

the changes are small, the trends will be amplified in plots of $\Delta d (= d_3 - d_2)$, $\Delta\phi (= \phi_2 - \phi_1)$, and $\Delta\alpha (= \alpha_1 - \alpha_3)$ vs the α 's, d 's, and ϕ 's. The changes will presumably be higher for the α_1 vs ϕ_2 plot. $\Delta\alpha (= \alpha_1 - \alpha_3)$ vs $\Delta\phi$ or vs Δd plots should also show ascending trends.

Since ϕ_2 changes more than ϕ_1 along the rotation we expect better correlations vs ϕ_2 than vs ϕ_1 . Moreover, severe scatter in the correlations due to errors in the measured values are expected since the overall changes in bond lengths and angles along the rotation are not very large. Several plots are given in supplementary material Figures S4–S30. For convenience they were treated as linear even when the scatter was appreciable, and the slope of many correlations are given in Table III.

Calculated and experimental d_1 vs ϕ_2 plots (Figure S4) show a descending trend, d_1 vs ϕ_1 plots show large scatter, d_2 vs ϕ_1 and d_3 vs ϕ_2 (Figure S5) plots show an ascending trend. Calculated and experimental d_2 vs ϕ_2 and d_3 vs ϕ_1 show negative trends (Figures S6–S15). The derived $\Delta d (= d_3 - d_2)$ vs $\Delta\phi (= \phi_2 - \phi_1)$ correlation (Figure 6) demonstrates the scatter observed in most of the experimental correlations.

Experimental plots of angle α_2 vs ϕ_1 show a large scatter. The calculated plot shows an ascending trend. The complementary α_2 vs ϕ_2 plots (Figures S16–S18), of α_1 vs ϕ_1 (Figures S19–S22) and (with a large scatter) for α_3 vs ϕ_2 plots, show descending trends. Ascending trends with appreciable scatter were observed for the calculated α_3 vs ϕ_1 , α_1 vs ϕ_2 , and $\Delta\alpha$ vs $\Delta\phi$ plots. Scatters were also observed in the α_2 vs $\Delta\phi$ plots which show descending trend (Figures S23–S25). The sum $\phi_1 + \phi_2$ for **2** generally increases during the one-ring flip process. The expected decrease of α_2 vs $\phi_1 + \phi_2$ is displayed in the calculated and experimental plots (Figures 7 and S26). For few non-hydrogen-bonded compounds $\phi_1 + \phi_2 > 90^\circ$ in the ground state, but the overall trend parallels the calculated plots.

In the bond length vs bond angle correlations (Figures S27–S29) d_1 vs α_2 plots are reasonably linear with a positive slope. d_2 vs α_1 and d_3 vs α_3 plots show descending trend with scatter. Calculated d_2 vs α_3 and d_3 vs α_1 plots show severe scatter with ascending trend. The experimental ascending Δd vs $\Delta\alpha$ plot for

non-hydrogen-bonded benzophenones (Figure S30) is one of the best correlations.

Consequently, correlations exist between various structural parameters of the benzophenones and are frequently amplified in the hydrogen-bonded systems. Since the one-ring flip is the favored rotational route, the trends indicated by both the experimental correlations and the MM calculations predict the changes in the structural parameters accompanying rotations of the rings. For example, from Figures S4B, S5, S15, and S22, d_1 for the hydrogen-bonded systems decreases by 0.02 Å, d_3 increases by 0.015 Å for non-hydrogen-bonded systems, α_2 decreases by ca. 3° and α_1 increases by ca. 3.5° , during the rotation. Both calculated and observed Δd vs $\Delta\phi$ plots (Figure 6) indicate an increase of 0.04 Å in Δd from the equilibrium value to the value in the rotational transition state, where $\Delta\phi \approx 90^\circ$.

Conclusions

In contrast with the 1,1-diarylethylenes which show a one-ring/two-ring flip dichotomy of rotational pathways, helical benzophenones undergo a helicity reversal process exclusively via a one-ring flip process. This is ascribed to the larger Ar—C=X conjugation energy for X = O (benzophenones) than in X = CR₂ (1,1-diarylethylenes). The structural correlation method is used for tracing the preferred rotational mechanism, and for grossly evaluating the structural parameters of the transition state. A complementary analysis of X-ray data and calculation can be used to derive reliably these structural parameters.

Acknowledgment. We are grateful to the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel, and The Bat-Sheva de Rothschild Fund for support of this work.

Registry No. 2, 119-61-9.

Supplementary Material Available: Figures S1–S30 of correlations between various bond lengths, bond angles, and torsional angles for benzophenones and calculations of changes in these parameters for the one-ring flip of **2** (24 pages). Ordering information is given on any current masthead page.

Proton Transfers among Oxygen and Nitrogen Acids and Bases in DMSO Solution

Calvin D. Ritchie* and Shanzheng Lu

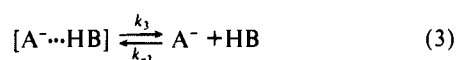
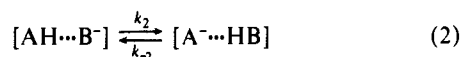
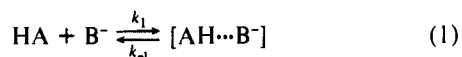
Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. Received May 14, 1990

Abstract: Rate constants for the proton-transfer reactions between conjugate acids and bases of several amines, phenols, carboxylic acids, and the solvated proton in DMSO-*d*₆ at 20 °C have been determined by the use of NMR line-shape analysis. Equilibrium constants for the same reactions are obtained from the p*K*_a's of the acids in dimethyl sulfoxide, some of which have been reported in earlier work and the rest obtained in the present work by use of Bordwell's indicator techniques. All of the reactions have rate constants considerably below expected diffusion-controlled limits for the proton transfers in the thermodynamically favorable direction, and several of the reactions, including the identity reactions of carboxylic acids, have kinetic deuterium isotope effects, *k*_H/*k*_D, between 0.8 and 1.3. For reactions of *N,N*-dimethylbenzylammonium ion with several phenoxides, carboxylates, and solvent, the rate constants for transfers in the unfavorable directions show a reasonable Brønsted correlation with $\beta \approx 1$ and a reasonably constant reverse rate constant of $\approx 3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. The data clearly indicate that the proton-transfer step is not rate-limiting in these reactions. Most likely, desolvation is involved in the rate-limiting steps, but the rate constants are not simple functions of acidities as might have been expected if hydrogen bonding of acid to solvent were the major factor involved in the solvation. Other factors, particularly dispersion interactions of solvent with solutes, are discussed. We suggest that the formation of an acid–base complex with proper orientation to allow contact between the proton and the basic site is rate-determining and involves desolvation along with detailed steric interactions of the acid–base pair.

Eigen's classic studies¹ established the fact that proton transfers between electronegative atoms (specifically, O, N, and F) in

aqueous solution frequently occur with diffusion-limited rates in the thermodynamically favorable direction. In the three-step

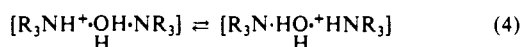
mechanism proposed in those studies



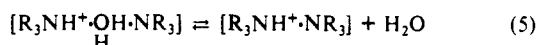
either k_2 or k_{-2} , whichever is for the thermodynamically favorable direction, is larger than k_{-1} or k_3 , respectively, for such "normal" reactions.

Rate constants for the formation of simple encounter complexes in eq 1 or the reverse of eq 3 can be calculated from diffusion theory² and are expected to be between 10^9 and $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ near 25 °C and only weakly dependent on structures of the acids and bases. Equilibrium constants for the formation of "noninteracting" encounter complexes have been estimated^{3,4} to be approximately 10^{-1} M^{-1} so that k_{-1} for reaction 1 is expected to be approximately 10^{10} – 10^{11} s^{-1} near 25 °C. Thus, for a thermodynamically favorable proton transfer occurring by the mechanism of reactions 1–3, reaction 1 will be rate-determining if $k_2 > 10^{11} \text{ s}^{-1}$, or, stated differently, if $\Delta G_2^\ddagger < 1.5 \text{ kcal/mol}$.

Unfortunately, the encounter complexes, $[\text{AH}\cdots\text{B}^-]$ and $[\text{A}^-\cdots\text{HB}]$ may not be "noninteracting", and the interactions within them may differ markedly even for similar acids and bases. It is known, for example, that for proton transfers in water between some amines and ammonium ions a water molecule between the acid and base relays the proton:⁴



Grunwald⁴ has argued that the solvent-separated complex is always the first formed; it can undergo either the relayed proton transfer or a conversion to a nearest-neighbor complex



followed by a direct proton transfer. Whether a particular acid–base pair undergoes a relayed or a direct proton transfer depends on the relative rates of reactions 4 and 5. With successive replacements of the hydrogens of ammonia with methyl groups, the rate constants for reaction 4 show little change but those for reaction 5 decrease markedly. For ammonia–ammonium ion transfers, the direct reaction is operative, whereas for methylamine–methylammonium ion the direct and the relay reactions occur competitively and for trimethylamine–trimethylammonium ion only the relay reaction can be detected. The decrease in rate of reaction 5 with increasing methyl substitution was attributed to dispersion interactions of solvent with the polarizable methyl groups increasing the energy required for solvent removal.

Hydrogen-bonding interactions must also be present in the encounter complexes. Eigen¹ first suggested the role of these interactions, and we⁵ emphasized the importance of the existence of at least one localized lone pair of electrons on the basic site in allowing fast proton transfers. In aqueous solution, the important hydrogen bond need not be directly from acid to base. Ahrens and Maass⁶ report rate constants for proton transfers from carboxylic acids to carboxylates, ammonium ions to amines, ammonium ions to thiolates, and thiols to thiolates. They interpret their data in terms of the strengths of the hydrogen bonds between the acids and bases, but these are probably in the solvent-separated complexes between acids and water and between water and bases. It has been established that the identity proton transfers between benzoic acids and the corresponding carboxylates in methanol take

place by the relay mechanism,⁷ and it is believed that most proton transfers between oxygen and nitrogen acids and bases in hydroxylic solvents occur by this path.⁸

Although a fair number of proton transfers between electronegative atoms do indeed^{1,2,8,9} occur in the favorable direction with rate constants of $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$, there are a surprising number of apparently simple proton transfers in water that occur at rates considerably below this. Grunwald reports,¹⁰ without comment, a rate constant of $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the identity exchange of *N,N*-dibenzylmethylammonium ion with *N,N*-dibenzylmethylamine in water at 30 °C by the water-relay path. A rate constant of $3.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 30 °C for the water-relayed identity exchange of triethanolamine with triethanolammonium ion was attributed⁸ to an unfavorable solvent orientation influenced by "...polar substituents or centres of van der Waals attraction...". In methanol solution, a remarkably small rate constant of $4.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 30 °C for the relayed proton transfer between *N,N*-diethyl-*m*-toluidine and its conjugate acid was attributed⁸ to "steric effects". There have been a number of examples reported by Bernasconi¹¹ for slow proton transfers to amines and phenoxides from the ammonium ions formed by amine–electrophile combination reactions in 50% water–dimethyl sulfoxide solution. A fairly typical example is a rate constant of $5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the proton transfer to *p*-cyanophenoxide ion from the ammonium ion adduct of 1,1-diphenyl-2,2-dinitroethylene and morpholine; the proton-transfer reaction has an equilibrium constant of nearly 10^5 . Even the reaction of propionic acid with acetate ion has a reported⁶ rate constant of only $3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 20 °C in water, and the identity exchange of acetic acid with acetate ion is estimated⁹ to have a barrier of $\Delta G_2^\ddagger \approx 5 \text{ kcal/mol}$ for reaction 2. The barrier was postulated to arise from some type of solvent reorganization requirement.

Since the solvent relay mechanism is possible only in solvents capable of both accepting and donating hydrogen bonds, direct proton transfers must occur in non-hydroxylic solvents and we might expect to see patterns of reactivity considerably different from those seen in water.

There have been only scattered reports of rate constants for simple proton transfers between electronegative atoms in non-hydroxylic solutions uncomplicated by ion pairing, homoconjugate formation, or other aggregation phenomena. Delpuech¹² has reported a study of the rate of isomerization in DMSO of *cis*-*cis*-2,6-dimethyl-*N*-methylpiperidinium ion to the *trans*,*trans* ion, which is believed to proceed by rate-limiting deprotonation and fast inversion about nitrogen. He finds $k = 6.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for protonation of the amine by solvated proton and $k = 2.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for transfer from the ammonium ion to the amine. He cites earlier studies in which he found $k = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the proton transfer from ammonium ion to ammonia and $k = 2.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for that from trimethylammonium ion to trimethylamine, both in DMSO solution. Kreevoy¹³ has reported rate constants $k = 1.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for protonation of tribenzylamine and $k = 4.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for protonation of *N,N*-dimethylbenzylamine, both by the solvated proton in DMSO at 25 °C. We have recently reported¹⁴ a rate constant $k = 2.8 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ for the favorable protonation of tribenzylamine by trifluoroacetic acid at 20 °C in DMSO. Rate constants for proton transfers involving thiols/thiolates,¹⁵ alcohols/alkoxides,¹⁶ and acetylenes/acetylides,¹⁷ all in DMSO, have also been reported,

(7) Grunwald, E.; Meiboom, S. *J. Am. Chem. Soc.* **1963**, *85*, 2047.

(8) Grunwald, E.; Eustace, D. In *Proton-Transfer Reactions*; Caldin, E., Gold, V., Eds.; Chapman and Hall: London, 1975; pp 103–120.

(9) Hibbert, F. *Adv. Phys. Org. Chem.* **1986**, *113*.

(10) Grunwald, E.; Ralph, E. K. *J. Am. Chem. Soc.* **1967**, *89*, 4405.

(11) Bernasconi, C. F. In *Techniques and Applications of Fast Reactions in Solution*, Gettins, W. J., Wyn-Jones, E., Eds.; Reidel: Dordrecht, 1979; pp 453–462.

(12) Delpuech, J. J.; Bianchin, B. *J. Am. Chem. Soc.* **1979**, *101*, 383.

(13) Kreevoy, M. M.; Wang, Y. *J. Phys. Chem.* **1977**, *81*, 1924.

(14) Ritchie, C. D.; Lu, S. *J. Am. Chem. Soc.* **1989**, *111*, 8542.

(15) Delpuech, J. J.; Nicole, D. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1025.

(16) Delpuech, J. J.; Nicole, D. *J. Chem. Soc., Perkin Trans. 2* **1977**, 570.

(17) Chrisment, J.; Delpuech, J. J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 407.

(1) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

(2) Caldin, E. F. *Fast Reactions in Solution*; Blackwell: Boston, 1964; pp 10, 11.

(3) Cox, M. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1978**, *100*, 5956.

(4) Grunwald, E.; Ku, A. Y. *J. Am. Chem. Soc.* **1968**, *90*, 29.

(5) Ritchie, C. D. *J. Am. Chem. Soc.* **1969**, *91*, 6749.

(6) Ahrens, M. L.; Maass, G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 818.

Table I. UV-Vis Spectral Parameters for Indicators in DMSO

indicator	λ , nm	ϵ_{acid}^a	ϵ_{base}^a
2,6-(NO ₂) ₂ -4-ClPhOH	480	0.0	9.6×10^3
	354	3.72×10^3	8.42×10^2
	374	7.68×10^2	1.51×10^4
2,6-Cl ₂ -4-NO ₂ PhOH	315	8.08×10^3	2.99×10^3
	430	0.0	2.67×10^4
	374	7.68×10^2	1.51×10^4
2,4-(NO ₂) ₂ PhOH	306	1.06×10^4	1.17×10^3
	374	7.68×10^2	1.51×10^4
	432	0.0	1.65×10^4
2,6-(<i>t</i> -Bu) ₂ -4-NO ₂ PhOH	302	5.50×10^3	2.45×10^3
	327	8.39×10^3	1.9×10^2
	455	0.0	3.52×10^4
9-cyanofluorene	302	2.55×10^3	3.80×10^4
	327	0.0	9.32×10^3
	455	0.0	1.38×10^3
<i>p</i> -NO ₂ PhOH	322	1.01×10^4	6.57×10^2
	436	0.0	3.12×10^4

^a Molar absorptivity in units of M⁻¹ cm⁻¹.

but the data are, at best, questionable since the pK_a values used differ by up to 8 units from those obtained by Bordwell.¹⁸

The ready availability of high-field FT-NMR spectrometers now makes it possible to study proton-transfer reactions in reasonably dilute solutions in solvents such as DMSO. In the present paper, we report rate and equilibrium constants for proton transfers among several amines, phenols, and carboxylic acids and their conjugate bases in DMSO-*d*₆ solution and the determination of kinetic deuterium isotope effects on several of these.

Experimental Section

Materials. Chemicals other than those enumerated below were commercial reagent-grade products used as received.

DMSO-*d*₆ (99.9%, Cambridge Isotope Laboratories) was purified as described earlier¹⁹ for ordinary DMSO. Water content of the freshly purified material, determined by ¹H NMR spectrometry, was typically $\approx 4 \times 10^{-4}$ M, and deuterium content was >99.9%.

Standard aqueous solutions of sodium hydroxide and of hydrochloric acid were prepared by dilution of commercial concentrates (J. T. Baker Dilut-it) with distilled water that had been stored under argon. These solutions were used for the titrations of the acids and bases listed in the following text to verify purity as stated in each case; standard indicators were used for detection of end points.

Potassium dimsyl solutions, in both ordinary and deuterated DMSO, were prepared from potassium hydride reaction with the solvents essentially as described by Bordwell.¹⁹

2,6-Di-*tert*-butyl-4-nitrophenol was prepared as described by Bordwell²⁰ and recrystallized several times from ethanol/water. The potassium salt of the phenol was prepared by treating the phenol with a slight excess of potassium hydroxide in 2-propanol; the precipitated salt was recrystallized several times from water containing ca. 1 M KCl. The potassium aryloxide was dried in a vacuum oven at 45 °C overnight. UV-vis spectral characteristics of the phenol and phenoxide are shown in Table I.

2,6-Di-*tert*-butyl-4-nitrophenol-*d*₁ was obtained by recrystallizing the phenol three times from ethanol-*d*₁/deuterium oxide. The ¹H NMR spectrum of the phenol in DMSO-*d*₆ indicated no residual OH (δ 8.52) protons.

2,6-Dinitro-4-chlorophenol was prepared by adding, dropwise with stirring, 20 mL of concentrated nitric acid to a solution of 5 g of *p*-chlorophenol in 20 mL of concentrated sulfuric acid while the temperature of the solution was maintained below 45 °C by occasional cooling with an ice bath. Approximately 5 min after the addition was complete, the reaction mixture was poured onto ice, and when the ice had melted, the precipitate was filtered off. The crude product was recrystallized several times from ethanol/water. UV-vis spectral characteristics of the phenol and corresponding phenoxide are shown in Table I.

Potassium 2,6-dichloro-4-nitrophenoxide and potassium 2,6-dinitro-4-chlorophenoxide were prepared by mixing a solution of the phenol in ethanol with an approximate equivalent of potassium hydroxide dissolved

in water. The precipitate that formed was filtered off and recrystallized several times from ca. 35% ethanol in water. UV-vis spectral characteristics of the phenoxides are shown in Table I.

2,4-Dinitrophenol (Aldrich) containing ca. 15% water was recrystallized several times from ethanol. UV-vis spectral characteristics of the phenol are shown in Table I.

Potassium 2,4-dinitrophenoxide was prepared by adding an approximate equivalent of solid potassium hydroxide to a hot solution of the phenol in ethanol. The salt crystallized as the solution cooled and was recrystallized several times from ca. 70% ethanol in water. UV-vis spectral characteristics of the phenoxide are shown in Table I.

9-Cyanofluorene was prepared as described by Bordwell.¹⁹ UV-vis spectral characteristics of 9-cyanofluorene and its conjugate base are shown in Table I.

Trifluoroacetic acid (Aldrich) was analyzed as 99.7% pure by titration with standard sodium hydroxide. The acid was stored in a tightly capped container in a refrigerator.

Dichloroacetic acid and difluoroacetic acid (Aldrich) were both analyzed as $100 \pm 0.3\%$ pure by titrations with standard sodium hydroxide.

Cyanoacetic acid (Aldrich) was vacuum sublimed to obtain colorless crystals that analyzed to be 99.8% pure by titration with standard sodium hydroxide.

Potassium difluoroacetate was prepared by neutralization of 5 g of the acid dissolved in 25 mL of water with 3.5 g of potassium carbonate. The volume of the resulting solution was reduced to 10 mL by evaporation, and 30 mL of ethanol was then added. Crystals formed as this solution cooled and were filtered off and recrystallized twice from 3:1 ethanol/water.

Potassium diphenylacetate was prepared by adding an approximate equivalent of solid potassium hydroxide to a hot solution of diphenylacetic acid in ethanol. When all of the potassium hydroxide had gone into solution, the solution was cooled and then diluted with an equal volume of diethyl ether. Crystals formed within a few minutes and were filtered off and recrystallized twice from 1:1 ethanol/ether.

Trifluoromethanesulfonic acid (Aldrich) was distilled at atmospheric pressure under argon.

Tribenzylamine (Eastman Kodak) was recrystallized from hexane before use.

N,N-Dimethylbenzylamine (Aldrich) was vacuum distilled and stored under argon.

Instrumentation. NMR spectra were obtained on a Varian Model VXR-400S spectrometer equipped with a programmable thermostated probe. The NMR spectra were simulated on an Apollo DN3000 workstation interfaced to a Hewlett-Packard Model 7475A plotter.

UV-Vis spectra were obtained with a Varian Cary Model 210 spectrophotometer.

Methods. All solutions were prepared and stored under argon atmospheres by use of the three-way stopcock, gas-tight syringe technique described by Bordwell.¹⁹ Quantitative dilutions were made by use of glass-bore micrometer syringes (Gilmont S-1100 or S-1200) having Teflon plungers and O-rings and Luer fittings that accommodated either a stainless steel or Teflon syringe needle. In order to conserve the purified DMSO-*d*₆, master solutions were prepared and multiply diluted, when necessary, in 1.0–10.0-mL volumetric flasks. The 10.0-mL volumetric flasks were fitted with small standard-taper three-way stopcocks. The 1.0-mL volumetric flasks were closed with small three-way inert valves (Hamilton Co. 86727) with male Luer connectors (Hamilton 35030) fitted to the flasks by means of custom-made Teflon bushings. Custom-made Teflon bushings were also used to fit these valves to standard UV-vis spectrophotometer cells. The valve openings were large enough to accommodate syringe needles, and the valves were used in exactly the same manner as the three-way stopcocks for transfers of solutions under argon. Hygroscopic solid samples were weighed on a Cahn gram electrobalance and transferred to dried argon-flushed volumetric flasks in an argon-filled glovebag. Transfers of solutions under argon protection to NMR tubes were accomplished in a manner similar to the three-way stopcock technique by use of a simple T-tube; one end of the cross was fitted with an O-ring-type thermometer adapter through which the NMR tube was inserted, while argon was passed in through the base and out the other end of the cross of the T. The NMR tube was flushed with argon by another line attached to a syringe needle reaching to the bottom of the tube. After being filled with the reaction solution, the NMR tube was pushed up through the cross of the T-tube and capped while a good flow of argon was maintained. A thin layer of paraffin wax (Parafilm) was wrapped around the edge of the plastic cap to provide a tight seal.

The determinations of pK_a values in DMSO utilized Bordwell's indicators.¹⁸ Techniques were similar to those described previously²¹ except

(18) Bordwell, F. G. *Accs. Chem. Res.* **1988**, *21*, 456. See also: Bordwell, F. G.; Algrim, D.; Fried, H. E. *J. Chem. Soc., Perkin Trans. 2* **1979**, 726.

(19) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006.

(20) Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; Drucker, G. E.; Gerhard, J.; McCollum, G. J.; Van Der Puy, M.; Vanier, N. R.; Matthews, W. S. *J. Org. Chem.* **1977**, *42*, 326.

(21) Ritchie, C. D.; VanWerth, J. E.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1982**, *104*, 3491.

Table II. pK_a Values in DMSO at 25 ± 2 °C

acid	pK_a	indicator (pK_a) ^a
CF ₃ COOH	3.51 ± 0.04	2,6-(NO ₂) ₂ -4-ClPhOH (3.56)
(C ₆ H ₅) ₂ CHCOOH	10.9 ± 0.05	<i>p</i> -NO ₂ PhOH (10.78)
N≡CCH ₂ COOH	8.20 ± 0.08	9-cyanofluorene (8.36)
CF ₂ HCOOH	6.45 ± 0.10	2,6-(<i>t</i> -Bu) ₂ -4-NO ₂ PhOH (7.34)
Cl ₂ CHCOOH ^b	6.05 ± 0.05	2,4-(NO ₂) ₂ PhOH (5.06) 2,6-(<i>t</i> -Bu) ₂ -4-NO ₂ PhOH (7.34)
Cl ₃ PhOH	6.65 ± 0.05	2,6-(<i>t</i> -Bu) ₂ -4-NO ₂ PhOH (7.34)
Bz ₃ NH ⁺ ^c	3.64 ± 0.05	2,6-(NO ₂) ₂ -4-ClPhOH (3.56)
Bz(CH ₂) ₂ NH ⁺ ^d	7.60 ± 0.10	2,6-(<i>t</i> -Bu) ₂ -4-NO ₂ PhOH (7.34)

^a Values are from ref 18 or primary sources given there. ^b The pK_a for dichloroacetic acid was incorrectly listed as 6.4 in ref 18. ^c This value was previously reported in refs 13 and 14. ^d Kreevoy in ref 13 reported $pK_a = 7.59$ apparently using a pK_a of 7.6 for the indicator. Our NMR data on solutions of the acid and indicator require the $pK_a = 7.6$, taking the indicator $pK_a = 7.34$.

that titrations were not carried out in the spectrophotometer cell. Master solutions of the indicators, acids, and conjugate bases were prepared and measured (by micrometer syringe); portions of these were mixed, diluted in volumetric flasks, and then transferred to 1.0-mm- or 1.0-cm-path spectrophotometer cells for measurement. At least three widely different acid to base ratios were used with each indicator. Analyses utilized the absorbances at wavelengths reported in Table I.

NMR spectra were obtained on solutions in "ultra-thin-wall" tubes (Wilmad 545-PPT). Temperature control during data collection was by means of the standard programmable thermostated probe set at 20 °C. Suppression of the DMSO-*d*₆ peak at δ 2.5 was employed by using the low-power decoupler with sufficient power (instrument setting was usually 15 dB below the nominal 1 W) to avoid data overflow. For the very dilute solutions used, 1500–4000 transients at 8-s acquisition time each were required for good signal to noise ratios. All solutions prepared for ¹H NMR spectra contained ca. 10⁻³ M cyclohexane, δ 1.4, as an internal standard. Sweep range was normally δ 0–10 for ¹H NMR, and 32K double-precision data points were collected, resulting in a resolution of 0.125 Hz.

For ¹⁹F NMR at 376.29 MHz, we arbitrarily take chemical shifts relative to an assumed value of δ -76.00 for a mixture of 0.8 mL of trifluoroacetic acid and 0.1 mL of DMSO-*d*₆, which was used as an external standard for all runs. Solutions prepared for ¹⁹F NMR spectra were usually in ordinary DMSO containing at least 10% of DMSO-*d*₆ to serve as a frequency lock. For the study of trifluoroacetic acid/trifluoroacetate exchange, the spectra were obtained for δ -78.4 to -67.8; for study of the difluoroacetic acid/difluoroacetate exchange, the range was δ -127.5 to -116.9 with a resolution of 0.125 Hz.

NMR spectra of the nonexchanging acid species of moderately strong acids (CF₃COOH and tribenzylammonium ion) were obtained on solutions containing ca. 10⁻¹ M of a strong acid to inhibit ionization; trifluoromethanesulfonic acid ($pK_a = 0.3^{18}$) was used for ¹H NMR spectra, and 5-nitrobarbituric acid ($pK_a = 0.8^{18}$) was used for ¹⁹F NMR spectra. The spectra of the nonexchanging anionic basic species were obtained on solutions of the potassium salts, either prepared as described above or formed in solution by addition of a slight excess of potassium dimethyl solution to a solution of the acid species.

Results and Treatment of Data

pK_a 's in DMSO. The pK_a values determined in this work and the indicators used in each case are reported in Table II.

Dynamic NMR Studies. FORTRAN programs were written to carry out the calculations of NMR spectra of the exchanging systems by the use of the density matrix formalism.²² Four basic types of systems were encountered in the present study: (1) Singlet/singlet exchange was studied in the cases of the 3,5-protons of 2,6-di-*tert*-butyl-4-nitrophenol exchanging with the 3,5-protons of the corresponding phenoxide, the methyl proton of diphenylacetic acid exchanging with the methyl proton of the corresponding carboxylate, and the fluorines of trifluoroacetic acid exchanging with those of the trifluoroacetate. (2) Singlet/doublet exchange was studied in the cases of the benzyl protons of tribenzylamine exchanging with those of tribenzylammonium ion and the benzyl protons of dimethylbenzylamine exchanging with those of dimethylbenzylammonium ion. (3) Doublet/doublet exchange was studied in the case of the fluorines of difluoroacetic acid ex-

Table III. NMR Spectral Parameters for Spin Systems Studied

species	obs	δ^a	<i>J</i> , Hz	<i>T</i> ₂ ^b , s
(C ₆ H ₅ CH ₂) ₃ N	benzyl H	3.50		0.93
(C ₆ H ₅ CH ₂) ₃ NH ⁺	benzyl H	4.32 (d)	5.2, HCNH	1.06
(C ₆ H ₅ CH ₂)(CH ₃) ₂ N	benzyl H	3.37		1.2
(C ₆ H ₅ CH ₂)(CH ₃) ₂ NH ⁺	benzyl H	4.28 (d)	5.5, HCNH	1.4
F ₂ CHCOOH	methyl H	6.31 (t)	53, FCH	1.7
F ₂ CHCOO ⁻	methyl H	5.48 (t)	57, FCH	2.2
F ₂ CHCOOH	F	-126.0 (d)	53, FCH	1.5
F ₂ CHCOO ⁻	F	-119.2 (d)	57, FCH	1.5
2,6-(<i>t</i> -Bu) ₂ -4-NO ₂ PhOH	aryl H	8.01		2.0
2,6-(<i>t</i> -Bu) ₂ -4-NO ₂ PhO ⁻	aryl H	7.68		3.1
Ph ₂ CHCOOH	methyl H	5.06		1.5
Ph ₂ CHCOO ⁻	methyl H	4.49		0.90
CF ₃ COOH	F	-73.6		1.9
CF ₃ COO ⁻	F	-71.8		3.0

^a Peak position or center of a multiplet. ¹⁹F chemical shifts are relative to an arbitrary δ -76 for 8:1 trifluoroacetic acid/DMSO external reference. ^b From the reciprocal of half of the peak width at half-height for the non-exchanging species in DMSO.

changing with those of difluoroacetate ion. (4) Triplet/triplet exchange was studied for the methyl proton of difluoroacetic acid exchanging with the methyl proton of difluoroacetate ion. The pertinent NMR characteristics of the individual species are given in Table III. The ¹⁹F NMR spectra of trifluoroacetic acid and of difluoroacetic acid under "nonexchange" conditions in the absence of the corresponding acetates show a sharp singlet and a sharp doublet, respectively. Long-range coupling between the carboxylic O-H proton of the acids and the fluorines, which might have been expected to broaden these peaks, is undoubtedly wiped out by the rapid exchange of the acidic protons with "free" protons in solution. The use of the peak widths from these spectra to calculate the "phenomenological *T*₂" values causes no significant error in the simulations of the spectra of the exchanging acids and acetates when both are present at comparable concentrations.

The FORTRAN program accepted initial input of the peak positions, coupling constants, phenomenological *T*₂ values of the two exchanging species, the peak height of the highest peak in the spectrum of the exchanging system, and the frequency range and scale to be treated. It then interactively allowed variations of the chemical relaxation time and the relative populations of the two exchanging species, producing a plotted spectrum on semitransparent paper for each variation. These plotted spectra were overlaid on the experimental spectra for comparisons. Variations of parameters continued until subjectively best fits of simulated and experimental spectra were obtained. In nearly every case, the simulated spectrum was within the line thickness of the experimental spectrum.

We define the relative populations P_{acid} and P_{base} of an acid species HB₁ and its conjugate base B₁

$$P_{acid} \equiv \frac{[HB_1]}{[HB_1] + [B_1]} \quad P_{base} \equiv \frac{[B_1]}{[HB_1] + [B_1]} \quad (6)$$

and an exchange time τ_{ex} , for the interconverting HB₁/B₁ system

$$\frac{1}{\tau_{ex}} = \frac{P_{acid}}{\tau_{(HB_1)}} = \frac{P_{base}}{\tau_{(B_1)}} \quad (7)$$

where $\tau_{(HB_1)}$ and $\tau_{(B_1)}$ are the usual chemical relaxation times²² of the species HB₁ and B₁, respectively.

The relaxation time, $\tau_{(HB_1)}$, is inversely related to the rate of conversion of the observed acid to the base species. The rates obeyed the equation

$$\frac{\text{rate}}{[HB_1]} = \frac{1}{\tau_{ex} P_{acid}} = \frac{1}{\tau_{(HB_1)}} = \sum_j k_j [B_j] = k_p \quad (8)$$

where the index *j* is over all base species in solution and the last equality defines the pseudo-first-order rate constant for the conversion of HB₁ to B₁. Plots of the pseudo-first-order rate constants versus concentration of a particular base, keeping all others constant, gave the individual second-order rate constants, *k_j*, for the proton-transfer reactions. Some fairly typical plots are shown in Figure 1.

(22) Kaplan, J. I.; Fraenkel, G. *NMR of Chemically Exchanging Systems*; Academic Press: New York, 1980.

Table IV. Rate Constants for Proton Transfers in DMSO at 20 °C

HA ^a	B ^a	log K_{eq}^b	log k_f^c	log k_r^d	$k_f(H)/k_f(D)$
Bz ₃ NH ⁺	DMSO-d ₆	-4.8 ^{e,f}	-0.8 ^e	4.0 ^f	1.2 ± 0.2
Bz ₃ NH ⁺	CF ₃ COO ⁻	-0.1	2.3 ^f	2.4 ^f	1.1 ± 0.2
Bz ₃ NH ⁺	2,6-Cl ₂ -4-NO ₂ PhO ⁻	0.9	5.2	4.4	
Bz ₃ NH ⁺	2,6-(NO ₂) ₂ -4-ClPhO ⁻	0.0	4.9	4.9	
Bz(CH ₃) ₂ NH ⁺	DMSO-d ₆	-8.8 ^e	-2.2 ^{e,g}	6.6 ^g	
Bz(CH ₃) ₂ NH ⁺	CF ₃ COO ⁻	-4.1	2.6	6.7	
Bz(CH ₃) ₂ NH ⁺	Cl ₂ CHCOO ⁻	-1.6	4.9	6.5	
Bz(CH ₃) ₂ NH ⁺	F ₂ CHCOO ⁻	-1.2	4.8	6.0	
Bz(CH ₃) ₂ NH ⁺	2,6-(<i>t</i> -Bu) ₂ -4-NO ₂ PhO ⁻	-0.3	6.3	6.6	
Bz(CH ₃) ₂ NH ⁺	Bz(CH ₃) ₂ N	0.0	5.6	5.6	
Bz(CH ₃) ₂ NH ⁺	NCCH ₂ COO ⁻	0.6	6.6	6.0	
2,6-(<i>t</i> -Bu) ₂ -4-NO ₂ PhOH	2,6-(<i>t</i> -Bu) ₂ -4-NO ₂ PhO ⁻	0.0	6.4	6.4	1.3 ± 0.2
CF ₃ COOH	DMSO-d ₆	-4.7 ^e	3.6 ^e	8.3	
CF ₃ COOH	CF ₃ COO ⁻	0.0	≤5.7	≤5.7	
Ph ₂ CHCOOH	Ph ₂ CHCOO ⁻	0.0	6.0	6.0	
F ₂ CHCOOH	F ₂ CHCOO ⁻	0.0	6.5	6.5	1.0 ± 0.2
F ₂ CHCOOH	2,6-(<i>t</i> -Bu) ₂ -4-NO ₂ PhO ⁻	0.9	5.5	4.6	1.0 ± 0.2
F ₂ CHCOOH	2,6-Cl ₂ -4-NO ₂ PhO ⁻	-1.9	5.1	7.0	
F ₂ CHCOOH	2,4-(NO ₂) ₂ PhO ⁻	-1.3	6.2	7.7	
F ₂ CHCOOH	Cl ₃ PhO ⁻	0.3	6.3	6.0	

^a Key: Bz = benzyl, Ph = phenyl. ^b $\log K_{eq} = pK_a(BH) - pK_a(HA)$; K_{eq} is unitless. ^c Rate constant for transfer from HA to B, units of $M^{-1} s^{-1}$. ^d Rate constant for transfer from BH to A, units of $M^{-1} s^{-1}$. ^e Unitless equilibrium constant and second-order rate constant obtained by treating the solvent as an ordinary reactant with concentration of 14 M. ^f Previously reported in ref 14. ^g Data from ref 13.

We attempted to determine the rate constant for the identity reaction of trifluoroacetic acid with trifluoroacetate ion but found the pseudo-first-order rate constant to be essentially independent of trifluoroacetate ion concentrations up to ca. 6×10^{-2} M. The first-order rate constant for transfer from trifluoroacetic acid to solvent was found to be $7.0 \times 10^4 s^{-1}$, and this produces a coalesced peak in the ¹⁹F NMR spectrum having a width of ≈ 3 Hz. Further narrowing to a limit of ≈ 0.8 Hz should be observed for increasing rate, and assuming that we would have observed a decrease of ≈ 1 Hz in line width, we set an upper limit of ca. $6 \times 10^5 M^{-1} s^{-1}$ on the rate constant for the identity exchange. The line does narrow to ≈ 2.0 Hz for a solution containing 0.17 M trifluoroacetate and 0.09 M trifluoroacetic acid, but we suspect that ion pairing and homoconjugate formation are present at these high concentrations and make any interpretation questionable.

Rates of the deuteration of tribenzylamine by solvated deuteron and by trifluoroacetic acid-*d* were determined with commercial trifluoroacetic acid-*d* (Cambridge Isotope Laboratories, 99.8% D) just as we have described for the normal acid.¹⁴ The water content of the solvent was much less than 10% of the concentration of trifluoroacetic acid-*d* in all of the solutions used and could be disregarded.

Deuterium isotope effects on the identity and cross-reactions of difluoroacetic acid and 2,6-di-*tert*-butyl-4-nitrophenol were studied by the use of the deuterated phenol and potassium difluoroacetate both in the DMSO-*d*₆ containing slightly less than 10^{-3} M water and in DMSO-*d*₆ in which 2×10^{-3} M D₂O was purposely added. We present evidence in the next section that water does not participate in the reactions studied here. However, the studies of the identity reaction of the phenol required concentrations of less than 10^{-3} M of the phenol, and for those solutions containing only the "residual" H₂O, significant amounts of both phenol and phenol-*d* were present. Any significant differences in rates of reactions of the H and D compounds would have resulted in distortions of the line shapes for the aryl protons from those for either the H or D compound alone; such distortions were not observed, confirming the small isotope effects calculated from the studies with added D₂O in which the amounts of phenol were insignificant. The identity reaction of difluoroacetic acid-*d* was studied in solutions prepared from potassium difluoroacetate (ca. 10^{-3} M) and 2,6-di-*tert*-butyl-4-nitrophenol-*d* (ca. 10^{-2} M); at equilibrium, the concentration of the aryloxyde (ca. 10^{-3} M) was small enough that the major contribution to the observed conversion of CF₂HOOD to CF₂HCOO⁻ was by the carboxylate ion. The pseudo-first-order rate constants obtained were "corrected" for the contribution from the aryloxyde ion by use of the rate constant obtained from studies of the carboxylic acid-

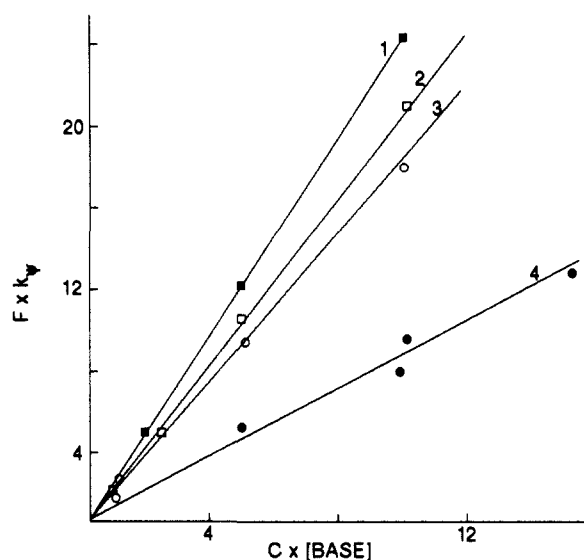


Figure 1. Plots of pseudo-first-order rate constants (s^{-1}) versus base concentrations (M). Rate constants: (1) conversion of 2,6-di-*tert*-butyl-4-nitrophenol to corresponding phenoxide versus concentration of the phenoxide, $C = 10^4$, $F = 10^{-2}$; (2) conversion of *N,N*-dimethylbenzylamine versus concentration of 2,6-di-*tert*-butyl-4-nitrophenoxide ion, $C = 10^3$, $F = 10^{-3}$; (3) conversion of tribenzylammonium ion to tribenzylamine versus concentration of 2,6-dichloro-4-nitrophenoxide ion, $C = 10^3$, $F = 10^{-2}$; (4) conversion of tribenzylammonium ion to tribenzylamine versus concentration of 2,6-dinitro-4-chlorophenoxide ion, $C = 10^3$, $F = 10^{-2}$.

d/carboxylate conversion at higher, varying, concentrations of the aryloxyde ion (solutions prepared from the deuterated phenol, the potassium salt of the phenol, and the potassium difluoroacetate) while the carboxylate ion concentration was constant.

The rate constants and isotope effects obtained are reported in Table IV.

Absence of Participation of Water. Freshly purified solvent contained, typically, $\approx 4 \times 10^{-4}$ M H₂O. With extremely careful applications of the techniques described in the Experimental Section, it was possible to maintain the water concentrations at $\leq 10^{-3}$ M throughout an NMR experiment. In a few cases where technique was relaxed, solutions containing as much as $\sim 1 \times 10^{-2}$ M water were used in this work. Since exchanging acids and bases were usually present at concentrations well below 10^{-2} M, it is important to establish that the "traces" of water present do not participate significantly in the reactions studied.

Kreevoy¹³ studied the effect of water concentration on the exchange reactions of tribenzylammonium and *N,N*-dimethylbenzylammonium ions with solvent in DMSO and found a linear dependence of rate of exchange on water concentration. The rate constants for water-catalyzed exchanges were $76 \text{ M}^{-1} \text{ s}^{-1}$ for tribenzylammonium ion and $1 \text{ M}^{-1} \text{ s}^{-1}$ for *N,N*-dimethylbenzylammonium ion. In no case studied in the present work would the contribution of these catalyzed exchanges by $\sim 10^{-2} \text{ M}$ water amount to more than a few percent of the measured pseudo-first-order rate constants for the amine-ammonium ion exchanges.

In DMSO solutions containing $\approx 2 \times 10^{-5} \text{ M H}^+$, the water peak in the NMR spectrum at δ 3.33 is noticeably broadened; at higher concentrations of H^+ , it disappears completely. This is almost certainly caused by exchange of the water protons with the solvated proton. A solution of 0.1 M trifluoromethanesulfonic acid in DMSO-*d*₆ shows a somewhat broad ($\sim 25\text{-Hz}$) peak at δ 13.5, which should be close to that of the solvated proton. (From $\text{p}K_{\text{a}} = 0.3$, the acid should be ca. 90% dissociated.)

Carboxylic acids in unbuffered solutions at concentrations of $\approx 0.1 \text{ M}$ in DMSO-*d*₆ show moderately broad NMR peaks near δ 15; CF_3COOH has δ 15.5, CF_2HCOOH has δ 14.6, and $\text{Cl}_2\text{-CHCOOH}$ has δ 14.5. All of these unbuffered solutions have H^+ concentrations $> 10^{-5} \text{ M}$, and as mentioned above, the water peak at δ 3.33 is missing. Similarly, $\approx 0.1 \text{ M}$ 2,6-di-*tert*-butyl-4-nitrophenol has a slightly broad peak at δ 8.5. Undoubtedly the broadness of the peaks is caused by a moderately rapid exchange of the "trace" water protons, solvated protons, and carboxylic acid or phenol protons in the unbuffered solutions.

For all of the studies of identity and cross-exchanges of phenols and carboxylic acids, with the exception of trifluoroacetic acid, the solutions have proton concentrations $\ll 10^{-5} \text{ M}$. In these solutions, the trace water protons appear at δ 3.33. At buffer concentrations of $< 10^{-3} \text{ M}$, the water peak is quite narrow but does show significant broadening with increasing concentrations of any buffer pair. Typical cases were as follows: for solutions containing 2,6-di-*tert*-butyl-4-nitrophenol/phenoxide ion at equal concentrations of $1 \times 10^{-3} \text{ M}$, both the water peak and the phenol peak have widths of $\sim 3 \text{ Hz}$; for difluoroacetic acid/difluoroacetate ion at equal concentrations, the water peak has a width of $< 3 \text{ Hz}$ at acid concentration of $5 \times 10^{-4} \text{ M}$ but the width increases to $\sim 100 \text{ Hz}$ at acid concentration of $5 \times 10^{-3} \text{ M}$; for diphenylacetic acid/diphenylacetate ion at equal concentrations, the water peak has a width of $\sim 20 \text{ Hz}$ at acid concentration of $1 \times 10^{-3} \text{ M}$ and broadens to $\sim 50 \text{ Hz}$ at acid concentration of $2 \times 10^{-3} \text{ M}$. In all cases, the width of the water line was much smaller than the pseudo-first-order rate constant for the proton exchange being observed.

These observations clearly show that proton exchanges of the acids and bases with water at the low water concentrations maintained in these studies are much slower than the reactions with which we are concerned here. The indications are clear, however, that the exchanges with water do occur and could complicate studies carried out with higher concentrations of water. Although we did not attempt accurate measurements of the exchange rates with water, it appears that the line width of the water peak increases with both concentration of acid and concentration of base in the buffer systems. It seems quite likely that the reaction causing the broadening of the water line is a relayed proton transfer from the buffer acid through water to the buffer base just as discussed in the introduction for transfers in aqueous solution.

Accuracies of Rate Constants Reported. There are four factors of which we are aware that limit the accuracies of the rate constants that we report.

First and most serious, the line-shape fittings, even in the most favorable cases studied, give imperceptible differences in visual "goodness" for 5% variations in exchange times, τ_{ex} . The uncertainties in exchange times become greater at both limits of slow "exchange broadening" of the separate lines and fast "exchange narrowing" of the coalesced lines. Since our second-order rate constants are obtained from slopes of plots of $1/\tau$ versus concentrations, these uncertainties in τ become magnified. Even for

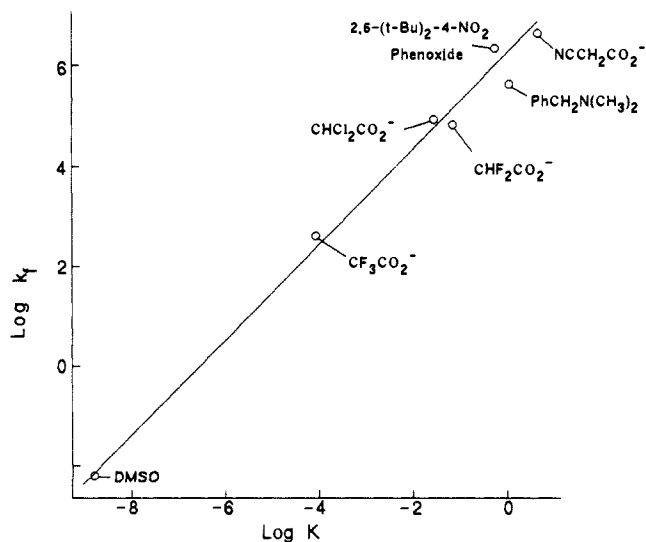


Figure 2. Brønsted plot for reactions of *N,N*-dimethylbenzylammonium ion with bases in DMSO.

the most favorable cases, we doubt that our rate constants are accurate to better than $\pm 10\%$. We estimate that the worst cases are no worse than $\pm 30\%$.

Second, temperature control by the standard thermostated probe is unlikely to be much better than $\pm 1 \text{ }^\circ\text{C}$. This would lead to a variation of $\sim \pm 5\%$ in a rate constant for a reaction with an activation energy of 10 kcal/mol .

Third, the use of multiple dilutions of small volumes of solutions to prepare the final reaction mixtures can lead to appreciable errors in concentrations. We estimate that this source could lead to errors in the final second-order rate constants of as much as $\pm 5\%$.

Fourth, activity coefficients for ionic species in DMSO, relative to the infinitely dilute standard state, are likely to become appreciably different from unit at ionic strengths above $\sim 10^{-3} \text{ M}$. We commented in an earlier paper¹⁴ that the apparent $\text{p}K_{\text{a}}$ of tribenzylammonium ion varied linearly with the square root of the ionic strength in DMSO solutions. We have found identical behavior for *N,N*-dimethylbenzylammonium ion, but the ionic strengths used are much lower than those that were necessary for the study of the tribenzylammonium ion exchanges. None of the rate constants that we report are "corrected" for activity coefficients. Such corrections could be appreciable, particularly for the reactions of the ammonium ions with anionic bases. In the present studies, we have kept ionic strengths as low as possible, but uncertainties from activity coefficients could be as much as $\sim \pm 10\%$ in some of the second-order rate constants.

All of these factors taken together could easily lead to uncertainties $\pm 50\%$ in the rate constants, ± 0.2 in the log k 's, reported in Table IV. For the isotope effects that we have studied, the similarities of conditions used for the normal and isotopically substituted exchanges and the direct comparisons of pseudo-first-order rate constants should result in less than this maximum uncertainty in $k_{\text{H}}/k_{\text{D}}$; we estimate an uncertainty of $\pm 20\%$ in these.

Discussion

The near-unity kinetic isotope effects on the proton-transfer reactions virtually exclude the possibility of the actual proton transfers being the rate-determining steps of these reactions. This conclusion is strengthened by the Brønsted plot of the rate constants for proton transfers from *N,N*-dimethylbenzylammonium ion to a series of bases shown in Figure 2. The slope of the line is 0.94. We believe that this number is insignificantly different from 1.0. The rate constants for the reverse, thermodynamically favorable proton transfers from the conjugate acids to *N,N*-dimethylbenzylamine are nearly constant; excluding the identity reaction of the amine, they range from $1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for difluoroacetic acid to $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for trifluoroacetic acid.

Brønsted plots, Figure 3, for other series in Table IV are essentially scatter diagrams, but the ranges of rate and equilibrium

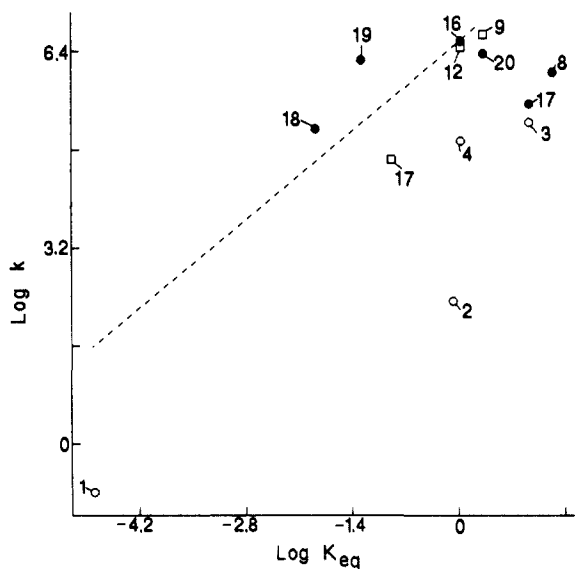


Figure 3. Brønsted plots for several series of reactions. Open circles are for reactions of tribenzylammonium ion with bases, filled circles are for reactions of difluoroacetic acid with bases, and squares are for reactions of 2,6-(*t*-Bu)₂-4-NO₂PhOH with bases. The numbers correspond to the order of listing in Table IV. The dashed line has a slope of 1.00.

constants for any one acid or one base are much smaller than the range for *N,N*-dimethylbenzylammonium ion reactions.

Kreevoy¹³ reported a Brønsted slope of 0.59 for the thermodynamically favorable protonation of a series of aryl-substituted tribenzylamines in DMSO by the solvated proton. This is difficult to understand in view of our observation of a near-unity k_H/k_D for the protonation of tribenzylamine. Kreevoy points out, however, that the reliability of the slope depends on the inclusion of the point for protonation of *N,N*-dimethylbenzylamine. If this point is excluded, five of the seven tribenzylamines have rate constants for proton transfer to solvent that differ by less than a factor of 2 from one another, from $2.5 \pm 0.4 \text{ s}^{-1}$ for tris(4-methylbenzyl)amine to $4.9 \pm 1.3 \text{ s}^{-1}$ for tris(3-methoxybenzyl)amine. This is still surprising; for these transfers in the unfavorable directions, we would have expected a Brønsted slope near unity. In any case, our observation of an isotope effect of 1.2 ± 0.2 on the protonation of tribenzylamine argues strongly against a rate-determining proton-transfer step.

The near-constancy of the rate constants for the thermodynamically favorable proton transfers to *N,N*-dimethylbenzylamine and for the identity reactions of 2,6-di-*tert*-butyl-4-nitrophenol and of difluoroacetic acid at a value well below that expected for diffusion control requires that the rate-controlling step has an appreciable barrier. The most likely source of this barrier is the desolvation of the acid and base species in order to form a "nearest-neighbor" complex.

If this is correct, one might have expected several things that are not observed. If the major solvent-solute interaction to be overcome in desolvating the solutes were hydrogen bonding of acid to solvent, stronger acids would have stronger hydrogen bonds and should react more slowly in favorable or balanced reactions than weaker acids. We find, however, that the identity exchange of diphenylacetic acid, $pK_a = 10.9$, is somewhat slower than the identity exchange of difluoroacetic acid, $pK_a = 6.4$. As Jencks²³ has pointed out for reactions in water, one would also expect that Brønsted slopes of greater than unity for the unfavorable transfers and negative slopes for favorable transfers would result from the stronger hydrogen bonding of stronger acids to solvent or the stronger hydrogen bonding of solvent to stronger bases. In accord with this expectation, decreasing rate constants for increasing basicity of amines in their reactions as nucleophiles toward a phosphate ester have been reported.²⁴ None of the proton-transfer

reaction series reported in Table IV show this behavior.

In fact, there are no reports of negative or greater than unity Brønsted slopes for proton-transfer reactions between electro-negative atoms even in hydroxylic solvents.^{1,6,9} Brønsted slopes of unity for unfavorable reactions changing over a narrow range of ΔpK_a s near 0 to slopes of 0 for favorable transfers are the "normal Eigen behaviors" most frequently seen. Since these reactions are believed to occur by relay through a solvent molecule, it might be argued that no desolvation is required in these reactions. However, the reactions of HCN with bases in water²⁵ have been shown to occur by a direct transfer mechanism not involving an interposed water molecule; for reactions of carboxylates and of moderately basic amines, the Brønsted slopes are very close to unity, and the reverse, thermodynamically favorable, reactions have rate constants of $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Similarly, reactions of the C(2)-hydrogen of 3,4-dimethylthiazolium ion and of 3-(cyano-methyl)-4-methylthiazolium ion with bases in D₂O were argued²⁶ to involve a direct proton transfer, and for all but the strongest bases, the reverse protonations of the C(2) anions by the conjugate acids of the bases are diffusion-controlled with rate constants of $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. No trend toward lower reverse rate constants is seen for the stronger acids with either the thiazolium species or cyanide ion.

Reactions of dimethyl-9-fluorenylsulfonium ion and two ring-substituted derivatives with bases in water show curved Brønsted plots, with the slopes approaching very close to unity for carboxylate ion and weakly basic amine bases.²³ Kinetic isotope effects on the reactions decrease as the base strength decreases, becoming quite small for the weakest bases; for cyanoacetate ion, $k_H/k_T = 2.8$. The reverse, thermodynamically favorable, proton transfers from the stronger carboxylic acids and ammonium ions to the fluorenyl ion have rate constants that appear to have leveled out at $\sim 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Reactions of *tert*-butylmalononitrile with bases in aqueous solution²⁷ show very similar behavior, with small isotope effects ($k(\text{H}_2\text{O})/k(\text{D}_2\text{O}) = 1.1$ for *tert*-butylmalononitrile with acetate ion) and a "limiting" rate constant of $\sim 3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for protonation of the *tert*-butylmalononitrile anion by the stronger acids. In both of these cases, the rate constants for the thermodynamically favorable proton transfers appear to have reached limiting values well below the expected diffusion-controlled rates and to show no signs of decreasing with increasing acid strength.²⁸

Grunwald has reported⁷ an increasing rate constant with increasing acidity for the identity reactions of several substituted benzoic acids in methanol solution and has noted⁴ that the rates of desolvation of amines in water sometimes decrease with decreasing basicity of the amines. This behavior, and the similar decrease in rate of conversion of solvent-separated to nearest-neighbor amine-ammonium ion complexes, was attributed to a dominant role of London dispersion interactions between the solutes and solvent.²⁹ The entire question as to the relative contributions of hydrogen bonding and other solvent-solute in-

(24) Jencks, W. P.; Haber, M. T.; Herschlag, D.; Nazaretian, K. T. *J. Am. Chem. Soc.* **1986**, *108*, 6100.

(25) Bednar, R. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 7117; **1985**, *107*, 7126.

(26) Washabaugh, M. W.; Jencks, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 674, 683.

(27) Bruce, T. J.; Pratt, R. F. *J. Org. Chem.* **1972**, *37*, 3563. See also: Hibbert, F.; Long, F. A.; Walters, E. A. *J. Am. Chem. Soc.* **1971**, *93*, 2829. Hojatti, M.; Kresge, A. J.; Wang, W. *J. Am. Chem. Soc.* **1987**, *109*, 4023.

(28) It is particularly puzzling that the two apparently quite different systems, involving the highly delocalized fluorenyl ions and the much more localized malononitrile anion, behave so similarly while they behave so differently from the cyanide ion and the thiazolium zwitterion systems in reactions with carboxylic acids and ammonium ions. Reactions of the carbanions with the proton are more "reasonable". For the protonations of both *tert*-butylmalononitrile anion and malononitrile anion by solvated proton in water,²⁷ $k \approx 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, while protonation of dimethyl-9-fluorenylsulfonium ylide has $k \approx 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and that of the 2-nitro-substituted ylide has $k \approx 3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Stated differently, the reactions of water, as a base, show large positive deviations from the Brønsted plots for the malononitriles, but much smaller deviations for the dimethyl-9-fluorenylsulfonium ions.

(29) Grunwald, E.; Lipnick, R. L.; Ralph, E. K. *J. Am. Chem. Soc.* **1969**, *91*, 4333.

(23) Murray, C. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1990**, *112*, 1880.

interactions to the solvation energies of ammonium ions is unsettled.^{30,31}

On the basis of these considerations, we believe that desolvation energies of the acidic and basic species are not dominated by hydrogen bond energies and that desolvation could be the source of at least part of the observed barriers in the direct proton transfers in solution.

Our data, however, seem to rule out any general mechanism in which the acid and the base species are independently desolvated in rate-determining steps. Particularly pertinent to this point are the identity and cross-reactions of difluoroacetic acid and 2,4-di-*tert*-butyl-4-nitrophenol: the rate constant for the thermodynamically favorable proton transfer from difluoroacetic acid to the phenolate is significantly smaller than the rate constants for either identity reaction. If the mechanism of the reaction involved independent desolvation of acid and base, followed by rapid proton transfer, the cross-reaction should have a rate constant no less than twice that of the slowest identity reaction.³² If the desolvation of acid and base occurred in one step, such as in the conversion of a solvent-separated to a nearest-neighbor complex, or were concerted with proton transfer, but still involved simple additive contributions from the two partners, the "intrinsic" barrier for the cross-reaction would be the average of the barriers for the two identity reactions and the actual barrier for an appreciably favorable cross-reaction could be lower, but not higher, than the "intrinsic" barrier.^{33,34}

Any general mechanism for the reactions must involve specific interactions between acid and base at the transition state of the rate-determining step in order to accommodate the observations of the cross and identity rates reported here.

The point that must be borne in mind in trying to formulate a mechanism for these reactions is that the actual proton transfer is not rate-determining. This means that the proton transfer in the favorable direction is faster than the *reverse* of the preceding rate-determining step. If some sort of desolvation is rate-determining, then the reverse, solvation, must be slower than the proton transfer. Since solvation must be fairly fast,^{8,10,26} certainly not much less than 10^{10} s^{-1} , the proton transfers must be fast indeed. Examination of molecular models indicates that even in cases such as the identity exchange of 2,6-di-*tert*-butyl-4-nitrophenol there are conformations that allow contact between the phenolate oxygen and the proton of the phenol without strain. Since the proton transfers of the type studied here can probably occur with, at most, very small barriers at contact distances,³⁵ there appears to be no problem with fast transfer *once the proper conformation of the acid-base pair is attained*.

Kreevoy³⁶ has considered the consequences of proton transfers occurring with very small or no potential energy barriers. One possibility is that the entire reaction occurs in a single step without

intermediates. The transition state for such a process would involve heavy-atom motion, with little or no motion of the proton, along the reaction coordinate. The rapidity of the proton motion could also lead to nonequilibrium of solvent with the charge distribution of the acid-base pair and produce a dynamical contribution to the barrier for the reaction. We believe that it is conceptually simpler to consider the present results in terms of the usual three-step mechanism, eqs 1-3, but recognize that the intermediates may have vanishingly short lifetimes³⁷ and that "classical" transition-state theory may not be appropriate.

Peters³⁸ generated the ion pairs of benzophenone ketyls and dialkylaniline cation radicals photochemically and then observed the proton transfer within the ion pair. He argues that the rate-determining step of the reaction is a reorientation of the partners within the ion pair prior to the proton transfer.

We suggest that it is the formation of a properly oriented and spaced nearest-neighbor "reactive complex" that is the rate-determining step in the proton transfers between electronegative atoms in DMSO solution. Some desolvation must be involved in the formation of the complex and could depend on both hydrogen-bonding and dispersion interactions of both the acid and base with solvent. The proper orientation depends on the detailed shapes of both the acid and the base of the pair; they must fit together to allow contact between the basic site and the proton. The complex could also involve favorable dispersion interactions between the acid and base moieties, although Grunwald's data^{7,8,10,29} indicate that these interactions do not contribute substantially in the rate-determining desolvation steps for amine-ammonium ion reactions.

According to this situation, tertiary amines with large bulky groups, such as tribenzylamine show exceptionally slow rates of proton transfer because, in addition to desolvation requirements, restrictive geometries must be attained that allow contact of the basic atom with the proton. Since detailed fits of acid and base are required, identity and cross-reactions are not simply related. The fact that the reaction of 2,6-di-*tert*-butyl-4-nitrophenol with *N,N*-dimethylbenzylamine is faster than the reaction of the less bulky difluoroacetic acid with the same amine could be ascribed either to favorable dispersion interactions of the phenol with amine or to stronger solvation of difluoroacetic acid due to hydrogen bonding. The slower identity reaction of diphenylacetic acid than of difluoroacetic acid can be attributed to the greater dispersion interactions with solvent in the diphenylacetic acid case, while the slower identity reaction of trifluoroacetic acid than of difluoroacetic acid might result from the stronger hydrogen bond of trifluoroacetic acid with solvent.

The question of concertedness in the desolvation of reactants and formation of the reactive complex is an interesting one somewhat related to that addressed by Hibbert⁹ regarding transfer of an intramolecularly hydrogen-bonded proton to a base. If it were necessary to completely remove at least one solvent molecule from a reactant acid or base before development of favorable interactions, such as (but not necessarily limited to) hydrogen bonding, between the acid and base in the complex, we would expect to observe appreciable barriers to the formation of the complexes producing rate constants well below the diffusion limit of $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The fact that the protonation of trifluoroacetate ion by solvated proton approaches diffusion control and the rate constant of $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for ammonia-ammonium ion transfer in DMSO¹² suggests that desolvation can be compensated by favorable interactions between the reaction partners. Both of these cases involve reactions of very small unhindered species that could easily allow a concerted process.

Size of the acid and base, alone, appears not to be the primary factor in determining whether or not rates can reach diffusion control, and the separation of hindrance to the concerted desolvation from effects involved in attaining proper orientation and distance for proton transfer is difficult. For aqueous solution, the similar behaviors of small cyanide ion²⁵ and the fairly large

(30) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311; **1976**, *98*, 318.

(31) Jones, F. M., III; Arnett, E. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 263. Taft, R. W.; Taagepera, M.; Summerhays, K. D.; Mitsky, J. *J. Am. Chem. Soc.* **1973**, *95*, 3811.

(32) This lower limit would be for a case in which desolvation of either the acid or base of the slowest identity reaction was the entire source of the barrier. Since the proton transfer of an identity reaction has only a 50% probability, the factor of 2 occurs for the cross reaction.

(33) Ritchie, C. D. *Physical Organic Chemistry, The Fundamental Principles*, 2nd ed.; Dekker: New York, 1989; pp 243-248.

(34) Although Marcus theory is usually applied to the proton-transfer step, the general ideas can be applied to the complex formation just as well. The simplest version of Marcus theory³³ gives $\log k_{AB} = \frac{1}{2}(\log k_{AA} + \log k_{BB} + \log K_{AB})$. The two other pairs in which we have studied both identity reactions and the cross-reaction show small deviations from this "Marcus" behavior. For dimethylbenzylamine-2,6-di-*tert*-butyl-4-nitrophenol, the calculated $\log k_{AB}$ is 6.1 and the observed is 6.6; for difluoroacetic acid-dimethylbenzylamine, the calculated value is 6.6 and the observed is 6.0, both for transfers in the favorable direction.

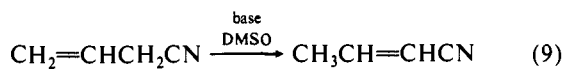
(35) Ritchie, C. D.; King, H. F. *J. Am. Chem. Soc.* **1966**, *88*, 1069; **1968**, *90*, 825, 833, 838. Scheiner, S. *Acc. Chem. Res.* **1985**, *18*, 174. Scheiner, S.; Latajka, Z. *J. Phys. Chem.* **1987**, *91*, 724.

(36) Kreevoy, M. M.; Truhlar, D. G. In *Investigations of Rates and Mechanisms of Reactions*, 4th ed.; C. F. Bernasconi, Ed.; Wiley: New York, 1986; Chapter 1. See also: Hynes, J. T. *Annu. Rev. Phys. Chem.* **1985**, *36*, 573-97.

(37) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161.

(38) Manning, L. E.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 6452.

thiazolium zwitterion²⁶ discussed above are pertinent. For DMSO solution, Bordwell³⁹ has reported a study of the base-catalyzed isomerization of 3-butenitrile to 2-butenitrile



which proceeds by deprotonation and reprotonation. From the estimated $\text{p}K_a$ of 22.5 for 3-butenitrile, the $\text{p}K_a$'s of the catalyzing bases, and the rate constants for the isomerization, we can estimate rate constants for protonation of the carbanion (at the 2-position) by the conjugate acids of the bases. For protonation of the carbanion by cyclohexylammonium ion ($\text{p}K_a = 11.1$) and by thiophenol ($\text{p}K_a = 10.3$), $k \approx 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Protonations by phenols and carboxylic acids are only somewhat slower: $k \approx 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $\text{p}K_a = 10.0$ for 2,3,4,5-tetrachlorophenol and $k \approx 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $\text{p}K_a = 11.0$ for benzoic acid. It is also

(39) Bordwell, F. G.; Hughes, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 4737.

pertinent to note in Table IV that the protonation of difluoroacetate ion by 2,4-dinitrophenol is considerably faster than those by the 2,6-disubstituted phenols.

The major fault with the postulation of desolvated, highly oriented, and specifically interacting complexes prior to proton transfer is that it provides enough flexibility to accommodate nearly any results. Nevertheless, we cannot see a simpler alternative. It is clear from the results presented here that proton transfers between electronegative atoms are considerably more complicated than previously thought and that the complications must arise from processes other than the actual proton transfer.

Acknowledgment. We acknowledge several helpful discussions with Dr. R. J. Kurland. Dr. Dinesh Sukumaran has helped clarify several points of NMR theory and has contributed substantial technical assistance with the NMR spectrometer. This research was supported by NSF Grant CHE-8603895. The Varian Model VXR-400S spectrometer used in this work was purchased under Department of Education Grant 2-2-01011.

E2-E1cB Borderline: Elimination Reactions of 2-(2,4,6-Trinitrophenyl)ethyl Halides in Aqueous Solution

Joseph R. Gandler,* Joey W. Storer, and Douglas A. A. Ohlberg

Contribution from the Department of Chemistry, California State University, Fresno, California 93740-0070. Received May 9, 1990

Abstract: The base-promoted elimination reactions of 2-(2,4,6-trinitrophenyl)ethyl halides in aqueous solution have been investigated. The relative rate constant ratios for elimination of fluoride, chloride, bromide, and iodide are 1:1.6:4.7:3.9, 1:1.9:4.3:8.5, and 1:2.2:10.2:14.7 for the hydroxide ion, trifluoroethoxide ion, and hexafluoroisopropoxide ion promoted reactions, respectively. This small spread in relative halogen leaving group abilities extends a previously reported trend of decreasing sensitivity to the identity of the leaving halogens as the β -aryl substituent is made more electron withdrawing in the series 2-phenylethyl, 2-(*p*-nitrophenyl)ethyl, 2-(2,4-dinitrophenyl)ethyl, and 2-(2,4,6-trinitrophenyl)ethyl halides. The fluoride to chloride rate constant ratio, however, shows little or no change for the 2-(2,4-dinitrophenyl)ethyl (2.0) and 2-(2,4,6-trinitrophenyl)ethyl (1.6) derivatives. The reactions are general-base promoted, with Brønsted β values increasing in the order 0.37:0.41:0.49:0.54 for the iodide, bromide, chloride, and fluoride substrates. The Brønsted β values reported here are consistent with a previously reported trend of decreasing β values for strongly activated 2-arylethyl derivatives as the β -aryl substituent is made more electron withdrawing, e.g., $\beta = 0.61, 0.46,$ and 0.41 , for 2-(*p*-nitrophenyl)ethyl bromide, 2-(2,4-dinitrophenyl)ethyl bromide, and 2-(2,4,6-trinitrophenyl)ethyl bromide, respectively. A similar decrease is observed for the 2-(2,4-dinitrophenyl)ethyl ($\beta = 0.43$) and 2-(2,4,6-trinitrophenyl)ethyl ($\beta = 0.37$) iodides, but little or no change is observed for the corresponding chlorides and fluorides ($\beta \sim 0.50$). Rate constants for the hydroxide ion promoted reaction are about 100-fold smaller than expected on the basis of reactions of other 2-arylethyl derivatives, including the *p*-nitrophenyl and the 2,4-dinitrophenyl compounds, and suggest steric hindrance to resonance by the two *o*-nitro groups. Taken together, these results are consistent with an E2 ($A_{\text{XH}}D_{\text{H}}D_{\text{N}}$) mechanism for the iodide and bromide substrates and a reaction coordinate that has a large component of hydron transfer. The mechanisms of reaction of the fluoride and chloride substrates are, however, not established by these results, but a change to an E1cB_{irr} ($A_{\text{XH}}D_{\text{H}} + D_{\text{N}}$) mechanism appears possible.

Base-promoted elimination reactions of 2-arylethyl derivatives have been extensively studied and have played an important role in better understanding the relationship between the structure of the E2 transition state and changes in reactant and catalyst structure and reaction conditions.¹⁻⁶ Changes in the structure of the E2 transition state are important because these changes can give rise to changes in reaction mechanism, structure-reactivity

behavior, regioselectivity, and stereochemistry.¹⁻⁶

As the β -aryl substituent becomes more electron withdrawing in this series, there is evidence for a decrease in the extent of leaving group bond cleavage in the E2 transition state¹⁻⁶ as measured by decreases in heavy-atom leaving group^{2,7,8} and α -secondary-hydrogen⁹ isotope effects and other measures of leaving-group bond cleavage, including values of ρ_{lg} ¹⁰ and β_{lg} ¹¹ and the relative leaving group abilities of halide ions.¹² As a result

(1) For a recent review on alkene-forming elimination reactions see: Gandler, J. R. In *The Chemistry of Double-bonded Functional Groups*; Patai, S., Ed.; Wiley: Chichester, 1989; Vol. 2, Part 1.

(2) Saunders, W. H., Jr.; Cockerill, A. F. *Mechanisms of Elimination Reactions*; Wiley: New York, 1973; Chapter 2.

(3) More O'Ferrall, R. A. In *The Chemistry of the Carbon-Halogen Bond*; Patai, S., Ed.; Wiley-Interscience: New York, 1973; Part 2.

(4) Fry, A. *Chem. Soc. Rev.* **1972**, *1*, 163.

(5) Bartsch, R. A.; Zavada, J. *Chem. Rev.* **1980**, *80*, 453.

(6) Bunnett, J. F. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 225.

(7) Bourns, A. N.; Smith, P. J. *Can. J. Chem.* **1974**, *52*, 749.

(8) Grout, A.; McLennan, D. J.; Spackman, I. H. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1758.

(9) (a) Cockerill, A. F. *Tetrahedron Lett.* **1969**, 4913. (b) Foud, F. M.; Farrell, D. G. *Tetrahedron Lett.* **1978**, 4735.

(10) Banger, J.; Cockerill, A. F. *J. Chem. Soc. B* **1971**, 498.

(11) Gandler, J. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 1937.

(12) Saunders, W. H., Jr. *Acc. Chem. Res.* **1976**, *9*, 19.