ON THE KINETICS OF METHYL FREE RADICALS, II.

The Velocity Constant of the Association Reaction between Methyl Radical and Iodine Atom.

By Jiro Osugi.

It is widely informed that the association reaction between two atoms is a termolecular process, but the association between free radicals and atoms has not yet been experimentally elucidated. In the first report, the author concluded from the experimental evidences that the association between methyl radical and iodine atom is a bimolecular process, and that the velocity constant of the reaction may be 1.09×10^{14} cc/mol sec.

In the present report, the author analysed the curves of the pressure change after the shutting off light which were obtained from the same experiments as reported before, and calculated the velocity constant of the reaction from the reaction velocity after the shutting. No one has determined the velocity constant of the reaction.

Apparatus and experimentals.

The apparatus was the same as reported before. The experimental method was also the same, but the rotating velocity of the film-roller of the oscillograph used was made higher and the reaction velocity after the shutting off light was made easier to measure. The following additional experiments were performed. The pressure change due to the absorption of infra-red rays was measured by means of a I KW tungsten lamp and yellow-brown glass filter. The time interval of the shutting and opening of the shutter was recorded on the film by means of a photo-cell.

Method of analysis.

The general figure of the pressure change curve is the same as shown in the case of recombination of hydrogen by Dr. Shida[1]. When the methyl iodide contained in the reaction vessel is illuminated by ultra-violet rays, methyl radical and iodine atom are formed. The pressure increase due to the heat of the

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1) S. Shida, *This Journal*, 16, 44 (1942)

association reaction between methyl radical and iodine atom is recorded on the film. The pressure increase takes a finite value when the reaction heat is equal to the cooling (stationary state), and after the shutting off light the increased pressure falls to the initial pressure within a few seconds. Methyl radical and iodine atom do not disappear at a moment after the shutting, but they associate according to their own mechanism. We can, therefore, obtain the relation between the reaction velocity of the association and the time after the shutting by the, following analysis of the curve after the shutting. Dr. Horiba's thermal analysis of reaction velocity gives the homogeneous reaction velocity in gaseous phase by the following equation,

$$K \frac{dx}{dt} = \frac{d(\Delta p)}{at} + k\Delta p.$$ (1)

where

$$K = \frac{nRQ}{S\sigma V}.$$ (2)

The sign and the value of the constants are the same as described in the previous report. The reaction heat Q is taken to be 96 Kcal which will be examined later on.

Experimental results.

The pressure change obtained from the curve after the shutting off light and the reaction velocity calculated by the equation described above are shown in Table 1, where Δp is the pressure change, t time, $\frac{dx}{dt}$ the reaction velocity of the association, k the cooling constant, K the constant given by Eq. (2), λ the sensitivity of the manometer (mmHg per mm on film).

Table 1

A. CH_3I: 11.07 cmHg, $K = 6.953 \times 10^8$ (mmHg cc/mol), $k = 0.478$ (sec^{-1}),
temp.: 28.7°C, $\lambda = 1.26 \times 10^{-3}$ (mmHg/mm).

t (0.0083 sec)	ΔP (10^{-3} mmHg)	$\frac{d(\Delta P)}{dt}$ (10^{-3} mmHg/sec)	$k\Delta P$ (10^{-3} mmHg/sec)	$\frac{dx}{dt}$ (10^{-12} mol/sec cc)
0	11.20		5.35	7.69
2	11.17	2.36	5.34	4.29
4	11.13	3.35	5.31	2.82
6	11.06	3.99	5.28	1.85
8	11.00	4.37	5.25	1.27

B. CH_3I: 5.87 cmHg, $K=1.509 \times 10^9$ (mmHg cc/mol), $k=1.192$ (sec^{-1}),
Ar: 17.49 cmHg,   temp.: 23.7°C, $\lambda=4 \times 10^{-4}$ (mmHg/mm).

t (0.0083 sec)	ΔP (10^{-3} mmHg)	$\dfrac{d(\Delta P)}{dt}$ (10^{-3} mmHg/sec)	$k\Delta P$ (10^{-3} mmHg/sec)	$\dfrac{dx}{dt}$ (10^{-12} mol/sec cc)
0	7.81		9.31	6.17
1	7.79	2.19	9.29	4.70
2	7.77	3.52	9.26	3.81
3	7.74	4.77	9.23	2.95
4	7.71	5.57	9.19	2.40
5	7.67	6.18	9.14	1.96
6	7.61	6.60	9.07	1.64

C. CH_3I: 7.96 cmHg, $K=8.258 \times 10^8$ (mmHg cc/mol),
CO_2: 30.13 cmHg, $\lambda=1.09 \times 10^{-3}$ (mmHg/mm), $k=0.670$ (sec^{-1}),   temp.: 25°C.

t (0.0083 sec)	ΔP (10^{-3} mmHg)	$\dfrac{d(\Delta P)}{dt}$ (10^{-3} mmHg/sec)	$k\Delta P$ (10^{-3} mmHg/sec)	$\dfrac{dx}{dt}$ (10^{-12} mol/sec cc)
0	11.54		7.73	9.36
2	11.49	3.92	7.70	4.57
4	11.41	5.07	7.65	3.12
6	11.33	5.94	7.59	1.99
8	11.22	6.47	7.52	1.26

The relations between the reaction velocity obtained above and the time are shown in Fig. 1. We can obtain the reaction velocity constant from these
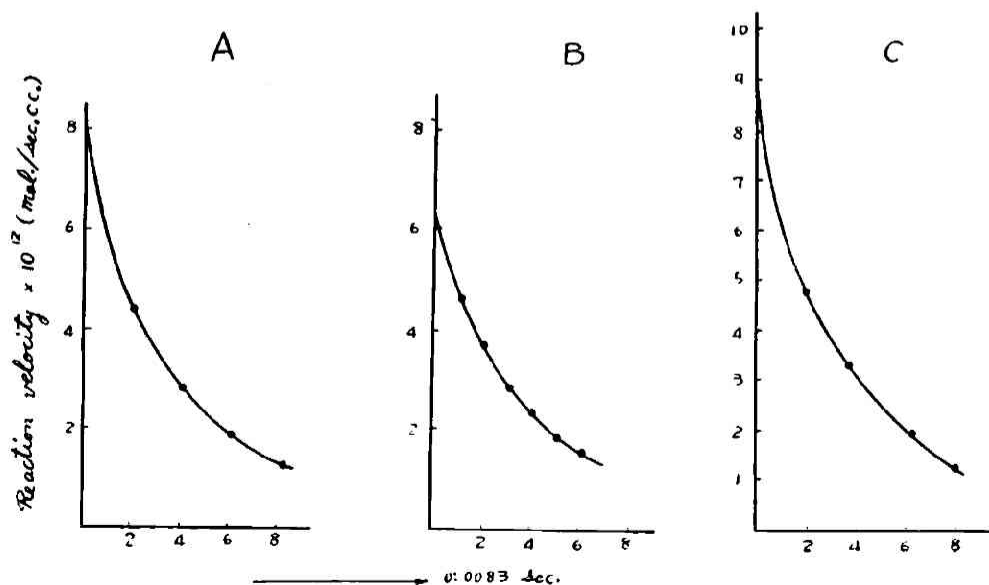

Fig. 1   Relations between the reaction velocity and the time.

results as follows.

It was proved in the previous report that the association between methyl radical and iodine atom was a bimolecular process. As the concentrations of methyl radical and iodine atom, both of which are produced by the decomposition of methyl iodide, are equal, we can assume the decreasing velocity of the concentration of methyl redicals as the velocity of the association reaction,

$$-\frac{d(CH_3)}{dt} = k_2(CH_3)^2, \tag{3}$$

$$\frac{1}{(CH_3)} = k_2 t + c',$$

where k_2: bimolecular reaction velocity constant,

            c' : integration constant.

Taking the moment of the shutting as $t=0$ and the stationary concentration of methyl radical as $(CH_3)_0$,

$$c' = \frac{1}{(CH_3)_0},$$

$$\therefore \quad k_2 t = \frac{1}{(CH_3)} - \frac{1}{(CH_3)_0}, \tag{4}$$

And assuming the velocity given by Eq. (3) as V and the value in stationary state as V_0,

$$(CH_3) = \sqrt{\frac{V}{k_2}}, \quad \text{and} \quad (CH_3)_0 = \sqrt{\frac{V_0}{k_2}}.$$

From Eq. (4), we can obtain the following relations,

$$\sqrt{k_2} t = \sqrt{\frac{1}{V}} - \sqrt{\frac{1}{V_0}}, \tag{5}$$

$$k_2 = \left(\frac{\sqrt{\dfrac{1}{V}} - \sqrt{\dfrac{1}{V_0}}}{t}\right)^2. \tag{6}$$

The velocity constants can be calculated from Eq. (6) and are shown in Table 2.

As the velocity constants have a constant value regardless of the presence of inert gases, we can conclude as in the previous report, that the reaction occurs in the bimolecular mechanism. And the velocity constant is

$$k_2 = 0.55 \times 10^{14} \text{ cc/mol sec.}$$

The linear relations between $\sqrt{\dfrac{1}{V}}$ and t are given by Eq. (5) and shown in Fig. 2. The linearities obtained are satisfactory.

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Table 2

Exp. A.

t (0.0083 sec)	V (10^{-12} mol/sec cc)	$\sqrt{V}$ (10^{-6})	$\dfrac{1}{\sqrt{V}}$ (10^6)	k_2 (10^{14} cc/mol sec)
0	7.69	2.77	0.36	
2	4.29	2.07	0.48	0.54
4	2.82	1.68	0.60	0.50
6	1.85	1.36	0.73	0.56
8	1.27	1.13	0.89	(0.63)
				mean 0.53

Exp. B.

t (0.0083 sec)	V (10^{-12} mol/sec cc)	$\sqrt{V}$ (10^{-6})	$\dfrac{1}{\sqrt{V}}$ (10^6)	k_2 (10^{14} cc/mol sec)
0	6.17	2.48	0.40	
1	4.70	2.17	0.46	0.49
2	3.81	1.95	0.51	0.44
3	2.95	1.72	0.58	0.51
4	2.40	1.55	0.65	0.53
5	1.96	1.40	0.71	0.56
6	1.64	1.28	0.78	0.57
				mean 0.52

Exp. C.

t (0.0083 sec)	V (10^{-12} mol/sec cc)	$\sqrt{V}$ (10^{-6})	$\dfrac{1}{\sqrt{V}}$ (10^6)	k_2 (10^{14} cc/mol sec)
0	9.36	3.06	0.33	
2	4.57	2.14	0.47	0.71
4	3.12	1.77	0.57	0.52
6	1.99	1.41	0.71	0.58
8	1.26	1.12	0.89	(0.71)
				mean 0.60

Considerations.

The author will now examine the experimental methods performed and the results obtained.

The time taken for shutting the shutter is found to be about $\dfrac{1}{100}$ sec. from the measurements which are recorded on the film by means of a photo-cell.   So
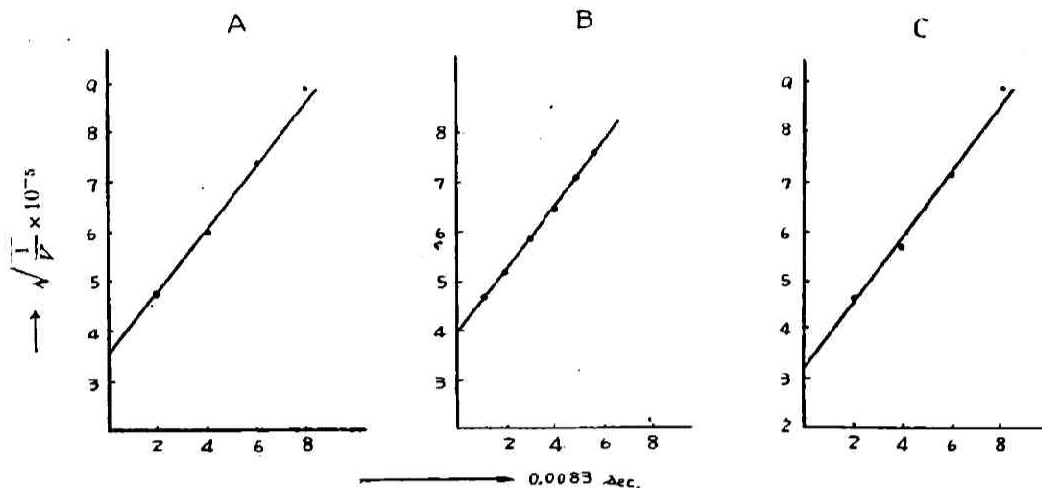
Fig. 2   Linear relations between $\sqrt{\dfrac{1}{V}}$ and the time.

the values determined within $\dfrac{1}{100}$ sec. after the shutting are not reliable.

The ultra-violet absorptions of methyl iodide have been measured by many investigators.[2] Though their results are not necessarily consistent, it is surely ascertained that the continuous spectra ranging from 3300Å to 2100Å are attributed to the decomposition of methyl iodide into methyl radical and iodine atom, either of which is excited in electronic levels[3]. In the calculation of the reaction velocity by Eqs. (1) and (2), it is reasonable to consider that the reaction heat Q is not equal to the energy of $C-I$ bond but to the energy of the bond plus that of the excitation. For the energy of excitation will be preserved for a moment in a radical or atom.* In the present experiment, the author take 96 Kcal as the reaction heat from the spectroscopic evidences†. It seems to be due

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* The vibrational levels of methyl iodide are excited by infra-red rays. The pressure increase due to the excitation can be measured by the present apparatus. The experiments on measuring and analysing the pressure change after the shutting off light which is caused by the molecules internally excited were performed. From the results, the author observes that the cooling constant tends to become the slightly smaller value within $\dfrac{1}{100} \sim \dfrac{2}{100}$ sec. after the shutting, but the effect is not certain from the consideration of the time for shutting. As to the electronic excitation, however, the preservation time of the internal energy will be surely longer.

† From due considerations of the spectra of a high pressure mercury lamp filtered with nickel chloride solution, the experimental evidence that the effective rays for the reaction were cut off completely by the insert of a glass plate, and the extinction coefficient of methyl iodide, the author took 96 Kcal (2950 Å) as the reaction heat.

2) D. Porret and C. F. Goodeve, *Trans. Farad. Soc.*, **33**, 690 (1937)

   G. Herzberg and G. Scheibe, *Z. Physik. Chem.*, **7**, 390 (1930)

   Y. Hukumoto, *Sci. Report Tohoku Imp. Univ.*, **21**, 906 (1932)

   T. Iredale and A. G. Mills, *Proc. Roy. Soc.*, A**133**, 430 (1931)

3) J. E. Lennard-Jones, *Trans. Farad. Soc.*, **30**, 70 (1934)

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to the decrease of the excitation energy that the linear relations shown in Fig. 2 can not be held after $\frac{8}{120}$ sec.

The mean valve of the velocity constants calculated from the values—from $\frac{2}{120}$ sec. to $\frac{6}{120}$ sec.—is

$$k_2 = 0.55 \times 10^{14} \text{ cc/mol sec.}$$

The value calculated from the collision theory is 1.09×14^{14} cc/mol sec. as reported before. The agreement is sufficient.

Bawn[4] calculated the equilibrium constant of the reaction $CH_3I \rightleftarrows CH_3 + I$ by the partition functions and estimated the velocity constant of the association by using the velocity constant of unimolecular decomposition of CH_3I. The value is

$$k_2 = 1.2 \times 10^{15} \text{ cc/mol sec.} \quad \text{at } 600°K,$$

and the corrected value is

$$k_2 = 8.2 \times 10^{14} \text{ cc/mol sec.} \quad \text{at } 280°K.$$

This theoretical value is rather larger as compared with the value obtained in the present experiment.

The time (mean life) required to decrease the concentration of methyl radical to its half value can be calculated by Eq. (4). The mean interval of collisions between methyl radical and iodine atom can be calculated by the collision theory. These values are compared in Table 3. The conclusion that the association reaction occurs in every bimolecular collision is also confirmed from these results.

Table 3

Exp. No.	A	B	C
Mean life (sec)	$\frac{1}{20.6}$	$\frac{1}{18.4}$	$\frac{1}{22.7}$
Mean collision interval (sec)	$\frac{1}{28.7}$	$\frac{1}{26.5}$	$\frac{1}{30.8}$

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4) C. E. H. Bawn, *Trans. Farad. Soc.*, 31, 1536 (1935)