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Solvent Effects on ρ Values of the Hammett Equation

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The effects of selvents on ρ values have been systematically treated as a two-variable problem within a linear free-energy relationship framework. It is assumed that the standard activation free energy is a continuous function of σ, a substituent variable, and ξ, a solvent variable. The applicability of the resultant equations is proved by a test of the dissociation constants (obtained from the literature) of benzoic acids in various solvents. As a result, it is proposed that these effects on ρ values can be explained in terms of the interaction or cross-term of σ and ξ. The application to the reaction rates of a typical Menschutkin reaction, obtained by experiments in ten non-aqueous solvents, suggests that the solvent dependence in these reactivities is much more complicated.

Systematic studies of the substituent effects of the dissociation constants of organic acids in solution have been carried out comprehensively by many authors since the proposal of Hammett's equation.[1] The relationships between the ρ values and the environmental changes have also been the subject of some studies.[2,3]

Concerning the effects of solvent on the ρ values, Wynne-Jones[4] discussed the relative acid strengths of some acids in such hydroxylic solvents as water, methanol, and ethanol; he suggested the inverse proportionality of these values to the dielectric constants of the solvents used. Furthermore, Kilpatrick and his co-workers[5] confirmed Wynne-Jones's results on the dissociations of acids in aqueous dioxane; however, they indicated that this relationship was limited to solvents with dielectric constants larger than ~25. In low dielectric solvents (lower than ~25) it did not hold; here the dipole-dipole interaction may dominate. Recently, Grunwald[6] proposed a linearity between the ρ values and his Y_0 values for the dissociation of anilinium ions.

On the other hand, the existence of a linear dependence of ρ values on the reciprocals of the absolute temperatures has also been reported.[2,3] Separating the external contributions to the thermodynamic quantities from the internal ones, Hepler[7] established the dissociation of phenols in an aqueous solution and supported the concept of the existence of a linear relation.

The interest in the effects of solvents on the ρ values, one of the Hammett reaction parameters, has prompted the present authors to initiate this project in the hope of establishing a more systematic treatment of the solvent effects on the Hammett constants. It seems that these problems may be treated as a two-variable problem by considering that both the standard activation free energy for the reaction and the standard free-energy changes in the equilibrium are continuous functions of x and y; x and y standing for the characteristics of the substituent, *i. e.*, σ, and the characteristics of such environmental factors as the solvent properties and the temperatures respectively.

Taylor's expansion theorem is used to treat this problem. Equation (1) represents this theorem for the standard free-energy change, $\Delta F°$, which is a continuous function of foth x and y:[8]

$$\Delta F°(x, y) = \Delta F°(0, 0) + \left(\frac{\partial \Delta F°}{\partial x}\right)_{0,0} x + \left(\frac{\partial \Delta F°}{\partial y}\right)_{0,0} y + \left(\frac{\partial^2 \Delta F°}{\partial x \partial y}\right)_{0,0} x \cdot y + \frac{1}{2}\left(\frac{\partial^2 \Delta F°}{\partial x^2}\right)_{0,0} x^2 + \frac{1}{2}\left(\frac{\partial^2 \Delta F°}{\partial y^2}\right)_{0,0} y^2 + 0(x^3, y^3) \quad (1)$$

Here the subscripts indicate the arbitrarily-destinated conditions.

If a linear free-energy relationship is assumed with regard to x and y, the terms of the second and higher powers of x and y, except for the fourth on the right hand side of Eq. (1), can be omitted. Therefore, Eq. (2) can be written as:

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[1] L P. Hammett, *J. Am. Chem. Soc.*, **59**, 96 (1937).

[2] P. R. Wells, *Chem. Revs.*, **63**, 171 (1963).

[3] H. H. Jaffe, *ibid.*, **53**, 191 (1953).

[4] W. F. K. Wynne-Jones, *Proc. Roy. Soc. (London)*, **A140**, 440 (1933).

[5] J. H. Elliott and M. Kilpatrick, *J. Phys. Chem.*, **45**, 454 (1941).

[6] E. Grunwald and B. Gutbezahl, *J. Am. Chem. Soc.*, **75**, 559 (1953).

[7] L. G. Hepler, *ibid.*, **85**, 3089 (1963).

[8] W. Kaplan, "Advanced Calculus," Addison-Wesley Publishing Co., Massachusetts, U. S. A. (1952), p. 369.

$$\Delta F^\circ(x,y) = \Delta F^\circ(0,0) + \left(\frac{\partial \Delta F^\circ}{\partial x}\right)_{0,0} x + \left(\frac{\partial \Delta F^\circ}{\partial y}\right)_{0,0} y + \left(\frac{\partial^2 \Delta F^\circ}{\partial x \partial y}\right)_{0,0} x \cdot y \qquad (2)$$

Then, using Eq. (4), Eq. (2) can be rewritten as follows:

$$\Delta F^\circ(x,y) = \Delta F^\circ(0,0) + A_0 x + B_0 y + \left(\frac{\partial A}{\partial y}\right)_0 x \cdot y \qquad (3)$$

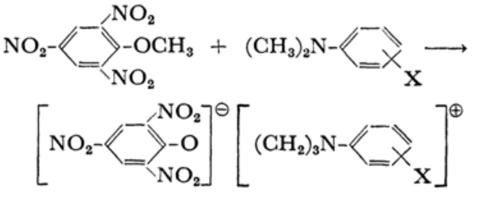
$$\left(\frac{\partial A}{\partial y}\right)_0 = \left(\frac{\partial B}{\partial x}\right)_0 \qquad (4)$$

Eq. (4) is based on the mathematical theory that the order of differentiation is immaterial because ΔF° is the "property" of the reaction system⁹⁾ and because it has been assumed that all the derivatives concerned are continuous in the domain considered.

This equation (3) is essentially the same as that of Miller¹⁰⁾ provided that $\partial A/\partial y$ or $\partial B/\partial x$ is constant. Especially if $\partial A/\partial y$ or $\partial B/\partial x$ is zero, this situation shows that x and y contribute to ΔF° independently; the resultant equation (5) has been useful for the separation of the factors in the substituent effects, *i. e.*, polar, steric, resonance, and so on.¹¹⁾

$$\Delta F^\circ(x,y) = \Delta F^\circ(0,0) + A_0 x + B_0 y \qquad (5)$$

In order to examine the usefulness of such a treatment of the solvent effects, the dissociation constants of substituted benzoic acids in various aqueous solvents were compared with many literature values, and then the rates of a Menschutkin-type reaction series (I) were followed in various non-aqueous solvents which had not hitherto been studied. This reaction was chosen for the present research because it was expected that the ρ values might be liable to variation in proportion to the solvent changes, since in acetone this value was significantly large.³,¹²⁾



(I)

Results and Discussion

The Application of Eqs. (3) and (4) to the Solvent Effect. Usually, as has been seen in may results, if the Hammett rule holds good in one solvent, it is valid also in other solvents so far as the non-charged substituents are concerned.³,¹³⁾ Moreover, if the linear free-energy relationship is assumed also for solvent variation, x and y in Eq. (3) may be replaced by σ and ξ, the characteristic features of a solvent. We can also replace ΔF° with the equilibrium constant, K. Thus Eqs. (3) and (4) yield:

$$\log\left(\frac{K_\sigma{}^\xi}{K_0{}^0}\right) = \rho_0\sigma + \zeta_0\xi + \left(\frac{\partial \rho}{\partial \xi}\right)_0 \sigma \cdot \xi \qquad (6)$$

$$\left(\frac{\partial \rho}{\partial \xi}\right)_0 = \left(\frac{\partial \xi}{\partial \sigma}\right)_0 \qquad (7)$$

Now it does not appear that ξ can be uniquely determined by such a special characteristic of a solvent as $1/D$ or $(D-1)/(2D+1)$. Therefore, ξ will be here defined as the logarithmic ratio of the equilibrium constant in a standard solvent to that in others when the unsubstituted reactant is used; that is to say, log $(K_0{}^{\text{other solv}}/K_0{}^{\text{reference}})$ (the subscript indicates the substituent and the superscript indicates the solvent). ζ is a measure of the susceptibility of a given reaction series to the ξ defined above.

Equation (6) contains the interaction or the cross term of σ and ξ. This term may be used to explain the solvent effects on ρ and the substituent effects on ζ if these effects are two sides of one thing; that is to say, Eq. (7) is valid. Equations such as Eq. (7) have been frequently used in the form of pK(H_2O) *vs.* pK(other solvent).¹⁴⁾ The arising of this cross-term suggests how the contribution of σ to ΔF° affects the contribution of ξ to ΔF°.

To begin with, the above treatment should be applicable to the thermodynamic equilibrium constants, K_{th}, of benzoic acids in various solvents, for σ may depend on the solvent although it is defined as the logarithmic ratio of the thermodynamic ionization constants of substituted benzoic acid to that of unsubstituted acid in an aqueous solution. Moreover, the thermodynamic values should be used for theoretical treatment.¹⁵⁾ Fortunately, the true acid strengths of benzoic acid and its derivatives have been studied by many workers.

Table 1 shows the ξ values for several solvents, which have been calculated by using the average values of these data taken from the references, together with the dielectric constants (ξ is defined as $\log(K_0{}^{\text{other solvent}}/K_0{}^{H_2O})$). Figure 1 represents the plots of $\log(K_\sigma{}^{\text{other solvent}}/K_\sigma{}^{H_2O})$ *vs.* ξ. The

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9) K. S. Pitzer and L. Brewer, Revised Edition of Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y. (1961).

10) S. I. Miller, *J. Am. Chem. Soc.*, **81**, 101 (1959).

11) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, New York, N. Y. (1956), Chapter 8.

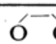
12) E. Hertel and J. Dressel, *Z. Phys. Chem.*, **23**, 281 (1933).

13) C. D. Richie and E. S. Lewis, *J. Am. Chem. Soc.*, **84**, 591 (1962).

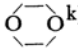
14) For example, L. P. Hammett and L. A. Wooten, *ibid.*, **57**, 2289 (1935); B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac and A. J. Parker, *ibid.*, **88**, 1911 (1966).

15) J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939).

TABLE 1. ξ VALUES[a] OF SOLVENTS FOR THE DISSOCIATION OF BENZOIC ACID AT 25°C

Solvent	H_2O[c,d,g,r]	10 w% MeOH[s]	20 v% MeOH[e,n]	10 w% $(CH_3)_2CO$[h]	20 v% EtOH[e]	20 w% [k,p]	40 v% MeOH[e]	25 w% $(CH_3)_2CO$[h]
ξ	0.00	−0.187	−0.26	−0.25	−0.28	−0.668	−0.744	−0.795
D_{25}[b]	78.6		71.5	73.0	72.7	60.83	63.49	64.0

Solvent	50 v% CH_3OH[e]	40 v% EtOH[e,f]	30 w% [k,p]	50 v% EtOH[e]	60 v% MeOH[n]	40 w% [k,p]	80 v% MeOH[e,n]	70 v% EtOH[e,f]
ξ	−0.95	−1.02	−1.08	−1.34	−1.34	−1.594	−1.093	−1.935
D_{25}[b]	59.03	66.2	51.9	60.8	54.34	43.0	44.43	47.9

Solvent	50 w% [k,p]	80 v% EtOH[e]	90 v% EtOH[e]	95 v% EtOH[e]	61.0 w% [k]	95 v% MeOH[n]	100% MeOH[l,m,g]	100% EtOH[j,l]
ξ	−2.18	−2.25	−2.51	−2.72	−2.80	−3.27	−5.20	−5.94
D_{25}[b]	34.3	43.0	38.75	35.75	25.1	36.04	32.61	24.2

Solvent	i-PrOH[u]	c-HexOH[u]	50 v% Butyl cellosolve[o]	C_4H_9OH[k]	$(CH_2OH)_2$[k]	$C_6H_5OCH_3$[u]	20% Sucrose[t]
ξ	(−6.72)[v]	(−7.14)[v]	(−1.45)[v]	(−4.41)[v]	(−3.447)[v]	(−1.51)[v]	(+0.02)[v]
D_{25}[b]				17.7	37.7	4.30	

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a) ξ is defined as $\log(K_0^{\text{other solvent}}/K_0^{H_2O})$, where $\log K_0^{H_2O}$ has a value of −4.203; average value, Refs. c, d, g, and r.

b) Dielectric constants of aq. EtOH and of aq. dioxane obtained from the interpolation of Timmermans' data; J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Amsterdam, The Netherlands (1950).

c) A. Bieber, *Z. Elektro. Chem.*, **55**, 250 (1951).

d) L. P. Hammett, *J. Am. Chem. Soc.*, **57**, 2289 (1953).

e) W. L. Bright and H. T. Briscoe, *J. Phys. Chem*, **37**, 789 (1933).

f) E. Grunwald and B. J. Berkowitz, *J. Am. Chem. Soc.*, **73**, 4939 (1951).

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

h) J. F. J. Dippy, S. R. C. Hughes and B. C. Kitchiner, *J. Chem. Soc.*, **1964** 1275.

i) H. Goldschmidt, *Z. Physik. Chem.*, **112**, 429 (1924).

j) E. Larsson, "Untersuchungen über die Elektrolytische Dissoziation einiger Elektrolyte in Äthylalkolischer Lösung," Dissertation, Lund (1924).

k) J. H. E. Elliott and M. Kilpatrick, *J. Phys. Chem.*, **45**, 454 (1941).

l) I. D. Tabagua, M. M. Tsurtsumiya and N. A. Izmailov, *Tr. Sukhumsk. Gos. Ped. Inst.*, **15**, 103 (1962); *Chem. Abstr.*, **60**, 14370 (1964).

m) *Ibid.*, **15**, 119 (1962); *Chem. Abstr.*, **60**, 14373 (1964).

n) A. L. Bacarella, E. Grunwald, H. P. Marshall and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955).

o) E. Berliner and E. A. Blommers, *J. Am. Chem. Soc.*, **73**, 7479 (1951).

p) H. S. Dunsmore and J. C. Speakman, *Trans. Faraday Soc.*, **50**, 236 (1954).

q) M. Kilpatrick and Arenberg, *J. Am. Chem. Soc.*, **75**, 3812 (1953).

r) R. A. Robinson and A. I. Biggs, *Australian J. Chem.*, **10**, 128 (1957).

s) H. N. Parton and J. Rogers, *Trans. Faraday Soc.*, **38**, 238 (1942).

t) J. F. J. Dippy, *J. Chem. Soc.*, **1944**, 411.

u) (i) V. I. Dulova and D. R. Galieva, *Dolklady Akad. Nauk Uzbek SSR*, **1960**, No. 9, 42-4; *Chem. Abstr.*, **56**, 4140b (1962). (ii) V. I. Dulova and T. A. Maslentsova, *ibid.*, **1960**, No. 2, 27—30; *Chem. Abstr.*, **56**, 8069e (1962).

v) Values in parentheses show the non-thermodynamical ionization constants.

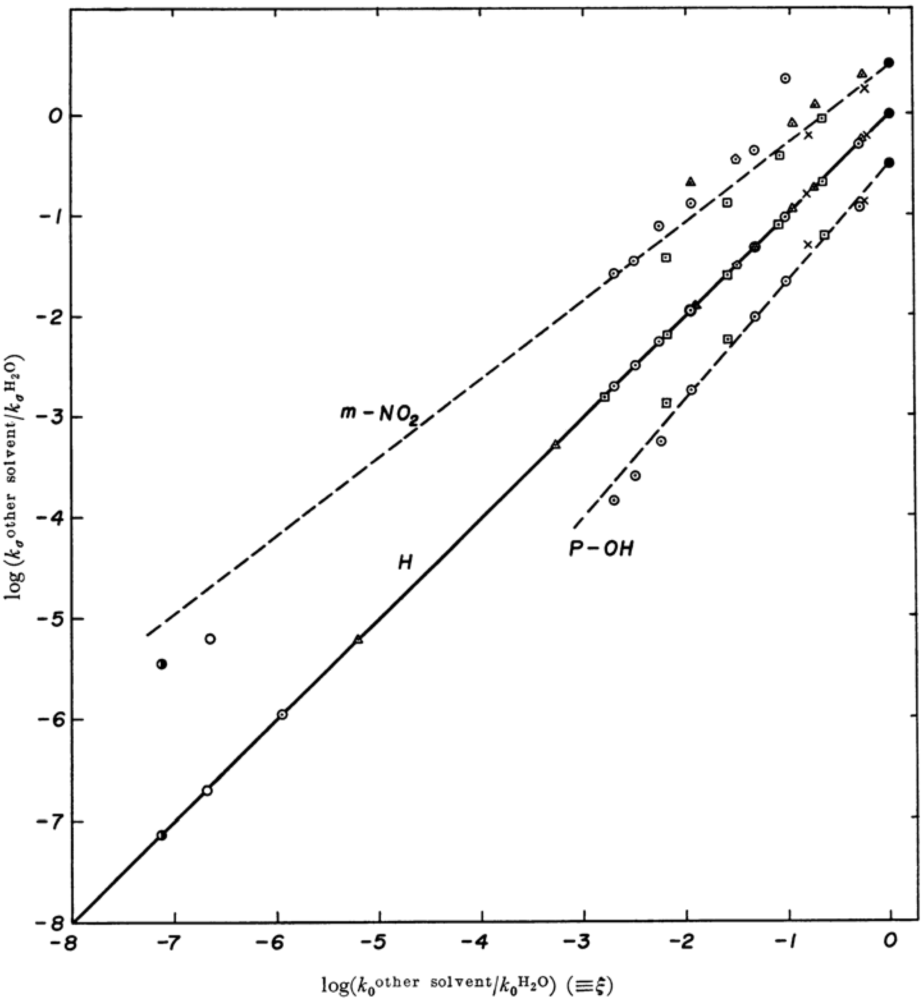

Fig. 1. The representation of linear free energy relationship with regard to solvent variations for the equilibrium constants of benzoic acid and its derivatives at 25°C. The log($k_\sigma^{\text{other solvent}}$/$k_\sigma^{H_2O}$) scale is displaced 0.5 to the upward or downward for m-NO_2 or p-OH derivatives for avoiding confusion. ●, Water; ×, water-acetone mixture; △, water-methanol mixture; ⊙, water-ethanol mixture; ⊡, water-dioxane; ○, isopropanol; ◑, hexanol; ⬠, anisole. See references in Table 1.

slope of this figure results in ζ (ζ_0 is equal to 1.00 according to the definition of ξ). The existence of a relation of the type of Eq. (7) is clearly shown in Figs. 2 and 3; this proves that the variation in the ρ values with the properties of the solvents arises from the cross-interaction of σ and ξ. Figure 2 shows that ρ decreases linearly with an increase in ξ; that is to say, the more polar the solvents are, the smaller this value becomes.

In order to discuss further details of the solvent effect on the ρ value, the relationship between ξ and the dielectric property of the solvent should be examined. As is shown in Fig. 4, an approximately linear relationship exists between ξ and $1/D$, the reciprocal of the dielectric constant, but in aqueous dioxane it is not observed. This is very similar to the situation which Hyne explained as the effect of specific solvation.[16] Judging from this point of view, in this case it may also be considered that dioxane-water mixed solvents have a larger dielectric character than expected and that they affect this equilibrium. The reason why the interaction term has some value is explained if only σ contains some component varying with the solvent.

On the other hand, the effects of the field in which the solute are located are taken as among the most important factors which contribute to the cross-interaction between σ and ξ. Dewar

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16) J. B. Hyne, *J. Am. Chem. Soc.*, **85**, 304 (1963).

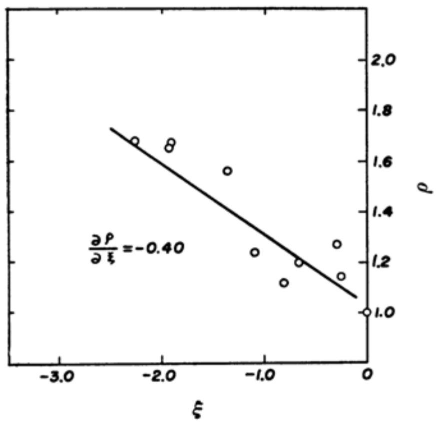

Fig. 2. Plot of ρ *vs.* ξ for the dissociations of benzoic acid and its derivatives.

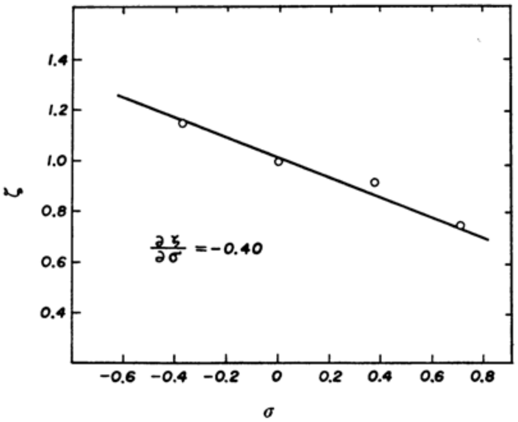

Fig. 3. Plot of ζ *vs.* σ for the dissociations of benzoic acid and its derivatives.

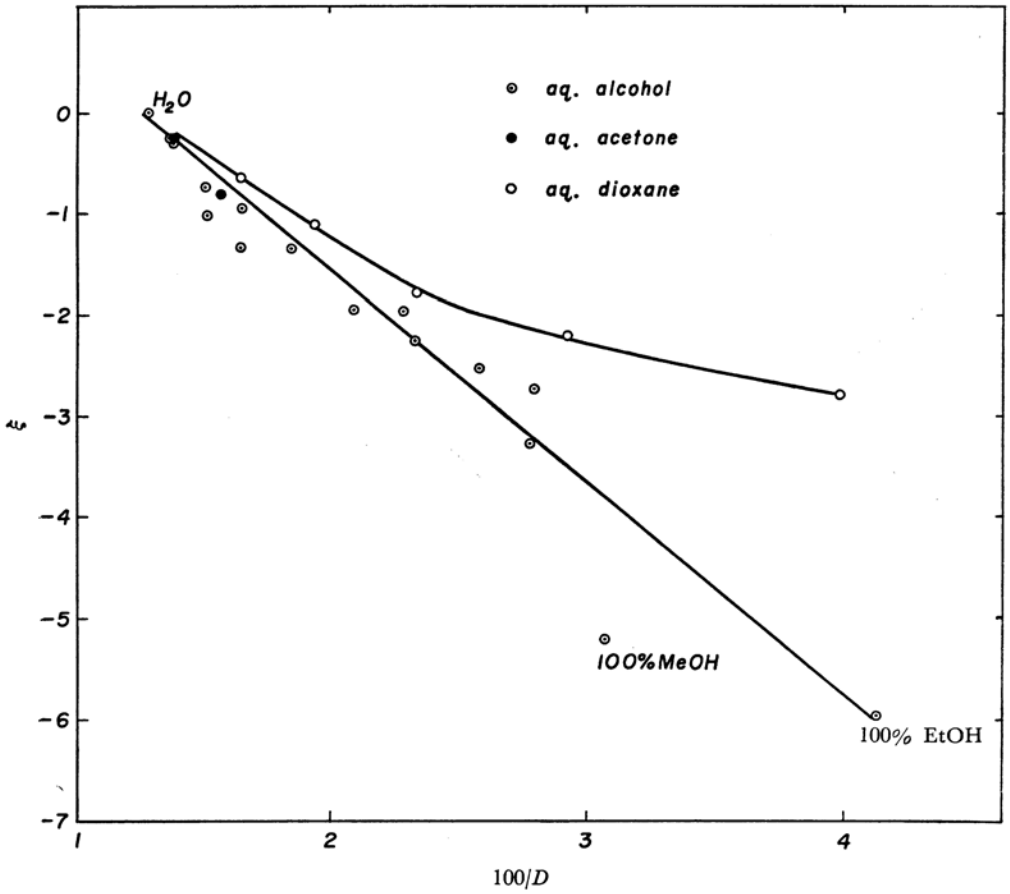

Fig. 4. The relationship between ξ, defined for the dissociation constants of benzoic acid, and $1/D$ for various aqueous solvents.

et al.[17] have emphasized the importance of this factor in a substituent effect. Thus, it seems reasonable that the field effect of each substituent results in the variation in ρ with ξ, as Willi has also suggested.[18]

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[17] M. J. S. Dewar and P. J. Grisdale, *ibid.*, **84**, 3539 (1962).

[18] A. V. Willi, *Helv. Chem. Acta*, **40**, 2032 (1957).

Usually this effect results from both the electrostatic contribution described as $1/D$ and the non-electrostatic (*i. e.,* specific) solvent effect. However, in the equilibrium under consideration, it seems that only the former acts on this effect (Fig. 4). The slope of such a linear plot (Fig. 2) may give a relative measure of the field effect which depends on the type of reaction.

The same treatment is applicable to the other dissociation equilibrium, those of anilinium ions or bicyclo[2.2.2]octane-1-carboxylic acid.[13] Equation (7) holds good for these series. The results of Grunwald showed that the ξ of the former equilibrium is linearly dependent on his Y_0[6] values and then he used the similar equation as Eq. (7) for the prediction of ρ values in several solvents.

On the other hand, the sign of the interaction constant[19] is negative, which seems to be generally true for the equilibrium with a positive ρ value. Over the range of negative ξ values, *i. e.,* in solvents less polar than water, the electron-withdrawing ability of a substituent in this situation increases the force driving for an equilibrium more than that in the additive relation which comes into existence when the interaction term is equal to zero. This can be explained if it is considered that the electron-withdrawing substituent operates to stabilize the carboxylate anion directly through space. The less polar the solvent is, the larger the degree of this effect becomes.

The Non-Aqueous Solvent Effects on ρ Value. It should be noted that the above treatment is also applicable to the variation in the velocity coefficient, k, with both substituents and solvents, using the concept of the theory of the absolute reaction rate;[20] *i. e.,* the standard activation free energy of a reaction is the thermodynamic property. Equation (8) is derived as:

$$\log\left(\frac{k_\sigma{}^\xi}{k_0{}^0}\right) = \rho_0\sigma + \zeta_0\xi + \left(\frac{\partial\rho}{\partial\xi}\right)_0\sigma\cdot\xi \qquad (8)$$

Few systematic studies have been carried out on the non-aqueous solvent effects on the ρ value. Regarding this problem, the present authors have, however, obtained some results of the Menschutkin-type reaction I (Table 2).

Figure 5 shows a Hammett plot based upon some of these data. The correlation coefficient of this plot from Table 2 is good in every solvent except in methanol.[21] This means that the substituent effects on the rates of these reactions can be expressed sufficiently in terms of a simple Hammett substituent constant, and that the reaction mechanisms are not influenced by the change in substituents. Also, it must be emphasized that for even this reaction of the highly hindered system (2,4,6-trinitro substituted reactant), the Hammett relationship holds good. This observation, as has been suggested by Taft,[22] seems to be attributable to the fact that the steric requirement of the reaction is not influenced by the variation in the substituent at the *m*- or *p*-position.

The non-aqueous solvent effects on the ρ value are extremely complex in the reaction under examination, as is shown in Table 2. However, a clear tendency is observed; the ρ values in aromatic solvents are all larger in absolute value than those in other solvents. The above-mentioned treatment has been applied to this reaction. We chose benzene as the standard solvent, and ξ was defined as log $(k_0{}^{\text{other solvent}}/k_0{}^{\text{C}_6\text{H}_6})$. The plot of log $(k_\sigma{}^{\text{other solvent}}/k_\sigma{}^{\text{C}_6\text{H}_6})$ against ξ (not shown) gives two distinctly different lines, which is equivalent to the fact that the two Hammett plots intersect with each other. The substituents also influence the mode of the variation in the logarithm of the rate constant with the solvent. The solvent constant can not be determined *a priori*. In this respect, the solid and dashed lines in Fig. 6 were drawn in to show that the solvents fall naturally into two groups: group a, along the dashed line in Fig. 6, consists of benzene, *p*-xylene, bromobenzene, and chloroform, while group b, along the solid line in Fig. 6, consists of tetrahydrofuran, methyl ethyl ketone, methanol, and acetonitrile. It goes without saying that Eq. (7) holds for each group. Nitrobenzene shows, however, a deviation from these two lines. The absolute value of ρ decreases with an increase in the solvent polarity in the members of group b, but in the members of group a this tendency is just reversed. In other words, $\partial\rho/\partial\xi$, the measure of the sensitivity to the field effects, is positive in group b and negative in group a since the reaction under consideration has a negative value of ρ.

It is now necessary to review the non-aqueous solvent effects on the kinetics of this type of reaction. A linear dependence of ξ on the $(D-1)/(2D+1)$ function can be expected from the first approximation of Kirkwood's theory[23] for dipole-dipole reactions, but no such simple relationship is observed in group a. Recently Reinheimer *et al.*[24] correlated the abnormally-high reactivity of the

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19) The terms $\partial\rho/\partial\xi$ and $\partial\zeta/\partial\sigma$ mean the interaction constants of σ and ξ when it is constant, as is shown in Figs. 2 and 3, judging from the similarity to the estimation of energy levels for polyatomic molecules. See, for example, Ref. 11, p. 503.

20) S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York (1940).

21) As the concurrent methanolysis of the reactant occurs, the pseudo second-order rate constants in methanol must be calculated after a consideration of this solvolysis. For this reason, in methanol the correlation is worse than in other solvents.

22) R. W. Taft, Jr., *J. Am. Chem. Soc.,* **74**, 3120 (1952).

23) J. G. Kirkwood, *J. Chem. Phys.,* **2**, 351 (1934).

24) J. P. Reinheimer, J. D. Harley, and W. W. Meyers, *J. Org. Chem.,* **28**, 1575 (1963).

Table 2. Rate constants of the reaction between *N,N*-dimethylaniline or its derivatives and 2,4,6-trinitroanisole and ρ values in various solvents at 50±0.1°C

Solvent	Substituent								
	Rate constant,$^{a)}$ k, $l\cdot mol^{-1}\cdot hr^{-1}$						$n^{e)}$	ρ	$r^{f)}$
	None	m-NO$_2$	m-Cl	m-CH$_3$	p-CH$_3$	p-OCH$_3$			
Benzene	0.112$^{b)}$	0.00156$^{b)}$	0.0105$^{b)}$	0.182$^{b)}$	0.375$^{b,c)}$	0.701$^{b)}$	6	−2.724	−0.999
p-Xylene	0.0821$^{b)}$	0.00115$^{b)}$	0.00661$^{b)}$	0.133$^{b)}$			4	−2.669	−0.998
Nitrobenzene	0.7645$^{c)}$	0.01095$^{b)}$	0.0777$^{b)}$	1.15$^{c)}$	2.32$^{c)}$	4.74$^{c)}$	6	−2.67	−0.999
Bromobenzene	0.278$^{b)}$ (0.317)	0.00267$^{b)}$	0.0230$^{b)}$	0.521$^{c)}$			4	−2.931	−1.000
Acetonitrile	0.579$^{c)}$	0.0142$^{b)}$	0.0773$^{b)}$	0.862$^{c)}$	1.59$^{c)}$	3.18$^{c)}$	6	−2.373	−0.999
Methanol	0.578$^{c)}$	0.0169$^{d)}$		1.089$^{c)}$ 1.143$^{g)}$		1.726$^{c)}$ 1.51$^{g)}$	4	−2.114	−0.993
Methyl ethyl ketone	0.374$^{c)}$	0.00891$^{b)}$	0.0461$^{b)}$	0.558$^{c)}$	0.9865$^{c)}$		5	−2.335	−0.999
Tetrahydrofuran	0.2375$^{b)}$	0.00551$^{b)}$	0.0290$^{b)}$	0.393$^{c)}$	0.676$^{c)}$	1.53$^{c)}$	6	−2.463	−0.998
Chloroform	0.419$^{b)}$	0.00335$^{b)}$	0.0322$^{b)}$	0.651$^{c)}$			4	−2.947	−1.000
Carbon disulfide		0.0009$^{b,h)}$		0.215$^{b)}$			2	−3.05	

a) Average value for at least two runs. Deviation of average value not less than 0.5 but not more than 2%.
b) Value by initial rate method.
c) Value by integral rate method.
d) Value obtained without consideration of methanolysis of trinitroanisole.
e) Number of substituents for determination of ρ.
f) Correlation coefficient of Hammett plot.
g) Value obtained by considering methanolysis of trinitroanisole through initial rate method.
h) Less accurate than other.

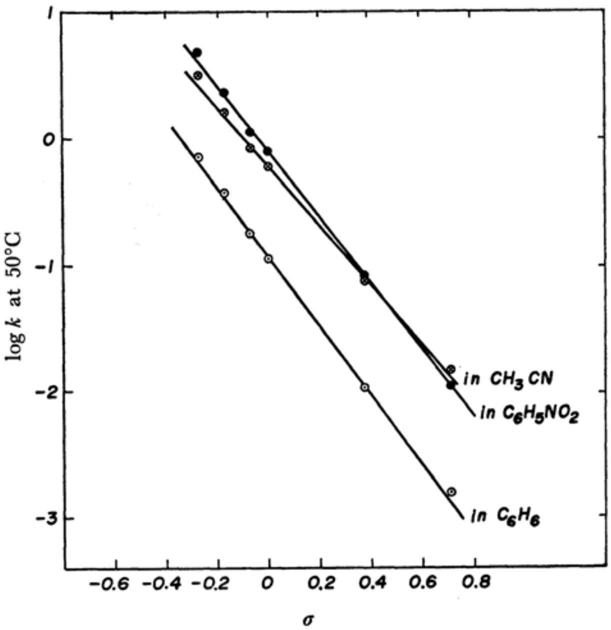

Fig. 5. Hammett plots of the reaction (I), ●, in nitrobenzene; ⊗, in acetonitrile; ⊙, in benzene.

Menschutkin reaction in aromatic solvents with the non-electrostatic properties of these solvents. On examination of the data described in the literature[24] and the data at hand, it can be said that the electron density in the aromatic nucleus seems to play a role in determining the kinetics of this type of reaction in aromatic solvents. There seems to be a specific solvation of a leaving anion in a transition state by aromatic solvents. This effect is clearly in the sequence: nitrobenzene>bromobenzene>benzene>toluene>*p*-xylene. For example, in such aromatic solvents as toluene or *p*-xylene, containing electron-releasing substituents, the rate of this type of reaction is slower than in other solvents.

On the other hand, it has also been noticed that a transition state assumed to be close enough to picrate, the reaction product, may be considerably sensitive to the non-electrostatic or diffusion factor of solvent effects.[25]

These factors may cause a difference in the mode of the variation in ρ with the solvent between the members of group a and those of group b. However, the explanation of this difference must be reserved until it is confirmed that this behavior is not unusual for the Menschutkin type of reaction in non-aqueous solvents; we shall continue our examination on this problem.

Experimental

Kinetic Procedure. It was conductmetrically verified by Hertel and Dressel[12] that the reaction (I) strictly follows the bimolecular rate law and that it is practically completed through the scheme. However, the formation of picrates enabled us to follow the kinetic runs by the convenient spectroscopic technique. The stock solution was introduced into a reaction vessel with a capacity of 50 m*l*, equipped with a slender and long-necked flask, and placed in a thermostat held at 50±0.1°C; then the stock solution of dimethylaniline or its derivatives was added. The sampling solution from this vessel was extracted three times with a constant volume of a water-benzene mixture so that the picrate produced might be obtained as an aqueous solution. This solution was diluted to a concentration favorable for measuring the optical density of the solution. In the experiments using nitrobenzene as the solvent, the water layer was further washed with benzene in order to prevent the contamination by this solvent from markedly affecting the optical densities of the water layer. The optical density of the samples was obtained over the range of 360—400 mμ at intervals of 10 mμ on a Hitachi spectrophotometer EPU-2A, using quartz cells 1.0 cm thick.

These salts appear to be completely dissociated in water. To check this point, the molecular extinction coefficients, ε, of *N,N,N*-trimethylanilinium and *p*-tolyl-*N,N,N*-trimethylanilinium picrate were measured. The calibration curves which were obtained in the range of 360—400 mμ at intervals of 10 mμ obeyed Beer's law excellently in each case. The results are given in Table 3. The table shows that these coefficients are essentially identical with each other, so the data of the *N,N,N*-trimethylanilinium salt were taken for the calculation of the rate constants.

A typical run, the reaction of *m*-methyl-dimethylaniline with 2,4-6-trinitroanisole in tetrahydrofuran at 50°C, is shown in Fig. 7, where D and D_∞ are the

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25) E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 4517 (1964).

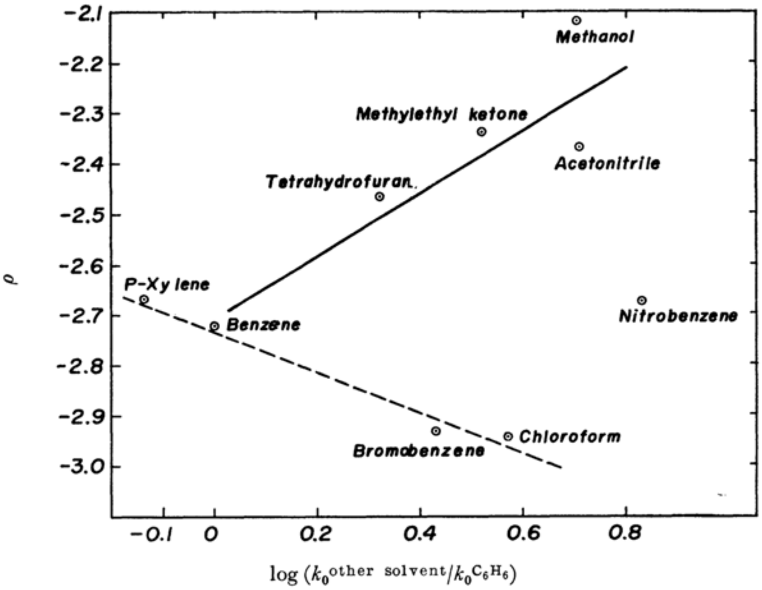

Fig. 6. The relationship between ρ and log ($k_0^{\mathrm{other\ solvent}}/k_0^{\mathrm{C_6H_6}}$) as the solvent parameter for the reaction (I).

TABLE 3. MOLECULAR EXTINCTION COEFFICIENTS OF SOME PICRATES IN WATER

Picrates, λ, mμ	360	370	380	390	400
Sodium	14080	13090	11730	10780	9870
N,N,N-Trimethylanilinium	13990	12890	12890	11670	9796
p-Methylphenyltrimethyl-ammonium	13960	13050	11850	10860	10010

optical densities of the samples in water at finite and infinite times respectively. Since the optical density is proportional to the concentration of the picrate produced, the second-order rate constant can be obtained by multiplying the slope of such a figure by εl (l indicates the cell length; 10 mm). In the case of slower reactions the method of initial rates was carried out in order to estimate the rate constants by the equation: $\mathrm{d}D/\mathrm{d}t = (k/\varepsilon l)D^{\mathrm{a}}{}_{\infty}\cdot D^{\mathrm{b}}{}_{\infty}$. The rate constants obtained by the two procedures agree with each other within 10%, as is shown in the case of bromobenzene in Table 2. The concentrations used in the calculation of the velocity constants were the concentrations at the temperature of the experiment by correcting for solvent expansion. The densities of THF at several temperatures were calculated by the usual manner using one experimental value, d_{20}.[26]

At least one duplicate experiment was always performed with a different initial concentration. As a result, it was observed that the rate coefficient is independent of the concentration. In methanol, however, it was observed that the rate of the methanolysis of trinitroanisole is comparable to the rate of the reaction of *m*-nitro-dimethylaniline with trinitroanisole. The estimation of the rates of the methanolysis of trinitroanisole in methanol was carried out by the initial rate method. The plot of D against t gives a straight line through the zero point. The slope of this plot was $(5.38\pm0.21)\times10^{-3}\,\mathrm{hr}^{-1}$ for the pseudo first-order methanolysis rate (the average value of three independent runs). Using this value, the rate coefficients of the reaction between *m*-methyl- or *p*-methoxy-*N,N*-dimethylaniline and trinitroanisole in methanol were given in the following form:

$$k=\frac{1}{a\cdot b}\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_0=\frac{k_{\mathrm{methanolysis}}}{b}$$

where $(\mathrm{d}x/\mathrm{d}t)_0$ was obtained by means of Newton's numerical differential equations.[27]

The rate of the reaction between *m*-nitro-dimethylaniline and trinitroanisole in methanol was obtained by the method of Andrews and Young[28] using the following equation:

$$\frac{(\mathrm{d}x/\mathrm{d}t)_0}{[\mathrm{TNA}]_0}=k[\mathrm{DMA}]_0+k_{\mathrm{methanolysis}}$$

A plot of $(\mathrm{d}x/\mathrm{d}t)_0/[\mathrm{TNA}]_0$ *vs.* $[\mathrm{DMA}]_0$ was a straight line the slope of which gave k.

Table 2 gives the results for the reaction rates in various solvents obtained as has been described above.

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[26] J. H. Perry, "Chemical Engineer Handbook," 4th ed., McGraw-Hill Book Co., New York (1963).

[27] M. Oiwa, "Hanno Sokudo Keisanho, (Measurement of the Reaction Rates)," Asakura Shoten, Tokyo (1962), p. 86.

[28] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed., John Wiley and Sons, New York, N. Y. (1953), p. 369.

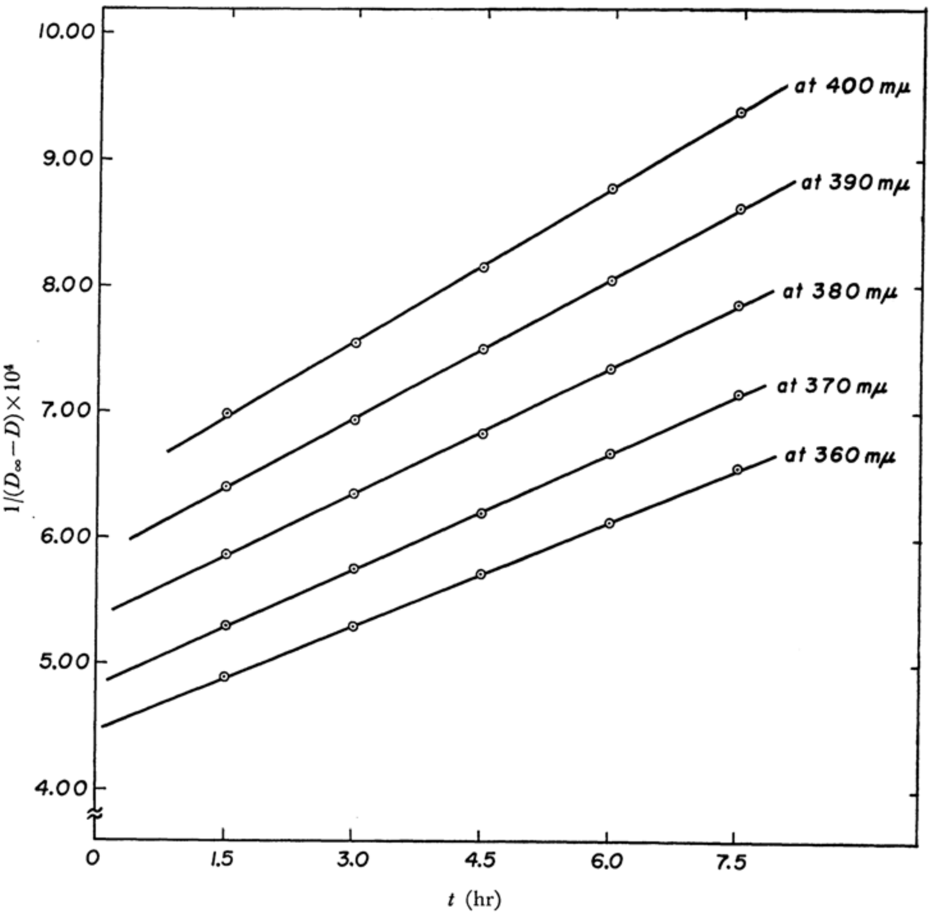

Fig. 7. A typical run for the reaction between *m*-methyl-dimethylaniline and trinitroanisole in tetrahydrofuran at 50°C.

Materials. The *N,N*-dimethylaniline, from Wako Pure Chemicals, was purified according to the procedure described by Fieser[29] and stored in an atmosphere of dry nitrogen until use.

The *p*-methoxy-, *p*-methyl-, *m*-chloro-, and *m*-methyl-*N,N*-dimethylanilines were prepared according to the directions of Fukui *et al.*[30] from commercial *p*-methoxy-, *p*-methyl-, *m*-chloro-, and *m*-methylanilines respectively. The purification of these materials was similar to that of *N,N*-dimethylaniline. The purity of these samples was assured to be sufficient by elemental analysis, infrared spectroscopy, and gas chromatography, in which only a single peak was observed in every case, using two solid supports, P. E. G. 6000 and Silicone D. C. 550.

The *m*-nitro-*N,N*-dimethylaniline was prepared by the usual method of nitration[31] and recrystallized from 95% ethanol at least four times; mp 57—58°C, lit. 57—58°C.[32]

The 2,4,6-trinitroanisole (TNA) was prepared by the reaction[33] of dissolved sodium hydroxide in methanol at 0—5°C with picryl chloride (which was taken from picric acid and phosphorus pentachloride), recrystallized from methanol several times, and dried over silica gel in a desiccator; mp 67—68°C, lit. 67—68°C.[32] Found: C, 34.71; H, 2.35; N, 17.05%. Calcd for $C_7H_5N_3O_7$: C, 34.58; H, 2.0; N, 17.28%.

The *N,N,N*-trimethylanilinium- and *p*-methylphenyltrimethylammonium picrates were prepared from equimolar quantities of amines and anisole at 50°C in THF and were recrystallized from water until a constant melting point was obtained; mp 120—120.5°C and 195—196°C[33] respectively. The sodium salt was prepared from picric acid and sodium hydroxide in boiling water and recrystallized. These salts were dried in an Abderhalden flask for several hours at the boiling point of acetone and then used to obtain the molecular extinction coefficients in water. Benzene, *p*-xylene, and bromobenzene were shaken with concentrated sulfuric

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[29] L. F. Fieser, "Experiments in Organic Chemistry," Maruzen, Tokyo (1957).

[30] K. Fukui, Y. Inamoto, S. Takase and T. Kitano, *Kogyo Kagaku Zasshi (J. Chem. Soc., Japan, Ind. Chem. Sect.)*, **62**, 531 (1959).

[31] "Org. Synth.," Coll. Vol. 3, p. 658 (1955).

[32] R. C. Farmer, *J. Chem. Soc.*, **1959**, 3425.

[33] J. B. Ramsey and E. L. Colichman, *J. Am. Chem. Soc.*, **69**, 3043 (1947).

acid several times until no further discoloration was observed; they were then washed with water, about 10% aqueous potassium hydroxide, and again with water, dried over calcium chloride, and distilled. The center fraction was further distilled twice from phosphorus pentoxide.

The nitrobenzene and methyl ethyl ketone were commercial reagents used without further purification. After drying with calcium chloride and then phosphorus pentoxide, they were distilled three times. The center fraction was collected for use.

The tetrahydrofuran was refluxed with potassium hydroxide and distilled. After drying and refluxing with sodium wire, the center fraction was redistilled. It was stored over sodium wire and then further distilled before use.

The acetonitrile was dired over phosphorus pentoxide, distilled, and treated as before. The center franction was stored over phosphorus pentoxide and distilled before use.

The methanol,[34] chloroform,[35] and carbon disulfide[36] were purified as has been described in the literature.

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[34] A. A. Maryott, *J. Am. Chem. Soc.*, **63**, 3079 (1941).

[35] S. O. Morgan and H. H. Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

[36] E. E. Ogg and J. W. Williams, *J. Am. Chem. Soc.*, **50**, 2894 (1928).