

ON THE KINETICS OF METHYL FREE RADICALS, I.

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

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Since Herzfeld's remark,¹⁾ the association reaction between two atoms has been generally considered to require the third body for the formation of a stable diatomic molecule. When more complex particles (radicals or molecules) take part in an association reaction, they can combine in a bimolecular process.

The present report concerns chiefly to the association reaction between methyl radical and iodine atom, and to the question whether they can combine bimolecularly or termolecularly.

The experimental method is Dr. Horiba's established "Thermal analysis of chemical reaction velocity."²⁾

Apparatus and Materials.

The experimental apparatus is the same as adopted for the thermal analysis in gaseous phase.³⁾ The chief parts consist of a cylindrical reaction vessel with a quartz window, a gas refining apparatus, a light source, and a differential manometer on the basis of electric capacity change. The sensitivity of the manometer is about 4/10000 mm Hg, being corrected and controlled when required.

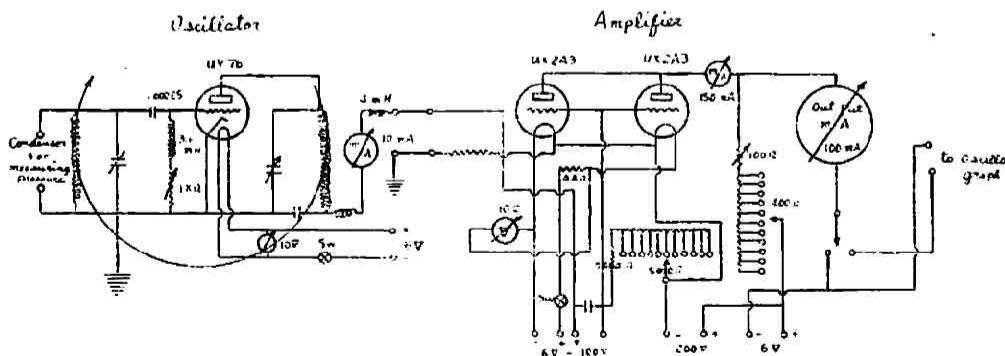


Fig. 1 Electric circuit for measuring pressure.

1) K. F. Herzfeld, *Z. Physik.*, **8**, 132 (1922)

2) S. Horiba, *This Journal*, **11**, 439 (1937)

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

The electric oscillating and amplifying circuit for measuring pressure is shown in Fig. 1. One of the correction figures of the pressure measurements is shown in Fig. 2. The satisfactorily linear relations between the pressure changes and the deflections (on the film) are obtained. The light source is high pressure mercury lamp with the filter of a nickel chloride solution. The effective wave length is about 2950 Å, being determined by the spectroscopic method.

Methyl iodide was synthesized from methanol, iodine and phosphorus, and was repeatedly distilled and dried, and was further purified by distillation in vacuum before its introduction to the reaction vessel. The composition of argon given by Teikoku Sanso Co. was as follows: Ar: 86%, N₂: 14%, O₂: 0.01%. Liquid carbon dioxide was purified in gaseous phase, its purity being more than 99.5%.

Methods.

The association reaction between methyl radical and iodine atom is the reverse process of the photolysis of methyl iodide by which methyl free radical and iodine atom are formed.⁴⁾ The photochemical decomposition of methyl iodide by ultra-violet rays has low quantum yield (about 2/1000)⁵⁾. This means that the association between methyl radical and iodine atom is almost complete. The velocities of the association were measured from the pressure increases due to the reaction heat.

The reaction velocity in homogeneous gas phase is given by the following equation in the method of thermal analysis of reaction velocity,

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

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

$$\frac{dx}{dt}; \text{ reaction velocity (mol/sec. cc)}$$

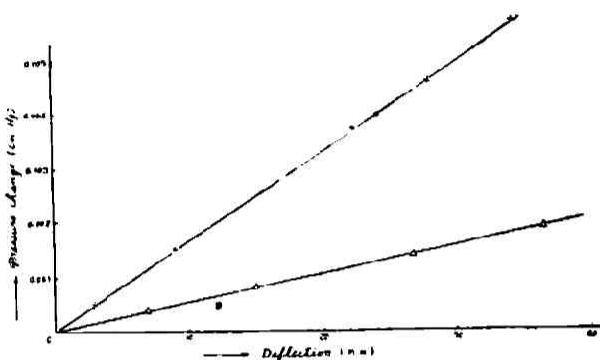


Fig. 2 Relations between pressure changes and deflections.

4) J. Osugi: *This Journal*, **18**, 1 (1944)

5) W. West and L. Schlessinger: *J. Am. Chem. Soc.*, **60**, 961 (1938)

- ΔP : pressure increase due to reaction heat,
 k : cooling constant*, n : number of mols of gas in reaction vessel,
 R : gas constant, Q : heat of reaction,
 S : specific heat,† σ : specific gravity,
 V : volume of reaction vessel (71.64 cc).

The reaction velocity in a photochemical stationary state is briefly given by the equation,

$$K \frac{dx}{dt} = k \Delta P.$$

In the present paper the studies of the stationary reaction velocities under various experimental conditions are reported.

Experimental Results.

a. The relation between the reaction velocity and the pressure of methyl iodide.

The reaction velocity of the association reaction was measured under various pressures of methyl iodide and a definite intensity of light source. The relations between the reaction velocity and the pressure of methyl iodide are given in Fig. 3. The reaction velocity is directly proportional to the pressure of methyl iodide.

b. The relations between the reaction velocity and light intensity.

The relations between light intensity and currents of the mercury lamp are

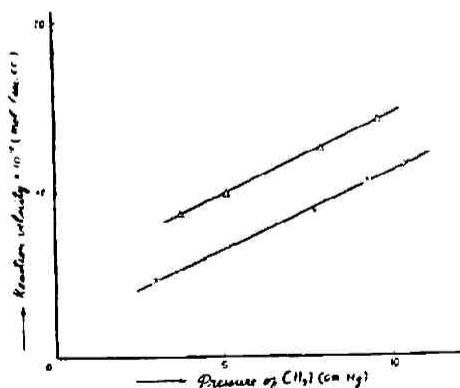


Fig. 3 Relations between reaction velocities and pressures of CH₃I.

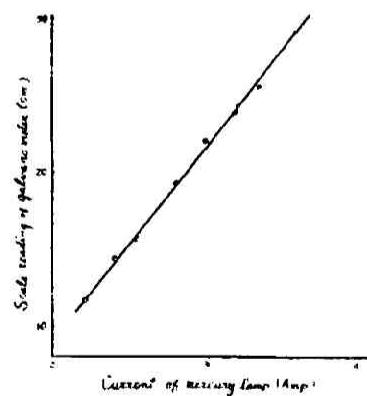


Fig. 4 Relations between light intensity and currents of mercury lamp.

* Cooling constant k is obtained by the following equation from the cooling curve of the shutting off light.

$$k = -\frac{1}{\Delta P} \cdot \frac{d(\Delta P)}{dt}.$$

† Specific heat S is obtained from the calculated value of C_P and the value of $\tau = C_P/C_V$.

ON THE KINETICS OF METHYL FREE RADICALS, I

89

linear as shown in Fig. 4. Light intensity was measured by means of a photoelectric cell and a galvanometer. The relations between the reaction velocities and the currents of the mercury lamp are linear under a definite pressure of methyl iodide as shown in Fig. 5.

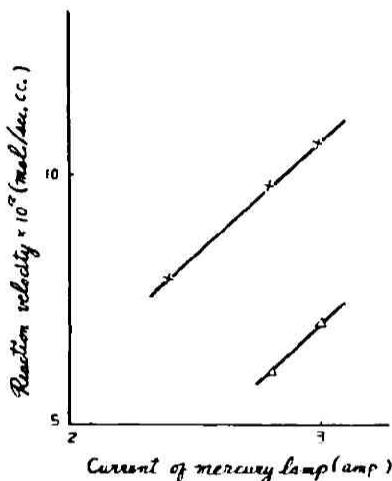


Fig. 5 Relations between reaction velocity and light intensity.
x; 9.32 cmHg of CH_3I
 Δ ; 5.27 cmHg of CH_3I

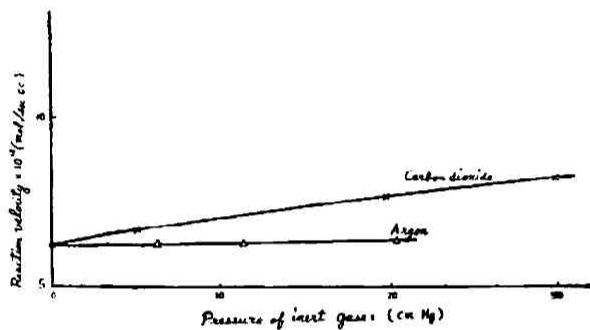


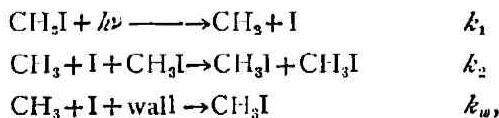
Fig. 6 Effect of inert gases on the reaction velocity.

c. The influences of inert gases.

When inert gas at various pressures, argon and carbon dioxide, are added to methyl iodide at a definite pressure, the relations between the reaction velocity in a definite light intensity and the pressure of inert gas are shown in Fig. 6.

Considerations.

It has not been proved whether the association reaction between radical and atom is of a bimolecular process or termolecular one. It is a matter of importance to determine the mechanism of the association reaction. If the process is termolecular, the wall of the reaction vessel has a great ability as the third body of the reaction at the pressure of the present experiments. We can not neglect the association on the wall as compared with a homogeneous termolecular reaction. In the experiments shown in Fig. 3,



where k_1 , k_2 etc. are the reaction velocity constants.

In a stationary state,

$$\frac{d[\text{CH}_3]}{dt} = k_1 [\text{CH}_3\text{I}] I_0 - k_2 [\text{CH}_3][\text{I}] [\text{CH}_3\text{I}] - k_w [\text{CH}_3][\text{I}] = 0,$$

$$\therefore [\text{CH}_3][\text{I}] = \frac{k_1 [\text{CH}_3\text{I}] I_0}{k_2 [\text{CH}_3\text{I}] + k_w} = \frac{k_1 I_0}{k_2 + k_w / [\text{CH}_3\text{I}]},$$

where I_0 is the intensity of light source.

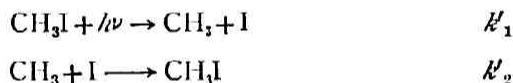
As the reaction velocities are measured in the present experiments from the homogeneous pressure increases due to the reaction heat,

$$-\frac{d[\text{CH}_3]}{dt} = k_2 [\text{CH}_3][\text{I}] [\text{CH}_3\text{I}],$$

$$\therefore \text{reaction velocity} = -\frac{d[\text{CH}_3]}{dt} = \frac{k_1 k_2 [\text{CH}_3\text{I}] I_0}{k_2 + k_w / [\text{CH}_3\text{I}]} . \quad (1)$$

The termolecular mechanism can not elucidate the linear relation as shown in Fig. 3, and also shown in Fig. 6 if the pressure of inert gas [X] be taken as the third body in association process.

If the process is bimolecular,



and in a stationary state,

$$\frac{d[\text{CH}_3\text{I}]}{dt} = k'_1 [\text{CH}_3\text{I}] [I_0] - k'_2 [\text{CH}_3][\text{I}] = 0,$$

$$\therefore [\text{CH}_3][\text{I}] = k'_1 [\text{CH}_3\text{I}] I_0 / k'_2,$$

$$\therefore \text{reaction velocity} = -\frac{d[\text{CH}_3]}{dt} = k'_1 [\text{CH}_3] I_0 .$$

We can understand the linear relations as shown in Figs. 3 and 5 from the standpoint of bimolecular mechanism. The velocity increase shown in Fig. 6 may be due to the fact that the homogeneity of the reaction becomes more perfect in the presence of any inert gas.

As the experimental facts can be elucidated in the light of binary collision mechanism instead of triple collision, we can conclude that the association reaction between methyl radical and iodine atom is a bimolecular process.

The velocity constant of a bimolecular reaction k_2 is generally given from the collision theory by the following equation,

$$k_2 = N_0 (r_A + r_B)^2 \sqrt{\frac{8\pi k T}{\mu}} \cdot e^{-E/kT}, \quad (2)$$

ON THE KINETICS OF METHYL FREE RADICALS, I

91

where N_0 : Avogadro number, μ : reduced mass,
 r_A, r_B : molecular radius, E : activation energy,
 k : Boltzmann constant.

From the facts that the activation energy of monomolecular decomposition of CH_3I is equal to the energy of the C—I bond in Ogg's experiment⁶⁾ and that the photolysis of CH_3I has low quantum yield⁹, we can estimate that the activation energy of the association between methyl radical and iodine atom is zero. Therefore, the velocity constant of the association reaction between methyl radical and iodine atom can be calculated by Eq. (2)*.

$$k_2 = 1.09 \times 10^{14} \text{ cc/mol sec.}$$

This value of the velocity constant may be correct at least in its order.

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6) R. A. Ogg, *J. Am. Chem. Soc.*, **56**, 526 (1934)

* Molecular radius of methyl radical is assumed to be equal to that of methane.