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Reaction Rates in Binary Mixed Solvents. VI.[1] An Sn Ar Reaction in a Methanol-Acetonitrile Mixture

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The present authors have previously developed a method of estimating the solvation patterns of the solute species involved in a reaction by analyzing the relation between the observed rate constants and the composition of the solvent.[1–3]

Since many data on rate constants and solvent activity coefficients were accumulated for **Sn Ar** reactions by Parker *et al.*,[4,5] the reaction is very appropriate for a discussion of the validity of our methods and the consistency between our method and Parker's parameters.

When an inorganic salt is involved as a reactant, one of the most important problems is how to evaluate the salt effects on reaction rates.[6] In some cases, these effects were ascribed to the incomplete dissociation of the inorganic salt in non-aqueous solvents;[7–10] in other cases, there are different reasons.[11–13]

In this report, first we will describe the quantitative treatment of the dependence of the observed rate constant on the initial concentration of potassium thiocyanate, a nucleophile; next, we will consider the solvation patterns of the species involved in the reaction based on the present authors' method and Parker's parameters.

Experimental

Materials. 2,4-Dinitroiodobenzene was prepared by refluxing 2,4-dinitrochlorobenzene and sodium iodide in dimethylformamide.[14] The crude product was recrystallized three or four times from a benzene-petroleum benzin mixture.

Potassium thiocyanate and sodium thiocyanate of a guaranteed-grade reagent were dried over silica gel.

The solvents used were purified by a method described elsewhere.[15,16]

Kinetic Procedure. The reaction rates were measured by two methods. In the first, a solution of 2,4-dinitroiodobenzene was added to a solution of potassium thiocyanate in a long-necked reaction vessel maintained at the reactions temperature. Aliquots of 5 m*l* were withdrawn at given intervals from the vessel. In the other method, the reaction were carried out in a high-pressure glass vessel with a volume of *ca.* 20 m*l* with a stainless steel screw stopper.

In either case the reactions were stopped by pouring the reaction mixture into a vessel containing water and light petroleum. After the extraction of inorganic salts from the organic layer, the concentration of the iodide ion produced was determined potentiometrically using a silver nitrate solution.

Results and Discussion

Salt Effects. The reaction followed the second-order kinetics for each run. The rate expression can then be written as follows:

$$\frac{dX}{dt} = k_{obs}\,(\text{2,4-dinitroiodobenzene})(\text{KSCN}) \qquad (1)$$

where X denotes the concentration of iodide ions formed in the reaction. The observed rate constant, k_{obs}, decreased as the initial concentration of potassium

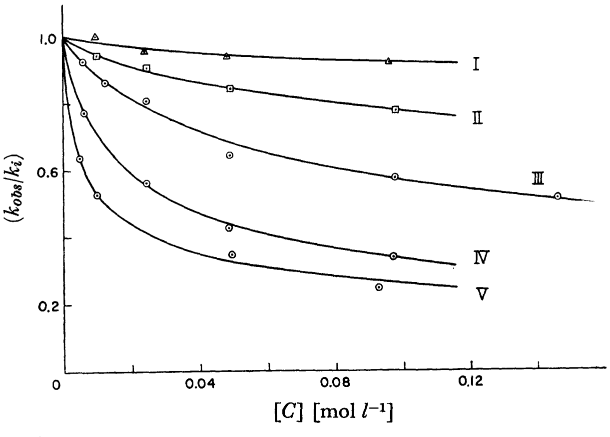

Fig. 1. The dependence of observed rate constants on the initial concentration of a nucleophile.
I, 2,4-dinitroiodobenzene+KSCN in pure methanol; II, 2,4-dinitroiodobenzene+KSCN in methanol (10 mol%)-acetonitrile (90 mol%) mixture; III, 2,4-dinitroiodobenzene +KSCN in pure acetonitrile; IV, 2,4-dinitroiodobenzene+NaSCN in pure acetonitrile; V, 2,4-dinitroiodobenzene+KSCN in pure acetone; ———, calculated values; △, ⊡, ⊙, observed values

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thiocyanate increased. Typical examples are shown in Fig. 1. The experimental error of each rate constant was estimated to be less than ±2% from duplicate runs.

The method of analyzing the salt effects is based on the Acree hypothesis.[6–10,17] According to this hypothesis, the observed rate constants are expressed as sums of two components, *i.e.*, a rate constant for free ions, k_i, and a rate constant for ion pairs, k_{ip}, as follows:

$$k_{obs} = k_i\alpha + (1-\alpha)k_{ip} \tag{2}$$

where α stands for the degree of dissociation of potassium thiocyanate.

Since, for an ion pair, a thermodynamic dissociation constant, K_d, and a dissociation constant defined in terms of the concentration, K_c, are expressed by Eq. (3),[10] Eq. (2) can be rearranged to Eq. (4):

$$K_d = C\alpha^2 f_\pm^2/(1-\alpha) = K_c f_\pm^2 \tag{3}$$

$$k_{obs} = [\{-K_c+(K_c^2+4K_cC)^{1/2}\}/2C](k_i-k_{ip}) + k_{ip} \tag{4}$$

where $f_\pm$ and C stand for an activity coefficient and the stoichiometric concentration of potassium thiocyanate.

The experimental results were analyzed on the basis of Eq. (4) using a NEAC 2200—500 computer by the steepest descent method; the calculated values of k_i, k_{ip}, and K_c are listed in Table 1. The lines in Fig. 1 show the values calculated on the basis of these parameters.

TABLE 1. CALCULATED VALUES OF k_i, k_{ip}, AND K_c AT 40°C

Solvent	Nucleophile	$10^5\times k_i$	$10^5\times k_{ip}$	K_c
Acetonitrile	NaSCN	72.0	—	0.0165
Acetonitrile	KSCN	69.1	—	0.0635 (0.0380[19])
Acetonitrile Methanol (90:10 mol%)	KSCN	17.7	8.28	0.0827
Acetonitrile Methanol (70:30 mol%)	KSCN	5.04	4.34	0.0804
Acetonitrile Methanol (50:50 mol%)	KSCN	2.89	2.43	0.0819
Acetonitrile Methanol (25:75 mol%)	KSCN	2.03	1.79	0.0850
Methanol	KSCN	1.95	1.56	0.0909[a]
Acetone	KSCN	1125	96.6	0.0045 (0.0034[18])

Unit: k_i and k_{ip} : ($l\cdot$mol$^{-1}\cdot$sec^{-1}), K_c; (mol$\cdot l^{-1}$)

Values in parentheses show the dissociation constant determined by conductivity measurements.

a) The value from the reference[20] was used for the calculation.

Rate Constant in Binary Mixed Solvents. As a first approximation, assuming that the difference in k_i between methanol and acetonitrile results from the specific solvation of the thiocyanate ion by methanol and that all the other systems, *i.e.*, thiocyanate ion-acetonitrile, 2,4-dinitroiodobenzene-solvent mixtures and an activated complex-solvent mixture, form ideal solutions, by simplifying Eqs. (13) and (14) in Part IV[3] of this series the following equations are obtained:

$$(k_1/k_4) = (K_r+1) = 35.4 \tag{5}$$

$$\ln k_{\mathrm{mix}} = x_1 \ln k_1 + x_4 \ln k_4 + x_4 \ln (K_r+1) - \ln (x_4K_r+1) \tag{6}$$

where methanol is indicated by the subscript 4 and where K_r refers to the equilibrium constant of the hypothetical reaction of methanol with the thiocyanate ion. The solid curve in Fig. 2 is the theoretical value calculated from these equations.

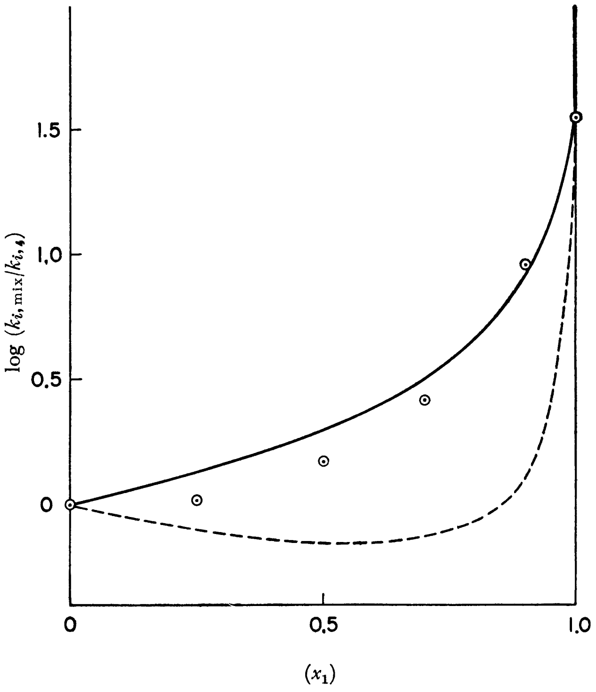

Fig. 2. Comparisons of calculated values with observed values. ———, calculated values by first model; ------, calculated values by the second model; ⊙, free ion rate constants

In the second approach, the concept of solvent activity coefficients[4] has been taken into account.

The relation between the solvent activity coefficient reported by Parker *et al.*,[4] γ, and the activity coefficient used by the present authors,[2] β_i, is given by Eq. (7), and the coefficient,$^4\gamma^1$, can be correlated to the equilibrium constant of the hypothetical reaction, K, on the basis of the definition of Ref. 2, when a solute is more stabilized in the solvent 1 than in the solvent 4.

$$^4\gamma^1 = (\beta_1/\beta_4) = (^1\gamma^4)^{-1} = 1/(K+1) \tag{7}$$

Making use of the following solvent activity coefficients,[4] the relation,[2] Eq. (11), and several rules,[2] the final equation for rate constants in mixed solvents is obtained as follows:

$$\log {}^0\gamma^s_{\mathrm{SCN}^-} = 2.6\ ^{4)} \tag{8}$$

$$\log {}^0\gamma^s_{\mathrm{RX}} = -0.4\ ^{4)} \tag{9}$$

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$$\log {}^{0}\gamma_{\mathrm{M}}^{s}{*} = 0.65\ \text{[21]} \tag{10}$$

$$k_{\mathrm{mix}} = k_0 \frac{(\beta_{\mathrm{SCN}^-,\mathrm{mix}} \beta_{\mathrm{RI},\mathrm{mix}})}{\beta_{\mathrm{M}*,\mathrm{mix}}} \tag{11}$$

$$\begin{aligned} \ln k_{\mathrm{mix}} = {} & x_1 \ln k_1 + x_4 \ln k_4 \\ & + x_4 \ln (K_{\mathrm{SCN}^-} + 1) - \ln (x_4 K_{\mathrm{SCN}^-} + 1) \\ & + x_1 \ln (K_{\mathrm{RX}} + 1) - \ln (x_1 K_{\mathrm{RX}} + 1) \\ & - \{x_4 \ln (K_{\mathrm{M}*} + 1) - \ln (x_4 K_{\mathrm{M}*} + 1)\} \end{aligned} \tag{12}$$

where the subscript 1 refers to acetonitrile, and the subscript 4, to methanol, and where $K_{\mathrm{SCN}^-} = 3.97 \times 10^2$, $K_{\mathrm{RX}} = 1.51$, and $K_{\mathrm{M}}* = 3.47$.

The values calculated by means of Eq. (12) are shown by a dotted curve in Fig. 2.

Of the three solvent activity coefficients, that of the thiocyanate ion is the largest; this is equivalent to the idea that the rate of the reaction is controlled by the strong solvation of the thiocyanate ion by methanol. In the former treatments, this factor has been taken into account as the hypothetical reaction of thiocyanate ion with methanol. In the latter treatments, the solvent activity coefficients have been transformed into equilibrium constants in order to reproduce Parker's concept in our model.

Both models can explain the general behavior of the rate constant in a mixed solvent, and there is consistency between our model and the solvent activity coefficient reported by Parker *et al.* in that a strong solvation of the thiocyanate ion by methanol is the main factor making the rate in methanol slower than in acetonitrile.

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[21] $\log {}^{0}\gamma_{\mathrm{M}}^{S}{*}$ was estimated by means of the relation[4]:

$$\log {}^{0}\gamma_{\mathrm{M}}^{s}{*} = \log {}^{0}\gamma_{\mathrm{SCN}^-}^{s} + \log {}^{0}\gamma_{\mathrm{RX}}^{s} - \log (k^s/k^0)$$