curve, the concentration of quinoline at each time, t, could be determined.

Results. For the determination of substituent effects and solvent effects, all kinetics experiments were carried out at 76.4 ± 0.2 °C. To obtain the Arrhenius plot (ln k vs. $1/t$) additional runs were made at 86.4 ± 0.2 and 96.4 ± 0.2 °C.

Rate data of each kinetics experiment are shown in Table I. The method of least squares was used to derive the average slope of each reaction plot from the raw data.

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Registry No.—**1a,** 56346-06-6; **1c,** 65815-43-2; **1d,** 65815-44-3; **1e,** 65815-45-4; **1f,** 65815-46-5; **1g,** 65815-47-6; **1h,** 65815-48-7; **1i,** 65815-49-8; **2a,** 65847-84-9; (*Z*)-**2c,** 65815-50-1; (*E*)-**2c,** 65815-51-2; **2d,** 65815-52-3; **2e,** 65815-53-4; **2f,** 65815-54-5; **2g,** 65847-83-8; **2h,** 65815-55-6; **2i,** 65815-56-7; quinoline, 91-22-5; ethyl benzoylacetate, 94-02-0; *p*-methoxybenzoyl chloride, 100-07-2; *m*-chlorobenzoyl chloride, 618-46-2; ethyl *p*-methoxybenzoylacetate, 2881-83-6; benzoyl chloride, 98-88-4; ethyl *p*-nitrobenzoylacetate, 838-57-3; *p*-toluyl chloride, 874-60-2; ethyl *p*-fluorobenzoylacetate, 1999-00-4.

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Rate of Deprotonation of Phenylnitromethane by Hydroxide Ion in Aqueous Dimethyl Sulfoxide and Aqueous Methanol[1]

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The rates of deprotonation of phenylnitromethane by hydroxide ion in aqueous dimethyl sulfoxide and aqueous methanol have been measured at 20, 30, and 40 °C under pseudo-first-order conditions using the stopped-flow technique. The various solvents (vol %) used, the second-order rate constants ($k_2 \times 10^{-2}$ M^{-1} s^{-1}) found at the three temperatures, ΔH^* (kcal/mol), and ΔS^* (cal/mol deg), respectively, are as follows: 20% methanol, 1.54, 2.97, 5.78, 11.4, −9.4; 50% methanol, 2.22, 4.39, 8.44, 11.6, −8.3; 33.3% Me_2SO, 3.22, 6.43, 9.42, 9.2, −15.5; 50% Me_2SO, 13.8, 20.8, 36.9, 8.3, −15.8; and 66.7% Me_2SO, 10.47, 17.03, 24.60, 7.2, −15.6. A plot of log k_2 (25 °C) vs. ΔpK for the aqueous Me_2SO solutions gave a least-squares slope (β) of 0.58 ($r = -0.997$). The Brønsted β coefficient calculated on the basis of the enhanced basicity of hydroxide ion in these mixtures thus agrees closely with that obtained for aqueous solutions by variation in the type and strength of the bases employed. The constancy of the entropy of activation in Me_2SO–water mixtures suggests that solvent reorganization is very similar in each solvent and that the differences in rate can be attributed to the increased strength of the interaction between the solvent and the incipient water molecule.

Interest in proton transfer reactions is promoted by their formal simplicity. The accumulated evidence points to the mechanism shown in eq 1–3, in which charge types are not shown.[2]

$$\text{H–A} + \text{B} \rightarrow \underset{1}{\{\text{A–H} \cdots \text{B}\}} \quad (1)$$

$$\{\text{A–H} \cdots \text{B}\} \rightarrow \underset{2}{\{\text{A} \cdots \text{H–B}\}} \quad (2)$$

$$\{\text{A} \cdots \text{H–B}\} \rightarrow \text{A} + \text{H–B} \quad (3)$$

Species **1** and **2** represent hydrogen-bonded encounter complexes, and reactants and products can be free species or ion pairs.

Carbon acids are expected to behave qualitatively differently than oxygen or nitrogen acids because of the inability of the former to hydrogen bond in the encounter complex. Both carbonyl[3] and nitro compounds[4] have been studied extensively with a view toward defining the structure of the transition state in deprotonation reactions in aqueous solution. Many weaker acids have been studied in nonaqueous

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Table I. Rate Constants for Phenylnitromethane Reacting with Hydroxide Ion

Solvent[a]	t, °C	$k_2 \times 10^{-3}$, $M^{-1}\,s^{-1}$[b]	n[c]	r[d]
Water[e]	25.0	0.151		
20.0% MeOH	20.0	0.154 ± 0.023	5	0.999
	25.0	0.215		
	30.0	0.297 ± 0.054	6	0.997
	40.0	0.578 ± 0.169	6	0.996
50.0% MeOH	20.0	0.222 ± 0.038	5	0.999
	25.0	0.314		
	30.0	0.439 ± 0.084	5	0.999
	40.0	0.844 ± 0.244	5	0.999
33.33% Me_2SO	20.0	0.322 ± 0.041	7	0.995
	25.0	0.448		
	30.0	0.643 ± 0.202	6	0.994
	40.0	0.942 ± 0.252	6	0.999
50.00% Me_2SO	20.0	1.38 ± 0.21	5	0.999
	25.0	1.73		
	30.0	2.08 ± 0.22	5	0.998
	40.0	3.69 ± 0.18	4	0.999
66.67% Me_2SO	20.0	10.47 ± 1.79	5	0.997
	25.0	13.28		
	30.0	17.03 ± 2.36	5	0.998
	40.0	24.60 ± 0.89	5	0.999

[a] Volume percent. [b] The values in this column are least-squares slopes for the plot of pseudo-first-order rate constants vs. hydroxide ion concentration. The deviation given is the difference between the least-squares slope and the k_2 calculated for the point furtherest from the line. Values at 25 °C are interpolated from the Arrhenius equation. [c] Number of different hydroxide ion concentrations used. [d] Correlation coefficient truncated at three decimal places. [e] Taken from ref 7.

solutions.[2b,5] For the deprotonation of nitro compounds, Bordwell and his co-workers have concluded that in the transition state the proton is approximately half-transferred, even for reactions of fairly large $\Delta G°$ values, and that rehybridization of the carbon center has progressed only slightly from sp^3 to sp^2. These conclusions were based on substituent effects on both rate and equilibria in the ionization of substituted aryl nitromethanes and aryl nitroethanes,[6a] deuterium isotope effects,[6b] and structural effects on the protonation rates of nitronate anions.[6c] Keefe and Munderloh have supported this view, based on their study of the reaction of phenylnitromethane and its deuterated analogue with 15 bases in aqueous solution.[7]

Bell and Cox have reported an interesting study of the inversion of (−)-methone in Me_2SO–water mixtures.[8] They were able to correlate rate changes in these solvents with the enhanced basicity of hydroxide ion, as reflected in H_- values.[9] The Brønsted β value for the reaction calculated from these variations in the basicity of the medium agreed quite closely with that determined for acetone reacting in aqueous solution with bases of strengths approaching that of hydroxide ion.

Our interest in extending this latter approach to the study of phenylnitromethane was twofold. We wanted to see if the Brønsted β coefficient determined in this fashion would agree with the one determined in the standard manner by Keefe and Munderloh and if the activation parameters found for the reaction in aqueous Me_2SO would be interpretable in terms of the previously suggested structure of the transition state.[6b] The results of this study are described below.

Experimental Section

Phenylnitromethane was prepared by the procedure of Kornblum, Smiley, Blackwood, and Iffland.[10] The crude product boiled at 75–85 °C (3.5 mm) and a redistilled sample had bp 68–69 °C (0.7 mm). Stock solutions were prepared by dissolving weighed amounts in the appropriate Me_2SO–water mixtures or in absolute methanol. Three different concentrations were prepared in each solvent mixture by dilution of a small aliquot of the stock solution with solvents containing excess potassium hydroxide. Molar absorptivities were obtained from the slope of the linear plot (r > 0.996) of absorbance vs. concentration. In aqueous methanol, the anion showed λ_{max} at 293.5 nm with log a = 4.33. The appropriate values in aqueous Me_2SO are as follows: 33.3% Me_2SO, 300 nm, 4.38; 50.0% Me_2SO, 303 nm, 4.31; 66.7% Me_2SO, 308.5 nm, 4.25.

Dimethyl sulfoxide (Aldrich Chemical Co.) was stirred overnight with calcium hydride and distilled at 20 mm. A middle-boiling fraction had bp 86 °C. Aqueous mixtures were prepared by mixing appropriate volumes of Me_2SO or reagent grade (Mallinckrodt) methanol with distilled, demineralized, freshly boiled water. Solutions of potassium hydroxide were prepared by diluting aliquots of carbonate-free, ~1 M base in either water or 33.33% (v/v) Me_2SO with appropriate solvent to prepare ~0.1 M solutions. These were standardized against potassium acid phthalate and were subsequently diluted to the concentration range of 10^{-2}–10^{-4} M for use in kinetic studies.

Deprotonation kinetics were followed by ultraviolet spectroscopy using a Durrum stopped flow spectrophotometer. The analogue photomultiplier output representing absorbance changes was stored in a Physical Data Model 514A, 10-bit transient recorder and was analyzed by means of a varian 620-l computer. Runs were made under pseudo-first-order conditions, with base concentrations ranging from 10 to 100 times that of the nitro compound. Good first-order kinetics were followed, and analyses characteristically were made using 3 half-lives. Data were analyzed using the expression in eq 4, in which S_∞ and S_t represent a signal proportional to the absorbance at infinity and at time t, respectively.

$$\ln (S_\infty - S_t) = -k_\Psi t + \ln (S_\infty - S_0) \qquad (4)$$

Least-squares analysis of the regression of ln ($S_\infty - S_t$) on time gave correlation coefficients better than −0.99. Such analyses typically utilized 300–600 data points.

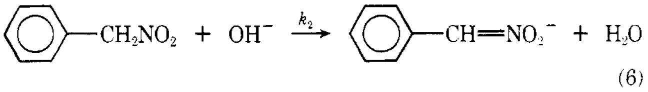
The second-order rate constants were calculated by use of eq 5, in which $\{OH^-\}$ represents the constant concentration of hydroxide ion.

$$k_\Psi = k_2\{OH^-\} \qquad (5)$$

A plot of k_Ψ vs. $\{OH^-\}$ is linear (r > 0.994) and must pass through the origin. Because of this latter requirement, the origin was included as a fixed data point in the analysis.

Results and Discussion

The rates of deprotonation of phenylnitromethane, eq 6, by hydroxide ion in a variety of Me_2SO–water and methanol–water mixtures have been determined at 20, 30, and 40 °C, using the stopped flow technique.



(6)

The second-order rate constants are collected in Table I. The rate constant is relatively insensitive to the change from water to methanol–water, as seen from a mere doubling of k_2 at 50 vol % (30.9 mol %) methanol. In contrast, the change from water to 66.67 vol % (33.63 mol %) Me_2SO results in an 88-fold increase in k_2. These findings are consistent with changes in the basicity of the media.

Bowden[9] has summarized much previous work dealing with acidity and basicity in strongly basic media. The basicity of a medium is given by the expression in eq 7, in which pK_a refers to the ionization of an indicator in water and the concentration terms refer to ionization in the medium in question.

$$H_- = pK_a - \log(\{HA\}/\{A^-\}) \qquad (7)$$

H_- therefore represents the increase in the basicity of the medium over pure water brought about by changing activity coefficients. Methanol–water mixtures are anomalous in that there is a *very slight decrease* in H_- at a given hydroxide ion concentration in changing from pure water to pure methanol. The basicity of aqueous methanol solutions is therefore not expected to deviate significantly from that of pure water.

On the other hand, Me_2SO–water mixtures show an orderly

Table II. Δp*K*'s for Phenylnitromethane and Water in Aqueous Me_2SO at 25 °C

Solvent[a]	Mol % of Me_2SO[b]	log k_2	Δp*K*[c]	Excess basicity[d]
Water	0	2.18[e]	−8.83	0.00
33.33% Me_2SO	11.24	2.65	−9.76	0.96
50.00% Me_2SO	20.21	3.24	−10.83	1.87
66.67% Me_2SO	33.63	4.12	−12.14	3.09

[a] Volume percent. [b] All calculations involving densities used those of J. M. G. Cowie and P. M. Toporowski, *Can. J. Chem.*, **39**, 2240 (1961). [c] Calculated from eq 9 with p*K* for phenylnitromethane of 6.88 (ref 6a). [d] Excess basicity is defined as $H_- - pK_w - \log\{OH^-\} + \log a_{H_2O}$ (ref 11). [e] Taken from ref 7.

increase in H_- from 12.04 for 0.011 M hydroxide ion in pure water to ~22.5 for the same concentration in 95 mol % Me_2SO, and Cox and Stewart[11] have shown that H_- rises rapidly as the last traces of water are removed from the mixture. The enhanced basicity in aqueous Me_2SO is attributed to the competition between hydroxide ions and Me_2SO molecules for hydrogen bond formation with donor water molecules, resulting in an increase in the activity of the hydroxide ion as the Me_2SO content increases.[9]

In their study of the inversion of (−)-methone, Bell and Cox[8] derived Δp*K* values as a function of solvent composition based on eq 8 and 9.

$$pK_{H_2O} = H_- + \log(\{H_2O\}/\{OH^-\}) \qquad (8)$$

$$\Delta pK = pK^0_{SH} - H_- - \log(\{H_2O\}/\{OH^-\}) \qquad (9)$$

Equation 8 gives the expected change in the ionization constant of water, while eq 9 gives the difference in p*K* between the ionization of (−)-menthone in water and the ionization of water in aqueous Me_2SO mixtures. A plot of log k_2 vs. Δp*K*, the usual Brønsted relationship, gave a slope of 0.48 as the Brønsted β coefficient. This compared well with the β value of 0.54 which had been determined for acetone reacting in water with bases of strength up to that of hydroxide ion.

Analogous Δp*K* values for the present study are shown in Table II. These values were calculated by use of 6.88 as the p*K* for phenylnitromethane in water.[6a] The H_- values used were obtained by linear interpolation of those reported by Bowden.[9] The assumption of Bell and Cox that $H_- - \log\{OH^-\}$ is independent of the small hydroxide ion concentrations used in this study was also made. A plot of log k_2 vs. Δp*K* gave a least-squares slope (β) of 0.58 ($r = -0.997$). Not surprisingly, a plot of log k_2 vs. excess basicity, as defined by Cox and Stewart,[11] was also linear ($r = 0.996$) and gave nearly the same slope (0.63). Keefe and Munderloh[7] have tabulated the results for the reaction of phenylnitromethane with 14 oxygen and nitrogen bases and with fluoride ion in aqueous solution. They reported a Brønsted β coefficient of 0.57. The agreement between the β value determined in their study and the one reported here indicates that the measurement of deprotonation rates as a function of aqueous Me_2SO composition provides a satisfactory approach to the determination of β for nitro compounds, just as it does for ketones.

It has been pointed out on the basis of both theory[6a,12] and experiment[4c,6a] that Brønsted coefficients are not necessarily good indicators of transition state structure in proton-transfer reactions, despite the fact that Brønsted plots sometimes show the expected curvature.[2a,13] Whether or not a Brønsted plot shows curvature is frequently open to interpretation, and Kemp and Casey[14] have argued that most proton transfers that have been studied give plots that are linear over remarkably large Δp*K* ranges. In contrast, Hupe and Wu[15] have recently reported a definitive case in which distinct curvature is seen in the Brønsted plot for deprotonation of 4-(*p*-nitrophenoxy)-2-butanone by an homologous set of bases. They suggest that curvature due to changes in transition state bond orders is essentially not observable over the Δp*K* range accessible with the single substrate and homologous set of catalysts typically employed in constructing a Brønsted plot. Instead, they propose that curvature may result from a compromise between the forces of charge stabilization by solvent molecules and the unfavorable energy required to leave solvent molecules in position after proton transfer has occurred.

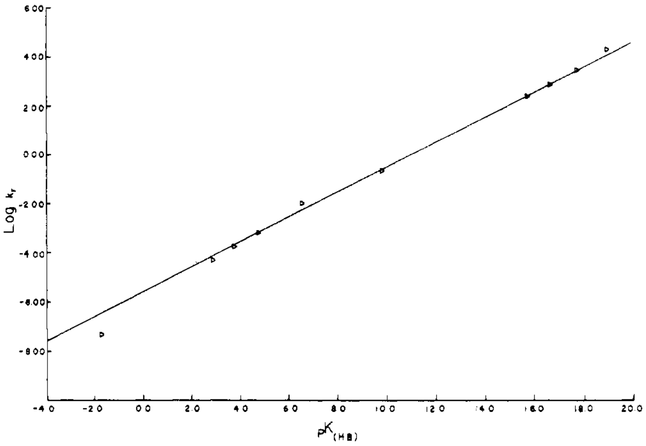


Figure 1. Plot of the logarithm of the rate constant (25 °C) vs. p*K* for the conjugate acids of oxygen bases used for the deprotonation of phenylnitromethane. Because the point for water ($pK_{(HB)} = -1.86$) deviates significantly, this point was not included in the calculation of the least-squares line shown. The data points for aqueous solutions were taken from ref 7.

In this connection it is interesting to examine the combined data of Keefe and Munderloh[7] and the present study. Reanalysis of the previously reported results by means of a plot of log k_2 vs. pK_{HB} gave a slope of 0.56 with a correlation coefficient of 0.974, which reflects a slight scatter of points. A plot containing only the seven points for oxygen bases gave a β of 0.53 with $r = 0.987$. Addition of the three points for aqueous Me_2SO solutions results in a β of 0.50 and r of 0.994. Interestingly, visual inspection of the plot, shown in Figure 1, reveals that the point for hydroxide ion in water is cleanly on the line, although that for water falls somewhat below it. These combined data clearly indicate that there is no curvature in this case for a series of homologous bases representing a difference of ~16 p*K* units. The continued linearity of the plot is remarkable for two reasons. First, the activation parameters for the reaction in water differ significantly from those for the reaction in aqueous Me_2SO (vide infra), which suggests that solvational factors are greatly different in the two types of solvents. Consequently, a difference in w_r (the energy required to bring the reactants together, including solvational energy[15]) might have been expected, and this could have modified the slope and/or the intercept in passing to the mixed solvents. Second, the H_- scale in the range presently applied is based on changes in the ionization constants of aromatic amines. Because these acids are structurally dissimilar to carbon acids nonparallel changes in ionization behavior might have been expected. Again, in this respect, phenylnitromethane compares to (−)-methone in introducing no irregularities. Despite these possible complications, the plot continues linearly even though the reaction is carried out under very different solvational circumstances. This behavior is compatible with the interpretation that lack of curvature stems from the essential lack of rehybridization of the central carbon atom as the transition state is reached. Curvature may possibly mean that there is extensive charge delocalization accompanied by structural reorganization as the transition state is attained.

Table III. Activation Parameters for the Deprotonation of Phenylnitromethane by Hydroxide Ion at 25 °C

Solvent[a]	E_a[b]	ΔH^*[b]	ΔS^*[c]
Water[d]	12.2	11.6	−9.4
20.00% MeOH	12.0	11.4	−9.4
50.00% MeOH	12.2	11.6	−8.3
33.33% Me_2SO	9.8	9.2	−15.5
50.00% Me_2SO	8.9	8.3	−15.8
66.67% Me_2SO	7.8	7.2	−15.6

[a] Volume percent. [b] Kcal/mol. [c] Cal/mol deg. [d] Taken from ref 7.

The activation parameters for the deprotonations are collected in Table III. Again, there is a close correspondence between the values for the reaction in aqueous methanol and in pure water. The presence of Me_2SO in the solvent mixture causes a trend toward smaller activation enthalpies. Differences in reaction rate constants are based solely on the enthalpy differences, because the entropy of activation for the reaction is virtually identical in the three mixtures studied and is more negative than in water and methanol–water mixtures.

Caldin, Jarczewski, and Leffek[16] reported activation parameters for the reactions in acetonitrile solution of *p*-nitrophenylnitromethane with tri-*n*-butyl- and triethylamine. These reactions have enthalpies of 6.0 and 6.7 kcal/mol and entropies of −25.2 and −22.1 cal/(mol deg), respectively. The low enthalpies of activation were attributed to the weakness of the bond between the hydrogens and the aliphatic carbon atom, and the large negative entropies of activation were interpreted as an indication of a transition state that is more strongly solvated than the initial state. The values in Table III seem to reflect the same solvational phenomena, in that the enthalpies of activation and entropies of activation are smaller in the mixed solvents than in water. If the proton is partly transferred in the transition state, loosening of the C–H bond and partial formation of an O–H bond should render the proton more susceptible to solvational interaction in the transition state than when it is firmly bonded to the carbon atom in the reactant. Thus, the difference in attractive solvational interactions between incipient water molecule and the hydroxide ion is greater than that between the incipient phenylmethanenitronate anion and the phenylnitromethane molecule. This effect is progressively magnified as the Me_2SO content increases, resulting in progressively decreasing enthalpies of activation. Structural tightening in the solvent is also apparently associated with these interactions, producing relatively large, negative entropies of activation. The constancy of ΔS^* in the three mixtures studied cannot be interpreted unambigously at present.

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Registry No.—Phenylnitromethane, 622-42-4; hydroxide ion, 14280-30-9; dimethyl sulfoxide, 67-68-5; methanol, 67-56-1.

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