shifts and equilibrium isotope effects at each position. Taking the shift of the CH of isopropyl cation ($\delta \sim 11$) as our model for δ_2 and using the experimental shifts in the low-temperature spectrum of norbornyl[5] lead to $\delta_1 = 2$ ppm and the average of δ_{6exo} and $\delta_{6endo} = 3$ ppm. If, as is commonly assumed through applying the Hammond postulate, the transition state for solvolysis is close to the ion, it is reasonable to use the measured *kinetic* deuterium isotope effects for solvolysis to model equilibrium isotope effects on the ion. Equililibrium deuterium isotope effects in systems involving simple acyclic tertiary ions were found to be very similar in magnitude to the kinetic isotope effects in *tert*-butyl solvolysis,[8a-d] so this choice seems appropriate for the classical ion model.

Kinetic deuterium isotope effects for solvolysis of norbornyl brosylate of $C_2 = 1.124$, $C_1 = 1.081$, $C_{6exo} = 1.09$, and $C_{6endo} = 1.07$ (all at approximately 25 °C in acetic acid) have been reported.[9a-d] The proton shift of the peak due the 1, 2, 6_{exo}, and 6_{endo} protons is the average of the individual shifts. The shifted peak in the fraction of molecules containing the deuterium on carbons 1, 2, or 6 is the same average altered by the isotope effects. Assuming an exponential temperature dependence in order to extrapolate the kinetic isotope effects to −43 °C, we predict an isotopic shift of 0.059 ppm *downfield* on the basis of this classical model through the use of a computer program that calculates the average frequencies weighted by the above isotope effects. This is clearly incompatible with the observed shift of 0.146 ppm *upfield*.

If the transition state for solvolysis coincided exactly with the symmetrically bridged cation, it would be expected that the kinetic isotope effects for C_2 and C_1 would be the same as well as those for C_{6exo} and C_{endo}. Clearly it does not. The sign of the isotope shift, reported here, shows that the stable ion differs considerably from this transition state and must be bridged.

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Registry No. Norbornyl cation, 24321-81-1; deuterium, 7782-39-0; norbornanone, 497-38-1.

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Cation–Anion Combination Reactions. 23. Solvent Effects on Rates and Equilibria of Reactions

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Abstract: Rate and equilibrium constants for the reactions of 3,6-bis(dimethylamino)xanthylium cation with several amines and thiolates in dimethyl sulfoxide solution have been measured. Assumptions used in previous work to estimate equilibrium constants in dimethyl sulfoxide solution are found to be incorrect. Conclusions reached from those assumptions are not supported by the present data, and there are no examples in the present or past work where solvent effects on rates are appreciably greater than those on the corresponding equilibria for simple bond-forming reactions. Equilibrium constants have also been determined for the reactions of thiophenoxide and trifluoroethoxide ions with (*p*-(dimethylamino)phenyl)tropylium ion in water. The kinetic reactivities of trifluoroethoxide relative to hydroxide ion and of thiophenoxide relative to alkanethiolates are much greater than the corresponding equilibrium reactivities. In addition, an example of a slow, rate-determining, proton transfer in the reaction of morpholine with 3,6-bis(dimethylamino)xanthylium cation in dimethyl sulfoxide has been found.

In several papers of the present series,[1,2] we have suggested the possibility that solvent motion along the reaction coordinate could be an important contribution to the activation barriers of ionic reactions in solution. Any case of a change of solvent causing a larger change in rate constant than in corresponding equilibrium constant for a simple combination reaction would provide strong support for the suggestion. It has proved difficult, however, to find reactions for which both rate and equilibrium constants can be determined in two fundamentally different solvents, such as water and dimethyl sulfoxide. By the use of seemingly reasonable assumptions to estimate the solvent effect on either rate[1] or equilibrium[2] and the solvent effect on the other quantity determined experimentally, it has been concluded that the reactions of triarylmethyl cations with azide ion and with amines show behavior supporting the concept.

Pyronin cation (3,6-bis(dimethylamino)xanthylium cation) has provided an opportunity to check some of our assumptions and estimates. Rate and equilibrium constants for a number of reactions of this cation in water have already been reported.[3] The cation is reasonably stable in dimethyl sulfoxide solution, and rate and equilibrium constants for reactions with several amines and thiolates in that solvent have now been determined.

The reaction of pyronin with morpholine in dimethyl sulfoxide has been found to involve a slow, rate-determining, proton transfer. Details of that reaction are reported here.

In addition, it has been possible to determine equilibrium constants for reactions of thiophenoxide and trifluoroethoxide ions with (*p*-(dimethylamino)phenyl)tropylium ion in water to check whether or not the kinetic reactivities of these ions can be related to equilibrium reactivities.

Experimental Section

Materials. Dimethyl sulfoxide was purified by the procedure described by Bordwell[4] and was stored and handled under argon atmospheres.

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Amines and thiols were commercial reagents further purified by distillation or vacuum distillation under argon protection. Trifluoroethylamine hydrochloride was reagent grade material used without further purification. Other amine hydrochlorides were prepared by adding 1 molar equiv of concentrated aqueous hydrochloric acid to an ethanol solution of the amine. All of the salts, except that from 2-methoxyethylamine, precipitated on concentrating the ethanol solutions on a steam bath and were recrystallized from ethanol or 2-propanol. The hydrochloride of 2-methoxyethylamine was obtained by evaporating the ethanol solution to dryness under reduced pressure, followed by drying under high vacuum. This salt was extremely hygroscopic and was handled only under a dry argon atmosphere. Purities of all of the hydrochlorides were verified to be better than 97% by potentiometric titration with standard 0.10 M silver nitrate solution.

The potassium salts of 3,5-dinitrobenzoic acid and of 2,4-dinitrophenol were prepared by adding 1 molar equiv of ethanolic potassium hydroxide to an ethanol solution of the acid. The salts precipitated on concentrating the solutions and were recrystallized from ethanol. The conjugate acids were reagent grade materials used without further purification.

Samples of 9-cyano- and 9-carbomethoxyfluorene were available from earlier studies.[2]

General Procedures. All solutions in dimethyl sulfoxide were prepared under argon atmospheres by utilizing the 3-way stopcock techniques described by Bordwell.[4] Solutions of liquid reagents were prepared volumetrically by the use of gas-tight syringes. Solid reagents were weighed by difference in tared flasks. The flasks were thoroughly flushed with argon before taring, and transfers were made in an argon-filled glovebag. The only exception to this procedure was for the preparation of solutions of pyronin. In that case, 0.3–0.5 mg of pyronin fluoborate was weighed on a Cahn Electrobalance and transferred, without protection, into a 150-mL flask. The flask was then repetitively evacuated and filled with argon before addition of solvent. The absorbances of the pyronin solutions at 555 nm were measured by mixing with pure dimethyl sulfoxide solution on the stop-flow spectrophotometer.

pK_a Measurements in Dimethyl Sulfoxide. The techniques and apparatus were the same as those described previously.[2]

The measurements for piperidinium and (2-methoxyethyl)ammonium ions were made by titration of a 4.5×10^{-4} M solution of 9-carbomethoxyfluorene with a 5.0×10^{-3} M solution of the amine. The absorbances of the solutions, in a 1.0-cm cell, were measured at 410 nm, the wavelength of maximum absorbance of the fluorenyl anion. The determination for morpholinium ion used 9-cyanofluorene as indicator and absorbances were measured at 420 nm. Other details were nearly indentical with those given for piperidinium ion.

The determination for (trifluoroethyl)ammonium ion was by titration of a 3.0×10^{-3} M solution of the potassium salt of 2,4-dinitrophenol with a 1.5×10^{-2} M solution of (trifluoroethyl)ammonium chloride. The absorbances, in a 0.10-cm cell, were measured at 435 nm.

Equilibrium and Kinetic Measurements. All equilibrium and kinetic measurements of the reactions of the cations were made on a stop-flow spectrophotometer specially designed to allow solutions to be introduced under inert atmospheres. General features of the instrument have been described in earlier papers.[1,2,6] Mixing time is ca. 2 ms. Reactions of pyronin in dimethyl sulfoxide solution were followed at 555 nm and utilized a 2.0-cm-path observation chamber. The studies of reactions of Malachite Green and of (*p*-(dimethylamino)phenyl)tropylium were carried out as described in earlier papers.[1,3,5,6]

Master solutions of reagents were prepared at concentrations great enough that at least 25 mg of solid reagents, or 0.10 mL of liquid reagents, was required for 25 mL of solution. This conserved solvent while still allowing accurate concentrations to be prepared. These master solutions were diluted, serially if necessary, and final reaction solutions were prepared in the flasks fitted for attachment to the stop-flow apparatus. Concentrations, and other details where pertinent, are given under Results.

Absorbances of the cation solutions mixed with pure solvent on the stop-flow spectrophotometer were measured immediately before each set of reaction measurements. These solutions were used within 1 h of preparation, although no decreases in absorbance were observed over times of several hours at least.

Pseudo-first-order rate constants were calculated from ca. 1000 absorbance readings, spanning 5–10 half-lives, for each reaction by nonlinear least-squares procedures. Root-mean-square deviations of absorbances from first-order kinetics were never greater than 5×10^{-3} unit and were usually less than 3×10^{-3} unit. "Infinity" absorbances from the least-squares procedure were used for the calculations of equilibrium constants.

Table I. pK_a Values in Dimethyl Sulfoxide[a]

acid	pK_a	acid	pK_a
$CF_3CH_2NH_3^+$	5.8	$CH_3CH_2CH_2SH$	17.0[b]
$CH_3OCH_2CH_2NH_3^+$	10.2	$CH_3O_2CCH_2SH$	13.0[b]
$CH_3CH_2CH_2CH_2NH_3^+$	11.1[c]	3,5-dinitrobenzoic acid	7.3[d]
morpholinium ion	8.7	triethylammonium ion	9.0[c]
piperidinium ion	10.6		

[a] At 25.0 ± 1 °C. [b] Value from ref 2. [c] Value from ref 8. [d] Value from ref 7.

Results

Acidities in Dimethyl Sulfoxide Solution. Equilibrium constants that were precise to ca. 0.05 log unit were obtained for at least 20%–90% conversions of the indicators in all cases. These equlibrium constants for the reactions with indicators are combined with the known pK_a's of the indicators to give the pK_a values shown in Table I. As in earlier work from this[2] and other[7] laboratories, we believe that these values are accurate to better than 0.1 pK unit.

The pK_a shown in Table I for (2-methoxyethyl)ammonium ion is 0.4 unit greater than the value previously reported.[2] In the earlier work, *p*-nitrophenol was used as the indicator and the pK_a of the indicator was taken to be 10.4. Bordwell[9] has recently reported a more reliable value of 10.8 for the pK_a of *p*-nitrophenol, which corrects the earlier value for the (2-methoxyethyl)ammonium ion to perfect agreement with the present value.

Table I also contains a number of previously reported pK_a values for reference in the following discussions.

Reactions of Amines. Under the conditions used in the present and earlier studies, the reactions of cations with amines are two-stage reactions:[3,10]

$$R^+ + BH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RBH^+ \tag{1}$$

$$RBH^+ + B' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RB + B'H^+ \tag{2}$$

where BH is the amine reactant, and B′ can be any base in solution. The extent of reaction of R^+ at equilibrium is given by eq 3, where A_0 and A_∞ are absorbances of the cation before

$$(A_0 - A_\infty)/A_\infty = ([RBH^+]_\infty + [RB]_\infty)/[R^+]_\infty = K_1[BH](1 + K_2[B']/[B'H^+]) \tag{3}$$

reaction and at equilibrium, respectively, all concentrations are those at equilibrium, and K_1 and K_2 are the equilibrium constants for reactions 1 and 2, respectively. Appropriate measurements at various concentrations of BH, B′, and B′H allow the calculation, in principle, of K_1 and K_2.

For the reactions of pyronin with 2-methoxyethylamine, *n*-butylamine, morpholine, and piperidine in dimethyl sulfoxide solution, we have used known concentrations of amine and corresponding amine hydrochloride to "buffer" reaction 2. For these reactions, quite low amine/ammonium ion ratios were possible, and reasonable calculations of both K_1 and K_2 were possible. In none of these cases, however, was it possible to attain conditions such that the K_2 term in eq 3 was negligible. The calculations of K_1 and K_2 were done by a nonlinear least-squares fitting of the A_∞ measurements. Values obtained for the product K_1K_2 are precise to better than ±20%, but the values of the individual constants are probably not reliable to much better than ±50%.

The study of the reactions of trifluoroethylamine with pyronin and Malachite Green in dimethyl sulfoxide and of the reactions of all amines in aqueous solution required the use large amine/ammonium ion concentration ratios to give measurable reactions at reasonable concentrations. For these reactions, only the product

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Table II. Rate and Equilibrium Constants for Amine Reactions[a]

amine	solvent	k_1, M^{-1} s^{-1}	K_1K_2, M^{-1}	K_1, M^{-1}	K_2
		Pyronin Reactions			
n-butylamine	Me_2SO	1.8×10^5	2.6×10^5	1.0×10^4	26.0
	H_2O[b]	9.5×10^2	5.5	5.5×10^{-1}	10.0[c]
$CH_3OCH_2CH_2NH_2$	Me_2SO	9.8×10^4	2.2×10^4	1.8×10^3	12.0
	H_2O	2.7×10^2	6.8×10^{-1}	6.8×10^{-2}	10.0[c]
$CF_3CH_2NH_2$	Me_2SO	3.6×10	2.7×10^{-1}	1.3×10^{-2}	20.0[c]
piperidine	Me_2SO	1.6×10^6	7.7×10^5	1.8×10^4	43.0
	H_2O	2.8×10^4	2.2×10	2.2	10.0[c]
morpholine	Me_2SO	1.1×10^6	1.9×10^4	3.0×10^2	65.0
	H_2O	7.1×10^3	1.0×10^{-1}	1.0×10^{-2}	10.0[c]
		Malachite Green Reactions			
$CF_3CH_2NH_2$	Me_2SO	2.9	2.2×10	1.1	20.0[c]
	H_2O[d]	1.1×10^{-1}	1.7×10^{-2}	1.7×10^{-3}	10.0[c]

[a] At 25.0 ± 1 °C. [b] Data from ref 3. [c] These are estimated values, as described in the text. [d] Data from ref 10.

K_1K_2 can be evaluated from the observations. Values were obtained by nonlinear least-squares fitting of the A_∞ values.

For the reaction of trifluoroethylamine with pyronin in dimethyl sulfoxide, triethylamine–triethylammonium ion buffers, prepared by the addition of triethylamine to solutions of trifluoroethylamine hydrochloride, were utilized. The known relative pK_a's of the two ammonium ions (Table I) allowed the calculation of K_1K_2 for the reactions with B′ = trifluoroethylamine.

Similarly, 3,5-dinitrobenzoate–3,5-dinitrobenzoic acid buffers were utilized in the study of the reaction of Malachite Green with trifluoroethylamine in dimethyl sulfoxide solution.

It was verified in all of these studies that there is no reaction of the cations with the buffers alone.

Values for K_1 and K_2 can be estimated by assuming that K_2 will be approximately the same as that found for other primary amines reacting with the cations. These estimates are shown in Table II.

The study of the reactions of pyronin with morpholine in aqueous solution utilized triethylamine–triethylammonium ion buffers at pH of 11.70, and those with 2-methoxyethylamine used the same buffer system at pH 10.66. The pH of the solutions were measured by using a glass electrode standardized with saturated $Ca(OH)_2$. The reaction of piperidine in aqueous solution was buffered with piperidine hydrochloride at pH ca. 11 (measured values). The reactions of hydroxide ion under the conditions used are much slower than any of the amine reactions studied. Values of K_1K_2 were obtained as described above, and the assumption that K_2 is approximately 10 for all of the amines[3,10] allows the estimates of K_1 shown in Table II.

Kinetics of the amine reactions were studied under the equilibrium conditions just discussed. All of the reactions, except that of morpholine with pyronin in dimethyl sulfoxide, showed forward pseudo-first-order rate constants directly proportional to the reacting amine concentration. Reaction 1 is the rate-determining step for these reactions. Calculated second-order rate constants were precise to better than ±10% over at least a fivefold variation in amine concentration. Values are reported in Table II.

The reaction of morpholine with pyronin in dimethyl sulfoxide was obviously different from the other amine reactions. At morpholine concentrations above 2×10^{-4} M, the initially observed absorbances (ca. 2-ms mixing time) were significantly lower than those of the pyronin solutions mixed with pure solvent. The further decreases in absorbance on the stop-flow time scales followed accurate first-order kinetics, but the pseudo-first-order rate constants were clearly more than first order with respect to morpholine concentrations. For those reactions that were slow enough to allow accurate extrapolation of absorbance to zero time, the assumption that reaction 1 had reached equilibrium on mixing led to a reasonably consistent value for the equilibrium constant, which was only slightly greater than that obtained from the equilibrium measurements described above. The observed pseudo-first-order rate constants for these cases were in fair accord with the kinetic scheme of reactions 1 and 2, with reaction 1 being a rapid equilibrium.

In order to sharpen the data and to avoid assumptions, we resorted to computer fitting of the data. The exact equations for consecutive, reversible, pseudo-first-order reactions 1 and 2 were programmed. Values for K_1 and K_2 were set to those reported in Table II, and k_1 and k_2 were varied by Gauss–Newton procedures to obtain a least-squares fit of the observed pseudo-first-order rate constants with the smaller of the two eigenvalues of the kinetic equations. The program also calculated the theoretical absorbances at 2 and 3 ms for comparison with the absorbances initially observed on the stop-flow spectrophotometer. The agreement was good in all cases. It was also verified that the program converged to the same values of k_1 and k_2 for widely different starting values. Thirteen kinetic experiments with morpholine concentrations from 1.0×10^{-4} to 1.1×10^{-3} M and pseudo-first-order rate constants from 5.2 to 420 s^{-1} were fitted with a root-mean-square deviation of 8.8% in the rate constants. The value of k_2 obtained is 1.6×10^6 M^{-1} s^{-1}, and the value of K_1k_2 (4.8×10^8 M^{-2} s^{-1}) is almost certainly accurate to better than ±10%. The uncertainty in K_1 decreases the accuracy of k_2 to an estimated ±50%. The value obtained for k_1 from these experiments (1.2×10^7 M^{-1} s^{-1}) is not reliable since the calculated value for k_{-1} is greater than k_2 (morpholine) at the highest morpholine concentration used. Thus, the kinetics are completely determined by K_1 and k_2.

To verify the reaction scheme and to obtain a value for k_1, the reactions were then studied in the presence of an added base, B′, that can react in the proton transfer step, but not react directly with the cation. From the equlibrium measurements described above, it was known that neither triethylamine nor 3,5-dinitrobenzoate ion reacts with pyronin at reasonable concentrations. Triethylamine–triethylammonium ion buffers with $[Et_3N] = 10[Et_3NH^+]$ and triethylamine concentrations from 1.0×10^{-3} to 1.0×10^{-2} M were tried first. The pseudo-first-order rate constants for the morpholine reaction in the presence of this buffer increased linearly with triethylamine concentration. Computer analysis of the data, analogous to that described above, gave a value of 3.0×10^4 M^{-1} s^{-1} for k_2', the rate constant for reaction 2 with B′ = triethylamine. Even at the highest triethylamine concentration, the rate does not depend on k_1.

The rates of reaction of morpholine with pyronin were dramatically increased by the presence of 3,5-dinitrobenzoate buffers in the range 10^{-4}–10^{-3} M, and at the higher buffer concentrations the rates became less than first order with respect to buffer concentration. With a buffer ratio, base/acid, of 10, the change of concentration of 3,5-dinitrobenzoate from 9.9×10^{-4} to 2.0×10^{-3} M increased the observed pseudo-first-order rate constant by ca. 30%. Computer fitting of the data gave k_2', the rate constant for reaction 2 with B′ = 3,5-dinitrobenzoate, as 3.1×10^6 M^{-1} s^{-1} and $k_1 = 1.1 \times 10^6$ M^{-1} s^{-1}.

The exact kinetic equations for reactions 1 and 2, with the rate constants reported in Table III, reproduced the experimental pseudo-first-order rate cosntants, initial absorbances, and "infinity" absorbances with satisfactory precision for all runs. For the runs without added buffers present, these fits were only marginally

Table III. Rate and Equilibrium Constants for Reactions of Morpholine with Pyronin in Dimethyl Sulfoxide

reaction[d]	k_f[a]	k_r[b]	K[c]
$P^+ + MH = PMH^+$	1.1×10^6	3.6×10^3	3.0×10^2
$PMH^+ + MH = PM + MH_2^+$	1.6×10^6	2.5×10^4	6.4×10
$PMH^+ + Et_3N = PM + Et_3NH^+$	3.0×10^4	2.7×10^2	1.1×10^2
$PMH^+ + ArCOO^- = PM + ArCOOH$	3.1×10^6	1.5×10^6	2.0

[a] Forward rate constant, $M^{-1}\ s^{-1}$. [b] Reverse rate constant, s^{-1} or $M^{-1}\ s^{-1}$. [c] Equilibrium constant for the reaction in the direction written, M^{-1} or unitless. [d] P^+ is the pyronin cation, MH is morpholine, and Ar is the 3,5-dinitrophenyl group. Reaction conditions, 25.0 ± 1 °C.

Table IV. Miscellaneous Rate and Equilibrium Constants

reaction[a] (solvent)	k, $M^{-1}\ s^{-1}$	K, M^{-1}
$P^+ + n\text{-}PrS^- = PSPr$ (Me_2SO)		4.4×10^{14}
$P^+ + n\text{-}PrSH = PSPr + H^+$ (Me_2SO)	2.9×10^2	
$P^+ + CH_3O_2CCH_2S^- = PSCH_2CO_2CH_3$ (Me_2SO)	2.0×10^9 [b]	1.2×10^{11}
$P^+ + CH_3O_2CCH_2SH = PSCH_2CO_2CH_3 + H^+$ (Me_2SO)	3.0×10^2 [b]	
$DMAPTr^+ + C_6H_5S^- = DMAPTrSC_6H_5$ (H_2O)	6.3×10^8	2.0×10^5
$DMAPTr^+ + C_6H_5SH = H^+DMAPTrSC_6H_5$ (H_2O)	5.0×10^4	2.0×10^3
$DMAPTr^+ + CF_3CH_2O^- = DMAPTrOCH_2CF_3$ (H_2O)	1.4×10^4 [c]	1.1×10^3 [c]

[a] Reaction conditions, 25.0 ± 1 °C. P^+ is the pyronin cation and $DMAPTr^+$ is the (p-(dimethylamino)phenyl)tropylium cation. [b] Tentative values; see text. [c] Values obtained at ionic strength of 0.07 M.

poorer than those obtained by full optimization of those runs alone. There is a great deal of coupling of the individual rate and equilibrium constants in the reaction scheme, which leads to estimated uncertainties of ca. ±50% for the values shown in Table III. Combined values, such as K_1k_2' and K_1K_2, are considerably more precise.

Reactions of Thiols with Pyronin in Dimethyl Sulfoxide. The determinations of equilibrium constants for the reactions of thiolates with pyronin in dimethyl sulfoxide required the use of extremely low thiolate concentrations. These were attained by the use of 3,5-dinitrobenzoate–3,5-dinitrobenozic acid buffers for both the 1-propanethiolate and the carbomethoxymethanethiolate reactions.

For the 1-propanethiolate reactions, buffer base concentrations ranged from 5×10^{-4} to 2×10^{-3} M, and thiol concentrations from 1×10^{-4} to 1×10^{-3} M, to provide thiolate concentrations on the order of 10^{-14} M. Under these conditions, the reactions reach equilibrium in 1–10 s. The equilibrium absorbances are in accord with the expected reaction of pyronin with thiolate to give thioether and allow the calculation of $K = 4.4 \times 10^{14}$ M^{-1} with a precision of ca. ±10%. With the very low thiolate concentrations, thiolate does not contribute significantly to the rates of reaction. With buffer concentrations of 1×10^{-3} M or less, the pseudo-first forward rates are directly proportional to thiol concentration and allow the calculation of the second-order rate constant reported in Table IV with a precision of better than ±10%. At the highest buffer concentrations used, 2×10^{-3} M, the equilibrium absorbances are in good agreement with values at lower buffer concentrations, but the rates of reaction are nearly a factor of 2 less than those at lower buffer concentration. We have not pursued the cause of this problem.

For the reactions of carbomethoxymethanethiolate, buffer base concentrations of 2×10^{-3} to 3×10^{-3} M and thiol concentrations of 1.0×10^{-4} to 5.0×10^{-4} M gave thiolate concentrations on the order of 10^{-11} M. The reactions reached equilibrium in times of a few seconds, and the equilibrium absorbances gave an equilibrium constant of 1.1×10^{11} M^{-1} with a precision of better than ±10%. The forward pseudo-first-order rate constants varied with both thiol and thiolate concentrations. Second-order rate constants calculated for the reactions of both thiol and thiolate show rather poor precision. It seems quite possible that the high buffer concentrations used in these studies are causing problems similar to those noted above for the 1-propanethiol reaction at high buffer concentrations. Values of the rate constants shown in Table IV are believed to be accurate to better than a factor of 2, and should be considered as tentative. Since it is almost certain that the thiolate ion reacts at a diffusion-controlled rate, we have not pursued the rate measurements.

Reaction of (*p*-(Dimethylamino)phenyl)tropylium Ion with Trifluoroethoxide Ion in Water. The rate constant for this reaction has been reported previously.[11] The equilibrium measurements required the use of fairly high ionic strength carbonate–bicarbonate buffers and trifluoroethanol concentrations of 0.1–1.3 M. Two sets of experiments, one at ionic strength of 0.35 M and the other at 0.07 M, were performed. The pH values of the solutions were calculated from the buffer ratios, the pK_a of 10.33 for bicarbonate, and activity coefficients from standard tabulations.[12] The activity of trifluoroethoxide ion was calculated from the pK_a of 12.4 for trifluoroethanol assuming an activity coefficient of unity for trifluoroethanol.

Absorbances observed on mixing the cation solutions with buffer solutions alone were significantly less than those obtained on mixing the cation solution with pure water. At pH 10.09 and ionic strength 0.35 M, the initially observed absorbance is 18.3% lower than that of the solution in pure water, and the further decrease in absorbance to 0 occurs with a pseudo-first-order rate constant of 0.108 s^{-1}. From previously reported rate constants for reactions of hydroxide ion and water,[13] a pseudo-first-order rate constant of 0.21 s^{-1} was expected. At the same pH but ionic strength 0.07 M, the initially observed absorbance is 12.6% lower than that of the solution in pure water, and the pseudo-first-order rate constant for further decrease to 0 is 0.20 s^{-1}. These experiments indicate that a very rapid reaction, either with buffer or a precipitation of the cation at high ionic strength, is followed by the expected slow reaction of hydroxide ion and water.

In the buffered solutions of trifluoroethanol, the initially observed absorbances are the same as those observed in the presence of buffer alone. There is then a further decrease in absorbance with pseudo-first-order rate constants directly proportional to trifluoroethoxide ion concentrations and on the order of 10–50 s^{-1}. These reactions reach equilibrium before there is any significant contribution from the hydroxide ion and water reactions. For the 0.07 M ionic strength solutions, the second-order rate constant calculated for the trifluoroethoxide ion reaction is in good agreement with the previously reported value; the 0.35 M ionic strength solutions gave a value ca. 20% lower.

The equilibrium absorbances observed for the trifluoroethoxide ion reactions gave equilibrium constants with good precision when the values of $(A_0 - A_\infty)/A_\infty$ were "corrected" for the buffer reaction by subtraction of 0.183 and 0.126 for the 0.35 and 0.07 M ionic strengths, respectively. At 0.07 M ionic strength, a value of 1.1×10^3 M^{-1} and, at 0.35 M, a value of 7.7×10^2 M^{-1} were obtained. The difference in these two values, which is slightly outside experimental uncertainties, could easily arise from salt effects on activity coefficients of cation, trifluoroethanol, and product ether.

Reaction of (*p*-(Dimethylamino)phenyl)tropylium Ion with Thiophenoxide Ion in Water. These reactions were studied in acidic solutions where there is some complication due to the protonation of the dimethylamino group of the product thioether. Measurements were carried out in dilute hydrochloric acid solutions at pH 2.3 and 2.6 and in acetate–acetic acid buffers at pH 3.83, 4.8, and 5.1. At pH 2.3, 2.6, and 3.8, the observed reaction is essentially

$$C_6H_5SH + p\text{-}(CH_3)_2NC_6H_4Tr^+ \rightleftarrows p\text{-}H(CH_3)_2N^+C_6H_4TrSC_6H_5 \quad (4)$$

and a consistent value of 2.0×10^3 M^{-1} was obtained from the

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Table V. Values of Log Π in Eq 5 and 6 for Change from Water to Dimethyl Sulfoxide

reaction[a]	$\Delta \log K$	ΔpK_a	$\log \Pi_0$ or Π_-
$P^+ + n\text{-}BuNH_2$	4.3	0.5	3.8
$P^+ + CH_3OCH_2CH_2NH_2$	4.5	0.8	3.7
$MG^+ + CF_3CH_2NH_2$	2.8	0.2	2.6
P^+ + piperidine	4.1	−0.5	4.6
P^+ + morpholine	4.5	0.2	4.3
$P^+ + n\text{-}PrS^-$	9.5	6.2	3.3
$P^+ + CH_3O_2CCH_2S^-$	8.8	5.0	3.8
$CV^+ + HOCH_2CH_2S^-$	8.1	5.7	2.4
$p\text{-}ClC_6H_4N_2^+ + CN^-$ [b]	6.8	3.8	3.0

[a] P^+ is the pyronin cation, MG^+ is Malachite Green cation, CV^+ is Crystal Violet cation, and $p\text{-}ClC_6H_4N_2^+$ is the *p*-chlorobenzenediazonium ion. [b] Data from ref 18 and 19.

equilibrium absorbances for the equilibrium constant of reaction 4. At pH of 4.8 and 5.1, the dissociation of the product of reaction 4 into thioether and proton and, to a lesser extent, the acid dissociation of thiophenol ($pK_a = 6.50^{12}$) give the expected variations in equilibrium absorbances. Straightforward treatment of all of the data, using the reported pK_a of thiophenol, allows the calculations of the equilibrium constant for the reaction of cation with thiophenoxide ion to form thioether and of the pK_a of the protonated thioether. Values are reported in Table IV. The pK_a of the product of reaction 4 is, as expected, slightly lower than that of *N,N*-dimethylanilinium ion ($pK_a = 5.2^{12}$), and the equilibrium constant for the reaction of thiophenoxide ion in water is, as expected, considerably smaller than that for the same reaction in methanol solution ($K = 9.1 \times 10^8$ M^{-1}).[5]

At pH 3.8 and greater, the reactions reach equilibrium before the initial observations on the stop-flow spectrophotometer. From the measurements at pH 2.3 and 2.6, second-order rate constants for reactions of both thiophenol and thiophenoxide ion were obtained and are reported in Table IV. Good precision was observed, and we believe that the values are accurate to ca. ±10%.

Discussion

Solvent Effects on Equilibria. In a recent paper,[2] we defined two functions, $\log \Pi_0$ and $\log \Pi_-$, that were expected to be independent of the identity of the cation and nucleophile for cation–nucleophile combination equilibria. In eq 5 and 6, $\Delta \log K$

$$\log \Pi_- \equiv \Delta \log K - \Delta pK_a = \log (\gamma_{R^+}\gamma_{HNuc}/\gamma_{H^+}\gamma_{RNuc}) \qquad (5)$$

$$\log \Pi_0 \equiv \Delta \log K - \Delta pK_a = \log (\gamma_{R^+}\gamma_{BH_2^+}/\gamma_{H^+}\gamma_{RBH^+}) \qquad (6)$$

is the change in the log of the equilibrium constant of reaction, ΔpK_a is the change in pK_a of the conjugate acid of the nucleophile produced by a change of solvent, and the γ's are activity coefficients of the subscripted species in the second solvent relative to a standard state in the first solvent. Equation 5 is applicable to the reactions of anionic nucleophiles, Nuc^-, and eq 6 to the reactions of neutral nucleophiles, BH.

Pertinent data from the present and previous work are shown in Table V for the solvent change from water to dimethyl sulfoxide. Our expectations are, at best, only roughly realized. It is particularly surprising that the values of $\log \Pi_0$ from reactions of primary amines with pyronin are not different from values of $\log \Pi_-$ for corresponding reactions of thiolates. Arguments were presented in the previous paper[2] for expecting $\log \Pi_0$ to be ca. 1.3 units smaller than $\log \Pi_-$. Those arguments also lead to the expectation that $\log \Pi_0$ values for reactions of secondary amines would be smaller than $\log \Pi_-$ values, while the data show that they are significantly larger. It is similarly disturbing that the $\log \Pi_0$ and $\log \Pi_-$ values for the triarylmethyl cations are smaller than the corresponding ones for pyronin reactions.

Although some solace may be gained from the fact that all of the log Π values, for cations of such different natures as pyronin and aryldiazonium ions and nucleophiles as different as thiolates and secondary amines, are equal to 3.5 ± 1.1 units; the more sobering practical conclusion must be that variations of up to ca. 2 log units in solvent effects on equilibrium constants result from noncancellations of activity coefficients even in carefully chosen systems. These variations are not easily rationalized, much less predicted.

Table VI. Solvent Effects on Rate and Equilibrium Constants[a]

reaction[a]	ref	solvent 1	solvent 2	$\Delta \log k^b$	$\Delta \log K^b$
$P^+ + n\text{-}PrS^-$	3	H_2O	Me_2SO	3.4[c]	9.5
$CV^+ + HOCH_2CH_2S^-$	2, 17	H_2O	Me_2SO	4.1	8.1
$p\text{-}ClC_6H_4N_2^+ + CN^-$	18, 19	H_2O	Me_2SO	5.4	6.8
$p\text{-}CH_3C_6H_4N_2^+ + CN^-$	18, 19	H_2O	Me_2SO	5.6	7.0
$MG^+ + CF_3CH_2NH_2$	10	H_2O	Me_2SO	1.4	2.8
$P^+ + n\text{-}BuNH_2$	3	H_2O	Me_2SO	2.3	3.8
$P^+ + CH_3OEtNH_2$		H_2O	Me_2SO	2.6	4.4
P^+ + morpholine		H_2O	Me_2SO	2.2	4.3
P^+ + piperidine		H_2O	Me_2SO	1.7	4.6
$P^+ + n\text{-}BuNH_2$	3	H_2O	MeOH	0.4	−0.5
$SP^+ + n\text{-}BuNH_2$	3	H_2O	MeOH	0.6	−0.2
$DMAPTr^+$ + EtGly[d]	10, 11	H_2O	MeOH	0.9	0.3
MG^+ + EtGly[d]	10, 11	H_2O	MeOH	0.7	0.5
$DMAPTr^+ + CF_3CH_2NH_2$	10, 11	H_2O	MeOH	0.7	1.3
$DMAPTr^+$ + morpholine	10, 11	H_2O	MeOH	0.9	1.0
$DMAPTr^+ + CH_3ONH_2$	10, 11	H_2O	MeOH	1.2	2.7
$DMAPTr^+ + PhNHNH_2$	10, 11	H_2O	MeOH	1.0	2.2
$DMAPTr^+$ + Semicarb[e]	10, 11	H_2O	MeOH	0.8	2.8
$DMAPTr^+ + C_6H_5S^-$	5	H_2O	MeOH	1.0[c]	3.9
$p\text{-}NCC_6H_4N_2^+ + CN^-$	18, 20	H_2O	MeOH	2.5	3.2

[a] Abbreviations are the same as in Tables IV and V. Source of the data is given if it is not from the present work. [b] Log *k* in solvent 2 minus that in solvent 1. [c] The rate in nonaqueous solvent is diffusion controlled. [d] *N*-Ethylglycine. [e] Semicarbazide.

Solvent Effects on Rate Constants. All of the data from our present and past work for reactions for which we have determined both rate and equilibrium constants in at least two solvents are collected in Table VI.

In the previous report[2] of rate constants for reactions of Malachite Green with primary amines in dimethyl sulfoxide, equilibrium constants for the reactions were estimated by the use of eq 5 and 6 and the conclusion was reached that the solvent change from water to dimethyl sulfoxide produced greater changes in rate constants than in the corresponding equilibrium constants. That conclusion is now shown to be false for the specific case of the reaction of Malachite Green with (trifluoroethyl)amine and, in general by analogy with the corresponding reactions of pyronin. The fallacy arose from the incorrect estimates of equilibrium constants, as discussed above. For all of the amine reactions, the solvent effect on log *k* is approximately one-half that on log *K*.

There are four examples in Table VI, all for the change of solvent from water to methanol, where changes in log *k* are greater than or in opposite direction to changes in log *K*. In all of these cases, the solvent effects on both quantities are fairly small. There is one further example worth mention. For the reaction of *p*-nitro Malachite Green with azide ion, the change of solvent from methanol to dimethyl sulfoxide produces a change in log *K* of 2.1 units.[1] The measured value of log *k* in methanol is 4.79. The reaction is too fast for measurement by stop flow in dimethyl sulfoxide, but a reliable lower limit, log $k \geq 7.0$, could be set. The change in log *k* is, therefore, greater than or equal to 2.2 units.

Although most of these examples are outside expected experimental uncertainties, the discrepancies between "normal" (i.e.; $0 \leq \Delta \log k/\Delta \log K \leq 1.0$) and abnormal behaviors are quite small. At best, they provide some support for a rather minor contribution of solvent reorientation effects[2] to the rates of these reactions. The major solvent effects are "normal" and consistent with normal solvations of transition states.

Slow Proton Transfers of Ammonium Ions. Our observations of slow proton transfers from the morpholine–pyronin adduct to bases in dimethyl sulfoxide solution are consistent with results from two previous studies of similar reactions.

Kreevoy[14] has reported a number of examples of slow proton transfers from the solvated proton in dimethyl sulfoxide solution

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

to tertiary amines, mostly substituted tribenzylamines. These are exothermic reactions with rate constants well below diffusion limits. For example, the rate constants for protonations of tribenzylamine and of *N*,*N*-dimethylbenzylamine are 1.8×10^4 M^{-1} s^{-1} and 4.2×10^6 M^{-1} s^{-1}, respectively. Kreevoy suggests that the slow rates are the result of the necessity for removing a solvent molecule from the proton before reaction.

Bernasconi has found slow proton transfers in 50% (vol) aqueous dimethyl sulfoxide for the reactions of the morpholine adducts of activated ethylenes with bases.[15,16] Bernasconi's results bear a striking similarity to those of the present study. In both the reactions of 1,1-dinitro-2,2-diphenylethylene[15] and of benzylidenemalononitrile[16] with amines, the slow proton transfer is observed for reaction of morpholine but not for reaction of piperidine. The proton transfers from the morpholine adduct of 1,1-dinitro-2,2-diphenylethylene to tertiary amines is slower than to morpholine, while the transfer to an anion, *p*-nitrophenoxide ion, is faster than that to morpholine. Bernasconi suggests that steric effects are responsible for the slow proton transfers from the ammonium nitrogens.

The fact that the slow proton transfers in both Bernasconi's and the present work are observed for morpholine but not for piperidine reactions probably does not indicate a large difference in the proton transfer rate constants for the two amines. Most likely, as Bernasconi argues,[15] the different behaviors are due to slightly different balances of competing reaction rates for the two amines. In the present case of reactions with pyronin, the proton transfer from the piperidine adduct to piperidine would have to have a rate constant of less than 5×10^6 M^{-1} s^{-1} in order to cause observable behavior in the pseudo-first-order rate constants in the concentration range studied. This is only slightly larger than the value reported in Table III for the corresponding reaction of morpholine.

Equilibrium Constants for Alkoxide and Thiophenoxide Reactions. The equilibrium constant that we find for the addition of trifluoroethoxide ion to (*p*-(dimethylamino)phenyl)tropylium may be compared with the corresponding one for addition of hydroxide ion, log $K = 6.65$.[13] The difference in values, 3.5 units, is only slightly greater than the difference in pK_a values of water (taken as 15.7) and trifluoroethanol, 3.3 units. The rate constant for reaction of trifluoroethoxide ion with the cation is 10 times greater than that for reaction of hydroxide ion. The conclusion, previously expected and now established, is that the greater kinetic reactivity of trifluoroethoxide than that of hydroxide ions cannot be due to a greater "carbon basicity" of the alkoxide ion.

The difference in pK_a's of thiophenol and carbomethoxymethanethiol in water, 1.5 units,[2,12] is very close to the difference of 1.4 units in the log K values for additions of the thiolates to (*p*-(dimethylamino)phenyl)tropylium ion.[17] Thiophenoxide ion, with a rate constant very near the diffusion limit, reacts 10 times faster than the alkanethiolate.[17] The greater kinetic reactivity of the thiophenoxide cannot be ascribed to greater equilibrium reactivity.

As long as the attaching atom of the nucleophile remains constant, the equilibrium reactivities of nucleophiles with cations closely parallel the basicities of the nucleophiles. Even this limited orderly behavior is not seen in the kinetics of reactions.

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Registry No. $CH_3OCH_2CH_2NH_2$, 109-85-3; $CF_3CH_2NH_2$, 753-90-2; *n*-PrS^-, 20733-14-6; *n*-PrSH, 107-03-9; $CH_3O_2CCH_2SH$, 2365-48-2; $CH_3O_2CCH_2S^-$, 64743-45-9; $C_6H_5S^-$, 13133-62-5; C_6H_5SH, 108-98-5; $CF_3CH_2O^-$, 24265-37-0; $HOCH_2CH_2S^-$, 57966-62-8; Me_2SO, 67-68-5; $DMAPTr^+$, 38054-74-9; CV^+, 7438-46-2; pyronin·BF_4^-, 85338-00-7; malachite green, 569-64-2; *n*-butylamine, 109-73-9; piperidine, 110-89-4; morpholine, 110-91-8.

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Rate Constants and Arrhenius Parameters for the Reaction of a Primary Alkyl Radical with Tri-*n*-butylgermanium Hydride[1]

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Abstract: The rate constants for hydrogen atom abstraction from tri-*n*-butylgermanium hydride by the 5-hexenyl radical, k_5, have been measured in octane as solvent at temperatures varying from 233 to 393 K. Over this temperature range the data can be represented by $\log k_5\ (M^{-1}\ s^{-1}) = (8.44 \pm 0.47) - (4.70 \pm 0.62)/\theta$, where $\theta = 2.3RT$ kcal/mol. At ambient temperatures this germanium hydride is only about $^1/_{20}$ as reactive toward primary alkyl radicals as the corresponding tin hydride. This should make it a useful probe for slow alkyl radical rearrangements.

The free-radical chain reaction of tri-*n*-butyltin hydride with alkyl halides[4] has proved to be a particularly valuable method for studying the rearrangements of alkyl radicals.[5] As early as 1966 Walling et al.[6] showed that the reaction of 5-hexenyl bromide with the tin hydride could be represented by eq 1-4. By measuring the relative yields of hexene and methylcyclopentane at various tin hydride concentrations, Walling was able to calculate the rate constant ratio, k_2/k_3.[6,7] The absolute value of the rate constant for H atom abstraction from the tin hydride by a primary alkyl

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