Cation–Anion Combination Reactions. XII.[1] Rates, Equilibria, and Activation Parameters for Reactions of Triarylmethyl Cations in Aqueous Solution

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Abstract: Rate and equilibrium constants for the reactions of *p*-methyl-*p*′-dimethylaminotriphenylmethyl, *p*-methoxy-*p*′-dimethylaminotriphenylmethyl, *p,p*′-dimethoxy-*p*″-dimethylaminotriphenylmethyl, and *p*-trifluoromethyl-*p*′,*p*″-bis(dimethylamino)triphenylmethyl cations with water and hydroxide ion in aqueous solutions have been determined. The measurement of equilibria between the cations, carbinols, amino-protonated carbinols, and amino-protonated cations allows the evaluation of the full set of equilibrium constants for the acid–base reaction scheme. The thermodynamic and kinetic parameters, $\Delta H°$, $\Delta S°$, ΔH^*, and ΔS^*, for reactions of Malachite Green and Crystal Violet cations with water, hydroxide ion, and cyanide ion are also reported. General base catalysis of the reactions of *p*-methyl-*p*′-dimethylaminotriphenylmethyl, Malachite Green, and Crystal Violet cations with water has been observed, and rate constants for catalysis by Dabco and by quinuclidine are reported. The rate constant ratios k_{OH}/k_{H_2O} and k_{OH}/k_{Dabco} show appreciable variations among different cations, but the ratio k_{H_2O}/k_{Dabco} is relatively constant. The data are discussed in the general context of reactions of cations in aqueous solution.

In the previous two papers of this series,[1] we have called attention to the unusual character of the reaction of water with cations in aqueous solution. In particular, it was shown that the reactions of water with various cations do not show the same regularity that is exhibited by a wide variety of other nucleophiles, and that the reaction of water with Malachite Green [bis(*p*-dimethylaminophenyl)phenyl methyl cation] exhibits general base catalysis.

Taft[2] has previously reported that reactions of water with a series of triarylmethyl cations show no relationship between rate and equilibrium constants. More recently, Bunting[3] has noted that the rate constant ratio k_{OH}/k_{H_2O} is quite constant for a number of quaternary ammonium heterocycles, but that the value of the ratio (*ca.* $10^7\ M^{-1}$) is quite different from that for the triarylmethyl cations (*ca.* $10^4\ M^{-1}$). Bunton[4] has reported that the tri-*p*-anisylmethyl cation shows $k_{OH}/k_{H_2O} = 10^{2.8}\ M^{-1}$. Bunton also reported that he was unable to detect general base catalysis of the reaction of water with this cation, but Wyatt[5] has now conclusively demonstrated that the reaction is catalyzed by Dabco (diazabicyclo[2.2.2]octane), trimethylamine, and triethylamine.

The present study was undertaken in order to obtain additional data concerning the k_{OH}/k_{H_2O} ratio for cations whose stabilities are intermediate between that of the tri-*p*-anisylmethyl and the Malachite Green cations, to further investigate the generality of general base catalysis for the reactions of water with these cations, and to obtain activation parameters for some of the reactions which might shed some light on the detailed natures of the reactions.

Experimental Section

Materials. Samples of Malachite Green and Crystal Violet tetrafluoroborates were available from our previous work.[1] Samples of *p*-trifluoromethyl(Malachite Green)carbinol, *p*-methyl-*p*′-dimethylaminotriphenylmethanol, *p,p*′-dimethoxy-*p*″-dimethylaminotriphenylmethanol, and *p*-methoxy-*p*′-dimethylaminotriphenylmethyl tetrafluoroborate were obtained as a gift from Eastern Research Laboratories of the Dow Chemical Co.[6]

Commercial samples of Dabco were recrystallized from heptane and sublimed under reduced pressure. Triethylamine was distilled from NaOH under argon and stored under an argon atmosphere. Sodium bicarbonate, disodium phosphate, and quinuclidine hydrochloride were high purity commercial materials used without further purification. Acid and base solutions were standardized by titration and were stored under an argon atmosphere.

Equipment. Spectra were recorded with a Cary Model 14 spectrophotometer, and kinetics were followed with either the Cary or a Gilford Model 240 spectrophotometer. Both spectrophotometers were equipped with thermostated cell blocks for 10-cm cells which maintained constant temperature of the solutions in the cells to within ±0.05°.

A Beckman Model 1019 pH meter equipped with glass and saturated calomel electrodes was used for pH measurements. The meter was standardized with commercial buffers accurate to 0.01 pH unit.

Equilibrium Measurements in Aqueous Solution. Master solutions of the buffer components were prepared, standardized against hydrochloric acid or sodium hydroxide, and mixed in the ratios required for the desired pH. The mixed solutions were diluted as necessary to produce a final ionic strength of $4.0 \times 10^{-2}\ M$.

Master solutions of the triarylmethyl carbinols or salts were prepared in either methanol or acetonitrile containing *ca.* $10^{-3}\ M$ HCl to stabilize the cations. From the known concentrations of the master solutions and the molar absorptivities of the cations, the necessary dilution to produce a final solution having a maximum absorbance of *ca.* 1.00 (10-cm path) was calculated. For each of the compounds, exactly the same volume of master solution was added to the range of buffers used in the measurements of the equilibrium constants. The concentrations of the dyes in the final solutions were in the range from 1 to $5 \times 10^{-6}\ M$.

The buffered solutions of the cations were maintained at the experimental temperature in a thermostated bath for *ca.* 24 hr to allow establishment of equilibrium. The spectra of the solutions in 10.0-cm cells were then recorded, and the pH of each solution was measured.

Acetic acid or malonic acid–sodium hydroxide buffers were used for the p*K* determinations on the *p*-methoxy-*p*′-dimethylaminotriphenylmethyl cation, *p*-methyl-*p*′-dimethylaminotriphenylmethyl cation, and *p*-trifluoromethyl(Malachite Green) cation. Both acetic acid–sodium hydroxide and sodium bicarbonate–HCl buffers were used for the measurements of the *p,p*′-dimethoxy-*p*″-dimethylaminotriphenylmethyl cation. The temperature dependence studies for the Malachite Green cation utilized Na_2HPO_4–$HClO_4$ buffers, and those for Crystal Violet utilized both Dabco–$HClO_4$ and triethylamine–$HClO_4$ buffers.

For each cation, at least two solutions were prepared in which the pH was low enough to allow determination of A_0, the limiting absorbance at low pH. Treatment of the data is described in the Results section.

Equilibrium Measurements in Aqueous Sulfuric Acid. Solutions of sulfuric acid were prepared by weighing portions of standardized concentrated H_2SO_4 and dilution with water. Values of H_0''' and of H_R were taken from Boyd's tabulations.[7]

Measured volumes of the master solutions of the cations, as described above, were added to the sulfuric acid solutions, and spectra were recorded in 10.0-cm cells.

Kinetic Measurements. Master solutions of buffer components and cations were prepared and standardized as described above to give initial absorbances of *ca.* 1.00 in the 10.0-cm cells. The initial concentrations of cations ranged from 1 to 5×10^{-6} *M*.

In the studies of the reactions of the cations with water, hydroxide ion, and cyanide ion, the buffer base concentration was always maintained at 2.0×10^{-3} *M*, and the buffer acid concentration was varied to give the desired pH. Ionic strengths were maintained by addition of appropriate amounts of $NaClO_4$ or $KClO_4$ to the solutions. Buffers consisting of Dabco-$HClO_4$ and of triethylamine-$HClO_4$ were used for all the cations, and dilute solutions of sodium hydroxide were also used in the studies of the Crystal Violet reactions. Potassium cyanide was used for the studies of the cyanide ion reactions.

Studies of general base catalysis were carried out in a manner similar to that described above, except that the buffer ratio was kept constant, and the buffer concentration was varied in a series of runs. In the studies of Dabco catalysis, ionic strength was maintained with either $NaClO_4$ or $KClO_4$, and in the studies of quinuclidine catalysis, ionic strength was maintained with KCl.

All reactions were followed for at least 8 half-lives.

Pseudo-first-order rate constants were calculated by minimization of the quantity

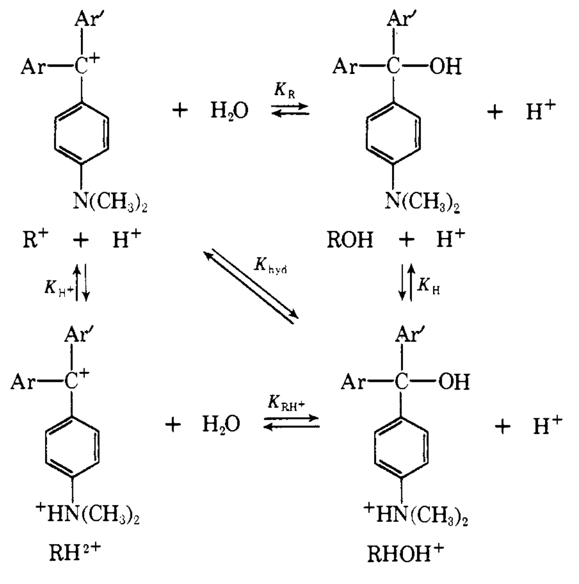
$$\sum_i [A_i - A_\infty - (\Delta A)\exp(-kt_i)]^2$$

with respect to k, ΔA, and A_∞, where A_i is the absorbance of the solution at time t_i, and k is the pseudo-first-order rate constant. Of the three equations resulting from this minimization, that for k cannot be solved analytically. The Fortran IV computer program used solves this equation by successive approximation to 0.1% accuracy in k. The root-mean-square deviation for all the kinetic runs made was less than or equal to the reading error of the absorbances recorded.

In all runs except those of Crystal Violet at low pH, the reactions proceeded to completion. For reactions of Crystal Violet at pH within 2 units of pK for this cation, the known pK and pH of the solution were used to calculate the forward and reverse rate constants from the observed pseudo-first-order rate constants.

In the studies of the reactions of cyanide ion and of general base catalysis, calculated rate constants for the reactions of hydroxide ion and water were subtracted from the observed pseudo-first-order rate constants. Plots of the "corrected" pseudo-first-order rate constants against cyanide or base concentration allowed the evaluation of the second-order rate constants.

Scheme I



$K_R = [ROH][H^+]/[R^+]$; $K_{RH^+} = [RHOH^+][H^+]/[RH^{2+}]$;

$K_{hyd} = [RHOH^+]/[R^+]$

$K_H = [ROH][H^+]/[RHOH^+]$; $K_{H^+} = [R^+][H^+]/[RH^{2+}]$

The following equilibrium constants were calculated from the data tabulated by Hepler[8] and were used in the calculations of second-order rate constants for reactions of cyanide and hydroxide ions: at 10°, pK_{HCN} = 9.64, pK_w = 14.532; at 25°, pK_{HCN} = 9.14, pK_w = 13.99; at 30°, pK_{HCN} = 9.10, pK_w = 13.839; at 50°, pK_{HCN} = 8.67, pK_w = 13.273; at 65°, pK_{HCN} = 8.33, pK_w = 12.908.

Results

Equilibrium Constants for Mono(dimethylamino)triarylmethyl Cations. The various acid-base equilibria in which the dimethylaminotriarylmethyl cations are involved in aqueous solution are diagrammed in Scheme I.[9]

The species R^+ and RH^{2+} show absorption in the visible spectrum which are quite different from one another. In dilute aqueous solutions, only the visible absorption spectrum of R^+ is observed, and the absorbance decreases with increasing pH as previously reported for Malachite Green derivatives.[1]

In the pH region where the absorbance due to R^+ is decreasing, a good isosbestic point is observed in the ultraviolet region of the spectrum, and the system behaves exactly as expected for a two-species, pH-dependent equilibrium. One can evaluate an apparent equilibrium constant, K_{app}, defined by

$$K_{app} = (A_0 - A)[H^+]/A \qquad (1)$$

where A is the absorbance of the solution at the given pH, and A_0 is the limiting absorbance at low pH, both measured at the wavelength of maximum absorbance of R^+. Values of K_{app} are reported in Table I.

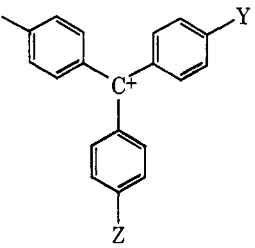
Since the equilibrium between R^+ and $RHOH^+$ is independent of pH, the ratio of the concentrations of these two species is constant for all dilute aqueous solutions, and the two species behave exactly as one. From the definitions of the equilibrium constants given in Scheme I and from eq 1, eq 2 is easily derived:

$$K_{app} = [ROH][H^+]/([R^+] + [RHOH^+]) = K_R/(1 + K_{hyd}) \qquad (2)$$

Ginzburg[10] first suggested the use of acidity functions for the determination of K_{hyd} for triarylmethyl cations. Ginzburg used the Hammett H_0 and the H_R functions for the purpose and found that the triarylmethyl cations did not precisely follow the theoretical behavior. The H_0''' acidity function, which was developed by the use of tertiary amine indicators,[7] is used in the present work. The indicators used to define this function are completely analogous to the present compounds in the K_H equilibrium process. Similarly, the H_R function was established by the use of triarylmethyl cations reacting according to the K_R process. Since $K_{hyd} = K_R/K_H$, we may expect that the K_{hyd} process will follow the function $(H_0''' - H_R)$, which becomes of appreciable magnitude in 5% by weight sulfuric acid.

For the three mono(dimethylamino) compounds studied in the present work, the spectra in aqueous sulfuric acid of less than 5% are identical with the spectra in dilute aqueous solution at pH less than pK_{app}. As the sulfuric acid concentration is increased, one first observes an increase in intensity of the R^+ spectrum, and, at higher concentrations of sulfuric acid, the spectrum shifts to that of the RH^{2+} species. At sulfuric acid concentrations in the range where the concentration of RH^{2+} becomes significant, good isosbestic points are observed as the spectrum shifts from that of R^+ to that of RH^{2+}. This clearly indicates that the conversion of $RHOH^+$ to R^+ is essentially complete at lower sulfuric acid concentrations that those at which the concentration of

Table I. Equilibrium Constant Data in Aqueous Solution for



X	Y	Z	T, °C	Acidity measure	Range	Value
$N(CH_3)_2$	CH_3	H[a]	25	pH	4.16–5.69	$pK_{app} = 5.00 \pm 0.02$
				$-H_0'''$	5.28–7.10	$pK_{H^+} = -6.65 \pm 0.02$
				$H_0''' - H_R$	0.19–1.07	$pK_{hyd} = -0.47 \pm 0.10$
$N(CH_3)_2$	OCH_3	H[b]	25	pH	4.23–5.82	$pK_{app} = 5.10 \pm 0.02$
				$-H_0'''$	4.54–5.91	$pK_{H^+} = -4.90 \pm 0.03$
				$H_0''' - H_R$	0.09–1.07	$pK_{hyd} = 0.10 \pm 0.04$
$N(CH_3)_2$	OCH_3	OCH_3[c]	25	pH	4.86–6.73	$pK_{app} = 5.80 \pm 0.03$
				$-H_0'''$	1.96–4.00	$pK_{H^+} = -3.45 \pm 0.05$
				$H_0''' - H_R$	0.09–0.19	$pK_{hyd} = 0.88 \pm 0.10$
$N(CH_3)_2$	$N(CH_3)_2$	CF_3	25	pH	5.06–6.28	$pK_{app} = 6.13 \pm 0.05$
$N(CH_3)_2$	$N(CH_3)_2$	H	10	pH	6.41–7.37	$pK_{app} = 7.05 \pm 0.01$[d]
			30	pH	6.36–7.32	$pK_{app} = 6.91 \pm 0.01$[d]
			50	pH	6.34–7.29	$pK_{app} = 6.81 \pm 0.01$[d]
$N(CH_3)_2$	$N(CH_3)_2$	$N(CH_3)_2$	25	pH	8.71–10.23	$pK_{app} = 9.39 \pm 0.07$[e]
			50	pH	8.30–9.54	$pK_{app} = 9.00 \pm 0.05$
			70	pH	7.71–8.86	$pK_{app} = 8.77 \pm 0.19$

[a] λ_{max} (R^+) 475, 355 nm; λ_{max} (RH^{2+}) 458, 380 nm. [b] λ_{max} (R^+) 500, 370 nm; λ_{max} (RH^{2+}) 475, 365 nm. [c] λ_{max} (R^+) dbl 538, 515, 404 nm; λ_{max} (RH^{2+}) 510, 387 nm. [d] Interpolated value of pK_{app} at 25° is 6.94. Reference 1 reports 6.92. [e] Reference 1 reports $pK_{app} = 9.36$ at 25°.

RH^{2+} becomes significant. Thus, the analysis of the spectra is quite simple since the molar absorptivity of R^+ can be taken from the spectra at the highest sulfuric acid concentrations before those at which absorbance due to RH^{2+} becomes observable.

From the spectral studies, both pK_{hyd} and pK_{H^+} can be determined if the acidity functions are valid for the present compounds. Values of these equilibrium constants are reported in Table I. The observed constancy of the calculated values over a range of sulfuric acid concentrations indicate the validity of the acidity functions as applied to these compounds.

Since Scheme I involves only three *independent* equilibrium constants, the determination of pK_{app}, pK_{hyd}, and pK_{H^+} allows us to calculate all five pK values for each compound. Values are shown in Table V.

The fact that the calculated values of pK_H for each of the compounds are nearly the same is in accord with expectations, since the structural differences in the three compounds are quite distant and isolated from the dimethylamino group, and furnishes some confirmation of the validity of the measurements of pK_{hyd} and pK_{H^+}.

Equilibrium Constants for Malachite Green, *p*-Trifluoromethyl(Malachite Green), and Crystal Violet. The values of pK_{app} for Malachite Green and for Crystal Violet at 25° have been reported previously.[1] The values obtained at other temperatures in the present study and the value at 25° for *p*-Trifluoromethyl(Malachite Green) are reported in Table I.

For these compounds with more than one dimethylamino group, it is not possible to determine K_{hyd} by studies in aqueous sulfuric acid since, even in dilute aqueous solution at low pH, the formation of the diprotonated carbinols becomes important. If we assume, however, that the basicity of the dimethylamino group of the carbinol is the same as that for the mono(dimethylamino) compounds except for statistical factors (*i.e.*, log 2 for Malachite Green derivatives, and log 3 for Crystal Violet), we can estimate values of K_{hyd}. With this assumption, pK_H for Malachite Green[11] and for *p*-trifluoromethyl(Malachite Green) is 5.17 and for Crystal Violet is 5.35.

Rearrangement of eq 2 gives:

$$K_R = K_{app}/(1 - K_{app}/K_H) \qquad (3)$$

From the data in Table I and the above estimates of pK_H, we conclude that $pK_R = pK_{app}$ within experimental accuracy for both Malachite Green and Crystal Violet. For *p*-trifluoromethyl(Malachite Green), we calculate $pK_R = 6.07$. The pK_{hyd} values for these cations are: 3.74 for Crystal Violet; 1.77 for Malachite Green; and 1.01 for *p*-trifluoromethyl(Malachite Green). Analogous estimation of the equilibrium constants for *p*-nitro(Malachite Green) from the previously reported[12] values of pK_{app} at 25° gives: $pK_R = 5.24$; $pK_{hyd} = 0.07$.

Standard treatment of the data for the temperature dependence of the pK's for Crystal Violet and Malachite Green gives the thermodynamic parameters for reaction of the cations with water. Combination of these values with $\Delta H° = 13.1$ kcal/mol and $\Delta S° = -21$ eu for the ionization of water at 25° [8] allows the calculation of $\Delta H°$ and $\Delta S°$ for reactions of the cations with hydroxide ion in water. These quantities are reported in Table V.

Kinetics of the Reactions of the Cations in Aqueous Solution. Rate constants for the reactions of the cations with water and hydroxide ion were calculated from the observed pseudo-first-order rate constants in buffered solutions with buffer base kept at less than 2×10^{-3} *M*. The data were treated with a weighted least-squares method which minimizes the per cent error in rate constants to obtain k_{OH} and k_{H_2O}. The rate constants obtained are summarized in Table II. The observed pseudo-first-order rate constants were always within ±10% of the calculated values and were generally within ±3%. In all cases studied, the pH range investigated was large enough that the values of both k_{H_2O} and k_{OH} should be accurate to better than ±10%.

Reactions of Malachite Green were studied at three ionic strengths at each temperature, as shown in Table II. It appears that k_{OH} decreases slightly with increasing ionic

Table II. Reactions of Cations with Water and Hydroxide Ion in Aqueous Solution

Cation[a]	N[b]	pH range studied	Ionic strength[c]	T, °C	k_{OH}[d]	k_{H_2O}[d]
Me,DMA	42	7.8–10.1	2.0×10^{-2}	25.0	17.9	5.51×10^{-3}
MeO,DMA	34	7.8–10.8	2.0×10^{-2}	25.0	15.8	4.60×10^{-3}
DiMeO,DMA	35	7.6–10.9	2.0×10^{-2}	25.0	13.0	2.29×10^{-3}
TFM-MG	25	7.6–10.8	2.0×10^{-2}	25.0	3.29	2.00×10^{-4}
MG	11	8.7–11.2	4.2×10^{-3}	10.2	0.582	4.85×10^{-5}
MG	6	9.0–11.1	8.4×10^{-3}	10.2	0.592	5.51×10^{-5}
MG	8	8.7–11.2	3.4×10^{-2}	10.2	0.472	4.76×10^{-5}
MG	13	8.4–10.9	4.2×10^{-3}	30.0	2.72	3.31×10^{-4}
MG	7	8.3–10.9	8.4×10^{-3}	30.0	2.60	3.33×10^{-4}
MG	6	8.3–10.9	3.4×10^{-2}	30.0	2.52	3.50×10^{-4}
MG	14	8.1–10.2	4.2×10^{-3}	49.0	11.5	1.70×10^{-3}
MG	11	8.3–10.2	8.4×10^{-3}	49.0	10.4	1.89×10^{-3}
MG	6	8.0–10.2	3.4×10^{-2}	49.0	8.72	1.97×10^{-3}
CV	25	10.3–11.4	8.4×10^{-3}	25.0	0.201	1.94×10^{-5}
CV	12	9.6–10.4	8.4×10^{-3}	49.3	1.54	1.92×10^{-4}
CV	7	9.2–10.0	8.4×10^{-3}	64.9	4.99	7.23×10^{-4}

[a] Me,DMA is *p*-methyl-*p*′-dimethylaminotriphenylmethyl cation; MeO,DMA is *p*-methoxy-*p*′-dimethylaminotriphenylmethyl cation; DiMeO,DMA is *p*,*p*′-dimethoxy-*p*′′-dimethylaminotriphenylmethyl cation; TFM-MG is *p*-trifluoromethyl-*p*′,*p*′′-bis(dimethylamino)-triphenylmethyl cation; MG is Malachite Green cation; CV is Crystal Violet cation. [b] Number of kinetic runs. [c] Maintained with $NaClO_4$ or $KClO_4$; units of *M*. [d] k_{OH} in units of M^{-1} sec^{-1}; k_{H_2O} in units of sec^{-1}.

Table III. Reactions of Cations with Cyanide Ion

Cation	N[a]	T, °C	Ionic strength	Range of CN^- concn	k_{CN}[b]
Malachite Green	5	10.2	4.2×10^{-3}	To 3×10^{-4}	0.132
	5	30.0	4.2×10^{-3}	To 4×10^{-4}	0.714
	5	49.0	4.2×10^{-3}	To 4.4×10^{-4}	2.64
Crystal Violet	6	25.0	8.4×10^{-3}	To 6×10^{-3}	5.38×10^{-2}
	6	49.3	8.4×10^{-3}	To 6×10^{-3}	3.02×10^{-1}
	5	64.9	8.4×10^{-3}	To 2.2×10^{-3}	1.19

[a] Number of kinetic runs. [b] Units of M^{-1} sec^{-1}.

strength, and that k_{H_2O} increases slightly with increasing ionic strength. The effects, however, are quite small for the highest ionic strength used in the present work (3.4×10^{-2} *M*) and are only slightly outside of the possible experimental error.

We have previously reported values for k_{OH} and k_{H_2O} for the reactions of Crystal Violet at 25°.[12] The present value found for k_{OH} is in excellent agreement with the value of 0.205 M^{-1} sec^{-1} previously determined. The value for k_{H_2O} in the present work is in poor agreement with the previously reported value of 3.5×10^{-5} sec^{-1}. On re-examination of the previous data, we find that we had neglected to correct the observed pseudo-first-order rate constants at low pH for the reversibility of the reaction. When this correction is made, the previous data show excellent agreement with the present.

Least-squares fits of the log *k* *vs.* $1/T$ data give the activation parameters shown in Table V. For Malachite Green, the data obtained at all three ionic strengths, along with previously reported data[12] at 25°, were all included in the calculation. The ΔS^* value for the reaction of Malachite Green with water is −21 eu, in good agreement with the value of −23 eu reported by Taft.[2]

Laidler[13] has reported a study of temperature and pressure effects on the rate constants for reaction of Malachite Green with 2.0×10^{-4} *M* sodium hydroxide in water and of Crystal Violet with 2.0×10^{-3} *M* sodium hydroxide in water. He reports $\Delta S^* = -10$ eu, $\Delta V^* = -12$ cm^3/mol for the Malachite Green reaction, and $\Delta S^* = -12$ eu, $\Delta V^* = 0$, for the Crystal Violet reaction. For the Malachite Green reaction, at 2.0×10^{-4} *M* hydroxide ion, the pseudo-first-order rate constant measured by Laidler is the sum of k_{H_2O} and $k_{OH}[OH^-]$. At 10, 30, and 49°, the hydroxide ion reaction accounts for 68, 61, and 54%, respectively, of the observed rate constant. Thus, Laidler's values of ΔS^* and ΔV^* for the Malachite Green reaction are not valid for either the reaction of water or of hydroxide ion alone. For the Crystal Violet reaction, however, the hydroxide ion concentration is high enough that the observed pseudo-first-order rate constant is more than 95% due to reaction of hydroxide ion at all temperatures studied. Thus, the values of ΔS^* and ΔV^* reported by Laidler for the Crystal Violet reaction should be fairly accurate for the hydroxide ion reaction. The reported value of ΔS^* is in good agreement with that found in the present study.

The pseudo-first-order rate constants obtained for reactions of Malachite Green and of Crystal Violet in buffered solutions with added potassium cyanide were corrected for the reactions of water and hydroxide ion as described in the Experimental Section. Plots of the "corrected" rate constants against cyanide ion concentration were fitted by least-squares to obtain the values of k_{CN} reported in Table III. It is conceivable that these values contain some contribution from general base catalysis of the reaction of water by cyanide ion. Since, however, Dabco and cyanide ion have similar basicities, and since the rate constant for Dabco catalysis of the water reaction is much smaller than the observed rate constant for reaction of cyanide ion, we believe that this contribution is negligible.

The value of k_{CN} for Crystal Violet at 25° is in only fair agreement with the previously reported[12] value of 6.3–6.7 × 10^{-2} M^{-1} sec^{-1} for comparable ionic strength. We believe that the present value is the more accurate because of the more accurate value of k_{H_2O} used in the present work.

Interpolation of the data for Malachite Green to obtain k_{CN} at 25° gives the value of 0.50 M^{-1} sec^{-1}, in excellent agreement with the values reported previously[12] at comparable ionic strength.

The activation parameters for the cyanide ion reactions, obtained by least-squares fit of the data in Table III, are shown in Table V.

Data pertaining to general base catalysis of the reactions

Table IV. Amine Catalysis of the Reactions of Cations with Water

Cation	Amine (concn range)	N[a]	T, °C	Ionic strength	k_{catal}[b]
Crystal Violet	Quinuclidine (to 5×10^{-2})	7	25.0	1.1×10^{-1} (Cl^-)	2.64×10^{-3}
Malachite Green	Quinuclidine (to 4×10^{-2})	5	25.0	1.1×10^{-1} (Cl^-)	4.19×10^{-2}
	Dabco (to 7×10^{-2})	5	49.0	8.4×10^{-3} (ClO_4^-)	1.28×10^{-2}
	Dabco (to 3×10^{-1})	7	49.0	3.4×10^{-2} (ClO_4^-)	1.2×10^{-2}
	Dabco (to 9×10^{-2})	5	10.2	3.4×10^{-2} (ClO_4^-)	6.7×10^{-4}
	Dabco (to 3×10^{-2})	6	10.2	8.4×10^{-3} (ClO_4^-)	6.1×10^{-4}
[c]	Dabco (to 2×10^{-2})	7	25.0	1.8×10^{-2} (ClO_4^-)	2.6×10^{-3}
Me,DMA[d]	Dabco (to 2.2×10^{-2})	13	25.0	4.0×10^{-2} (ClO_4^-)	3.3×10^{-3}

[a] Number of kinetic runs. [b] Units of M^{-1} sec^{-1}. [c] Data previously reported; see ref 11. [d] *p*-Methyl-*p*′-dimethylaminotriphenylmethyl cation.

Table V. Data Summary for Reactions of Cations in Aqueous Solution at 25.0°

	Cation[a]			
Quantity	Me,DMA	MeO,DMA	DiMeO,DMA	TFM-MG
pK_R	4.40	4.86	5.75	6.07
pK_{RH^+}	−7.32	−4.80	−2.57	
pK_{H^+}	−6.65	−4.90	−3.45	
pK_w	−0.47	0.10	0.88	1.01
pK_H	4.87	4.76	4.87	5.17
k_{OH}[b]	17.9	15.8	13.0	3.32
$k_{\mathrm{H_2O}}$[c]	5.51×10^{-3}	4.60×10^{-3}	2.29×10^{-3}	1.96×10^{-4}
k_{Dabco}[b]	4.7×10^{-2}			3.26×10^{-3}
$k_{\mathrm{OH}}/k_{\mathrm{H_2O}}$	3.25×10^{3}	3.45×10^{3}	5.68×10^{3}	1.69×10^{4}
$k_{\mathrm{OH}}/k_{\mathrm{Dabco}}$	3.8×10^{2}			1.0×10^{3}
$k_{\mathrm{H_2O}}/k_{\mathrm{Dabco}}$	1.2×10^{-1}			6.0×10^{-2}

	Cation		
	p-NO_2-MG[d]	MG	CV
pK_R	5.24	6.94	9.39
pK_w	0.07	1.77	3.74
k_{OH}[b]	5.64	2.18	0.201
$k_{\mathrm{H_2O}}$[c]	1.80×10^{-4}	2.11×10^{-4}	1.95×10^{-5}
k_{CN}[b]	0.92	0.51	5.38×10^{-2}
k_{Dabco}[b]		2.6×10^{-3}	[1.6×10^{-4}][e]
$k_{\mathrm{quinuclidine}}$[b]		4.2×10^{-2}	2.64×10^{-3}
$k_{\mathrm{OH}}/k_{\mathrm{H_2O}}$	3.13×10^{4}	1.03×10^{4}	1.03×10^{4}
$k_{\mathrm{OH}}/k_{\mathrm{Dabco}}$		8.4×10^{2}	[1.2×10^{3}][e]
$k_{\mathrm{H_2O}}/k_{\mathrm{Dabco}}$		8.2×10^{-2}	[1.2×10^{-1}][e]
$\Delta H^{\circ}_{\mathrm{H_2O}}$[f]		2.4	6.5
$\Delta H^{*}_{\mathrm{H_2O}}$[f]		16.3	17.5
$\Delta S^{\circ}_{\mathrm{H_2O}}$[g]		−23	−21
$\Delta S^{*}_{\mathrm{H_2O}}$		−21	−21
$\Delta H^{\circ}_{\mathrm{OH}}$[f]		−10.7	−6.6
$\Delta H^{*}_{\mathrm{OH}}$[f]		13.0	15.3
$\Delta S^{\circ}_{\mathrm{OH}}$[g]		−2	0
$\Delta S^{*}_{\mathrm{OH}}$[g]		−14	−10
$\Delta H^{*}_{\mathrm{CN}}$[f]		13.4	14.8
$\Delta S^{*}_{\mathrm{CN}}$[g]		−15	−15
$\Delta S^{*}_{\mathrm{Dabco}}$[g,h]		−27	

[a] Cation identification symbols are the same as those for Table II. [b] Units of M^{-1} sec^{-1}; at 25°. [c] Units of sec^{-1}; at 25°. [d] Data taken from ref 11; pK_R and pK_w recalculated as described in Results section. [e] The value of k_{Dabco} for Crystal Violet is estimated by assuming the relative rate constants for Malachite Green and Crystal Violet are the same as for quinuclidine. [f] Units of kcal/mol. [g] Units of cal deg^{-1} mol^{-1}. [h] $\Delta H^{*}_{\mathrm{Dabco}} = 13.0$.

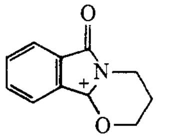
of the cations with water are shown in Table IV. The activation parameters for Dabco catalysis of the Malachite Green reaction are reported in Table V.

Discussion

General Base Catalysis of the Reactions of Cations with Water. The present work demonstrates the existence of general base catalysis of the reaction of water with triarylmethyl cations having pK_R's ranging from 4.4 to 9.4. We believe that general base catalysis is characteristic of the reactions of water with any cation of measurable stability in aqueous solution. This belief is based on several observations other than those reported in the present work.

Jencks[14] has recently reported a study of the reactions of

N,O-trimethylenephthalimidium cation



with a number of nucleophiles in aqueous solution. General base catalysis of the reaction of water by Dabco was observed, and the data give $k_{H_2O}/k_{Dabco} = 0.13$ *M*, in close agreement with the values found in the present study of triarylmethyl cations. The pK_R of the phthalimidium ion could not be directly measured but may be estimated as follows. The rate constant, k_{OH}, for reaction of the cation with hydroxide ion is reported as 4.6×10^6 M^{-1} sec^{-1}. The rate of the reverse reaction, which cannot be observed directly, may be estimated as equal to that for the analogous reaction of ethoxide ion, $k_{-OEt} = 3.3 \times 10^{-8}$ sec^{-1}. Thus, the equilibrium constant for the reaction of the cation with hydroxide ion is estimated to be 1.4×10^{14} M^{-1}, and pK_R is then -0.15. The phthalimidium cation is, then, more than 4 units less stable than the least stable of the triarylmethyl cations in the present study.

The reaction of tri-*p*-anisylmethyl cation ($pK_R = 0.82$) with water has now been shown to be catalyzed by Dabco, trimethylamine, and triethylamine.[5] Previous workers[4] had argued against the existence of general base catalysis for this reaction, based primarily on the observation of a very small solvent isotope effect, $k_{H_2O}/k_{D_2O} = 1.2$. The solvent isotope effect criterion is known to be unreliable for a number of cases.[15] We have shown, in previous work,[12] that the reaction of Crystal Violet with water shows little or no solvent isotope effect. The direct observation of general base catalysis of this reaction in the present work is another example, then, of the failure of the solvent isotope effect criterion for general base catalysis.

There are good indications that the reactions of water with cations even less stable than those discussed above are subject to general base catalysis. Goering[16] has reported the results of studies of the solvolyses of several benzhydryl derivatives in aqueous-organic solvents. Products from these reactions are formed by attack of nucleophiles on the solvent-separated ion pairs. The alcohol products formed show a slight predominance of retention of configuration. Since the only difference between ordinary solvent molecules and the solvent molecule which is part of the ion pair, at equilibrium, is the presence of the counterion, the observed retention must be due to an activation of solvent by the counterion; which is just another way of saying general base catalysis. It is possible that this is an example of "charge localization" catalysis rather than catalysis involving a strong contribution from the actual proton transfer,[17] but we see little experimental justification for this distinction in the present case. The cations involved in these reactions have pK_R's considerably less than -7, as reported by Deno.[18]

It thus appears that the reactions of water with cations having pK_R's ranging from -7 to $+9.4$ all are subject to general base catalysis. We will return to the subject of this generality after a discussion of the mechanism of the catalysis.

A plot of the log *k*'s for catalysis of the reactions of water with Malachite Green cation *vs.* the pK_a's of the conjugate acids of Dabco ($pK_a = 8.8$; statistical correction is $+0.3$), triethylamine ($pK_a = 10.9$; $\log k = -1.52$),[1] and quinuclidine ($pK_a = 11.1$) gives a Brφnsted slope, $\beta = 0.65$. Jencks[14] has presented the arguments that values of β other than zero and unity for reactions of this type are strong evidence against a two-step mechanism for the reaction:

$$R^+ + H_2O \overset{K_1}{\rightleftharpoons} ROH_2^+ \underset{k_{BH}[BH^+]}{\overset{k_B[B]}{\rightleftharpoons}} ROH + BH^+ \quad (4)$$

We believe, along with Jencks, that these reactions are concerted one-step processes not involving the formation of an ROH_2^+ intermediate.

Another strong argument against the two-step mechanism, also used by Jencks,[14] can be based on the magnitudes of the observed rate constants. Consider the reaction of Crystal Violet with water catalyzed by quinuclidine, with $pK_R = 9.4$, $k_Q = 2.6 \times 10^{-3}$ M^{-1} sec^{-1}, and $pK_a = 11.1$. The overall equilibrium constant for the reaction in eq 4, K_t, is given by:

$$K_t = K_1k_B/k_{BH} = K_R/K_{a(BH)} = 50 \quad (5)$$

Since the catalysis by quinuclidine shows no saturation effect, the mechanism of eq 4 requires that

$$k_Q = K_1k_B = 2.6 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1} \quad (6)$$

Combination of eq 5 and 6 then gives

$$k_Q/K_t = (K_1k_B)/(K_1k_B/k_{BH}) = k_{BH} = 5. \times 10^{-4} \quad (7)$$

From a variety of data, we may confidently expect k_B to lie in the range,[19] $10^7 < k_B < 10^{10}$, all in M^{-1} sec^{-1}.

From eq 4, it is easy to see that the pK_a of ROH_2^+ is given by

$$pK_{a(ROH_2^+)} = pK_{a(BH)} - \log(k_B/k_{BH}) = 11.1 - 3.3 - \log k_B \quad (8)$$

and from the limits set on k_B, the data require

$$-2.2 < pK_{a(ROH_2^+)} < 0.8 \quad (9)$$

Although accurate values of the pK_a's of the conjugate acids of alcohols are not known,[20] that for β-phenyl-β-hydroxypropionic acid has been estimated[21] as -7, and that for benzyl alcohol[22] appears to be less than -9. Even simple alkyl alcohols, such as 1-butanol, are estimated[20] to have pK_a's less than -4.

Thus, eq 9 gives an entirely unrealistic value for the pK_a of ROH_2^+, providing strong evidence against the two-step mechanism of eq 4. A value of k_B less than 20 M^{-1} sec^{-1} would be required to bring the pK_a into agreement with the above quoted data for the acidities of ROH_2^+ species.

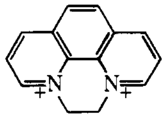
It may be of fundamental importance that for those alcohols, ROH, for which R^+ may exist as a carbonium ion in aqueous solution, there appears to be no evidence for existence of the species ROH_2^+. Deno[18,22] has noted in his studies of both benzhydryl and benzyl systems that the formation of carbonium ions appears not to be preceded by formation of appreciable amounts of ROH_2^+ species. For the 2,4,6-trimethylbenzyl alcohol, for example, the carbonium ion is half formed in 92% H_2SO_4 with no apparent formation of the protonated alcohol.[22] This indicates that the ROH_2^+ species in this case would have to have a pK_a of less than -9.3 on the H_0 scale.

It appears possible, on the basis of these observations, that protonated alcohol and solvated carbonium ion represent limiting equilibrium structures for such systems. That is, it seems quite possible that energy as a function of R-O distance for ROH_2^+ systems has a single minimum; in some cases, such as for primary alcohols, the system has an equilibrium R-O distance such that we recognize the species as a protonated alcohol; in other cases, the R-O distance is such that we recognize the species as a carbonium ion. These postulates help considerably in understanding the ubiquity of general base catalysis in the reactions of water with carbonium ions and provide a rationale for the unusual behavior of water as a nucleophile.[1]

We would also like to suggest that the rate constant ratio k_{H_2O}/k_{Dabco} may be a useful criterion for distinguishing between general base and nucleophilic catalysis. This suggestion is based on the observed near constancy of this ratio for all the cations in the present study, for Jencks' phthalimidium cation,[14] and for the tri-*p*-anisylmethyl cation.[5] The ratio varies by only a factor of *ca.* 3 (0.06 to 0.2) over the range of 9.5 p*K* units in stability of the cations. Jencks[23] has reported rate constants for nucleophilic catalysis of the hydrolyses of several acetate esters in aqueous solution, and we[24] have offered arguments supporting the classification of the Dabco reaction as nucleophilic, rather then general base, catalysis. The reported values of the ratio k_{H_2O}/k_{Dabco} are: 1.2×10^{-4} *M* for phenyl acetate; 8.3×10^{-6} *M* for *p*-nitrophenyl acetate; 1.5×10^{-7} *M* for 2,4-dinitrophenyl acetate; and 5.0×10^{-6} *M* for *N*-acetoxy-4-methoxypyridinium ion. These ratios are much smaller and much more variable than those found for the examples of general base catalysis.

The k_{OH}/k_{H_2O} Rate Constant Ratios. In marked contrast to the near constancy of k_{H_2O}/k_{Dabco}, the ratio k_{OH}/k_{H_2O} varies from 8.2×10^4 for the phthalimidium ion, through 3×10^4 to 3×10^3 for the triarylmethyl cations in the present study, down to 6.7×10^2 for the tri-*p*-anisylmethyl cation (all in units of M^{-1}). As Taft[2] has reported for a series of triarylmethyl cations, k_{H_2O} shows no correlation with K_R of the cations. The present data also show no correlation of k_{OH} with K_R. For example, k_{OH} for *p*-nitro-(Malachite Green) (pK_R = 5.24) is less than half as large as k_{OH} for the *more* stable *p,p′*-dimethoxy-p″-dimethylaminotriphenylmethyl cation (pK_R = 5.75). Both of these results are in accord with our earlier report of the absence of correlations of rate and equilibrium constants for cation-nucleophile reactions in general.[25]

In connection with the variability of the k_{OH}/k_{H_2O} ratios, we may also point out that several aryltropylium ions show values from 8.5×10^4 M^{-1} to 1.2×10^5 M^{-1} for this ratio, while the pK_R's of these cations range from 4.55 to 7.35. Bunting has reported[3] k_{OH}/k_{H_2O} ratios from 8.0×10^6 M^{-1} to 1.2×10^7 M^{-1} for four quaternary ammonium heterocycles with pK_R's ranging from 5.1 for *N*-methyl-4-nitroisoquinolinium ion to 9.54 for the dication:



The reactions of cyanide ion with several of the cations have also been studied. The rate constant ratios k_{OH}/k_{CN} are: 3.1 for tri-*p*-anisylmethyl cation;[4] 6.1 for *p*-nitro(Malachite Green); 4.3 for Malachite Green; and 3.7 for Crystal Violet. Some data are also available for the neutral nucleophile ethylamine, which give k_{OH}/k_{EtNH_2} values: 0.31 for tri-*p*-anisylmethyl cation;[4] 0.29 for Malachite Green; and 0.61 for *p*-dimethylaminophenyltropylium ion. Thus, in contrast to the wide variability of the k_{OH}/k_{H_2O} rate ratios, k_{OH}/k_{Nuc} for other nucleophiles are nearly constant for different cations, indicating that hydroxide ion is closely following the N_+ correlation[1] for these reactions.

These results confirm our earlier suggestion[1] that water is behaving quite differently from other nucleophiles in its reactions with cations. The constancy of the k_{H_2O}/k_{Dabco} ratio indicates that the "uncatalyzed" water reaction is quite similar to the catalyzed reaction. The large negative entropies of activation for both the "uncatalyzed" ($\Delta S^* = -21$ eu) and the Dabco catalyzed ($\Delta S^* = -27$ eu) reactions may also be an indication of the similarities of the reactions. It is somewhat disconcerting, however, that the entropy of activation for the reaction of Malachite Green with glycylglycine,[26] which reacts as a normal nucleophile,[1] is −28 eu, very close to that for the Dabco general base catalysis reaction.

It is unfortunate that we originally chose the reactions of water with cations as the standard reaction, with N_+ of water defined as zero, for the correlation of cation-nucleophile reactions.[1,25] It is now quite clear that the reactions of water are anomalous and do not fit the N_+ correlations with anywhere near the precision shown by other nucleophiles. Since the N_+ scale is a relative scale of reactivities, however, the fact that water does not obey the correlation does not affect the N_+ values given previously. This point is discussed further in the next paper in this series[24] where applicability, extensions, and limitations of the correlation are developed.

Nature of the Transition State for Cation-Anion Combination. Finally, we believe that the rather large negative entropies of activation for reactions of cyanide and hydroxide ions with Malachite Green and Crystal Violet are worthy of some comment. In particular, it is worth noting that ΔS^* for the reaction of hydroxide ion with both cations is more negative than ΔS° for the reactions. This means that ΔS^* is negative for both the forward, combination reaction, and for the reverse, dissociation reaction. In fact, since ΔS° is quite close to zero for both cations, ΔS^* for the reverse reaction is very nearly equal to ΔS^* for the forward reaction. Although we have not been able to measure ΔS° for the cyanide ion reactions, it seems likely that the same conclusions will be valid for these reactions as for the hydroxide ion reactions. The entropy of activation for the hydrolysis of *tert*-butyl chloride in water[27] is +14 eu, *ca.* 25 eu more positive than that for the dissociation of triarylmethanol or triarylmethyl cyanide, which points up the unusual character of the present reactions.

LeNoble[28] has commented on the unexpected $\Delta V^* = 0$ for the reaction of Crystal Violet with hydroxide ion (see the discussion of the validity of this measurement in the Results section of the present paper) which would be expected to give a fairly large positive ΔV^* from release of electrostricted water around the hydroxide ion.

For the same reasons, one expects the reaction of hydroxide ion with the triarylmethyl cations to give ΔS° greater than zero. The positive entropy from release of electrostricted water around hydroxide ion must be compensated by a negative entropy contribution from desolvation of the cation, or by a negative entropy contribution from solvation of the product triarylmethanol, or both.

The negative values of ΔS^* for these reactions (−10 to −15 eu) are slightly too large in magnitude to ascribe to the entropy of bringing two particles together in solution (*ca.* $-R \ln 55 = -8$ eu), and the fact that ΔS^* for the reverse reactions are also negative both indicate that solvation changes are the primary factor involved in these quantities. As Jencks[17] has argued, the entropy of bringing two particles together in solution can be considerably more negative than −8 eu if one considers the loss of rotational entropy of the particles. If this were the situation in the present case, however, we would not expect the negative entropy for the reverse reaction. We thus conclude that solvent must be more ordered at the transition state than at either reactant of product. Bunting[3] has reached similar conclusions for the reactions of water and hydroxide ion with several quaternary ammonium ions.

We suggest that the reactant cation has two solvation shells, as postulated by Frank[29] for other ions. The inner shell is expected to be electrostricted and more ordered than bulk solvent. The outer shell is expected to be highly disordered. Transfer of solvent from the outer shell into bulk solvent would produce a negative entropy contribution. If the transition state for the cation–anion combination reactions is such that part of this outer shell solvation around the cation has been released into bulk solvent, we then expect a negative entropy contribution to ΔS^*. Similarly, on going from the neutral product, Ar_3CX, to the transition state, the solvation around the developing cation and anion is largely electrostrictive, and the full second-shell solvation disorder has not been attained.

These postulates may ultimately help in understanding the relative reactivities of the cations, a topic which has caused some difficulties arising from the previously[1] postulated nature of the transition states.

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Cation–Anion Combination Reactions. XIII.[1] Correlation of the Reactions of Nucleophiles with Esters

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Abstract: The N_+ correlation of nucleophilic reactivities, previously shown to apply to the reactions of nucleophiles with organic cations, is now shown to apply to the reactions of nucleophiles with esters when explicit consideration of a two-step mechanism is included. The consideration of this mechanism requires that leaving-group abilities of attacking nucleophiles relative to leaving-group abilities of the ester leaving group be evaluated. This evaluation is accomplished by empirical data fitting under the stringent restriction that the leaving-group ability of a given group is assumed to be independent of other groups present in the intermediate. The new correlations extend previous observations to include reactions of 26 electrophiles and 52 nucleophiles. Interpretations of the correlations considerably extend and slightly modify earlier conclusions regarding the mechanisms of nucleophilic reactions with esters. The range of applicability of the N_+ equation documented in the present paper is far greater than could be anticipated on the basis of current theories of nucleophilic reactivity. Our own earlier rationalizations of these correlations are, at best, incomplete and need thorough reexamination.

The reactions of nucleophiles with acetate esters have been the subject of numerous experimental studies. The rate constants obtained in these studies, particularly those obtained by Jencks and his coworkers,[2-4] probably furnish the most extensive body of data obtained under a standard set of conditions that is available for any class of reactions. These data furnish a unique opportunity for testing of hypotheses concerning the effects of structure on reactivity.

Figure 1 shows plots of log *k* for reactions of nucleophiles with phenyl acetate (PA) *vs.* log *k* for reactions of the same nucleophiles with other acetate esters. Quite obviously, no simple general linear correlation is shown by these data. Previous interpretations of the rate data have relied on the application of the Brønsted catalysis relationship,[2-4] in which limited "structural families" of nucleophiles, such as primary amines, are examined individually.

The complexity of the general picture indicated in Figure 1 almost certainly has its origin in mechanisms of the reactions, and interpretations of the Brønsted relationships have centered on this point. Early discussions of the mechanisms of these reactions postulated the existence of a tetrahedral reaction intermediate. Somewhat later, strong arguments against the existence of the tetrahedral intermediate were advanced.[2] These arguments were based on the apparently reasonable assumption that such an intermediate would have to be at equilibrium with respect to proton-transfer