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Kinetics for Reversible Menschutkin Reactions. The Effects of Variations in Reactant Structures on the Sensitivity of the Reaction Rate to Solvent Variations

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The reaction rates and equilibrium constants for quaternization of *N,N*-dimethylaniline and its derivatives with methyl iodide have been measured in acetonitrile, acetone, tetrahydrofuran, nitrobenzene, benzene, benzyl alcohol, and methanol at various temperatures. There is an approximate tendency for the solvent dependence of the reaction rates to diminish linearly with increasing reactivity of nucleophile. This could be interpreted in terms of the theory of an absolute reaction rate and of the concept of the rise of interaction term. In this connection it was proposed that such a problem must be considered in terms of the unitary term of rates. Using the data of rates of the reaction between pyridine and methyl iodide in various solvents, the activity coefficients of dimethylaniline and its derivatives in methanol relative to that of pyridine are estimated. Some inferences have been drawn concerning the nature of S_N2 transition state from effects of solvents on both rates and equilibria.

The nucleophilic tendency for S_N2 reactions seems to be affected by the nature of electrophiles and of solvents, and also by temperature and pressure. The effects of variations in substrates on nucleophilic tendency have the subject of some authors.

However, the subject is not so simple as Swain and Scott considered.[1] From the study of Hine and Weimar on carbon basicity, correlation of nucleophilicity of bases with the hydrogen basicity is not always good.[2] Qualitatively the priciple of hard and soft acids and bases (HSAB) seems to be an explanation for this problem. Pearson *et al.*[3] explained qualitatively the fact that no good correlation exists for the difference between methyl iodide and *trans*-[Pt(py)$_2$Cl$_2$] in the variations of rates of reactions with charged and uncharged bases in terms of this principle. It seems, however, unlikely that there is no systematic tendency at all. For one thing it has been reported that there is a relatively simple linear relation between the nucleophilic tendency and the polarizability of leaving group.[4]

It should be noted that most experiments on these problems were carried out using the most complicating medium, water as solvent. It is yet uncertain whether the specificity of water as solvent contributes to the nucleophilic tendency in any way.

Thus it is of importance to examine the effects of solvents on nucleophilic tendency. For the Finkelstein or S_NAr reactions, Parker and his collaborators have tried to settle these effects on nucleophilic tendency by comparing the S_N2 reactivity in each solvent-solvent pair.[5] It remains to be proved whether the compilation of both charged

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[1] C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, **75**, 141 (1953).

[2] J. Hine and R. D. Weimar, Jr., *ibid.*, **87**, 3387 (1965).

[3] R. G. Pearson, H. Sobel and J. Songstad, *ibid.*, **90**, 319 (1968).

[4] a) R. E. Davis, *ibid.*, **87**, 3010 (1965); b) R. G. Pearson and J. Songstad, *ibid.*, **89**, 1827 (1967); c) G. Bartoli and P. E. Todesco, *Tetrahedron Lett.*, **1968**, 4867.

[5] R. Alexander, E. C. F. Ko, A. J. Parker and T. J. Broxton, *J. Amer. Chem. Soc.*, **90**, 5049 (1968) and references cited in this literature.

and uncharged nucleophiles should be made after due consideration of the solvent used. We have studied this type of problem within the linear free energy relationship framework of unchanged nucleophiles.[6] It has been proposed that the effects of solvents on the measure of sensitivity to the variations in nucleophiles (as an example, Hammett's ρ value) and the effects of variations in nucleophiles on the measure of sensitivity to the variations in solvents (denoted by ζ) are two aspects of the phenomenon. Therefore, the subject can be discussed as the factors influencing the value of ζ. The present paper reports a study of some factors influencing the dependence of the reaction rates of the quaternization of a base $R\cdot C_6H_4N(CH_3)_2$ with methyl iodide on solvent variations. The effects of R on ζ, the comparison of pyridine with dimethylaniline as a nucleophile, and the difference of ζ of the reaction based on methyl iodide and 2,4,6-trinitro-anisole or methyl picrate are reported here.

The reaction of dimethylaniline or its derivatives with methyl iodide have been followed in various solvents.[7] This reaction is of interest with respects to the occurrence of a reverse decomposition reaction at relatively low temperature. Rossell[7a] has made use of data for the series of this reaction to throw a doubt upon earlier views expressed by Glasstone *et al.*[8] of the resemblance of the transition state to quaternary ammonium salt produced. In this respect the present paper supports his view: The transition state is not as highly ionic as the quaternary ammonium salt.

Experimental

Materials. *N,N*-Dimethylaniline and its derivatives were prepared and purified as in our earlier work.[6] The purity was checked by glc in which only a single peak was observed. Methyl iodide was purified by the method of Cowley and Partington.[9] The purification procedure was repeated once a month. Various solvents used except acetonitrile were purified as in the previous paper. Acetonitrile was purified by the method of Coetzee *et al.*[10] The purification procedure was repeated once a week. The density of these solvents which were measured at a certain temperature agreed with the earlier values[11] within ±0.2%. Glc chart for solvents showed sufficient purity.

Apparatus and Kinetic Procedure. Pipettes were calibrated both with water and with each solvent, and burettes were calibrated with water. The experimental procedure of Rossell[7a] was used with the following modifications; (1) Aliquot portions withdrawn were analyzed for iodide by potentiometric titration with 0.005N to 0.01N silver nitrate and not with 0.02N silver nitrate as in the Volhard method. (2) Prevention of further reaction during the extraction was done by dilution with cold benzene rather than with light petroleum. (3) The reaction vessels were pyrex glass tubes which could be closed with a polyethylene plate in place of ampoules. Sealing could be omitted. Initial concentration of each reactant was 0.02—0.1M.

a) The Simple Kinetic Runs. The kinetics except for noted in the later section gave good second order rate constants in which the rate law is the simplest. When comparison was made of results obtained with independently prepared solutions, the reproducibility was within ±2% even in the worst case. Examples of the results are given in Fig. 1.

b) Kinetics Accompanying the Methanolysis of Methyl Iodide. Quaternization based on *N,N*-dimethylanilines in methanol gave good second order rate constants. The use of *N,N*-dimethyl-*m*-nitro aniline makes the kinetic run complicated, not because of the reverse decomposition reaction, but because of the slow rate of quaternization relative to the concurrent methanolysis of methyl iodide.[7b] However, analysis of the kinetic data through a way similar to our earlier paper[6] gave the rate constant with reasonable accuracy. The rate law used is

$$(\mathrm{d}x/\mathrm{d}t)_0 = k\cdot a\cdot b + k_{\mathrm{M}}\cdot a, \qquad (1)$$

where a and b are the initial concentrations of methyl iodide and *N,N*-dimethyl-*m*-nitroaniline, respectively, k is the second order rate constant, k_{M} is the first order rate constant of methanolysis of methyl iodide, and $(\mathrm{d}x/\mathrm{d}t)_0$ is the initial rate of the production of salt. Modification of equation (1) shows the linear relation between the term on the left hand side and b, *viz.*,

$$(\mathrm{d}x/\mathrm{d}t)_0/a = k\cdot b + k_{\mathrm{M}} \qquad (2)$$

Therefore k is given by the slope of this linear plot and

Table 1. The reaction rate for the quaternization based upon *N,N*-dimethyl-*m*-nitroaniline in methanol and the concurrent methanolysis rate constant of methyl iodide

	40°C	50°C	60°C
k, $\mathrm{M^{-1}\,hr^{-1}}$	0.0107	0.0273	0.0632
k_{M}, $\mathrm{hr^{-1}}$	4.96×10^{-4}	1.40×10^{-3}	3.51×10^{-3}

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[6] Y. Kondo, T. Matsui and N. Tokura, This Bulletin, **42**, 1037 (1969).

[7] a) In nitrobenzene, J. B. Rossell, *J. Chem. Soc.*, **1963**, 5183; H. Essex and O. Gelormini, *J. Amer. Chem. Soc.*, **48**, 882 (1926); b) In methanol, D. P. Evans, H. B. Watson and R. Williams, *J. Chem. Soc.*, **1939**, 1345; *ibid.*, **1939**, 1348; A. D. Harris and K. E. Weale, *ibid.*, **1961**, 146; c) In other solvents, W. C. Davies, *ibid.*, **1938**, 1865; R. A. Benkeser, C. E. DeBoer, R. E. Robinson and D.M. Sauve, *J. Amer. Chem. Soc.*, **78**, 682 (1956); W. C. Davies and R. G. Cox, *J. Chem. Soc.*, **1937**, 614.

[8] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York (1941), p. 419.

[9] E. G. Cowley and J. R. Partington, *J. Chem. Soc.*, **1938**, 977.

[10] J.F. Coetzee, G. P. Cunningham, D. K. McGuire and G. R. Padmanafhan, *Anal. Chem.*, **34**, 1139 (1962).

[11] J. Timmermans, "Physico - Chemical Constants of Pure Organic Compounds," Elsevier Publishing Com., Inc., Amsterdam (1950).

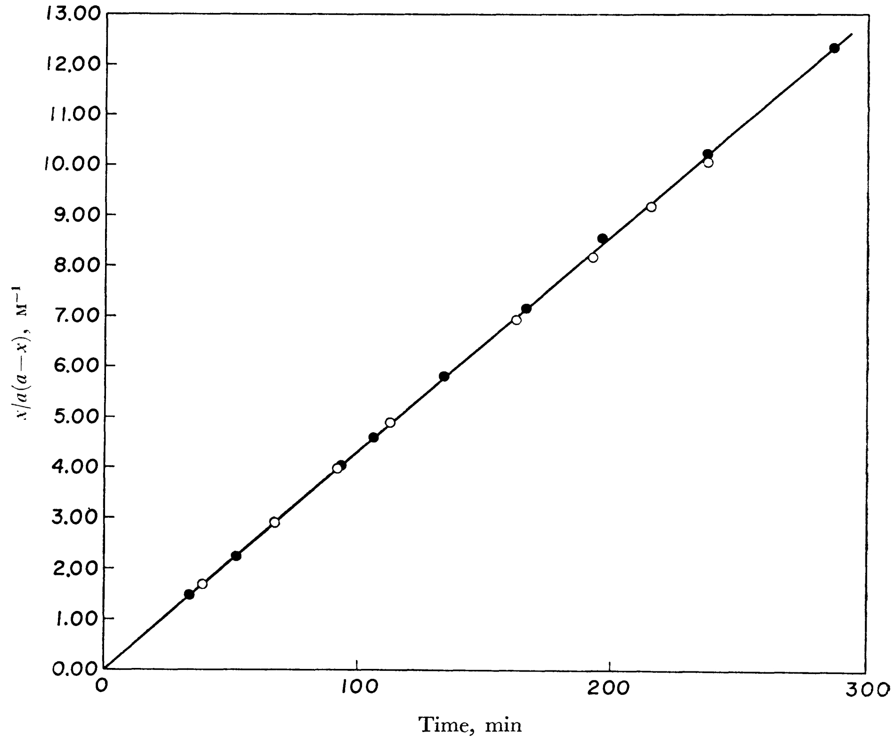

Fig. 1. Typical run for the reaction of *N,N*-dimethyl-*m*-toluidine with methyl iodide in acetonitrile at 40±0.1°C, ●: a=0.0945M, ○: a=0.02713M.

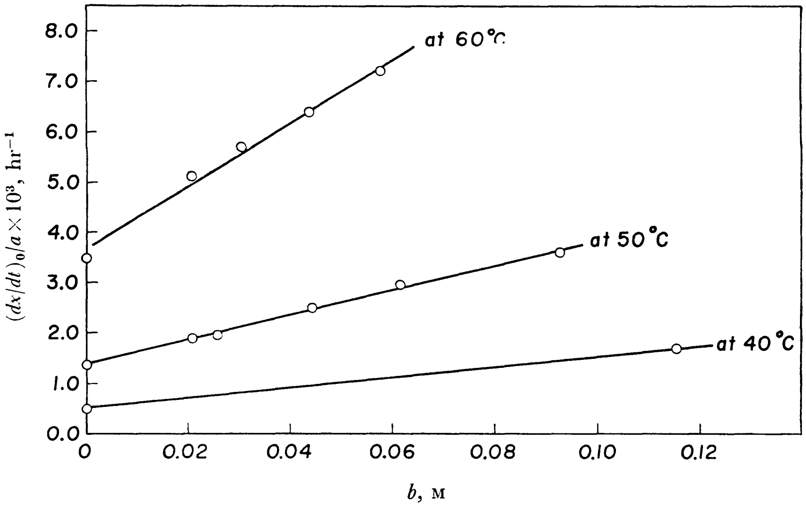

Fig. 2. The treatment of kinetic data for the reaction of *N,N*-dimethyl-*m*-nitroaniline with methyl iodide in methanol. See in text.

k_M by the intercept. Fig. 2 shows such plots. The results of k and k_M are given in Table 1. We believe that the accuracy of k by this method is no less than that of other methods. Both k and k_M show the Arrhenius relationship over the temperature range of experimental condition.

This type of correction was also made for the reaction of *N,N*-dimethyl-*m*-chloroaniline with methyl iodide. The reverse decomposition reaction might give a further complication, but it did not occur in methanol even at 70°C. The concentration of iodide at 20 half-lives period showed 100.3% completion for the reaction of *N,N*-dimethyl-*m*-toluidine with methyl iodide.

c) Kinetics Accompanying the Reverse Decomposition Reactions. Most of the present reactions show a rapid fall of the second order rate constants as the reaction proceeds. The higher the temperature and the more nonpolar the solvent is, the larger the decrease becomes.

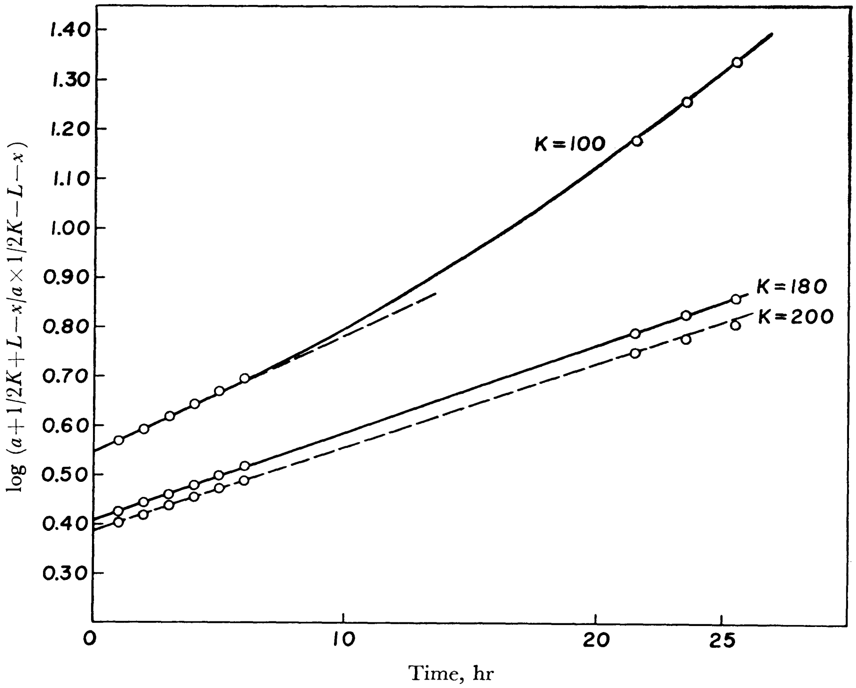

Fig. 3. Typical trial and error procedures of the treatment of kinetic data for the Menschutkin reaction containing the reverse decomposition of the salt. The reaction of dimethyl aniline with methyl iodide in nitrobenzene at 50°C.

The rate law is

$$dx/dt = k(a-x)^2 - k_d x \qquad (3)$$

where k_d is the first order rate constant for the reverse reaction based on ion-pair decomposition. The hypothetical equilibrium constant is

$$K = k/k_d. \qquad (4)$$

The use of Eqs. (3) and (4) gives

$$k \cdot t = 2.303/2L \log \{a+(1/2K)+L-x/a+(1/2K)-L-x\} \times \{a+(1/2K)-L/a+(1/2K)+L\}, \qquad (5)$$

where L is the parameter given by

$$L = \sqrt{1+4Ka} \,/\, 2K. \qquad (6)$$

The hypothesis used in the derivation might be proved to be right in terms of the linear relation between $\log\{a+(1/2K)+L-x/a+(1/2K)-L-x\}$ and time and the agreement of k obtained by the slope of this plot with k obtained from the initial slope of second order plot. The calculation for K was essentially the trial and error method, in which parameter K was adjusted so that the linear relation was obtained. The successive procedures are shown in Fig. 3. We could experimentally obtain the equilibrium point for some cases and show that the values obtained from the equilibrium point were in fair agreement with that from the hypothetical procedure. In the case of the reaction of *N*,*N*-dimethylaniline with methyl iodide in tetrahydrofuran (THF) at 50°C, for example, K through the former procedure is 0.432 and the latter value is 0.436. Even in acetonitrile, the most polar solvent in the present work, at 50°C, the decomposition of quaternary ammonium salt of *N*,*N*-dimethylaniline occurred, but in this case the degree of decomposition was *ca.* 2% after 100 hr and was too slow to obtain the value of K from the deviation of second order plot described above.

It is of interest that the rate of formation of iodide increases rapidly as soon as iodide precipitates and equilibrium is destroyed. These examples were observed in such solvents as benzene and THF. Measurement of k in the precipitation range was made on solutions ranging in concentration from *ca.* 0.08M to *ca.* 0.8M, but disagreement of each k value was over the experimental error as shown in Table 2. Thus the comparison for some nucleophiles in this solvent, was made with the same initial concentration.

Table 2. Dependence of k for a quaternization based on dimethylaniline in benzene at 50°C upon the initial concentrations of reactants (k in M^{-1} hr^{-1})

a	0.123	0.0890	0.820	0.194	0.0815	0.122
b	0.0459	0.0992	0.0862	0.194	0.768	0.0786
k	0.0260	0.0397	0.0612	0.0609	0.0778	0.0400

Results and Discussion

Tables 3 and 4 give results for reactions in various solvents at three to four temperatures. All reaction rate constants and equilibrium constants were calculated by the method of least squares and were corrected for the thermal expansion of the

TABLE 3. SUMMARY OF RATE CONSTANTS (k, in l mol^{-1} hr^{-1}) AT DIFFERENT TEMPERATURES IN VARIOUS SOLVENTS FOR QUATERNIZATION OF A BASE $R\cdot C_6H_4N(CH_3)_2$ WITH CH_3I

No.	R	30°C	40°C	50°C	60°C
		In CH_3CN			
1	p-CH_3	2.64	4.90	8.46	15.8
2	m-CH_3	1.345	2.57	4.66	8.24
3	H	0.913	1.725	3.12	5.83
4	m-Cl	0.105	0.208	0.396	0.772
5	m-NO_2	0.0180	0.0379	0.0767	0.143
		In $C_6H_5NO_2$			—
6	p-CH_3	1.62	3.06	5.60	9.79
7	m-CH_3	0.715	1.40	2.69	4.82
8	H	0.451	0.883	1.74	
9	m-Cl	0.0375	0.0809	0.176	0.365
10	m-NO_2	4.85×10^{-3}	0.0133	—	—
		In CH_3COCH_3			
11	p-CH_3	1.38	2.53	4.37	7.36
12	m-CH_3	0.731	1.325	2.30	4.16
13	H	0.492	0.925	1.58	2.81
14	m-Cl	0.0556	0.118	0.214	0.433
15	m-NO_2	9.78×10^{-3}	0.0177	0.0406	0.0674
		In CH_3OH			
16	m-CH_3	—	0.874	1.96	—
17	H	—	0.647	1.42	—
18	m-Cl	0.0265	0.0752	0.175	—
19	m-NO_2		0.0107	0.0273	0.0632
		In $C_6H_5CH_2OH$			
20	m-CH_3	0.833	1.79	3.72	7.13
21	H	0.644	1.32	2.76	5.36
22	m-NO_2	—	0.022	0.0499	—
		In THF			
23	p-CH_3	—	0.466	0.85	1.60
24	m-CH_3	0.158	0.304	0.493	0.714
25	H	—	0.168	0.327	0.528
26	m-Cl	—	0.0121	—	—
		In C_6H_6			
27	p-CH_3	—	0.099	—	—
28	m-CH_3	—	0.039	0.059	0.10
29	H	0.015	0.028	0.040	—
		In $CH_3COC_2H_5$			
30	p-CH_3	0.870	1.57	—	—
31	m-CH_3	0.464	0.852	1.55	—
32	H	—	0.560	1.03	—
		In C_6H_5Br			
33	m-CH_3	—	—	0.229	0.44

TABLE 4. SUMMARY OF EQUILIBRIUM CONSTANTS (K in l mol^{-1}) FOR QUATERNIZATION OF A BASE $R\cdot C_6H_4\cdot N(CH_3)_2$

Temperature	p-CH_3	m-CH_3	H	m-Cl	m-NO_2
		In CH_3CN			
60°	—	~1000	~1000	~50	3.7
		In $C_6H_5NO_2$			
30°	—	—	—	8.9	1.0
40°	—	—	—	5.0	0.44
50°	2000	450	180	2.3	—
60°	1000	200	66.7	1.7	0.22
		In CH_3COCH_3			
40°	—	—	—	5.2	—
50°	—	360	180	2.8	0.165
60°	~200	80	40	1.36	0.1
		In THF			
30°	—	2.66	—	—	—
40°	~4	1.84	1.00	0.041	—
50°	~2	1.17	0.434	—	—
60°	0.98	0.494	0.254	—	—
		In C_6H_6			
50°	—	0.40	—	—	—
60°	—	0.089	—	—	—
		In C_6H_5Br			
50°	—	0.75	~0.29	—	—
60°	—	0.33	—	—	—

solvent. The values of the equilibrium constants K were unfortunately the apparent values for the following reactions.

$$R\cdot C_6H_4\cdot N(CH_3)_2 + CH_3I \overset{K}{\rightleftarrows} R\cdot C_6H_4\cdot N(CH_3)_3{}^+\cdot I^-\text{(ion-pair)}$$

But the conclusion drawn from the relation based upon K may be the same.

The Unitary Term of k or K. It is necessary to compare the so-called unitary terms[12] of k or K, k_u or K_u when the effects of solvents on k or K and ζ are discussed in detail. The unitary part of k for the reactions under consideration is represented by

$$k_u = k \times 1000 d_{solv}/M_{solv} \qquad (7)$$

where k is the rate constant in common use whose dimension is M^{-1} time^{-1}, and d_{solv} and M_{solv} are the density of the solvent and the molecular weight of the solvent, respectively. The relation between k_u in Eq. (7) and the representation of k through the theory of absolute reaction rate,[13] given by the equation

$$k = k_g{}' \times r_A\cdot r_B/r_{M\ddagger} \times V_{solv.}/RT \qquad (8)$$

is self-evident, *viz.*,

$$k_u = k_g{}'' \times r_A\cdot r_B/r_{M\ddagger} \qquad (9)$$

In these equations r_A, r_B, and $r_{M\ddagger}$ are the activity coefficients, based upon the solvent standard state, of reactant amine, of methyl iodide, and of the activated complex of the transition state, respectively.

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[12] D. W. Gurney, "Ionic Processes in Solution," Dover Publication Inc., New York (1953), Chapter 6.

[13] Y. Kondo and N. Tokura, This Bulletin, **40**, 1433 (1967).

The unitary values of the activation parameters, $\Delta H_u^{\neq 0}$ and $\Delta S_u^{\neq 0}$ are given by

$$\Delta H_u^{\neq 0} = -\mathrm{R}T - \mathrm{R}\partial \ln k/\partial(1/T) - \mathrm{R}\partial \ln \mathrm{d}/\partial(1/T) \quad (10)$$

$$\Delta S_u^{\neq 0} = -\mathrm{R} - \frac{\mathrm{R}}{T}\partial \ln k\cdot \mathrm{d}/\partial(1/T) + \mathrm{R}\ln k_u - \mathrm{R}\ln\frac{\kappa T}{h} \quad (11)$$

where κ and h are Boltzman and Planck constants respectively, k_u being independent of the composition of the solution.[12] This correction for k mainly contributes to the change of entropy.

The essential point of the correction is in the choice of the standard state. The appropriate value for k is one mole per liter of solvent and that for k_u one mole per one mole of solvent. By comparing k_u for one solvent with that for others, the effects of solvents on the reaction rates and ζ may be discussed in terms of the commonly used activity coefficients through Eq. (9). All of the data will, therefore, be treated by using k_u in place of k. The above treatment is of course applied for the equilibrium constant K. The expression of K_u is

$$K_u = K_g' \times r_A \cdot r_B / r_{A^+\cdot B^-} \quad (12)$$

The Effects of Variations in Uncharged Nucleophiles on the Measure of k_u to Solvent Variations, ζ. The treatment is essentially the same as given previously.[6] The difference of ζ among nucleophiles arises from interaction term of the substituent variable and the solvent variable. Existence of the linear free energy relationship concerning the substituent change is necessary in order to treat the data in terms of this method. It is shown in Fig. 4. The expression of ζ for substituted dimethylanilines is defined by

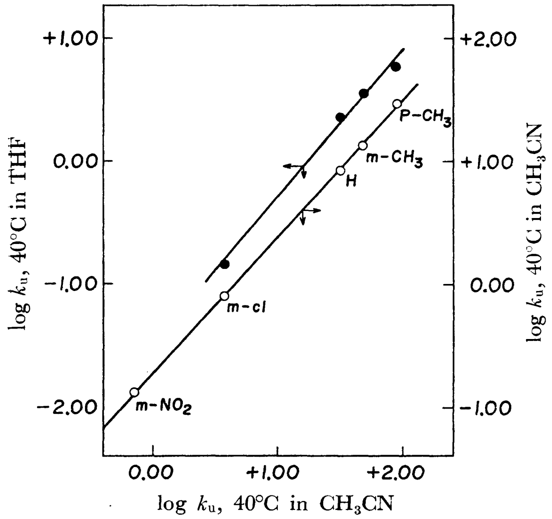

Fig. 4. The representation of the linear free energy relationships with respect to substituents.

$$\zeta = \delta_S \log k_u^X / \delta_S \log k_u^H \quad (13)$$

where δ_S means the differential with respect to the variations in solvents. The plot for this treatment is shown in Fig. 5, in which the slope gives the value of ζ. Deviation from this plot in some solvents is over the experimental error. But there is an approximate tendency for the dependence of ζ on the substituent. When the substituent is more electron donating, the value of ζ become smaller. This is illustrated in Fig. 6. The rate of reaction obtained by using a reactant with electron withdrawing substituent is more sensitive to solvent changes than others. In other words, the interaction constant between substituent variable and solvent variable has a positive value. The reason for the interaction between substituent variable and solvent variable might be interpreted in the following way. Equation (9) shows that these differences in ζ are not attributed to the effects of solvents on r_B, but to those on r_A or $r_{M^{\neq}}$, because by the first approximation the dependence of r_B on solvent change does not affect such a slope. Thus the substituent effect on the activity coefficients of either the reactant nucleophiles or of the activated complexes is somewhat modified by the nature of the solvent. The behavior is attributed to the latter for the following reasons. Firstly the modified Brϕnsted plot of $\delta_R \log k_u$ *versus* $\delta_R \log K_u$ has a relatively smaller slope than 1.00. Secondly the substituent effect in solvents with greater slopes is larger (see later section).

In terms of the solvent dependence of the Hammett's ρ value this explanation may be more clarified. That the slope of ζ *versus* σ has in general a positive value means that the value of ρ in more nonpolar solvent (in which the rate is slower) is more negative than that in polar solvent. There is a clear example of such a case; the difference of ρ in acetonitrile and that in methanol. The following equation which is derived from Eq. (9) will be applied.

$$\rho^{CH_3CN}\cdot\sigma_X = \rho^{CH_3OH}\cdot\sigma_X + \log\left({}^{CH_3CN}r_{AX}^{CH_3OH} / {}^{CH_3CN}r_{AH}^{CH_3OH}\right) - \log\left({}^{CH_3CN}r_{M^{\neq}X}^{CH_3OH} / {}^{CH_3CN}r_{M^{\neq}H}^{CH_3OH}\right) \quad (14)$$

In this equation ρ^{CH_3CN}, ρ^{CH_3OH}, and σ_X show Hammett's ρ in acetonitrile, in methanol, and substituent constant respectively. ${}^{CH_3CN}r_{AX}^{CH_3OH}$, ${}^{CH_3CN}r_{AH}^{CH_3OH}$, ${}^{CH_3CN}r_{M^{\neq}X}^{CH_3OH}$, and ${}^{CH_3CN}r_{M^{\neq}H}^{CH_3OH}$ denote the relative activity coefficient of the reactant, substituted amine and unsubstituted amine, and that of the activated complex with and without substituent, respectively. If the difference in quantity between ρ^{CH_3CN} and ρ^{CH_3OH} is attributed to the second term in Eq. (14), the relation of $|\rho|^{CH_3OH} < |\rho|^{CH_3CN}$ would be obtained because the solvation by methanol through hydrogen bonding will be diminished by the substitution

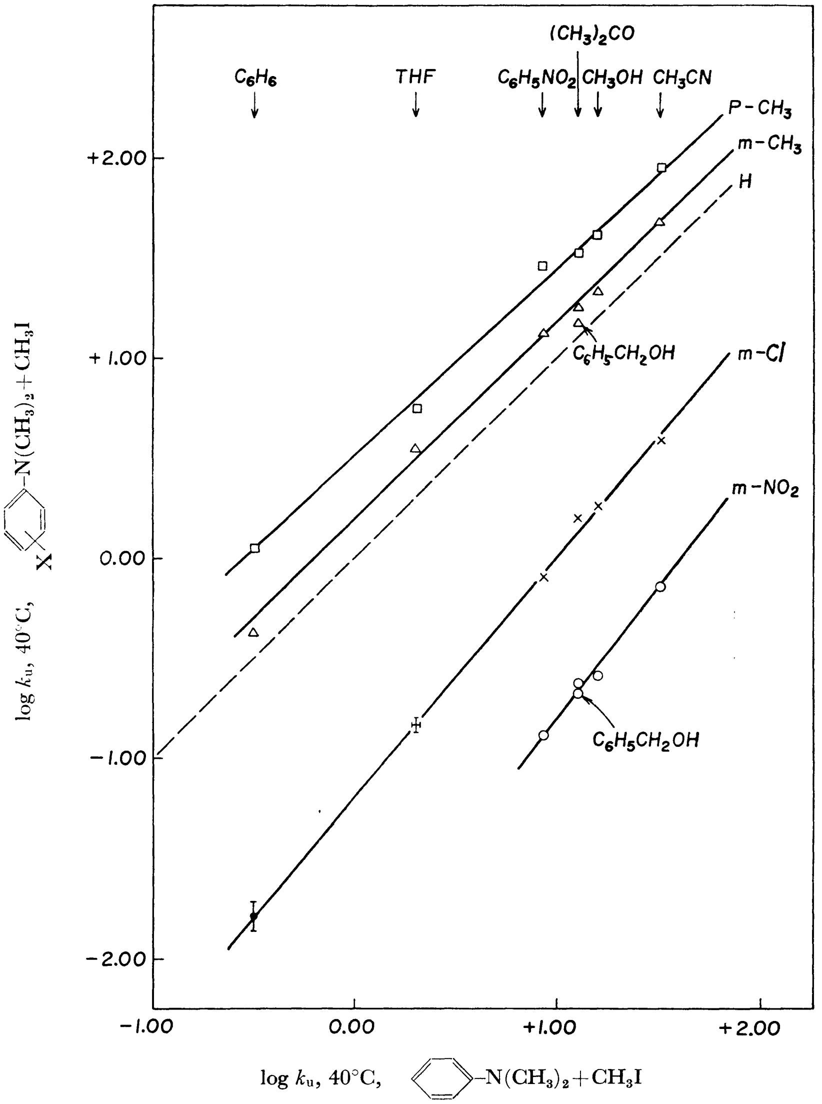

Fig. 5. The dependence of ζ on a few substituted nucleophiles at 40°C.

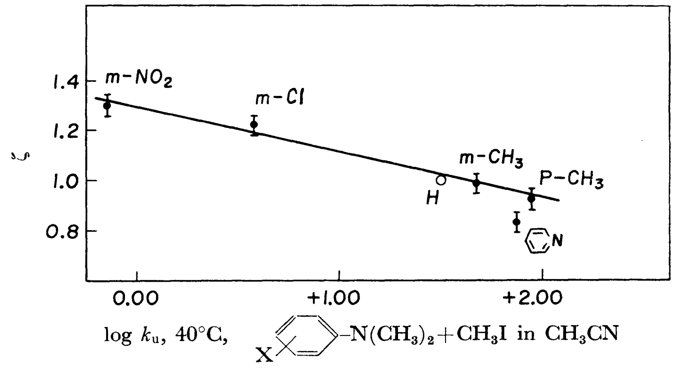

Fig. 6. The relationship between ζ and substituent variable.

of electron withdrawing group. The data show that this is not true unless the electron donating group (m-CH$_3$, p-CH$_3$) is introduced where a little downward deviation is observed (Fig. 5). The levelling off through the factor as expressed by the second factor in the right hand side of equation (14) was observed in liq. SO$_2$ which has strong solvation with amine bases.[14] A similar levelling off behavior is reported in ionizations of phosphines.[15]

Thus the substituent effect on ζ (Fig. 6) should result from the dependence of $\delta_R \log r_{M^{\ne}}$ on the solvent changes, and the deviation from these plots (Fig. 5) should be attributed to the dependence of $\delta_R \log r_A$ on the solvent changes. When pyridine is used as a nucleophile, the large deviation with regard to methanol (Fig. 7) clearly shows the existence of hydrogen bonding between pyridine and methanol.[16] The degree of divation expresses the difference between r_{Py} and r_{DMA} in methanol. For example, the relation of log $r_{DMA}^{CH_3OH}/r_{Py}^{CH_3OH}=0.70$ exists at 40°C.

It is of interest to examine the substituent effects on $\delta_S\,\Delta S_u^{\ne}$, the differences in $\Delta S_u^{\ne}$ among solvents. From the above explanation for ζ-δ relationship $\delta_S\,\Delta S_u^{\ne}$ must be larger by using the more electron withdrawing substituent. This is illustrated by the data in Table 5. Thus it also accounts for the fact that the interaction constant has positive value.

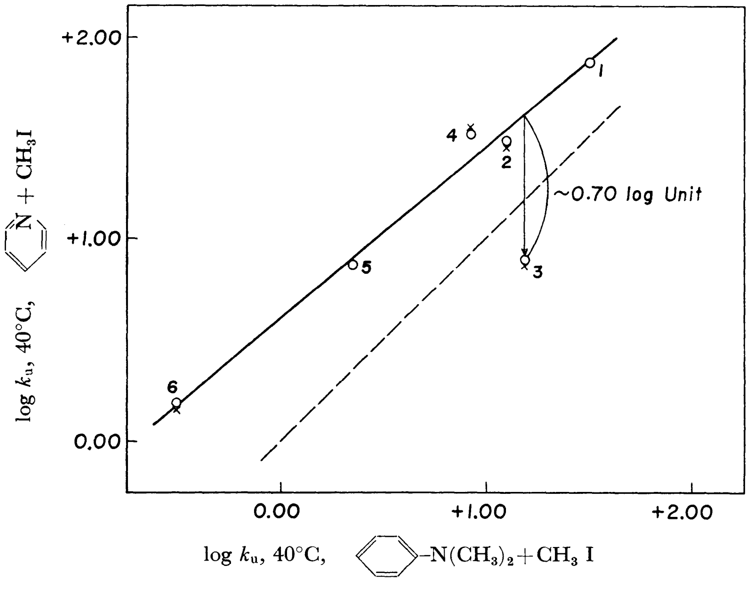

Fig. 7. The difference in ζ value between pyridine and dimethylaniline. The data of quaternization of pyridine are taken from the two previous reports. ○ is from N. Tokura and Y. Kondo, This Bulletin, **36**, 400 (1963), × is from H. Hartmann, H. Kelm and G. Rinck, *Z. Phys. Chem.*, **44**, 335 (1965). (1) CH$_3$CN, (2) (CH$_3$)$_2$CO, (3) CH$_3$OH, (4) C$_6$H$_5$NO$_2$, (5) THF, (6) C$_6$H$_6$.

TABLE 5. DIFFERENCE IN $\delta_s\,\Delta Su^{\ne}$, 50°C AMONG SOME SUBSTITUTED DIMETHYLANILINES

	p-CH$_3$	m-CH$_3$	H	m-Cl	m-NO$_2$
CH$_3$CN	0.00(−31.12)[a]	0.00(−31.56)[a]	0.00(−31.61)[a]	0.00(32.68)[a]	0.00(−33.84)[a]
(CH$_3$)$_2$CO	−3.58	− 3.78	− 4.51	−1.25	− 4.19
C$_6$H$_5$NO$_2$	−1.18	+ 0.15	+ 0.37	+3.44	+ 2.81
CH$_3$OH	+6.76[b]	+ 7.75[c]	+ 7.90[c]	+14.68	+14.22
THF	−2.9	−11.5	−10.5	+11.3	—

a) Values in parentheses represent the unitary term of the activation entropy in acetonitrile.
b) From the data given by Evans *et al.*, Ref. 7b.
c) Our data for m-CH$_3$ and H presented in Table 3 in this solvent are in fair agreement with the data by Evans *et al.* The activation parameters were calculated from both our data and theirs.

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

[15] W. A. Henderson, Jr., and S. A. Buckler, *J. Amer. Chem. Soc.*, **82**, 5794 (1960).

[16] E. Becker, *Spectrochim. Acta*, **17**, 436 (1961).

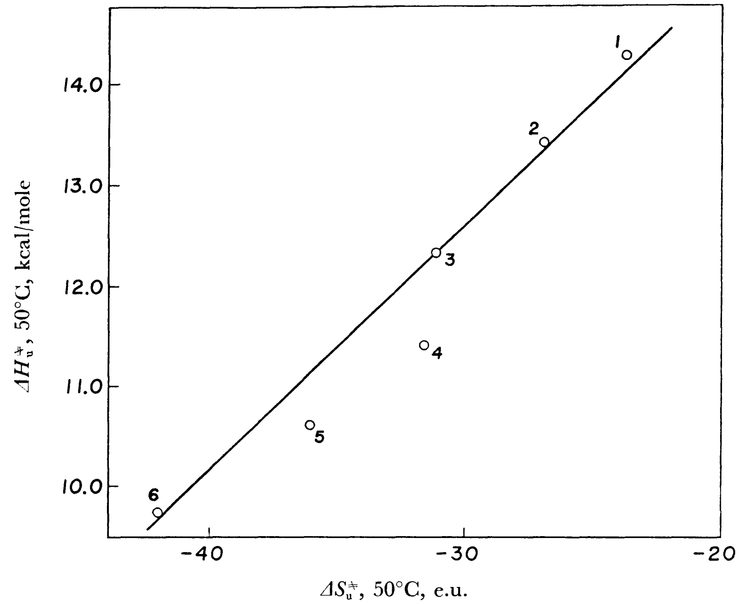

Fig. 8. The plot of $\Delta H_u^{\ddagger}$ *versus* $\Delta S_u^{\ddagger}$ for a reaction of *N,N*-dimethylaniline with methyl iodide.

There is another reason why the above tendency is denoted as the only "approximate" tendency at all. The order of the relative rates with respect to the solvent will be modified by the change of temperature. The degree of this modification is illustrated in the plot of $\Delta H_u^{\ddagger}$ *versus* $\Delta S_u^{\ddagger}$. Unless the so-called isokinetic linear relationship between these values exists, this relative order is modified. Figure 8 shows the approximate linearity between these two values.

The dependence of ζ on substituents which was explained on the basis of the above electrostriction theory will predict the variation of the pressure dependence of rates with the substitution of nucleophile. The substitution by the electron withdrawing groups will influence the pressure effect of rate by larger amount. In other words, the dependence of the volumes of activations on nucleophiles will be larger in so-called nonpolar solvents than in polar solvents. The solvent dependence of Hammett's ρ for the equilibria of a series of benzoic acids has been attributed to the activity coefficients of the carbonium ions.[6] For this type of equilibrium the pressure effect will be decreased by using the acids substituted by electron withdrawing groups. This was experimentally proved by Fischer *et al.*[17]

There is a case where the solvent effects of the nucleophilic tendency are mainly attributed to the relative activity coefficients of charged species i, $\delta_S \log r_i$. That is the Finkelstein reaction.[18] Thus the difference between charged and uncharged nucleophiles in the solvent dependence of the rate is clear. For the fomer the relative activity coefficients of the reactant bases are the main factor in determining the solvent dependence of ζ, but for the latter those of the activated complexes mainly affect the relative order of rates with solvent changes. Thus the compilation of both charged and uncharged reactants as nucleophiles is questionable, if the solvent used is taken into consideration.

Difference in the Factor Influencing the ζ between Methyl Iodide and Methyl Picrate. According to the compilation by Reinheimer *et al.*[19] the modification of the sensitivity of the rates to solvent changes caused by using EtI in place of EtBr for quaternization of pyridine may be made by a negligible amount at least in aromatic solvent. However, comparison of the present data with our previous data[6] shows that the ζ are markedly influenced by

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[17] A. Fischer, B. R. Mann and J. Vaughan, *J. Chem. Soc.*, **1961**, 1093.

[18] N. Tokura, preprint at the Symposium of Oxidation-Reduction in Non-Aqueous Solvent Systems, Kyoto, Oct., 1968, from the data of A. J. Parker in "Advances in Physical Organic Chemistry," Vol. 5, ed. by V. Gold, Academic Press, London, New York (1967), p. 173. Table 3 in this print is based on the reliable fact that the levelling off on anion solvation exists in these solvents, and not on the fact that in dipolar aprotic solvents the desolvation occurs with respect to small anion. *Cf.* R. F. Rodewald, K. Mahendran and R. Fuchs, *J. Amer. Chem. Soc.*, **90**, 6698 (1968).

[19] J. D. Reinheimer, J. D. Harley and W. W. Meyers, *J. Org. Chem.*, **28**, 1575 (1963).

the change of $CH_3Pic.$ to CH_3I. Figure 9 illustrates this situation. It is observed that the quaternization of *N*,*N*-dimethylaniline with methyl picrate is less sensitive to the variations in solvents than that with methyl iodide. The relation of $\zeta < 1.0$ is observed for methyl picrate. According to the interpretation of rate by the transition state theory (Eq.(9)) such a diffence should be attributed to the difference in the dependence on solvent variations between r_{CH_3I} and r_{CH_3Pic} or between $r_{M^{\neq},I}$ and

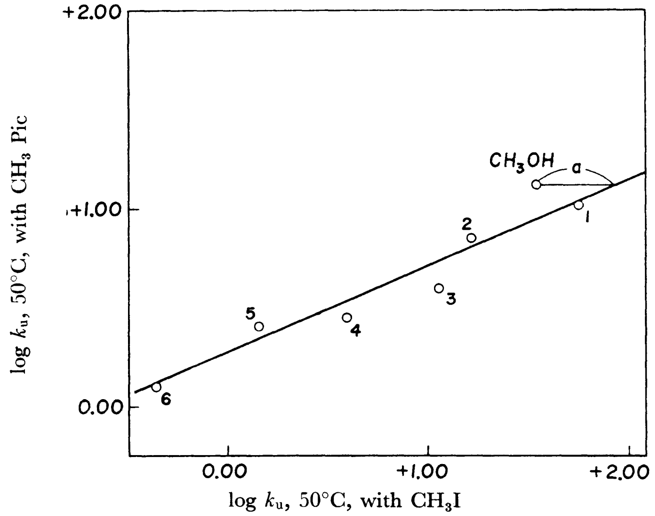

Fig. 9. The difference in ζ between the reaction of *N*,*N*-dimethylaniline with methyl iodide and that with methyl picrate. (1) CH_3CN, (2) $C_6H_5NO_2$, (3) $CH_3COC_2H_5$, (4) THF, (5) C_6H_5Br, (6) C_6H_6.

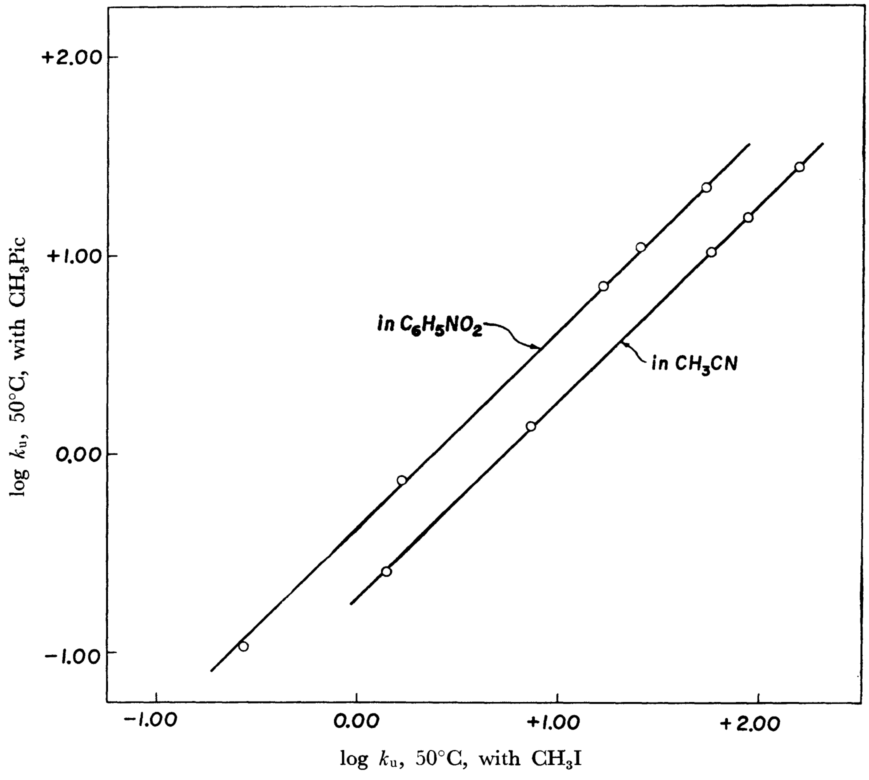

Fig. 10. The small difference in the substituent effects between the reactions with CH_3I and those with CH_3Pic both in $C_6H_5NO_2$ and in CH_3CN.

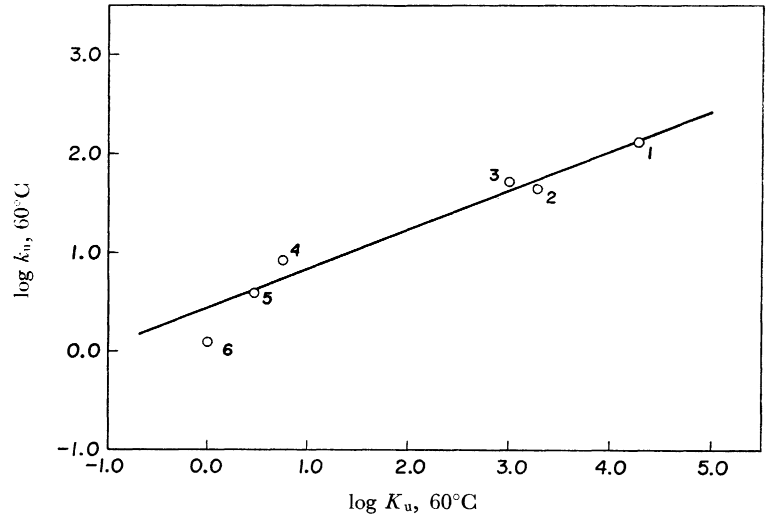

Fig. 11. The relationship between δ_S log k_u and δ_S log K_u for the relation of *m*-methyl-*N*,*N*-dimethylaniline with methyl iodide.
(1) CH_3CN, (2) $C_6H_5NO_2$, (3) $(CH_3)_2CO$, (4) THF, (5) C_6H_5Br, (6) C_6H_6.

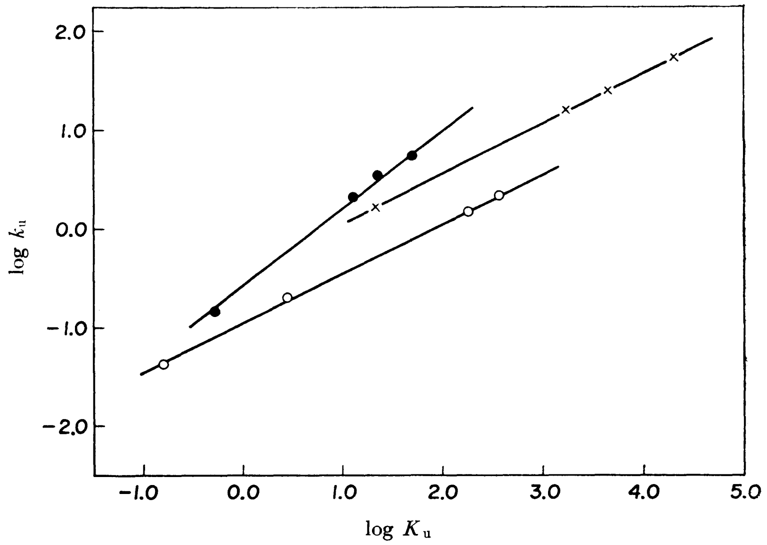

Fig. 12. Some of the modified Brønsted plots.
○ in $(CH_3)_2CO$ at 50°C
● in THF at 40°C
× in $C_6H_5NO_2$ at 50°C

$r_{\mathrm{M}^{\neq},\mathrm{Pic}}$. Although we have no data on $r_{\mathrm{CH_3I}}$ and $r_{\mathrm{CH_3Pic}}$ in various solvents, the existence of an approximately linear relationship as shown in Fig. 9 explains this behavior in terms of the difference in solvent dependence between $r_{\mathrm{M}^{\neq},\mathrm{I}}$ and $r_{\mathrm{M}^{\neq},\mathrm{Pic}}$. Our explanation is further supported by the fact that in the picrate there is large negative charge distribution and no net charge at any one atom.[20] The combination of this fact with the electrostriction theory leads to the following explanation; in the case of the transition state for the reaction with methyl picrate the negative charge distribution may be large. Thus, $r_{\mathrm{M}^{\neq},\mathrm{Pic}}$ may not become smaller even in polar solvents as $r_{\mathrm{M}^{\neq},\mathrm{I}}$ does, while in non-polar solvents the reverse relation may be true. There is less entropy loss accompanied with the electrostriction of solvent molecules along the reaction coordinate.

That the "completely" linear relation does not exist means that there is the difference in solvent effects between $r_{\mathrm{CH_3I}}$ and $r_{\mathrm{CH_3Pic}}$. A large devia-

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[20] E. Grunwald and E. Price, *J. Amer. Chem. Soc.*, **86**, 4517 (1964).

tion is observed in methanol. The experimental error of reaction rate was less than 0.02 log unit. The data of r_{CH_3I} in acetonitrile and in methanol at 25°C,3) $\log r_{CH_3I}^{CH_3CN} - \log r_{CH_3I}^{CH_3OH} \simeq 0.35$ is in accordance with this deviation 0.35 which is given as the distance, *a* in Fig. 9. This shows that the relation of $\log r_{CH_3Pic}^{CH_3CN} \simeq \log r_{CH_3Pic}^{CH_3OH}$ exists.

For both cases of CH_3Pic and CH_3I the relation of $|\rho|^{C_6H_5NO_2} > |\rho|^{CH_3CN}$ exists and in each solvent the differences in the substituent effects between CH_3I and CH_3Pic is apparently equal, as shown in Fig. 10. This seems to be inconsistent with the above discussion. But we can explain the relation similarly as in the previous section, if we assume that the substituent effects on the stability of each activated complex are almost independent of the leaving group.

The Nature of the S_N2 Transition State. The concept of Glasstone *et al.*8) about the stereochemistry of the S_N2 transition complex has been criticized by Rossell7a) and by Weale.21) Weale *et al.* studied the volume of activation for a reversible Menschutkin reaction, $CH_3I + C_6H_5\text{–}N(CH_3)\cdot(C_2H_5) \rightleftarrows C_6H_5\text{–}N(CH_3)_2{}^{\delta+}\cdot C_2H_5\cdots I^{\delta-}$ in acetone and showed that in absolute value the volume of activation is less than the change of volume accompanied with an equilibrium between reactant and product as ion-pair. Rossell criticized the relevance of the view of Glasstone *et al.* which was concluded from the similarity of $\varDelta S^\circ$ and $\varDelta S^{\neq}$ found in the reaction of dimethylaniline with methyl iodide in nitrobenzene. According to Rossell, "such a similarity is the exception rather than the rule."

If the solvent effects on the reaction rates are mainly attributed to the differences in the activity coefficients of the activated complexes among the variations of solvents, the dependence of k on the variations in solvents should be correlated with the dependence of K on those variations, and the slope of $\delta_S \log k_u$ *versus* $\delta_S \log K_u$ must show the degree of charge separation in the transition state. For the reaction of *m*-CH_3-DMA with CH_3I at 60°C Fig. 11 shows the approximate linear relation between $\delta_S \log k_u$ and $\delta_S \log K_u$ which has a relatively small slope. It can be considered that the nature of the transition state for the reactions is not very similar to that of the final product, quaternally ammonium salt. This result should be correlated with any relationship between $\delta_R \log k_u$ and $\delta_R \log K_u$ in each solvent. Figure 12 which shows a nearly linear relation22) among these values reflects the fact23) that the equilibrium between ions and ion-pairs is quite insensitive to the substituent effects. Figure 12 also shows the insensitivity of the reaction rate to substituent changes relative to that of the equilibrium constant.

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21) K .E. Weale, "Chemical Reactions at High Pressures," E. F. N. Spon Ltd., London (1967), p. 143.

22) The modified Brønsted type. This is an example for usually accepted generalization where relatively good correlation of carbon nucleophilicity exists in a series of bases with their carbon basicity, instead of with hydrogen basicity. See Ref. 2.

23) T. T. Denison and J. B. Ramsey, *J. Amer. Chem. Soc.*, **77**, 2615 (1955); G. W. Ceska and E. Grunwald, *ibid.*, **89**, 1371 (1967); N. N. Lichtin and P. D. Bartlett, *ibid.*, **73**, 5530 (1951).