dependence, runs were made with steady illumination at temperatures near 180° and 240°. The observed rate constant ratios k_2/k_3^2 were normalized to these temperatures by

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[11] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

using the activation energy differences reported by Trotman-Dickenson and Steacie,[8] $E_3-\frac{1}{2}E_2=9.7$ kcal for CH_3 and 10.3 kcal for CD_3. The experimental results are recorded in Table IV, which shows decided dependence of the ratio k_2/k_3^2 upon acetone pressure. Plots of the inverse k_3^2/k_2 against the inverse of the concentration of acetone give very satisfactory straight lines, as is shown in Fig. 3. The experimental results are therefore consistent with Eq. (10). The parameters of this equation for the three experimental conditions investigated are shown in Table V.

The experimental error in the values of k_3^2/k_a, which are equal to k_3^2/k_2 at high acetone pressures, is estimated at 10 percent, whereas there is an uncertainty of 30 percent in the ratios k_b/k_c, which are equal to those concentrations or pressures of acetone at which the recombination rate constant k_2 has fallen to one-half the limiting high-pressure value.

In the tenfold pressure range studied in these experiments, the recombination rate constant is reduced by a factor of 3 to 4. This pressure effect is shown to be independent of the absorbed light intensity (runs 62 and 63), even under conditions when the rate of methane production exceeds that of ethane. Further, the pressure effect is independent of the size of the reaction vessel (runs 66 to 70). This indicates that the heterogeneous recombination of the radicals is unimportant.

The runs with CO_2 added to the reaction mixture show a relatively small effect of CO_2 on the recombination rate constant. Even with approximately 40 mm of CO_2 added to 1 mm of acetone, the recombination rate constant is increased to a value characteristic of only 2-mm pressure of acetone. Carbon dioxide has apparently no effect on the rate of decomposition of acetone, as evidenced by unchanged rate of production of carbon monoxide. Hence its small effect on the ethane/methane ratio is due either to its low efficiency as the third body, or to a highly improbable cancellation of two opposing effects. One is the retardation of the diffusion of the radicals to the walls, and hence of the hypothetical heterogeneous recombination, the other is the accelerating third-body effect on the homogeneous recombination.

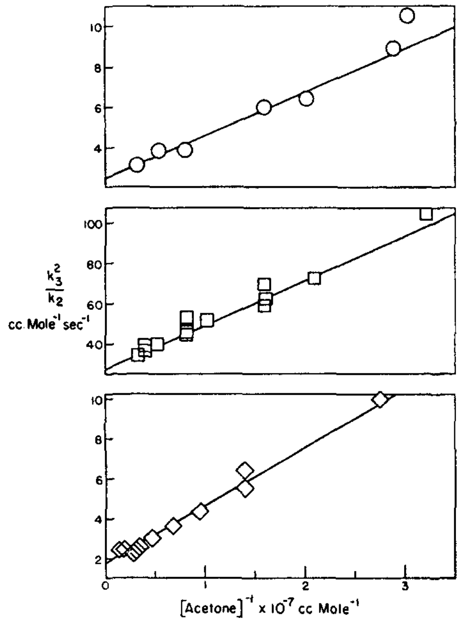

FIG. 3. Plots of the ratio k_3^2/k_2 against the inverse of acetone concentration. Circles are for CD_3 at 240°; squares for CH_3 at 240°; diamonds for CH_3 at 180°C.

It is rather unlikely that the observed reduction of the recombination rate at low pressures is due to the onset of competing reactions. One of them might be the formation of ethylene and hydrogen by the energy-rich ethane molecules. But Lossing and Tickner[4] observed no ethylene mass spectrometrically, under conditions even more extreme than those encountered in the present research. A disproportionation reaction $2CH_3 \rightarrow CH_4+CH_2$ has been reported by Bawn and Tipper,[12] but Bawn and Dunning[13] found no evidence of it and former authors estimate its activation energy as 8 kcal. This makes it unimportant in any case at the temperatures employed in the present experiments.

TABLE V. The pressure dependence parameters of the recombination rate constants.

Radical	Temp.	$\frac{k_3^2}{k_a}$ cc/mole sec	$\frac{k_b}{k_c}$ mole/cc	$\frac{k_b}{k_c}$ mm
CH_3	180	1.8	1.6×10^{-7}	4.5
CH_3	240	27	0.83	2.7
CD_3	240	2.4	0.88	2.8

Thus, there are strong reasons for believing that the observed change in the k_3^2/k_2 ratio is due to the third-body effect on the homogeneous recombination of methyl radicals. The magnitude of the observed effect—a change in the recombination rate constant by a factor of about four—is well outside the experimental errors. It may be noted that the earlier data of Trotman-Dickenson and Steacie,[8] obtained over the range of 4 to 100 mm at 150°, agree well with the presently observed pressure effect.

The pressure range in which the recombination rate constant becomes pressure dependent is consistent with Marcus'[14] theoretical treatment for the case of a loosely bound critical complex. But the presently observed ratio of the recombination constants for the normal and the deuterated radicals does establish a loosely bound complex. Thus, the data are consistent with Marcus' treatment, although we cannot agree with his conclusion that the experimental data favor a tightly bound critical complex.

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Slater's[15] classical treatment of the pressure dependence is interesting in that it predicts substantially identical behavior of the rate constants of the normal and the deuterated radicals—which is in accord with the present findings. Benson's[16] treatment of the pressure dependence suffers, we believe, from an oversimplification of the model. In conjunction with the present findings it leads to the conclusion that only three to four internal degrees of freedom participate in the distribution of energy in the energy-rich ethane molecules.

In conclusion a few comments on the apparent discrepancies in the absolute values of the recombination rate constants as obtained by several groups of workers. Gomer's results,[1] obtained by the same method, do not differ significantly from the present data and hence need no further comment. To make the work of Durham and Steacie[3] and Miller and Steacie[2] comparable with this research, one must apply corrections for the pressure effects on the recombination of methyl radicals and their reaction with nitric oxide. If the pressure dependence of the CH_3+NO reaction is the same as presently observed for the recombination rate, the collision efficiency for the recombination reaction, as calculated by Durham and Steacie, would have to be increased by a factor of about two hundred. The present discrepancy is only a factor of thirty and hence a lesser pressure dependence of the CH_3+NO reaction would bring these data into complete agreement. A discrepancy of about a factor of three between the low-temperature data of Ingold and Lossing[6] and the present measurements may be easily due to the low third-body efficiency of the inert gas (helium) which they used in addition to very low pressures of organic vapors. Such low efficiency is certainly not in conflict with the present observations on the effect of carbon dioxide. The rather strong negative temperature coefficient of the recombination rate, observed by Ingold and Lossing, is not consistent with the prediction of the absolute rate theory for the rate of formation of the critical complex. But the present interpretation of the low absolute magnitude of their recombination rate makes the stabilization of the energy-rich ethane molecules by collisions into the rate determining step. The Rice-Kassel theory of unimolecular reactions predicts a decrease in the lifetime of energy-rich molecules with rising temperature because of their rising energy content. It may well be that the temperature coefficient observed by Ingold and Lossing is due to this cause. If that is indeed true, it would appear that all the modern data on the recombination of methyl radicals are in substantial agreement among themselves and bear out very well most of the theoretical predictions.

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Absorption Coefficients of Gases in the Vacuum Ultraviolet. Part II. Nitrous Oxide

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Absorption coefficients of N_2O in the region 1080–2100A have been measured. Four continua were observed with maxima at 1820, 1450, 1285, and 1080A having f values of 0.0015, 0.0211, 0.367, and 0.1, respectively. The strongest absorption band in the ultraviolet lies at 1178A with an absorption coefficient of 3010 cm^{-1} at its maximum. A number of new bands were observed, and some of them classified. Some of the continua have been interpreted in terms of possible dissociation processes, and a potential energy diagram is presented.

SEVERAL investigators have studied the absorption spectrum of nitrous oxide in the vacuum ultraviolet. Leifson[1] observed two continuous bands, the first covering the region 2000–1680A and the second extending from 1550A to the transmission limit of fluorite. However, he did not observe any discrete bands. Sen-Gupta[2] also observed two continua in roughly the same regions. The most thorough and detailed work is that of Duncan[3] who studied the region 850–2200A. The near ultraviolet absorption spectrum of N_2O has been studied by a number of investigators.[4–6]

Absorption coefficients of N_2O in the region 1390–2200A were recently measured by Romand and Mayence[7] who studied the two continua mentioned above. They found the maxima to lie at 1450A and 1840A. There appear to be no other measurements of absorption coefficients in the vacuum ultraviolet. This paper will describe some absorption measurements made by a technique somewhat different from that of previous

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