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Reaction Rates in Binary Mixed Solvents. V[1]

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The rate constants of the Menschutkin reaction between methyl iodide and pyridine, *N,N*-dimethylaniline, 2,6-dimethylpyridine, and *N,N*-dimethyl-*o*-toluidine have been measured in a liq. SO_2-nitrobenzene mixture. These results have then been analyzed by the procedure described in a previous paper. The findings regarding the reactions of unsubstituted amines with methyl iodide have been explained theoretically by taking into account the specific solvation of amines by liq. SO_2 and that of an activated complex by a nitrobenzene solvent, whereas the behavior of the rate constants in the reactions of *o*-substituted amines in mixed solvents can be explained by assuming the specific solvation of an activated complex by liq. SO_2 only. In conformity with the above results and the difference in the effect of an *o*-methyl group on the reaction rates between liq. SO_2 and a nitrobenzene solvent, the mutual relation of the activation free energies of these reactions has been discussed.

In a previous paper of this series the present authors have discussed the theoretical procedure for analyzing the reaction rates measured in solvent mixtures. The additional possibility has been suggested that knowledge about the solvation phenomena of the solute could be drawn from an

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[1] Y. Kondo, Y. Honjo and N. Tokura, This Bulletin, **41**, 987 (1968).

analysis of the rate constants measured in mixed solvents which could not be drawn from an analysis of the reaction rates measured in pure solvents.

For a complete understanding of the reaction in solution it is necessary to summarize various informations originating from different sources.

One of the most useful methods of detecting the behavior of the solvent molecules near the reaction center is to examine the effect of the *o*-substitutent on the reaction rates in solution.[2-4] Accordingly, the effects of the *o*-methyl group on the rates of the Menschutkin reaction in liq. SO_2 have been compared with those in a methanol solvent,[3] and the difference in the behavior of the *o*-methyl group between these two solvents has been attributed to the specific solvation of the amines in liq. SO_2.[3]

In this paper the procedure for considering the mutual relation among activation free energies for the reactions in solution will be discussed by combining experimental results of different kinds obtained from different sources regarding the effects of an *o*-methyl group and the reaction rates in mixed solvents.

Experimental

Materials. The materials used in this experiment have been purified by methods described elsewhere.[3]

Kinetic Procedure. In most of all the kinetic runs given amounts of stock solutions of methyl iodide in liq. SO_2 were introduced into a reaction vessel containing given amounts of an amine solution in a nitrobenzene solvent, the mixture held at about −70°C by means of a pressure buret described elsewhere.[5a,5b] The reaction was started by placing the vessel into a thermostat bath held at the reaction temperature. The method of detecting the iodide ions produced during the reaction is almost the same as those described earlier.[3]

Typical results are shown in Table 1.

TABLE 1. RATE CONSTANTS OF THE REACTION BETWEEN PYRIDINE AND METHYL IODIDE IN THE LIQ. SO_2-NITROBENZENE MIXTURE

	50.0°C	40.0°C	30.0°C
$k\times10^4$	5.16	2.37	0.966
x	0	0	0
$k\times10^4$	7.39	3.05	1.15
x	0.190	0.228	0.190
$k\times10^4$	8.47	3.72	1.34
x	0.380	0.384	0.380
$k\times10^4$	9.24	4.08	1.61
x	0.598	0.604	0.598
$k\times10^4$	10.3	4.64	1.76
x	0.790	0.790	0.790
$k\times10^4$	21.3	11.1	5.52
x	1.0	1.0	1.0

k: $l\,mol^{-1}sec^{-1}$, x: mole fraction of nitrobenzene in a nitrobenzene - liq. SO_2 mixture.

Results

According to the theory developed in a previous paper[5] the logarithm of the rate constant has been plotted against the mole fraction of a nitrobenzene solvent (Figs. 1 and 2), the shapes of these curves

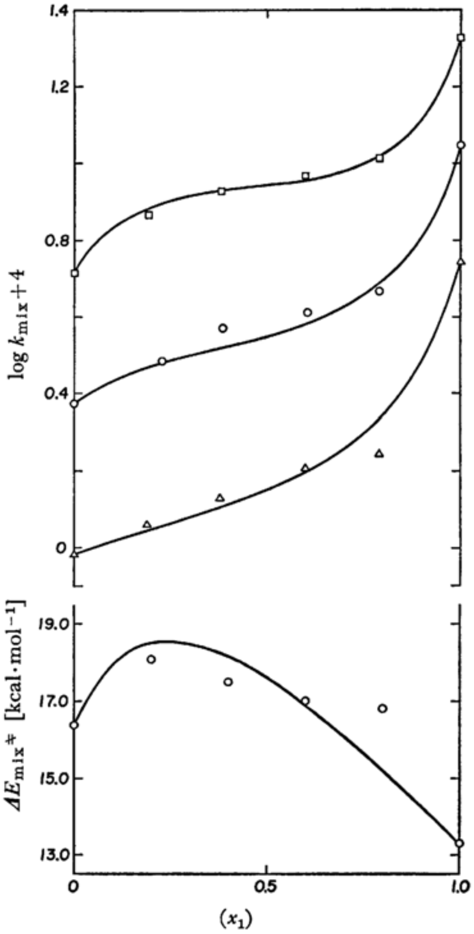

Fig. 1. Dependence of $\log k_{mix}$ and $\Delta E_{mix}^{\ddagger}$ for the reactions of pyridine with methyl iodide in liq. SO_2-nitrobenzene mixture upon mole fraction of nitrobenzene (x_1).

□ (50°C), ○ (40°C), △ (30°C): experimental results, —: calculated results

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[2] J. B. Hyne and R. Wills, *J. Am. Chem. Soc.*, **85**, 3650 (1963).

[3] Y. Kondo and N. Tokura, This Bulletin, **37**, 133 (1964).

[4] M. Hojo, M. Utaka and Z. Yoshida, *Yuki Gosei Kagaku Kyokai Shi (J. Syn. Org. Chem. Japan)*, **23**, 1034, 1040 (1965).

[5] a) N. Tokura, M. Matsuda and F. Yazaki, *Makromol. Chem.*, **42**, 108 (1960). b) N. Tokura, R. Asami, M. Matsuda and H. Negishi, *Kogyo Kagaku Zasshi (J. Chem. Soc., Japan, Ind. Chem. Sec.)*, **64**, 717 (1961).

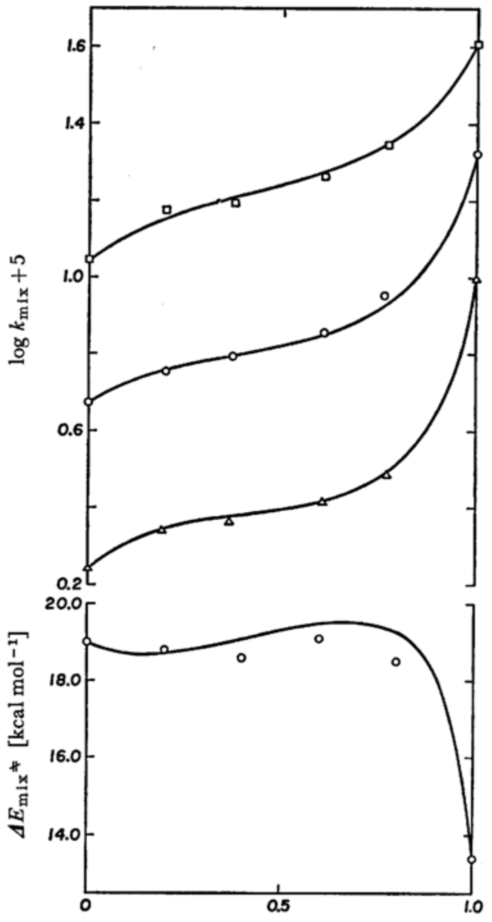

Fig. 2. Dependence of log $k_{\rm mix}$ and $\Delta E_{\rm mix}^{\ddagger}$ for the reaction of *N,N*-dimethylanilne with methyl iodide in liq. SO_2-nitrobenzene mixture upon mole fraction of nitrobenzene (x_1).
□ (50°C), ○ (40°C), △ (30°C): experimental results, —: calculated results

are obviously similar to that of curve 8 of model II in the previous paper.[1] The calculations were then made by taking the specific solvation of amines by liq. SO_2 and that of an activated complex by a nitrobenzene solvent into consideration. The interaction term, $\alpha_{14}x_1x_4$ and the molar volumes of the solvents which had been included in the original formula have been neglected in these calculations in order to make the computation easier.

$$\ln k_{\rm mix} = x_1 \ln k_1 + x_4 \ln k_4 + \{x_4 \ln(K_{\rm R}+1) - \ln(x_4K_{\rm R}+1) - x_1 \ln(K_{\rm A}+1) + \ln(x_1K_{\rm A}+1) - x_1x_4\alpha_{14}\} \quad (1)$$

$$\Delta E_{\rm mix}^{\ddagger} = x_1\Delta E_1^{\ddagger} + x_4\Delta E_4^{\ddagger} + x_1x_4\left\{\frac{\Delta H_{\rm A}^{\circ}}{(1+1/K_{\rm A})(x_1+1/K_{\rm A})} - \frac{\Delta H_{\rm R}^{\circ}}{(1+1/K_{\rm R})(x_4+1/K_{\rm R})}\right\} \quad (2)$$

The procedure of the calculation was as follows. (1) The calculated value of log $k_{\rm mix}$ have been best-fitted to the experimental values of log $k_{\rm mix}$ by searching for suitable values of both $K_{\rm A}$ and $K_{\rm R}$. (2) The enthalpy changes, $\Delta H_{\rm A}^{\circ}-\Delta H_{\rm R}^{\circ}$, have been computed from the rates of the variation in $K_{\rm A}$ and in $K_{\rm R}$ thus obtained with respect to the temperature. (3) The theoretical values of $\Delta E_{\rm mix}^{\ddagger}$ have been calculated from Eq. (2) by substituting into Eq.(2) the numerical values of $\Delta H_{\rm A}^{\circ}$ and $\Delta H_{\rm R}^{\circ}$ and of $K_{\rm A}$ and $K_{\rm R}$ obtained above.

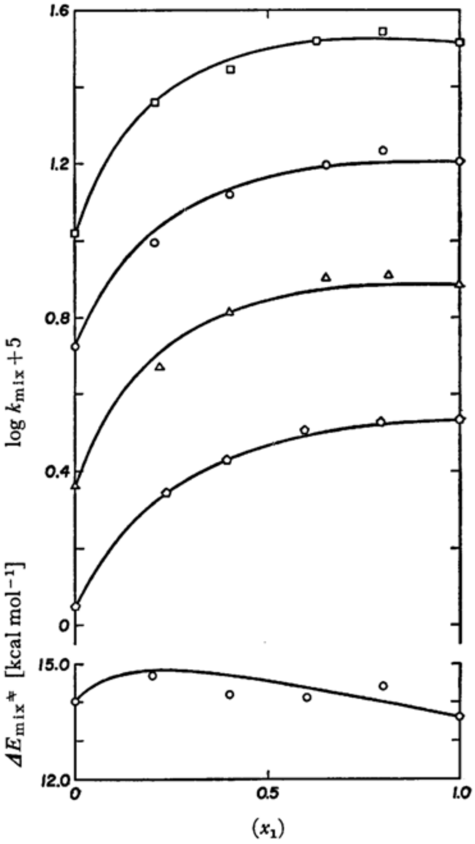

Fig. 3. Dependence of log $k_{\rm mix}$ and $\Delta E_{\rm mix}^{\ddagger}$ for reaction of 2,6-dimethylpyridine with methyl iodide in nitrobenzene - liq. SO_2 mixture upon mole fraction of liq. SO_2 (x_1).
□ (50°C), ○ (40°C), △ (30°C), ⬠ (20°C): experimental results, —: calculated results

These theoretical values are shown as smooth curves in Figs. 1, 2, 3 and 4.

As for the reactions of *o*-substituted amines, the results were analyzed by similar procedures except that only the specific solvation of an activated complex by liq. SO_2 has been taken into account. The parameters used in these calculations are summarized in Table 2.

Discussion

In these calculations the best values of $K_{\rm A}$ and $K_{\rm R}$ have been chosen without considering the boundary conditions, *i. e.*, Eqs. (3) and (4), which should

TABLE 2. THE PARAMETERS USED IN THESE CALCULATIONS

Reactions		Temperature					
		20°C	30°C	40°C	50°C	60°C	
Pyridine+MeI	K_A		1.5	3.0	6.0		$H_A{}^\circ=12.2$ (kcal mol^{-1})
	K_R		10	10	10		$H_R{}^\circ=0$ (kcal mol^{-1})
N,*N*-Dimethylaniline +MeI	K_A		4.0	3.0	3.0		$H_A{}^\circ=-3.8$ (kcal mol^{-1})
	K_R		17	11	6.0		$H_R{}^\circ=-10.2$ (kcal mol^{-1})
2,6-Dimethylpyridine +MeI	K_A	6.0	8.0	7.0	8.5		$H_A{}^\circ=2.2$ (kcal mol^{-1})
	K_R	0	0	0	0		$H_R{}^\circ=0$ (kcal mol^{-1})
N,*N*-Dimethyl-*o*-toluidine+MeI	K_A		7.5	7.0	6.5	6.0	$H_A{}^\circ=-1.5$ (kcal mol^{-1})
	K_R		0	0	0	0	$H_R{}^\circ=0$ (kcal mol^{-1})

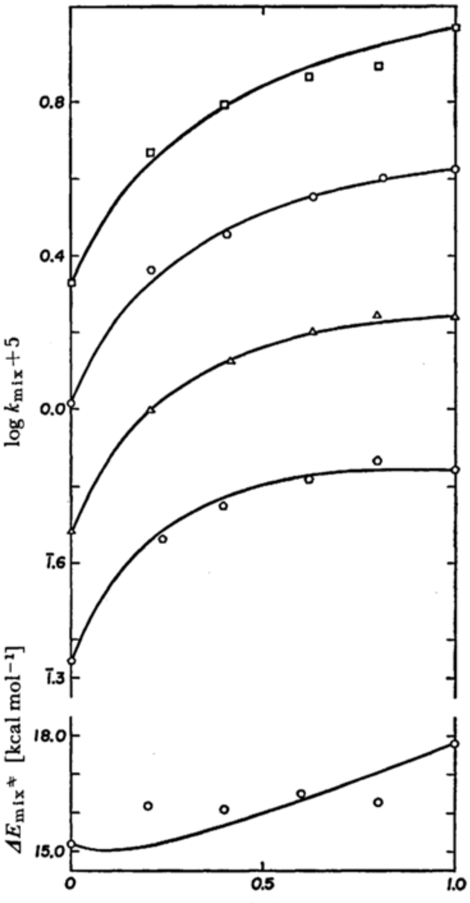

Fig. 4. Dependence of $\log k_{mix}$ and $E_{mix}{}^{\ddagger}$ for the reaction of *N*,*N*-dimethyl-*o*-toluidine with methyl iodide in nitrobenzene-liq. SO_2 mixture upon mole fraction of liq. SO_2 (x_1).
□ (60°C), ○ (50°C), △ (40°C), ⬠ (30°C): experimental results, —: calculated results

be satisfied whenever the model is self-consistent.

$$(k_1/k_4)=\exp(\alpha_{A1}-\alpha_{A4})\times\exp(\alpha_{B1}+\alpha_{M4}{}^{\ddagger})\times(K_A+1)(K_R+1)(V_1/V_4) \tag{3}$$

$$(\Delta E_1{}^{\ddagger}-\Delta E_4{}^{\ddagger})=\left\{\frac{\Delta H_A{}^\circ}{(1+1/K_A)}+\frac{\Delta H_R{}^\circ}{(1+1/K_R)}\right\} \tag{4}$$

However, if we try to describe an S-shaped curve like those in Figs. (1), and (2) by this model, values of both K_A and K_R must be chosen larger than those required by the boundary condition, Eq. (3).

One example of these situations is shown in Fig. 5, where the deviations from linearity, *i. e.*, $\Delta\log k_{mix}$, are calculated for various values of $(k_1/k_4)/(K_A+1)(K_R+1)$, which stand for the degree of consistancy.

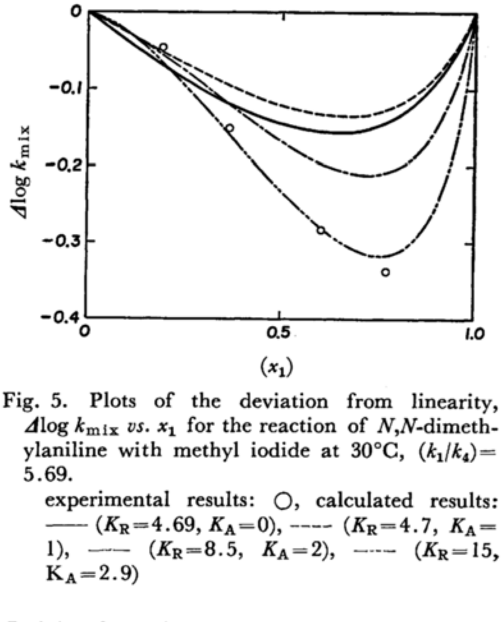

Fig. 5. Plots of the deviation from linearity, $\Delta\log k_{mix}$ *vs.* x_1 for the reaction of *N*,*N*-dimethylaniline with methyl iodide at 30°C, $(k_1/k_4)=5.69$.
experimental results: ○, calculated results: —— ($K_R=4.69$, $K_A=0$), ---- ($K_R=4.7$, $K_A=1$), —·— ($K_R=8.5$, $K_A=2$), -·-·- ($K_R=15$, $K_A=2.9$)

Judging from the above inconsistency, our model would be better applicable to the reaction rates of *o*-substituted amines than to those of unsubstituted amines; for unsubstituted amines the values of $(k_1/k_4)/(K_A+1)(K_R+1)$ are within the factor of three.

Though ΔE_{mix} could be fitted by this procedure to a considerable extent, the boundary condition, Eq. (4), could not be satisfied. The reason is the inconsistency described above. Therefore, the estimations of the theoretical values of $\Delta E_{mix}{}^{\ddagger}$ may be concluded to be richer in errors since, for these calculations, we have to rely only on the variation

TABLE 3. THE EFFECT OF *o*-METHYL GROUP IN LIQ. SO_2 AND IN A NITROBENZENE SOLVENT AT 40°C

Reaction	Solvent		
N,N-Dimethylaniline+MeI	$PhNO_2$	$k_H=21.0\times10^{-5}$ $k_{o-Me}=0.480\times10^{-5}$	$k_H/k_{o-Me}=43.7$
	Liq. SO_2	$k_H=4.69\times10^{-5}$ $k_{o-Me}=1.74\times10^{-5}$	$k_H/k_{o-Me}=2.69$
Pyridine+MeI	$PhNO_2$	$k_H=11.1\times10^{-4}$ $k_{o-Me}=5.31\times10^{-5}$	$k_H/k_{o-Me}=20.9$
	Liq. SO_2	$k_H=2.37\times10^{-4}$ $k_{o-Me}=1.60\times10^{-4}$	$k_H/k_{o-Me}=1.48$

k: $l\ mol^{-1} sec^{-1}$, k_H/k_{o-Me}; the ratio of the rate constants of the substituted and *o*-methyl substituted amines

in K_A and in K_R with a change in the temperature.

Although the above inconsistencies must be kept in mind, for the cases of unsubstituted amines the values of K_R are always larger than those of K_A, while for substituted amines only the values of K_A are needed for these calculations. In addition to these facts regarding the reactions of unsubstituted amines, the rate constants in a nitrobenzene solvent are larger than those in liq. SO_2. From these facts we can determine the positions of the activation free energies in liq. SO_2 relative to those in a nitrobenzene solvent.

As is shown in Table 3, the retarding effect by an *o*-substituted methyl group is more remarkable in a nitrobenzene solvent than in liq. SO_2. Consequently, the rate constants for the reactions of *o*-substituted amines become larger in liq. SO_2 than in a nitrobenzene solvent.

The difference in the effect of an *o*-methyl substituent between a methanol and a liq. SO_2 solvent has been attributed to the effect of the solvation of amines by liq. SO_2[3]. The addition compound formed from 2-methylpyridine and trimethyl boron has been reported to be less stable than that of 3- or 4-methylpyridine and trimethyl boron because of the *o*-methyl group.[6]

Therefore, if we assume that *o*-substituted amines are solvated to a lesser extent in liq. SO_2 than are unsubstituted amines, but that there is not much difference between the two in the solvation energy in a nitrobenzene solvent, we can determine the positions of the activation free energies of the former amines relative to those of the latter amines.

Summing up these conclusions, the following figure (Fig. 6) describes the mutual relations of the activation energies.

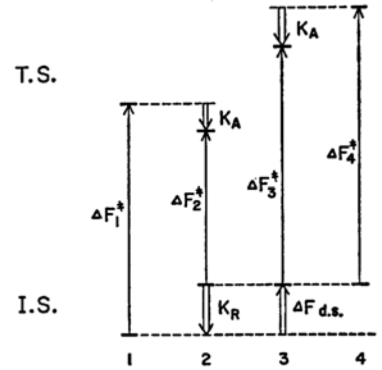

Fig. 6. The mutual relation of the activation free energies.
1: Unsubstituted amine+MeI in liq. SO_2
2: Unsubstituted amine+MeI in nitrobenzene
3: *o*-Substituted amine+MeI in liq. SO_2
4: *o*-Substituted amine+MeI in nitrobenzene
$\Delta F_{d.s.}$: desolvation free energy by the existence of *o*-methyl group

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6) H. C. Brown and G. K. Barbaras, *J. Am. Chem. Soc.*, **69**, 1137 (1947).