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Solvent Effects on ρ Values of the Hammett Equation. II.[1]

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The rates of reactions of *N,N*-dimethylbenzylamine or its derivatives with methyl iodide in fourteen nonaqueous solvents at 30°C have been studied. The effects of the solvents on reactivities and Hammett's ρ values have been examined. For establishing the relationship between ρ and solvent polarity, a unique solvent parameter for reactivity ξ_0 was defined, which measures the relative solvent polarity in determining the order of reaction rate with respect to solvent. There is a linear relationship between ρ and ξ_0, but protic and aromatic solvents show deviation from this relation in a particular way. The liner relationship provides a common basis for explaining both substituent and solvent effects. This suggests the importance of solvent reorientation accompanied by an activation process. It is argued that the hydrogen-bonded solvation of reactant amines and solvation of the leaving group are responsible for abnormal behaviors in protic and aromatic solvents.

Since the proposal of Hammett's equation, evidence has accumlated which indicates that the Hammett ρ value is not independent of solvent.[1,2] This indicates the importance of external factors contributing to the transmission of substituent effects. Sufficiently accurate data for a discussion of the effects of solvents on the ρ value have, however, been only recently reported. Wilcox and Leung examined the mode of substituent effects transmission and concluded the dominance of field effects.[3] For esterification of substituted benzoic acids by diphenyl diazomethane, Buckley *et al.* discussed the change of ρ values with solvent in terms of dielectric constant of solvent.[4] At least, the existence of solvent effects on the reaction constant cannot be expected from a purely inductive model.

On the other hand, solvent effects on reactivity have been discussed from some particular aspects by many authors. The classical treatment is based on the assumption that the solvent is a continuous dielectric medium and only provides an electrostatic field where the reaction can take place. The results show that such a classical concept cannot explain the solvent dependence on reactivity. Various ideas have been developed to account for the confusing solvent effects on rates and equilibria.[5] Many attempts have been made to correlate the rate constant with solvent solubility parameters.[6] However, attention has recently been focused on the importance of solvent reorientation which is associated with the activation process.[5,7] We think that in this concept there is a common basis in establishing the simple explanation for both substituent and solvent effects.

In order to gain pertinent information it is necessary to study a reaction system where the mechanism of reaction is least complicated. The change of mechanism accompanied by reactant variation seems to make the problem complicated.[8] Thus, it is of interest to study the solvent effects on ρ values for the reaction of S_N2 type. A method of treatment is given in previous papers.[1,9] In the present paper, we report the results of a study of solvent effects on ρ values for reactions of *N,N*-dimethylbenzylamine, (DMBzA) or its derivatives with methyl iodide. This system was chosen for the need of determining the rate constant in a wider range of solvents than in previous works.

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[1] Part I: Y. Kondo, T. Matsui, and N. Tokura, This Bulletin, **42**, 1037 (1969).

[2] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y. (1963), p. 178.

[3] C. F. Wilcox and C. Leung, *J. Amer. Chem. Soc.*, **90**, 336 (1968).

[4] A. Buckley, N. B. Chapman, M. R. J. Dack, J. Shorter, and H. M. Wall, *J. Chem. Soc., C*, **1968**, 631.

[5] C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Amer. Chem. Soc.*, **89**, 2063 (1967), and references cited.

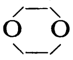
[6] A. P. Stefani, *J. Amer. Chem. Soc.*, **90**, 1694 (1968).

[7] G. Kohnstam, "The Transition State," The Chemical Society, Burlington House, London (1962), p. 179.

[8] E. Tommila *et al.*, *Ann. Acad. Sci. Fennicae II*, **91**, 10 (1959); A. Kivinen, *ibid.*, **108**, 33 (1961).

[9] T. Matsui and N. Tokura, This Bulletin, **43**, 1751 (1970).

Table 1. Rate constants for N,N-dimethylbenzylamine derivatives at 30.0°C[a]

NO.	σ[b]	m-CH_3 −0.069	H 0.000	m-Cl +0.373	m-NO_2 +0.710	p-OCH_3 −0.268	p-Cl +0.227	p-NO_2 +0.778
1	CH_3CN	230	206	97.0	48.4	311	121	43.6
2	$(CH_3)_2CO$	114	104	46.2	24.0	174	62.1	22.7
3	$C_6H_5NO_2$	145	125	46.6	19.0	223	67.0	20.6
4		24.0	22.2	7.7	3.05	38.2	10.6	2.40
5	THF	24.0	20.8	8.18	3.95	37.8	11.3	3.24
6	C_6H_6	8.13	7.07	2.36	0.751	13.2	3.04	0.595
7	CS_2	0.850	0.628	0.130	0.0288	1.31	0.210	0.0250
8	c-C_6H_{12}	0.0263	0.020	0.0030[c]	—	0.056	0.00405[c]	—
9	$C_6H_5CH_3$	5.17	4.31	1.44	0.459	8.10	1.80	0.348
10	C_6H_5Cl	16.0	12.7	3.46	0.939	23.2	5.18	0.888
11	C_6H_5Br	20.5	16.8	4.75	1.27	30.9	7.00	1.22
12	CH_3OH	9.90	9.32	5.40	3.33	12.4	6.71	3.27
13	C_2H_5OH	7.02	6.35	3.41	1.88	10.5	4.23	1.90
14	i-PrOH	5.16	4.58	2.17	1.07	7.13	3.00	1.15

a) Average value of rate constants in M^{-1} hr^{-1}.
b) Ref. 11.
c) Rate constant obtained by taking into account autocatalysis of quaternary salt (See Experimental).

Results and Discussion

Rate data for a series of N,N-dimethylbenzylamine for quaternisation by methyl iodide in various solvents are given in Table 1. All the rate constants were calculated by the method of least squares and were corrected for thermal expansion of solvent.

It is necessary to compare the unitary term of rate constant k_u in each solvent, instead of rate constant, in order to examine solvent effects on reactivities.[9] Hammett reaction "constant" is, however, a unitary quantity and independent of solution composition. In order to establish the relationship between ρ and solvent polarity, a solvent parameter for reactivity ξ_0 is defined by

$$\xi_0 = \log k_{u,0}/r_{CH_3I} - \log k_0{}^0 = \log r_{A0} - \log r_{M^{\neq}0} \qquad (1)$$

where r_{CH_3I}, r_{A0} and $r_{M^{\neq}0}$ are the activity coefficients based upon the solvent standard state of methyl iodide, unsubstituted amine and activated complex without substituent, respectively. $k_0{}^0$ denotes the hypothetical rate constant in gas phase of the reaction of unsubstituted amine with methyl iodide which is given by[10]

$$k_0{}^0 = \kappa \cdot K_0{}^{\neq}/R \cdot p^0_{A0} p^0_{B0}/p^0_{M^{\neq}0} \qquad (2)$$

Application of the Hammett equation to the data of Table 1, using σ values given by Brown andMcDaniel[11] gives the results in Table 2.[12] There is a discrepancy between ρ^m and ρ^p. Typical plots of the data are shown in Fig. 1. The results of log $k_{u,0}/r_{CH_3I}$ or ξ_0+log $k_0{}^0$ are given in Table 2. The activity coefficient of methyl iodide in various solvents were estimated from regular solution theory.[13] The r_{CH_3I}-values obtained in this way are compared with those determined experimentally in Table 3. The agreement between the calculated and found values is within the limit of analysis.

Relationship between ρ and ξ_0. The variation in ξ_0 with solvent is required for the changes of ρ values with solvents. Although in all solvents ρ^m is more negative than ρ^p, the mode of variation in ρ with ξ_0 is the same. The situation is illustrated by the plot of ρ against ξ_0 in Fig. 2. With respect to many solvents except for aromatic and alcoholic solvents there is a linear relationship between ρ and ξ_0. There is

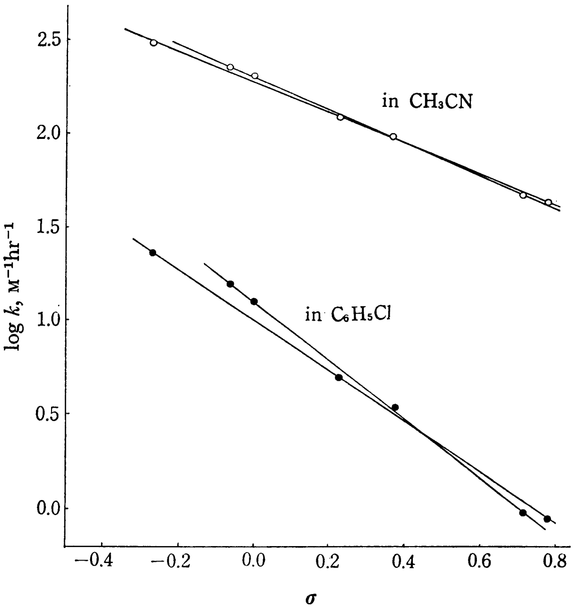


Fig. 1. Hammett plots of the reaction of N,N-dimethylbenzylamines with methyl iodide; ○, in CH_3CN; ●, in C_6H_5Cl.

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10) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, Inc., New York, N. Y. (1941), p. 400.

11) H. C. Brown and D. McDaniel, *J. Org. Chem.*, **23**, 420 (1958).

12) The referee commenting on the choice of substituent variables suggested that σ^0 should be chosen rather than σ for the present reaction system. However, the kinetic data correlate better with σ than with σ^0.

13) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, N. J. (1962), p. 102.

TABLE 2. HAMMETT EQUATION CORRELATIONS

No	Solvent	*meta* substituents				*para* substituents			
		$\log k_u^{0\,a)}$	$\log k_u^0/r_{CH_3I}$	ρ^m	$r^{0\,b)}$	$\log k_u^{0\,c)}$	$\log k_u^0/r_{CH_3I}$	ρ^p	$r^{b)}$
1	CH_3CN	3.588	3.337	−0.875	−0.9995	3.546	3.296	−0.815	−1.0000
2	$(CH_3)_2CO$	3.144	3.142	−0.886	−0.9985	3.132	3.130	−0.844	−0.9992
3	$C_6H_5NO_2$	3.074	3.017	−1.133	−0.9984	3.061	3.004	−0.987	−0.9994
4		2.387	2.387	−1.175	−0.9990	2.343	2.343	−1.150	−0.9999
5	THF	2.402	—	−1.077	—	2.138	—	−1.019	−0.9996
6	C_6H_6	1.886	1.854	−1.337	−0.9986	1.821	1.789	−1.286	−1.0000
7	CS_2	1.012	1.012	−1.869	−0.9998	0.895	0.895	−1.645	−0.9999
8	c-C_6H_{12}	−0.757	−0.881	−2.15	—	−0.908	−1.032	−2.31	—
9	$C_6H_5CH_3$	1.602	1.563	−1.341	−0.9991	1.525	1.486	−1.307	−1.0000
10	C_6H_5Cl	2.093	2.086	−1.579	−0.9996	1.992	1.985	−1.352	−0.9998
11	C_6H_5Br	2.197	2.196	−1.550	−0.9991	2.111	2.110	−1.342	−0.9998
12	CH_3OH	2.359	1.480	−0.617	−0.9993	2.334	1.455	−0.553	−0.9997
13	C_2H_5OH	2.029	1.681	−0.731	−0.9998	2.037	1.689	−0.706	−0.9959
14	*i*-PrOH	1.766	1.648	−0.874	−0.9996	1.761	1.643	−0.7575	−1.0000

a) Logarithm of unitary term of rate constant for the reaction of unsubstituted amine with methyl iodide.
b) Correlation coefficient of Hammett plot.
c) Logarithm of unitary term of rate constant for hypothetical of "*para*-unsubstituted amine" with methyl iodide.

TABLE 3. ACTIVITY COEFFICIENT OF METHYL IODIDE AT 30°C

Solvent[a)]	1	2	3	4	6	7	8	9	10	11	12	13	14
δ_1[b)]	12.1	9.57	10.9	9.87	8.95	9.87	8.13	8.85	9.40	9.77	14.2	12.6	11.4
$\log r_{CH_3I}$ (Experimental[c)])	0.493	0.346	—	—	—	—	—	—	—	—	1.01	—	—
(Calculated[d)])	0.251	0.002	0.06	0.00	0.03	0.00	0.12	0.039	0.007	0.007	0.879	0.348	0.118

a) The numbers in the table correspond to the numbers inTable 1.
b) Solubility parameters of solvent, $cal^{1/2}$ $cm^{-3/2}$.
c) Values calculated from the data given by Alexander *et al.* (Ref. 22). The reproducibility seems to be within ±0.2 log unit.
d) Values estimated from equation of $RT \ln r_{CH_3I} = V^0_{CH_3I}(\delta_1 - \delta_{CH_3I})^2$ where $V^0_{CH_3I}$ and δ_{CH_3I} are 63.02 cc/mol and 9.780 $cal^{1/2}cm^{-3/2}$, respectively.

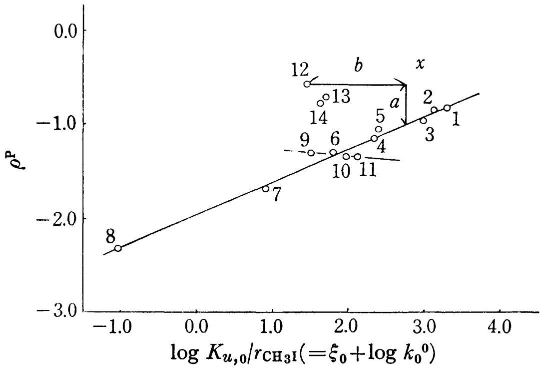

Fig. 2. Correlation of ρ^p with a solvent reactivity parameter. The numbers in the figure correspond to the numbers in Table 1.

a systematic trend that the lower the ξ_0 value the more negative the ρ value becomes.

The quantitative treatment reported previously is applied to the present system. The ρ value in an arbitrary solvent is given by

$$\rho = \rho^0 + (\partial\rho/\partial\xi_0)\xi_0 \tag{3}$$

where ρ^0 is the intrinsic ρ value. Modification of equation (3) shows the ρ value changes with the increase of solvent polarity as

$$\rho = \rho^0\{1 + 1/\rho^0 \cdot (\partial\rho/\partial\xi_0)\xi_0\} \tag{4}$$

The coefficient $1/\rho^0(\partial\rho/\partial\xi_0)$ is termed a leveling coefficient, because the value is in general negative,[14] and the second term in parentheses of Eq. (4) exerts a leveling effect upon substituent effects. For the present reaction the $\partial\rho/\partial\xi_0$ is 0.36, as shown in Fig. 2.

It is of interest to consider a necessary and sufficient condition for constancy of $\partial\rho/\partial\xi_0$. For deriving the condition we make use of the fact that the Hammett equation holds in all solvents. This is expressed in the form

$$\log k_x^0/k_0^0 = \rho^0\sigma, \quad \log r_{AX}/r_{A0} = \rho_A\sigma,$$
$$\log r_{M^{\neq}X}/r_{M^{\neq}0} = \rho_{M^{\neq}}\sigma \tag{5}$$

The ξ_0-value is split into ξ_{A0} and $\xi_{M^{\neq}0}$. The contribution of ξ_{A0} and $\xi_{M^{\neq}0}$ to ξ_0 is expressed by

$$\xi_0 = \log r_{A0} + (-\log r_{M^{\neq}0}) = \xi_{A0} + \xi_{M^{\neq}0} \tag{6}$$

Combination of these equations leads to the following expression for the $\partial\rho/\partial\xi_0$.

$$\begin{aligned} \partial\rho/\partial\xi_0 &= \partial\rho_A/\partial\xi_0 - \partial\rho_{M^{\neq}}/\partial\xi_0 \\ &= \partial\rho_A/\partial\xi_{A0} + \partial\rho_A/\partial\xi_{M^{\neq}0} \\ &\quad - \partial\rho_{M^{\neq}}/\partial\xi_{M^{\neq}0} - \partial\rho_{M^{\neq}}/\partial\xi_{A0} \end{aligned} \tag{7}$$

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[14] While $\partial\rho/\partial\xi_0$ is positive for reactions in which ρ^0 seems to be negative, negative $\partial\rho/\partial\xi_0$ values are obtained for reactions in which ρ^0 seems to be positive. The former case is observed in S_N2 type reactions, *viz.*, the present system and ionization of phosphines.[9] The latter case is observed in equilibria of proton acids[4] and esterification of benzoic acids.[4]

In general $\xi_{\mathrm{A}0}$ is independent of $\xi_{\mathrm{M}^{\neq}0}$, and Eq. (7) is modified to be

$$\partial\rho/\partial\xi_0 = \partial\rho_{\mathrm{A}}/\partial\xi_{\mathrm{A}0} - \partial\rho_{\mathrm{M}^{\neq}}/\partial\xi_{\mathrm{M}^{\neq}0} \tag{8}$$

Let us consider the requirement for constancy of $\partial\rho_{\mathrm{A}}/\partial\xi_{\mathrm{A}0}$ or $\partial\rho_{\mathrm{M}^{\neq}}/\partial\rho_{\mathrm{M}^{\neq}0}$. We assume that the ξ_x is represented by Eq. (9).

$$\xi_x = g(\xi)f(\sigma_x) \tag{9}$$

where $g(\xi)$ is a function depending upon the solvent, and $f(\sigma_x)$ is a function depending upon the substituent. It is easily shown that the $\partial\rho_{\mathrm{A}}/\partial\xi_{\mathrm{A}0}$ or $\partial\rho_{\mathrm{M}^{\neq}}/\partial\xi_{\mathrm{M}^{\neq}0}$ becomes independent of solvent. The reverse is also valid; the constancy of $\partial\rho_{\mathrm{A}}/\partial\xi_{\mathrm{A}0}$ or $\partial\rho_{\mathrm{M}^{\neq}}/\partial\xi_{\mathrm{M}^{\neq}0}$ leads to Eq. (9).

For constancy of $\partial\rho/\partial\xi_0$ the following condition is also required. The effects of solvents on reactivities are attributed to either r_{A} or $r_{\mathrm{M}^{\neq}}$. Uniqueness of $\partial\rho/\partial\xi_0$ which is observed with respect to many solvents (Fig. 2) shows that the conditions are satisfied. We believe that $r_{\mathrm{M}^{\neq}}$ is an important contributing factor to the changes of reactivities with solvents. Although the value of r_{A} has not been obtained experimentally, the situation may be valid.[15] Even in such a very non-polar solvent as cyclohexane, r_{A} may be nearly equal to unity and ρ_{A} is zero.[16]

It is instructive to consider whether theories proposed previously concerning r are satisfied with the condition expressed by Eq. (9). Kirkwood's first approximation[17] for the stability of dipole molecules in solution seems to fulfil the requirement. A solvent function $g(\xi)$ is a function of dielectric constant of solvent $D-1/2D+1$, and a structural function $f(\sigma_x)$ is a function of dipole moment and radius of molecules μ^2/γ^3. The theory cannot explain, however, the fact that the order of reactivity changes with solvents. In applications of the theory to solvent effects on reaction rates which have been carried out by Hartmann and Schmidt,[18] it is necessary to examine whether the solvents under consideration are satisfied with conditions mentioned by Kirkwood. The same situation holds in the application of regular solution theory to the explanation of solvent effects on reaction rates.[6] We must then consider another explanation of the linear relationship between $\rho_{\mathrm{M}^{\neq}}$ and $\xi_{\mathrm{M}^{\neq}0}$.

The concept that solvent reorientation makes a great contribution to activation thermodynamic parameters, in particular to activation entropies, may give a satisfactory explanation for the phenomenon. The following three considerations are required. First, the existence of Hammett's equation requires the condition that the reaction coordinate of activated complex remains constant within substituent changes. Second, the linear relationship between $\delta_x \log k$ and $\delta_x \log K$ requires that the degree of net charge development in the transition state of all substituted benzyl amines should be the same. Third, the linear correlation of $\delta_\xi \log k_u$ with $\delta_\xi \log K_u$ requires that the mechanism may remain constant within the solvents used.[9] These three requirements lead to the conclusion that the degree of charge distribution accompanied by an activation process varies with substituent, and the Hammett equation holds. Redistribution of electrical charge caused by a substituent affects the entropy change accompanied by solvent reorientation as the consequence of an activation. The situation is more clearly illustrated in Fig. 3. Slopes of the straight line can be determined by the ease of reorientation of solvents accompanied by an activation process. This ease is in the sequence: cyclohexane<carbon disulfide<benzene<dioxane<tetrahydrofuran<nitrobenzene<acetone<acetonitrile. The order is not related to solvent properties such as dielectric constant, solubility parameter.

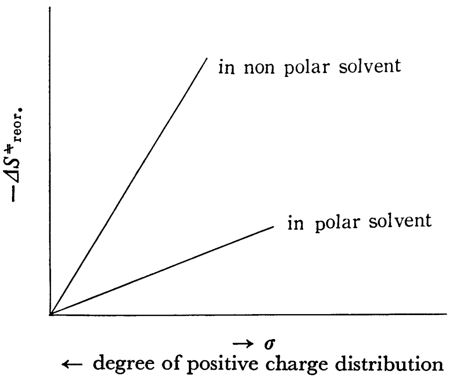

Fig. 3. Scheme for explaining the linear relationship between $\rho_{\mathrm{M}^{\neq}}$ and $\xi_{\mathrm{M}^{\neq}0}$.

Abnormal Behavior of ρ Values in Protic Solvents. Figure 2 shows that ρ values in protic solvents, *i. e.*, methanol, ethanol, and isopropanol, are more positive than expected from the small ξ_0 values in these solvents. Judging from the 1-1 hydrogen-bonded complex formations between alcohols and amines,[19] the first term on the right of Eq. (8) seems to play a still more important role. As a result of these relatively strong interactions, $\xi_{\mathrm{A}0}$ in alcohols is more negative than in other solvents. The interaction exercises a more profound influence upon the stability of amines with electron-donating substituents than that with electron-withdrawing substituents. Any deviation with regard to alcohols, as shown in Fig. 2, is thus observed.

The situation is quantitatively treated as follows taking the ρ value in methanol as an example. The method has been adopted to explain the solvent effects on the reaction of pyridine with methyl iodide. The logarithmic ratio of activity coefficient of benzylamine to that of dimethylaniline, $\log r_{\mathrm{A}x}^{\mathrm{CH_3OH}}/r_{\mathrm{DMA}}^{\mathrm{CH_3OH}}$ is determined by a deviation with regard to methanol from a plot of log $k_u(\mathrm{DMA}+\mathrm{CH_3I})$ *vs.* log $k_u(\mathrm{X{\cdot}DMBzA}+\mathrm{CH_3I})$ values for solvents. The plot of $\log r_{\mathrm{A}x}^{\mathrm{CH_3OH}}/$

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[15] Validity can be judged by volume change experiment for the solution processes. The excess volume of amines in various aprotic solvents is nearly equal to zero. H. Hartmann, H. D. Brauer, H. Kelm, and G. Rinck, *Z. Physik. Chem.*, (*Frankfurt*), **61**, 553 (1968).

[16] Dimerization phenomenon is considered to have important effect on activity coefficient of bases. According to Bruckenstein and Untereker (*J. Amer. Chem. Soc.*, **91**, 5741 (1969)), tertiary amines do not dimerize in hexane at the concentration used in the present work.

[17] J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

[18] H. Hartmann and A. P. Schmidt, *Z. Physik. Chem.*, (*Frankfurt*), **62**, 312 (1968).

[19] R. W. Taft, D. Gurka, L. Joris, P. von R. Schleyer, and J. W. Rakshys, *J. Amer. Chem. Soc.*, **91**, 4801 (1969), and the references cited. Data on excess volume of amines in alcohols (ref. 5) also show that amines are very stable in these solvents.

$r_{\mathrm{DMA}}^{\mathrm{CH_3OH}}$ *vs.* σ results in 0.38 for the value of ρ_{A} which is given as the distance *a* in Fig. 2. The deviation of point *x* in the figure from the straight line of usually accepted $\rho-\xi_0$ relationship is assigned to the log $r_{\mathrm{A}x}^{\mathrm{CH_3OH}}$ value and is expressed by the distance *b* in the figure. The condition expressed by the following equation is required.

$$\log r_{\mathrm{A}x}/r_{\mathrm{A}0} = 0.38\sigma_x;\ \log r_{\mathrm{A}0} = -1.30 \qquad (10)$$

ρ Values in Aromatic Solvents with Small Dielectric Constant. As shown in Fig. 2, ρ values in aromatic solvents with comparable dielectric constant with that of benzene decrease with increasing reactivities in the solvents. The negative sign of interaction between solvent- and substituent-variable is observed in the solvents. This is in striking contrast to the behavior of ρ values in other solvents. The behavior has also been observed for the reaction of *N,N*-dimethylanilines with methyl picrate.[1] The normal behavior of ρ values result from the important role of a specific solvation of a leaving anion in a transition state. This type of solvation may be closely related to the polarizability of aromatic nucleus in the solvents. The effect is in the sequence: toluene<benzene<chlorobenzene<bromobenzene.[1,20] The susceptibility of a leaving anion I(δ-) to the solvation seems to be dependent on the tightness[21] of developing charge δ-. Accordingly, the demand for solvation stabilization by the various transition states will vary with substituent. In the case of the electron-withdrawing substituents the departing charge δ- will be more localized than in the case of electron-donating substituents. The *I*(δ-) entity with tight character will have less solvation demand than will that with loose character. Thus the rate of quaternization of benzylamines substituted by electron-withdrawing groups is less sensitive to the effects of solvents in passing from toluene to bromobenzene than those substituted by electron-donating groups, the ρ values decreasing with the ξ_0 values in aromatic solvents.

Our explanation is in marked contrast to the view proposed by Alexander *et al.*[22] that "one cannot concentrate on only one end of a transition state." If it is so and the degree of solvent reorientation changes with only the net value of developing charge in the whole species of a transition state, a single straight line should be observed for $\rho-\xi_0$ relationship.

Experimental

Materials. *N,N*-dimethylbenzylamine and its derivatives were prepared according to Eliel *et al.*[23] from benzyl halide or its derivatives. Reagent grade benzyl chloride was obtained from Wako Pure Chemicals. *p*-Nitro- and *m*-nitrobenzyl bromides were prepared by bromination of *p*-nitro-[24] and *m*-nitrotoluene[25] respectively. *m*-Chlorobenzyl bromide was prepared according to the directions of Jenkins.[26] *p*-Methoxybenzyl chloride was prepared by the reaction of anisyl alcohol with hydrochloric acid.[27] *p*-Chlorobenzyl- and *m*-xylyl chloride were prepared by chlorination of *p*-chlorotoluene and *m*-xylene respectively according to Kharasch and Brown.[28] The prepared amines were dried over KOH pellet and distilled in a vaccum at least three times. The following boiling points were obtained: *N,N*-dimethylbenzylamine, 34—34.5°C/2 mmHg; *p*-methoxy-*N,N*-dimethylbenzylamine, 74—77°C/2.5 mmHg; *m*-methyl-*N,N*-dimethylbenzylamine, 85—85.5°C/19.5 mmHg; *m*-chloro-*N,N*-dimethylbenzylamine, 66—67°C/3 mmHg; *m*-nitro-*N,N*-dimethylbenzylamine, 112—114°C/3.5 mmHg; *p*-chloro-*N,N*-dimethylbenzylamine, 68—73°C/2.5 mmHg; *p*-nitro-*N,N*-dimethylbenzylamine, 125—127°C/6 mmHg. Purity of these samples was ascertained by gas-liquid chromatography, employing a Hitachi K53 gas chromatograph (Z 45 Column).

Methanol, tetrahydrofuran, acetonitrile, acetone, carbon disulfide, benzene, nitrobenzene, and bromobenzene were purified by the method previously described.[1,9] Toluene

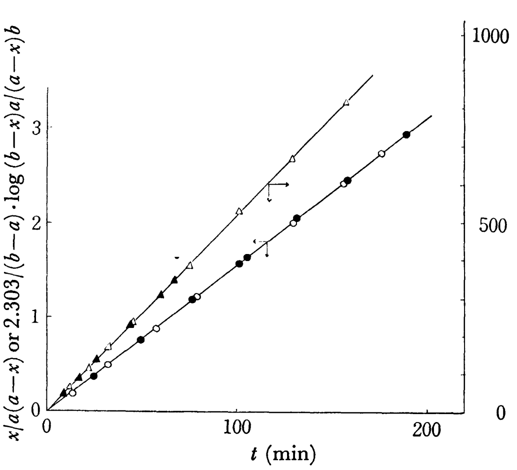

Fig. 4. Second-order rate plots for reactions of methyl iodide with *m*-nitro-*N,N*-dimethylbenzyl amine in chlorobenzene and with *p*-methoxy-*N,N*-dimethylbenzylamine in acetonitrile: in chlorobenzene, ○, $[\mathrm{CH_3I}]_0=0.0147$M, $[\mathrm{CH_3I}]_0/[\mathrm{Amine}]_0=1.00$; ●, $[\mathrm{CH_3I}]_0=0.0204$M, $[\mathrm{CH_3I}]_0/[\mathrm{Amine}]_0=2.98$; in acetonitrile, △, $[\mathrm{CH_3I}]_0=0.00301$M, $[\mathrm{CH_3I}]_0/[\mathrm{Amine}]_0=1.00$; ▲, $[\mathrm{CH_3I}]_0=0.00188$M, $[\mathrm{CH_3I}]_0/[\mathrm{Amine}]_0=1.64$.

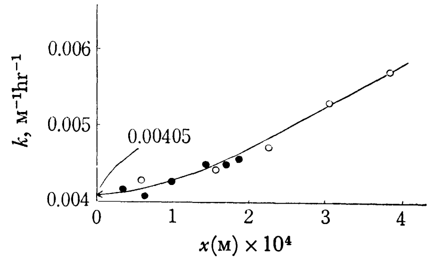

Fig. 5. Plot of second-order rate constants *vs.* concentration of salt produced for reaction of *p*-chloro-*N,N*-dimethylbenzylamine with methyl iodide in cyclohexane: ○, $[\mathrm{CH_3I}]_0=[\mathrm{Amine}]_0=0.0797$M; ●, $[\mathrm{CH_3I}]_0=[\mathrm{Amine}]_0=0.0623$M.

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and chlorobenzene were shaken with concentrated sulfuric acid several times and washed with water, aqueous potassium hydroxide, and then with water, dried over calcium chloride, and distilled. The center fraction was further distilled twice from phosphorus pentoxide. Cyclohexane,[29] ethanol,[30] and dioxane[31] were purified as described in literature. Isopropanol was purified by a method similar to that for ethanol.

Kinetic Procedure. The technique of the potentiometric kinetic measurements has been described in detail.[9] Reaction in solvents fitted into second order plots. Typical second order plots are shown in Fig. 4. Comparison was always made by results obtained with a different initial concentration. Reproducibility was mostly within ±1%. Initial concentration of each reactant was 0.002—0.02M except for the reaction in cyclohexane where the reactant solutoin of about 0.05M was used for kinetic measurements.

In two cases the second order rate constants increased as the reaction proceeded, a phenomenon reported by Laidler and Hinshelwood[32] and attributed to autocatalysis by quaternary salt. In the reaction of *p*-chloro-*N*,*N*-dimethylbenzylamine with methyl iodide in cyclohexane the increase was bout 50% at 0.5% conversion, and was somewhat larger for the reaction of *m*-chloro-*N*,*N*-dimethylbenzylamine with methyl iodide in the same solvent. In both cases plots of rate constants *vs*. concentrations of salts produced enable us to calculate the rate constant at zero conversion, as shown in Fig. 5. We believe that the constants obtained in this manner are accurate within about ±3%.

The reactions of *p*-nitro- and *m*-nitro-substituted amines with methyl iodide in cyclohexane were too slow to determine rate constants of these reactions with reasonable accuracy.

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