Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

The Velocity Constants of Free Ions and Ion Pairs. I

Yoshinobu Tanaka[a]; Norio Ise[a]
[a] Department of Polymer Chemistry, Kyoto University, Kyoto, Japan

To cite this Article Tanaka, Yoshinobu and Ise, Norio(1970) 'The Velocity Constants of Free Ions and Ion Pairs. I', Journal of Macromolecular Science, Part A, 4: 4, 825 — 849

To link to this Article: DOI: 10.1080/00222337008060984

URL: http://dx.doi.org/10.1080/00222337008060984

J. MACROMOL. SCI.–CHEM., A4(4), pp. 825-849, July, 1970

The Velocity Constants of Free Ions and Ion Pairs. I

YOSHINOBU TANAKA and NORIO ISE

Department of Polymer Chemistry
Kyoto University
Kyoto, Japan

SUMMARY

The specific velocity constants of free ion-molecule reactions and ion pair-molecule reactions are discussed. Assuming an equilibrium between solvated and desolvated reactive centers, the specific velocity constant of ion pair with a given charge-charge distance is expressed by

$$k = (\kappa kT/h)K^{\ddagger}K^{M}/(1 + \sum_{i} K^{i}[S_i]_a),$$

where κ is the transmission coefficient, **k** the Boltzmann constant, T the absolute temperature, **h** the Planck constant, $[S_i]_a$ the concentration of the solvent i, $K^{\ddagger}$ the equilibrium constant of activation, and K^M and k^i the equilibrium constants for solvation by the monomer M and by the solvent i, respectively. The K^M and K^i are derived from eletrostatic free energies for solvation. The apparent specific velocity constant is obtained by averaging the k's with respect to the charge-charge distance. The ratio of the reactivity of free ions and that of ion pairs is further calculated. Agreement with experiment is satisfactory.

INTRODUCTION

In this laboratory, the effects of the electric field on the rate of polymerization and on the degree of polymerization have been studied [1-10].

It was observed that an electric field increases the rate of polymerization and degree of polymerization in ionic polymerizations. The field effects have been qualitatively discussed in terms of the difference in the reactivity between free ions and ion pairs. The reactivities of free ions and ion pairs have been measured [11] but, to our knowledge, no theoretical study has been reported. The effect of solvation on the specific velocity constant has also been examined [12], but the effect has not been fully considered in theoretical treatments [13]. In this paper a preliminary theoretical study of the reactivities of ion pairs and free ions is presented. The specific velocity constants of free ion-molecule reactions and of ion pair-molecule reactions are derived and discussed.

THEORETICAL CONSIDERATIONS

1. Effect of Solvation on the Specific Velocity Constant

According to the theory of the absolute reaction rate for the reaction between an ion (or an ion pair) C^*_A and a molecule M

$$C_A^* + M \xrightarrow{k} C\text{-}M \qquad (1)$$

the specific velocity constant k is given by

$$k = \kappa \frac{kT}{h} \frac{[C^*\sim M]}{[C_A^*][M]} \qquad (2)$$

since reaction rate = $(\kappa kT/h)[C^*\sim M] = k[C_A^*][M]$. Here, $C^*\sim M$ denotes the activated complex, κ the transmission coefficient, k the Boltzmann constant, T the absolute temperature, and h the Planck constant. We assume that the reaction proceeds as follows: 1) C_A^* is solvated by $\Sigma_i n_i$ molecules of S_i; 2) One of the $\Sigma_i n_i$ molecules of S_i is desolvated, leaving only the naked surface of C_A^* accessible to the reactant molecule M; and 3) M reaches the naked reactive surface and forms an activated complex with with C_A^*. Here S denotes the solvent molecule and i the species of the solvent. Note that S_i represents all molecules except the reactant molecule M. This also includes the dipolar catalyst and impurity molecules.

We now assume the following equilibria:

$$C^* + M \overset{K^M}{\rightleftarrows} C^* \ldots M \qquad (3)$$

$$C^{*}\ldots M \underset{}{\overset{K^{\ddagger}}{\rightleftharpoons}} C^{*}\sim M \tag{4}$$

and

$$C^{*} + S_i \underset{}{\overset{k^i}{\rightleftharpoons}} C^{*}\ldots S_i \tag{5}$$

where C^{*} is the ion (or the ion pair) with the naked reactive surface, $C^{*}\ldots M$ the state in which a reactive surface of an ion or an ion pair is in contact with reactant molecule, $C^{*}\sim M$ an activated complex, $C^{*}\ldots S_i$ the ion (or the ion pair) solvated by S_i, and S_i the free solvent. Therefore, we have

$$[C^{*}] = [C^{*}_A] - \sum_i [C^{*}\ldots S_i] \qquad K^M = \frac{[C^{*}\ldots M]}{[C^{*}][M]}$$

$$K^{\ddagger} = \frac{[C^{*}\sim M]}{[C^{*}\ldots M]} \qquad K^i = \frac{[C^{*}\ldots S_i]}{[C^{*}][S_i]}$$

If $[S_i] >> [C^{*}\ldots S_i]$, we obtain the equation,

$$k = \kappa \frac{kT}{h} K^{\ddagger} \frac{K^M}{1 + \sum_i K^i[S_i]_a}$$

$$= \kappa \frac{kT}{h} K^{\ddagger} \frac{\exp\left(\frac{-\Delta G^M}{kT}\right)}{1 + \sum_i [S_i]_a \exp\left(\frac{-\Delta G^i}{kT}\right)} \tag{6}$$

where $[S_i]_a$ is the total concentration of the solvent S_i, and ΔG the free energy change for one molecule. In Eq. (6), the term $\kappa(kT/h)K^{\ddagger}$ is the rate constant obtained by the absolute rate theory for liquid reactions, and the term $K^M/(1 + \Sigma_i K^i[S_i]_a)$ the solvent effect.

C^{*}_A has many reactive surfaces with different reactivities. We assume that any particular C^{*}_A will be described by a characteristic reaction rate determined by the "rate-determining" surface, which gives the highest velocity for the process mentioned above. Within this assumption, the time fluctuations of the reaction rate on any reactive surface are neglected and the reaction rate of any C_A^* is assumed to be independent of the area of the rate-determining surface. Moreover, we assume that the equilibrium constant $K^{\ddagger}$ is independent of solvents and gegenions. In other words, the solvation to $C^* \ldots M$ is assumed to be the same as that to $C^* \sim M$, and the reaction a three-point reaction.

2. Model of the Ion-Molecule Reaction

The problem of calculating the ΔG's in Eq. (6) is intractable unless some simplifying assumptions are made. The model, shown in Fig. 1, satisfies the following assumptions:

1) The reactant ion, gegenion, solvent molecule, and molecular reactant are rigid spheres with radii, r_I, r_{II}, r_i, and r_M, respectively.

2) The reactant ion has an electric charge $z_I q$ at the center and has a reactive surface as dotted in Fig. 1. The center of the reactant ion is at the origin of the spherical polar coordinate system, and the center of the reactive surface is on the z axis.

3) The gegenion has an electric charge $z_{II} q$ at the center, and the center exists on the z axis. Both ions are unpolarizable.

4) The solvent molecule has a dipole moment μ_i at the center Q and an isotropic electronic polarization λ_i.

5) The reactant molecule has an "effective" dipole moment μ_M at the center Q and an isotropic electronic polarization λ_M. The effective dipole moment is given by

$$|\mu_M| = |\mu'_M| \cos\varphi \tag{7}$$

where μ'_M is the dipole moment of the reactant molecule, φ is the angle between μ'_M and $\overrightarrow{OQ}$ if the reactant ion has a positive charge, or the angle between μ'_M and $\overleftarrow{OQ}$ if the reactant ion has the negative charge.

6) The short-range interactions are negligible.

7) Solvation is defined as the state where an ion is in contact with a solvent molecule and

$$\overline{OQ} = r_I + r_i \tag{8}$$

By activated complex we mean that the reactive surface of an ion or an ion pair is in contact with reactant molecule and

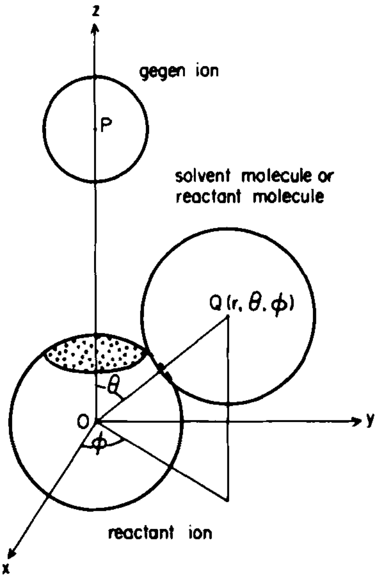

Fig. 1. Model.

$$\overline{OQ} = r_I + r_M \tag{9}$$

8) For simplicity, we assume that all molecules have the same radius, as given by

$$r_{III} = \frac{r_M + \sum_i^n r_i}{1 + n} \tag{10}$$

It is necessary to give a brief comment on the concept of "effective" dipole moment μ_M. Let the dipole moment of the reactant molecule μ'_M be fixed to the molecule as shown in Fig. 2. When the reactant ion is an anion, it has a tendency to approach to the positive side A of the reactant molecule. It would not always be possible that all reactant molecules react with the anion at A, for example, because of steric hindrance. The rate of reaction at B or C, however, should be smaller than that at A, since the anion approaches B or C less frequently than A. This difference between the rates of reaction at A, B, and C is taken into account in terms of the effective dipole moment. For example, in the case of the reaction at B, the

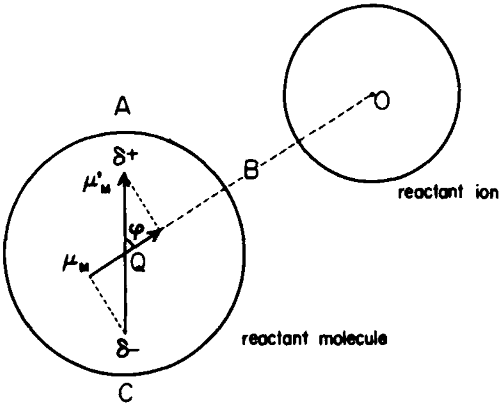

Fig. 2. Effective dipole moment.

effective dipole moment μ_M is the component along $\overrightarrow{QB}$ of the dipole moment μ'_M, and $|\mu_M| = |\mu'_M| \cos\varphi$, where $\varphi = \angle AQB$. An illustration for methyl iodide and ethyl iodide will be found in the latter part of this paper. It is known that anions that can react by the S_N2 mechanism approach the methyl iodide molecule along the direction of the C-I axis, along which the dipole moment μ'_M exists. In this case, therefore, $\varphi = 0$. Because of the steric hindrance by the CH_3 group, on the other hand, the direction of the approach of anions toward the ethyl iodide molecule is not on the axis of the dipole moment μ'_M. Thus, the φ value is not zero.

3. The Electrostatic Free Energy ΔG

The dielectric constant in the vicinity of ions is much lower than the macroscopic dielectric constant [14]. We assume that the dielectric constant at the point Q is unity. Therefore, the electric field strength at Q is given by

$$|E| = q\sqrt{\frac{z_I^2}{r^4} + \frac{z_{II}^2}{(R^2 + r^2 - 2rR\Theta)^2} - \frac{2z_Iz_{II}(R\Theta - r)}{r^2(R^2 + r^2 - 2rR\Theta)^{3/2}}} \qquad (11)$$

where q is the elementary charge, $r = OQ = r_I + r_{III}$, Θ is the cosine of the angle between the z axis and $\overrightarrow{OQ}$, and R is the distance between the reactant ion and the gegenion.

According to the Onsager theory [15], the potential energy of a molecule in a field E is given by

$$\epsilon = -\frac{D(D_0 + 2)}{2D + D_0} \cdot |\mu| \cdot |E| \cos\vartheta \tag{12}$$

where D is the dielectric constant, D_0 the internal dielectric constant of the molecule based on the electronic polarization, and ϑ the angle between **E** and μ. If we apply the Boltzmann distribution law for constant R and Θ, we obtain for the free energy of a molecule (as described in Appendix 2),

$$\Delta G_R^{\theta} = -\frac{D(D_0 + 2)}{2D + D_0} \cdot |\mu| \cdot |E| \cdot L\left(\frac{D(D_0 + 2)}{2D + D_0}|\mu| \cdot |E|/kT\right) - \frac{3D^2(D_0 + 2)}{2(2D + D_0)(2D + 1)}\lambda\, E^2 \tag{13}$$

where L denotes Langevin's function, and suffixes θ and R indicate that these parameters are fixed. Using D = 1 and $\exp(|\mu| \cdot |E|/kT) \gg 1$, and considering that the second term on the right-hand side is negligibly small, we have

$$\Delta G_R^{\theta} = -|\mu| \cdot |E| + kT \tag{14}$$

Generally, in order to obtain the specific velocity constant k_R for a given R, we should substitute Eq. (14) in Eq. (6) and find the maximum value of k_R^{θ} for various Θ using a trial and error method. For the general case this calculation is unfortunately complicated. When reaction systems satisfy the conditions given in the following section, however, the calculation is simpler.

4. Rate-Determining Surface

In this section we find a Θ value that determines the rate-determining surface. On differentiating Eq. (6) with respect to Θ we have

$$\frac{\partial k_R^{\theta}}{\partial \Theta} = \frac{\partial k_R^{\theta}}{\partial |E|} \cdot \frac{\partial |E|}{\partial \Theta} \tag{15}$$

where

$$\frac{\partial k_R^{\theta}}{\partial |\mathbf{E}|} = \frac{\kappa}{h} \cdot$$

$$K^{\ddagger} \cdot \frac{\exp\left(-1 + \frac{|\mu_M| \cdot |\mathbf{E}|}{kT}\right) \cdot \left[\, |\mu_M| + \sum_i (|\mu_M| - |\mu_i|)[S_i] \exp\left(-1 + \frac{|\mu_i| \cdot |\mathbf{E}|}{kT}\right)\right]}{\left[1 + \sum_i [S_i]_a \exp\left(-1 + \frac{|\mu_i| \cdot |\mathbf{E}|}{kT}\right)\right]^2} \tag{16}$$

and

$$\frac{\partial |\mathbf{E}|}{\partial \Theta} =$$

$$\frac{q^2 R \left\{ 2z_{II}^2 r^3 - z_I z_{II} \left[(R-r)^2 + 2rR(1-\Theta)\right]^{1/2} (R^2 - 2r^2 + rR\Theta)\right\}}{|\mathbf{E}| r^2 \left[(R-r)^2 + 2rR(1-\Theta)\right]^3} \tag{17}$$

Equation (16) shows that $\partial k_R^{\theta} / \partial |\mathbf{E}| > 0$ always when $|\mu_M| \geqq |\mu_i|$, and $\partial k_R^{\theta} / \partial |\mathbf{E}| < 0$ in most cases when $|\mu_i| > |\mu_M|$. Equation (17) shows that the sign of $\partial |\mathbf{E}| / \partial \Theta$ is the same as that of the terms

$$2z_{II}^2 r^3 - z_I z_{II} \left[(R-r)^2 + 2rR(1-\Theta)\right]^{1/2} (R^2 - 2r^2 + rR\Theta) \tag{18}$$

Equation (18) is positive for values of R which usually come into question. We therefore obtain the Θ values shown in Table 1 for determining the rate-determining surface. In this table, Θ_I is a limit imposed by the inaccessibility of reactant molecule to reactant ion as a result of steric hindrance and $\Theta_I \leq \Theta \leq 1$. Note that the following condition has to be satisfied in order for a reaction to take place:

$$R \geqq \Theta_I (r_I + r_{III}) \left(1 + \sqrt{1 + \frac{(r_{II} - r_I)(r_I + r_{II} + 2r_{III})}{\Theta_I^2 (r_I + r_{III})^2}}\right) \tag{19}$$

Table 1. Θ Determining the Rate-Determining Surface

	$r_I + r_{II} \leqq R < r_I + r_{II} + 2r_{III}$[a]	$r_I + r_{II} + 2r_{III} \leqq R$
$\frac{\partial k_R^\theta}{\partial \Theta} < 0$	$\Theta = \frac{R^2 + (r_I + r_{III})^2 - (r_{II} + r_{III})^2}{2R(r_I + r_{III})}$	$\Theta = 1$
$\frac{\partial k_R^\theta}{\partial \Theta} < 0$	$\Theta = \Theta_I$	$\Theta = \Theta_I$

[a] See Eq. (19).

5. The Apparent Specific Velocity Constant

According to Robertson and Acree [16], the apparent specific velocity constant is given by

$$k = \alpha k'' + (1 - \alpha)k' \tag{20}$$

where α is the degree of dissociation, and k'' and k' are the specific velocity constants of free ions and ion pairs, respectively. According to Bjerrum [17], a free ion and an ion pair may be distinguished by a critical distance R_c. We assume here that

1) The specific velocity constant of free ions is independent of R and is given by Eq. (6) at $R = \infty$ by

$$k'' = k_R(R = \infty) \tag{21}$$

2) The specific velocity constant of ion pairs is given by

$$k' = \int_{r_I + r_{II}}^{R_c} k_R \, P(R) \, dR \tag{22}$$

where P(R) is the probability for a gegenion to be at a distance R from a reactant ion. To obtain this probability, we calculate the potential energy of an ion pair, the distance between charge centers being R.

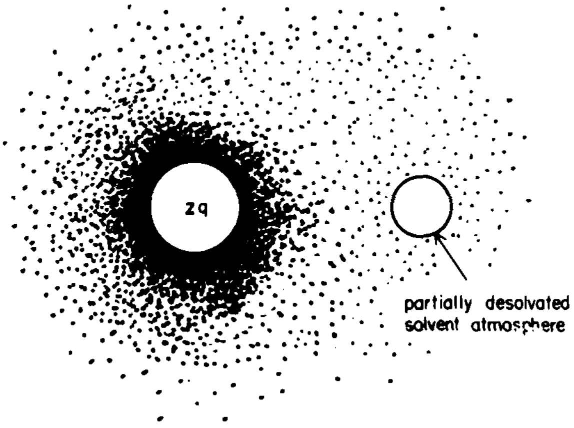

Fig. 3. Solvent atmosphere.

6. Solvent Atmosphere

In order to simplify the treatment, we further modify the above model for solvent molecules and we adopt a model, shown in Fig. 3, wherein the central ion is surrounded by a solvent atmosphere. When another ion or molecule approaches, the solvent atmosphere around this central ion is altered or "broken" and partial desolvation is said to occur. If we further assume that there is no interaction between the solvent atmospheres, then the potential energy is the sum of those of the independent solvent atmospheres.

The free energy of an S_i molecule at a distance r from the center of the ion is given by

$$\Delta G_i^r = -\frac{D^r(D_{oi}+2)}{2D^r + D_{oi}} |\mu_i| \cdot |E^r| L\left(\frac{D^r(D_{oi}+2)}{2D + D_{oi}} |\mu_i| \cdot |E^r|/kT\right) - \frac{3D^{r2}(D_{oi}+2)}{2(2D^r + D_{oi})(2D^r+1)} \lambda_i E^{r2} \qquad (23)$$

where the suffix r represents values at a distance r and D_{oi} is the internal dielectric constant of S_i molecule. If there is an equilibrium between the solvent molecules at distances r and ∞,

$$S_i^r + S_j^\infty \underset{\longleftarrow}{\xrightarrow{K_{ij}^r}} S_j^r + S_i^\infty \tag{24}$$

where the suffixes r and ∞ represente the distances, respectively, and the equilibrium constant K_{ij}^r is given by

$$K_{ij}^r = \frac{[S_j^r]\,[S_i^\infty]}{[S_i^r]\,[S_j^\infty]} \tag{25}$$

$$= \exp\,[(\Delta G_i^r - \Delta G_j^r)/kT] \tag{26}$$

We may consider $[S_i^\infty]$ equal to $[S_i]_a$ where the latter is the average concentration. The density of S_i at distance r from the center of an ion (ρ_i^r) is given by

$$\rho_i^r = \frac{[S_i]_a \exp\left(-\frac{\Delta G_i^r}{kT}\right)}{\sum\limits_i \frac{1}{\rho_i}[S_i]_a \exp\left(-\frac{\Delta G_i^r}{kT}\right)} \tag{27}$$

where ρ_i is the density in the pure state.

The potential energy of the complete (unbroken) solvent atmosphere around an ion is then given by

$$\epsilon_s^0 = 4\pi\int_{r_I}^{\infty} r^2 \sum_i \rho_i^r\,\Delta G_i^r\,dr \tag{28}$$

where the suffix s represents the potential energy of the solvent atmosphere. The potential energy ϵ_s^0 is, in other words, the solvation energy for an ion in mixed solvents. Here we assume that the dielectric constant has the macroscopic value. The convergency of the integral in Eq. (28) is proved in Appendix 1.

7. The Potential Energy of an Ion Pair

The potential energy of an ion pair is the sum of the potential energies of the interactions between an ion and its gegenion and of the solvent atmosphere around the ion pair. The potential energy between ions at distance R is given by

$$\epsilon_q = \frac{z_I z_{II} q^2}{DR} \tag{29}$$

The potential energy of the solvent atmosphere around an ion pair with an intercharge distance R is given by

$$(\epsilon_{SR} - \epsilon_s^0)_I + (\epsilon_{SR} - \epsilon_s^0)_{II} \tag{30}$$

where ϵ_s^0 is the potential energy given by Eq. (28) or the potential energy of the solvent atmosphere around an ion when its gegenion is at $R = \infty$, ϵ_{SR} is the potential energy of the solvent atmosphere around an ion when its gegenion is at distance R, and I and II denote a reactant ion and its gegenion, respectively. Since $\epsilon_{SR} = \epsilon_s^0 - \epsilon_{BSR}$, where ϵ_{BSR} is the potential energy of the solvent atmosphere replaced by the counterpart ion at distance R, then the potential energy of this ion pair is

$$\epsilon_R = \epsilon_q - (\epsilon_{BSR})_I - (\epsilon_{BSR})_{II} \tag{31}$$

By definition,

$$(\epsilon_{BSR})_I = 2\pi \int_{R-r_{II}}^{R+r_{II}} r^2 \left(1 - \frac{r^2 + R^2 - r_{II}^2}{2rR}\right) \sum_i \rho_i^r \, \Delta G_i^r \, dr \tag{32}$$

and

$$(\epsilon_{BSR})_{II} = 2\pi \int_{R-r_I}^{R+r_I} r^2 \left(1 - \frac{r^2 + R^2 - r_I^2}{2rR}\right) \sum_i \rho_i^r \, \Delta G_i^r \, dr \,. \tag{33}$$

If $\Sigma_i \, \rho_i^r \, \Delta G_i^r$ is equal to $\Sigma_i \, \rho_i^R \, \Delta G_i^R$, then

$$(\epsilon_{BSR})_I = \frac{4}{3} \pi r_{II}^3 \sum_i \rho_i^R \, \Delta G_i^R \tag{34}$$

and

$$(\epsilon_{BSR})_{II} = \frac{4}{3}\pi r_I^3 \sum_i \rho_i^R \Delta G_i^R \tag{35}$$

8. Distribution of the Distance R

For the intercharge distance R or an ion pair, the distribution functions of Bjerrum [17] and Fuoss [18] are known. Although the Fuoss function gives a more reasonable distribution, we use the much less complicated Bjerrum distribution function to define the ion pairs. Then

$$P(R)\,dR = R^2 \exp(-\epsilon_R/kT)\,dR \Big/ \int_{r_I+r_{II}}^{R_c} R^2 \exp(-\epsilon_R/kT)\,dR \tag{36}$$

and

$$\frac{1}{K_d} = \frac{4\pi N}{1000}\int_{r_I+r_{II}}^{R_c} R^2 \exp(-\epsilon_R/kT)\,dR \tag{37}$$

where K_d is the dissociation constant. If we assume that the activity coefficient ratio is unity, then

$$K_d = \frac{\alpha^2}{1-\alpha}[C^*]_a \tag{38}$$

Generally, $\alpha \ll 1$, and

$$\alpha \approx \sqrt{K_d/[C^*]_a} \tag{39}$$

The critical distance R_c, where the probability given by Eq. (36) is at a minimum for $R > 0$, cannot generally be easily estimated, because ϵ_R is usually unknown and different from the simple coulombic type. Finally, we get the specific velocity constant for free ions from Eqs. (6), (11), (14), and (21),

$$k'' = k\frac{kT}{h}K^{\ddagger}\cdot\frac{\exp\left(-1+\dfrac{|\mu_M|\cdot|z_I|q}{kTr^2}\right)}{1+\sum\limits_i [S_i]_a \exp\left(-1+\dfrac{|\mu_i|\cdot|z_I|q}{kTr^2}\right)} \tag{40}$$

and that for ion pairs from Eqs. (6), (11), (14), (22), and (36),

$$k' = \kappa \cdot \frac{kT}{h} K^{\ddagger} \cdot \frac{\displaystyle\int_{r_I + r_{II}}^{R_c} \frac{\exp\left(-\frac{\Delta G_R^M}{kT}\right)\exp\left(-\frac{\epsilon_R}{kT}\right)}{1 + \sum_i [S_i]_a \exp\left(-\frac{\Delta G_R^i}{kT}\right)} \cdot R^2\, dR}{\displaystyle\int_{r_I + r_{II}}^{R_c} R^2 \exp\left(-\frac{\epsilon_R}{kT}\right) dR} \tag{41}$$

where ΔG_R^M and ΔG_R^i are derivable from Eqs. (11), (14), and Θ (parameter of the rate-determining surface) values given in Table 1. ϵ_R is given by Eq. (31). The intergration in Eq. (41) can be carried out graphically. If we find the distance R_e where the probability $P(R)\, dR$ has its largest value in the range $R < R_c$, and the specific velocity constant at the distance R_e mainly determines the k', then we have approximately from Eqs. (6), (11), and (14)

$$k' = \kappa \cdot \frac{kT}{h} K^{\ddagger} \cdot \frac{\exp\left(-1 + \frac{|\mu_M| \cdot |E|_{R_e}}{kT}\right)}{1 + \sum_i [S_i]_a \exp\left(-1 + \frac{|\mu_i| \cdot |E|_{R_e}}{kT}\right)} \tag{42}$$

where $|E|_{R_e}$ is given by Eq. (11) when $R = R_e$. We note that, in the present treatment, R_e is equal to the closest distance of approach, because according to the distribution calculated by Eq. (36), the probability that the intercharge distance is equal to the closest one is extremely large. From consideration which will be given in forthcoming papers, this assumption is justified especially in reactions at rather higher temperatures and in solvents which bound both to cations and to anions. However, this assumption would not be justified especially in the cases of polymerizations of nonpolar monomers in polar solvents.

9. The Simplified Equations

To calculate the specific velocity constant according to Eq. (42) is generally quite complicated. However, the calculation is simplified in the following cases:

1) The reaction takes place between an ion or an ion pair and polar molecule in polar solvents.

In the case of reactions in polar solvents, we obtain

$$1 \ll \sum_i [S_i]_a \exp\left(-1 + \frac{|\mu_i| \cdot |E|}{kT}\right) \tag{43}$$

where $|E|$ is the field strength in the vicinity of ions. Therefore, in the case of reactions between an ion or an ion pair and a polar molecule in a polar solvent, we have from Eq. (40)

$$k'' = \kappa \frac{kT}{h} K^{\ddagger} \cdot \frac{1}{[S_i]_a} \exp\left[\frac{|z_I|q}{kTr^2} (|\mu_M| - |\mu_i)\right] \tag{44}$$

for a free ion, and also from Eq. (42)

$$k' = \kappa \frac{kT}{h} K^{\ddagger} \cdot \frac{1}{[S_i]_a} \exp\left[\frac{|E|Re}{kT} (|\mu_M| - |\mu_i|)\right] \tag{45}$$

for an ion pair.

2) The reaction takes place between an ion or an ion pair and a polar molecule in a nonpolar solvent. In this case,

$$k'' = \kappa \frac{kT}{h} K^{\ddagger} \cdot \frac{1}{[S_i]_a} \exp \frac{|\mu_M| \cdot |z_I| q}{kTr^2} \tag{46}$$

and

$$k' = \kappa \frac{kT}{h} K^{\ddagger} \cdot \frac{1}{[S_i]_a} \exp \frac{|\mu_M| \cdot |E| Re}{kT} \tag{47}$$

3) The reaction proceeds between an ion or an ion pair and a nonpolar molecule in a polar solvent. In this case we obtain

$$k'' = \kappa \frac{kT}{h} K^{\ddagger} \cdot \frac{1}{[S_i]_a} \exp \frac{-|\mu_i| \cdot |z_I| q}{kTr^2} \tag{48}$$

from Eq. (40) and

$$k' = \kappa \frac{kT}{h} K^{\ddagger} \cdot \frac{1}{[S_i]_a} \exp \frac{-|\mu_i| \cdot |E|_{Re}}{kT} \tag{49}$$

from Eq. (42).

We note here that Eqs. (44), (45), (48), and (49) also hold for mixtures of polar and nonpolar solvents.

DISCUSSION

The Reactivity Ration k''/k'

Based on the equations in Section 9, the reactivity ratios k''/k' are compared with experimental values. Table 2 shows the observed and calculated reactivity ratios in reactions between alkyl iodides and alkoxides [16].

Table 2. Reactivity ratio k''/k' (I)

Reaction[a]	k''/k' Observed	Calculated[c]
$CH_3I + C_2H_5O^-Na^+$	2.14	2.01
$CH_3I + C_2H_5O^-K^+$	1.84	1.94
$CH_3I + C_2H_5O^-Li^+$	3.53	2.03
$CH_3I + C_6H_5O^-Na^+$	5.91	6.42
$CH_3I + C_6H_5O^-K^+$	7.65	5.05
$CH_3I + C_6H_5O^-Li^+$	7.30	8.76
$C_2H_5I + C_6H_5O^-Na^+$	5.55	4.39
$C_2H_5I + C_6H_5O^-K^+$	5.15	3.82
$C_2H_5I + C_6H_5O^-Li^+$	5.83	6.42

[a] In ethanol, 25°C ($|\mu_i| > |\mu_M|$).

[b] S. F. Acree, *J. Amer. Chem. Soc.*, 37, 1902 (1945).

[c] Based on the values in Table 3.

The calculations were carried out by using the parameters given in Table 3. The effective dipole moment of CH_3I is equal to the dipole moment because

Table 3. [a]

Ion, molecule	$\|\mu'\|$ (D)	$\|\mu\|$ (D)	Radius, r (Å)	Reactive surface parameter (Θ_I)
CH_3I	1.35	1.35	2.93^b	–
C_2H_5I	1.78	1.40	2.93	–
C_2H_5OH	1.70	–	2.86^b	–
$C_2H_5O^-$	–	–	2.86^c	0.70
$C_6H_5O^-$	–	–	3.28^c	0.90
Na^+	–	–	0.95	–
K^+	–	–	1.33	–
Li^+	–	–	0.60	–

[a] Ref. 20.

[b] According to the equation $r^3 = \frac{3}{4\pi}\frac{M}{Nd} = 3.96396 \times 10^{-25}\frac{M}{d}$, where M = molecular weight, d = density (g/cm^3), and N = Avogadro number.

[c] The radii of $C_2H_5O^-$ and $C_6H_5O^-$ are assumed to be those of C_2H_5OH and C_6H_5OH, respectively.

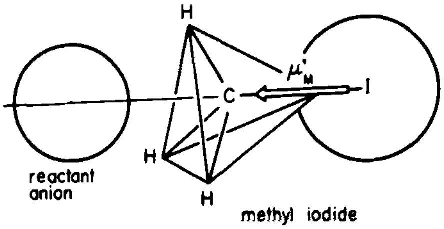

Fig. 4. Reaction of methyl iodide with an anion.

the reactant anion approaches the CH_3I molecule as shown in Fig. 4. The effective dipole moment of C_2H_5I is, on the other hand, not equal to the dipole moment.

In order to calculate the effective dipole moment by Eq. (7), we first obtain the direction of the dipole moment. It is assumed that the dipole moment vector μ'_M is the sum of the C–I bond moment vector μ_{C-I} and the C–C bond moment vector μ_{C-C}, and that these bond moment vectors

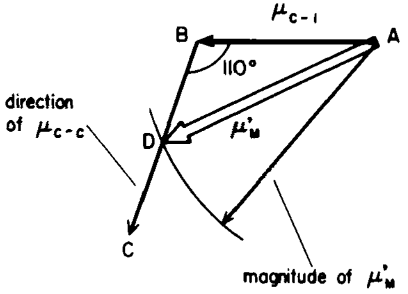

Fig. 5. Determination of the direction of dipole moment.

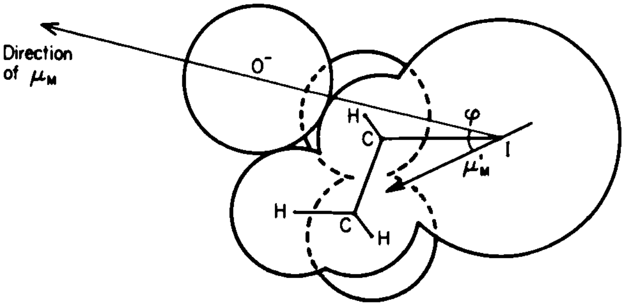

Fig. 6. Determination of the angle φ for the reaction of ethyl iodide with an anion. $O\bar{v}$, Pauling's radius 1.40 Å. I, van der Waals' radius 2.15 Å. H, van der Waals' radius 1.2 Å. C, radius 1.2 Å (C–H bond length). ∠CCI 110°. ∠CCH 109°28′.

lie along their respective bonds. Using these assumptions, we find that the angle between the vectors μ_{C-I} and μ_{C-C} is 110°. Here we know that the magnitudes of μ_{C-I} and μ'_M are 1.35×10^{-18} and 1.78×10^{-18} esu cm, respectively. As shown in Fig. 5, the vector μ_{C-I} and the direction of μ_{C-C} are drawn as AB and BC, respectively. Then, μ'_M is pivoted about A so that is scribes an arc subtended by D on the line BC. The vectors AD and BD are μ'_M and μ_{C-C}, respectively. Thus we obtain the angle between the C–I bond and μ'_M.

The reactant oxygen ion approaches the C_2H_5I along a direction with an angle φ with the dipole moment as shown in Fig. 6. Here it is assumed that the oxygen contacts with the first carbon atom at the smallest possible angle (φ). The effective dipole moment is then $|\mu'_M| \cos \varphi$.

The paramters Θ_I for $C_2H_5O^-$ and $C_6H_5O^-$ were assumed to be 0.70 and 0.90, respectively. This implies that the maximum values of θ of $C_2H_5O^-$ and $C_6H_5O^-$ are 45°35′ and 25°51′, respectively. These values seem to be reasonable, judging from the steric hindrance of the anions. In spite of the fact that these Θ_I values were used throughout for all gegen-cations and reactant molecules, the agreements between the observed and calculated k''/k' values are satisfactory.

Table 4 shows the reactivity ratios k''/k' of the reactions of p-nitrobenzyl bromide with the chloride and bromide ion [19]. The calculated values of k''/k' are obtained with the parameters given in Table 5. The dipole moments are obtained from the literature [20]. The effective dipole moment of p-nitrobenzyl bromide is assumed to be approximately equal to the dipole moment. The radii are taken from Pauling's data for the halogen and metal ions or from the structure of molecules by considering the longest intramolecular distance as the diameter for the others. The entire surface of the reactant anions, chloride and bromide ions, can be regarded as reactive, so the $\Theta_I = -1$.

From Table 4 it is clear that the calculations also generally agree quite well with the experimental results. Table 2 shows a most remarkable agreement for the variation of k''/k' with various gegenions, Na^+, K^+, and Li^+. In Table 4, however, the agreement is not so satisfactory for the reactions involving the bulky cations. The disagreement seems to be due to the assumption that the distance R_e where the probability $P(R)\,dR$ has its largest value is the closest one. According to our treatment, the dissociation of ion pairs is enhanced with the size of the ions, so that the probability $P(R)\,dR$ decreases with increasing R less steeply. Therefore, the contribution of the probability at R larger than R_e becomes more important, and hence, the use of R_e is no longer a satisfactory approximation. Actually, if we choose the distance $r_I + r_{II} + r_{III}$ instead of $r_I + r_{II}$, the disagreement becomes smaller as shown on the last line in Table 4.

CONCLUDING REMARKS

From the foregoing discussion, it is clear that the ratio of the reactivities of free ions (k'') and ion pairs (k') can be accounted for satisfactorily by using a simplified model. It is of interest to mention the implication of the final result at the extreme cases. Equations (44) and (45) give at $\Theta = -1$

$$\frac{k''}{k'} = \exp\left[(|z_I|q/kT)(|\mu_M| - |\mu_i|)/(R + r_I + r_{III})^2\right] \tag{50}$$

Table 4. Reactivity ratios k''/k' (II)

Reaction[a]	k''/k' Observed[b]	k''/k' Calculated[c]
NO_2  $CH_2Br + K^+Br^-$	8.2 ~ 21	6.69
NO_2  $CH_2Br + (CH_3)_4N^+Br^-$	2.4 ~ 6.8	8.58
NO_2  $CH_2Br + (C_2H_5)_4N^+Br^-$	1.7 ~ 2.5	6.05
NO_2  $CH_2Br + Rb^+Cl^-$	17 ~ 35	14.6
NO_2  $CH_2Br + (CH_3)_4N^+Cl^-$	2.4 ~ 6.2	11.2
NO_2  $CH_2Br + (C_2H_5)_4N^+Cl^-$	1.43 ~ 1.97	11.7
NO_2  $CH_2Br + (C_2H_5)_4N^+Cl^-$	1.43 ~ 1.97	3.38[d]

[a] In liquid SO_2 at 0°C ($|\mu_i| < |\mu_M|$).

[b] N. N. Lichtin, M. S. Puar, and B. Wasserman, *J. Amer. Chem. Soc.*, **89**, 6677 (1967).

[c] Based on values from Table 5.

[d] The distance at which the probability P(R) dR has its largest value is $r_I + r_{II} + r_{III}$.

and at $\Theta = 1$

$$\frac{k''}{k'} = \exp\left[(|z_I|q/kT)(|\mu_i| - |\mu_M|)/(R - r_I - r_{III})^2\right] \tag{51}$$

From Eqs. (50) and (51) we have the following relations:

	$\lvert\mu_i\rvert > \lvert\mu_M\rvert$	$\lvert\mu_M\rvert > \lvert\mu_i\rvert$
$\Theta = 1$	$k''/k' > 1$	$k''/k' < 1$
$\Theta = -1$	$k''/k' < 1$	$k''/k' > 1$

This shows that the reactivities are determined by the relative magnitudes of the effective dipole moments of the solvent and reactant molecules, and by the relative position of the reactant ion and molecule. It is interesting that the reactivity of free ions (k″) can be smaller than that of ion pairs (k′) under some conditions, though such a case has neither been found experimentally nor theoretically predicted so far.

Table 5. Parameter Value Used

Ion, molecule	$\lvert\mu'\rvert$ (D)	$\lvert\mu\rvert$ (D)	Radius, r(Å)	Reactive surface parameter (Θ_I)
Cl^-	–	–	1.81	-1
Br^-	–	–	1.95	-1
K^+	–	–	1.33	–
Rb^+	–	–	1.48	–
$(CH_3)_4N^+$	–	–	3.00	–
$(C_2H_5)_4N^+$	–	–	3.85	–
SO_2	1.61	–	2.59	–
NO_2  CH_2Br	3.58	3.58	4.05	–

Extension of the present treatment to polymerization reactions is possible and will be published later.

APPENDIX 1

Proof of the Convergency of the Integral in Eq. (28)

Substituting Eq. (23) into Eq. (28), we obtain

$$\epsilon_s^0 = -4\pi |z| q \sum_i |\mu_i| \cdot \rho_i^r \cdot \frac{D_{oi} + 2}{2D^r + D_{oi}} \int_{r_I}^{\infty} L\left(\frac{B}{r^2}\right) dr \; -$$

$$- \frac{4\pi |z|^2 q^2}{2r_I} \cdot \frac{3}{2D^r + 1} \sum_i \rho_i^r \frac{D_{oi} + 2}{2D^r + D_{oi}} \lambda_i \qquad \text{(A-1)}$$

if we assume that

$$|E^r| = \frac{|z_I| q}{D^r r^2}$$

and ρ_i^r and D^r are independent of r, where

$$B = [(D_{oi} + 2)/(2D^r + D_{oi})](|\mu_i| \cdot |z| q/kT)$$

From the expansion of the Langevin function, we have

$$\int_{r_I}^{\infty} L \frac{B}{r^2} \; dr = \int_{r_I}^{\infty} \left(\frac{B}{3} \frac{1}{r^2} - \frac{B^3}{45} \frac{1}{r^6} + \frac{2B^5}{945} \frac{1}{r^{10}} - \ldots \right) dr$$

$$= r_I \left\{ 1 \left(\frac{B}{3} \frac{1}{r_I^2} \right) - \frac{1}{5} \left(\frac{B^3}{45} \frac{1}{r_I^6} \right) \right.$$

$$\left. + \frac{1}{9} \left(\frac{2B^5}{945} \frac{1}{r_I^{10}} \right) - \ldots \right\} \qquad \text{(A-2)}$$

The series in the braces is obtained by multiplying term by term the two series,

$$\frac{B}{3} \frac{1}{r_I^2} - \frac{B^3}{45} \frac{1}{r_I^6} + \frac{2B^5}{945} \frac{1}{r_I^{10}} - \ldots$$

and

$$1 + \frac{1}{5} + \frac{1}{9} + \ldots + \frac{1}{1 + 4(n-1)} + \ldots$$

The former is the expansion of the Langevin function $L(B/r_I{}^2)$ and is convergent. The latter is easily proved to converge. Therefore, Eq. (A-2) is convergent and so is Eq. (28).

It should be noted that the convergence of ϵ_s^0 results by taking into consideration the partial orientation of the solvent molecules at a distance from the reactant ion, which is reflected in Eq. (23).

APPENDIX 2

Derivation of the Second Term in Eq. (13)

In Eq. (13), the first term is obtained by the Onsager theory [15], and the second term by the followings.

According to the Onsager theory, the component of an induced dipole moment which is parallel to **E** is obtained by

$$\frac{D(D_0 + 2)}{2D + D_0} \lambda \mathbf{E} \qquad \text{(A-3)}$$

The work for carrying the induced dipole moment from a distance of infinity to a point Q is obtained by

$$w_1 = -\frac{D(D_0 + 2)}{2D + D_0} \lambda |E| \cdot |G| = -\frac{3D^2(D_2 + 2)}{(2D + D_0)(2D + 1)} \lambda |\mathbf{E}|^2$$

where **G** is a cave electric field [15],

$$\frac{3D}{2D + 1} \mathbf{E}$$

According to electrostatics, the work for producing the induced dipole moment given by Eq. (A-3) is obtained by

$$w_2 = \int_0^{\ell} |G| q \, dl = \frac{3D^2(D_0 + 2)}{2(2D + D_0)(2D + 1)} \lambda |\mathbf{E}|^2$$

where

$$ql = \frac{D(D_0 + 2)}{2D + D_0} \lambda |E|$$

The free energy of the dipole moment that is induced by an ion electric field is, therefore, obtained by

$$w_1 + w_2 = -\frac{3D^2(D_0 + 2)}{2(2D + D_0)(2D + 1)} \lambda |E|^2 \tag{A-4}$$

Equation (A-4) is the second term in Eq. (13).

REFERENCES

[1] I. Sakurada, N. Ise, and T. Ashida, *Makromol. Chem.*, **82**, 284 (1965); **95**, 1 (1966).

[2] I. Sakurada, N. Ise, and S. Kawabata, *Makromol. Chem.*, **97**, 17 (1966).

[3] I. Sakurada, N. Ise, Y. Tanaka, and Y. Hayashi, *J. Polym. Sci., Part A-1*, **4**, 2801 (1966).

[4] I. Sakurada, N. Ise, and S. Hori, *Kobunshi Kagaku*, **24**, 145 (1967).

[5] I. Sakurada, N. Ise, and Y. Hayashi, *J. Macromol. Sci.–Chem.*, **A1**, 1039 (1967).

[6] I. Sakurada, Y. Tanaka, and N. Ise, *J. Polym. Sci., Part A-1*, **6**, 1463 (1968).

[7] I. Sakurada, N. Ise, and Y. Tanaka, *Polymer*, **8**, 625 (1967).

[8] I. Sakurada, N. Ise, Y. Hayashi, and M. Nakao, *Kobunshi Kagaku*, **25**, 41 (1968).

[9] I. Sakurada, N. Ise, H. Hirohara, and T. Makino, *J. Phys. Chem.*, **71**, 3711 (1967).

[10] N. Ise, H. Hirohara, T. Makino, K. Takaya, and M. Nakayama, *J. Phys. Chem.*, **74**, 606 (1970).

[11] For example, S. F. Acree, *J. Amer. Chem. Soc.*, **37**, 1902 (1915); N. N. Lichtin, M. S. Puar, and B. Wasserman, *J. Amer. Chem. Soc.*, **89**, 6677 (1967); D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 624 (1965).

[12] See, for example, J. Miller and A. J. Parker, *J. Amer. Chem. Soc.*, **83**, 117 (1961); A. J. Parker, *J. Chem. Soc.*, **1961**, 1328.

[13] E. D. Amis, *Solvent Effect on Reaction Rates and Mechanisms*, Academic, New York, 1966.

[14] J. B. Hasted, D. M. Ritson, and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948).
[15] L. Onsager, *J. Amer. Chem. Soc.*, **58**, 1486 (1936).
[16] H. C. Robertson and S. F. Acree, *J. Amer. Chem. Soc.*, **37**, 1902 (1915).
[17] N. Bjerrum, *Kgl. Danske Videnskab. Selskab*, 7(9), (1926).
[18] R. M. Fuoss, *Trans. Faraday Soc.*, **30**, 967 (1934).
[19] N. N. Lichtin, M. S. Puar, and B. Wasserman, *J. Amer. Chem. Soc.*, **89**, 6677 (1967).
[20] *Landolt-Börnstein*, Vol. I-3, 7th ed., Springer, Berlin, Göttingen, and Heidelberg, 1950.

Accepted by editor December 15, 1969
Received for publication December 23, 1969