homogeneous electron transfer and certainly, for a series of similar compounds, the correct relative rates. Extension of the present study to include a greater variety of compounds differing in electronic and structural features must be done to assess inductive (reflected in $\Delta F^{\circ\prime}$) and steric effects to rates of HETR. The spectroelectrochemical approach coupled with signal averaging and computerized digital simulation methods provides an opportunity to expand the scope of HETR studies; nearly any electrochemically active molecule or ion can be spectrally probed either directly or indirectly through some mediation scheme. Further, the resulting precision of the method now allows the effect of solvent, supporting electrolyte, temperature, etc., to be assessed for a wide variety of reacting pairs.

Acknowledgment. The authors acknowledge the financial support of the National Institutes of Health (Grant No. GM 14036) and the National Science Foundation (Grant No. GP 9306). Samples of 9,10-dimethylphenazine from E. T. Seo, TRW systems, Redondo Beach, Calif., and $Ta_6Br_{12}^{2+}$ by J. H. Espenson at Iowa State University are appreciated.

Kinetics of Proton-Transfer Reactions in Aqueous Solution. IV. The Brønsted Slope for Internally Hydrogen-Bonded Weak Acids

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Abstract: A kinetic and thermodynamic study has been carried out for the deprotonation by hydroxide ion of a series of closely related internally hydrogen-bonded weak acids. Five compounds have an ortho azo internal hydrogen bond; two have a salicylate internal hydrogen bond. Relaxation times as measured by a temperature-jump spectrometer at 15° and $I = 0.1$ were interpretable on the basis of the deprotonation reaction $OH^- + HA^z \rightleftharpoons A^{z-1} + H_2O$. Measured forward rate constants varied from 10^6 to 10^9 M^{-1} sec^{-1} for the pK range 9–12. On a plot of log k_f *vs.* pK_a, rate and equilibrium data were linearly related with a Brønsted coefficient $\alpha = 1.2$. This value was interpreted on the basis of Marcus' theory of Brønsted slopes as consisting of a "within-series" contribution to α of about 0.45, and a contribution of 0.75 due to changes in intrinsic properties of the compounds due to changes in structure.

Rate constants for proton-transfer reactions in aqueous solution have now been determined for many systems.[3–5] It is well established that the rates of all "normal" acid–base reactions (where the proton is attached to a singly bonded oxygen or nitrogen atom) are diffusion controlled, *i.e.*, reaction occurs as soon as the two reactants approach to within a critical distance. A diffusion-controlled reaction in water presupposes access of the solvent to the proton in order for transfer to occur *via* a skipping mechanism.[6] This is not the case where the proton participates in an internal hydrogen bond or is bonded to a carbon acid. In such instances the proton-transfer reaction may no longer be diffusion controlled and the rate constant becomes dependent on the ionization constant of the weak acid.[7,8] Such a functional dependence is represented by the Brønsted relationship $\alpha = \mathrm{d} \log k/\mathrm{d} \log K = -\mathrm{d} \log k/\mathrm{d}\mathrm{p}K$.

While the Brønsted equation can be "derived"[9] by relating $\Delta G^{\ddagger}$ and ΔG°, it is only recently that an attempt has been made to explore theoretical relations from which it can be derived. Marcus has modified the equations developed for his theory of weak-overlap electron-transfer reactions and applied them to elementary steps of proton-transfer reactions.[10] The fundamental equation relates the free energy activation barrier, ΔG^*, to an intrinsic barrier Λ (a reorganizational term) and to an extrinsic barrier $\Delta G^{\circ\prime}$, the free energy of reaction under the prevailing experimental conditions. The Brønsted coefficient is calculated from the relation $\alpha = \mathrm{d}\Delta G^*/\mathrm{d}\Delta G^{\circ\prime}$. The results of an extensive literature search[11] showed that the values of α so calculated agreed with the experimental values. The Brønsted coefficient for proton-transfer reactions was ~0.5, well within the limits of $0 < \alpha < 1$. In a later paper[12] Marcus pointed out that by using a more complete equation for α, his theory could also be used to account for unusual free energy slopes where $0 > \alpha > 1$.

The rate constants for proton transfer in pseudoacids have been well studied by classical[8] as well as relaxation techniques.[3–6] From the resulting Brønsted plots the limits on α, the Brønsted coefficient, have been substantiated as $0 < \alpha < 1$. With the utilization of rapid kinetic techniques, Brønsted plots over a sufficiently wide log k range could be made, and the expected curvature of α from $\alpha = 0$ to $\alpha = 1$ was observed for some

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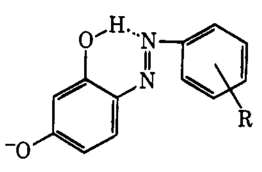
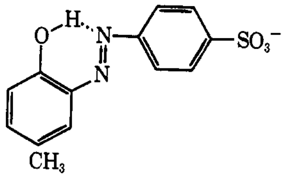
pseudoacids.[3] Also, correlations between rate and equilibrium constants for internally hydrogen-bonded acids could now be obtained. In an earlier paper[13] our data for some weak acids (including hydrogen-bonded and non-hydrogen-bonded systems) correlated well on a Brønsted plot with data from other laboratories. Several apparently parallel curves were observed, depending on the type of bonding present. The Brønsted coefficient for each of the curves was approximately unity for sufficiently high pK_a values. For low-pK_a systems, the rate constants approached the limiting value[3-5] for diffusion-controlled reactions ($k_f \sim 10^{10}$ M^{-1} sec^{-1}) for reaction of hydroxide anion with an acid. On the other hand, Marcus suggested[14] that if compounds having no internal hydrogen bond were removed from the Brønsted plot (Figure 2 of ref 13), a graph consistent with a slope of 0.5 might result for internally hydrogen-bonded weak acids, although there would be a large amount of scatter. This scatter might be accounted for by large structural changes from compound to compound in the series.

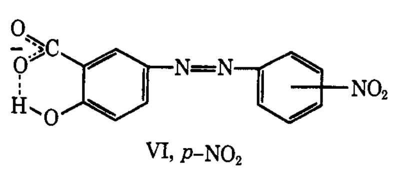
The purpose of this work was to study a series of closely related compounds, over a wide enough pK_a range, sufficiently carefully to allow an application of Marcus' theory to the data. It was particularly important to carry out the kinetic and thermodynamic measurements under identical conditions so that a detailed correlation might be made with confidence. We chose a series of substituted phenylazoresorcinol or -cresol compounds, all having an internal ortho azo hydrogen bond. The compounds studied were I, 4-phenylazoresorcinol; II, 4-(*p*-nitrophenylazo)resorcinol; III, 4-(*m*-nitrophenylazo)resorcinol; IV, 2,4-dihydroxy-4′-sulfonatazobenzene; V, 2-hydroxy-4-methyl-4′-sulfonatazobenzene; VI, alizarin yellow R; and VII, alizarin yellow G. The rate constants for most of these compounds have been reported[13,15] at temperatures other than 15°, the temperature at which this work was done.



I, R = H
II, R = *p*-NO$_2$
III, R = *m*-NO$_2$
IV, R = *p*-SO$_3^-$



V



VI, *p*-NO$_2$
VII, *m*-NO$_2$

Experimental Section

Materials. Compounds I, II, III, and VII were obtained as free acids and IV and VI as sodium salts from Eastman Kodak. I and IV were recrystallized twice from 100% ethanol; sodium salts were recrystallized from 70% alcohol-water. II was recrystallized twice from methanol; III was recrystallized from dioxane and then twice from ethanol. Melting points agreed with literature values.

Compound V was prepared by diazotization of Mallinckrodt A. R. sulfanilic acid monohydrate and subsequent coupling[16] to Matheson Coleman and Bell redistilled *p*-cresol. The dye was salted out with NaCl, filtered, and washed. It was recrystallized twice from a 75% alcohol-water mixture, powdered, dried for 3 hr at 110°, and stored in a dessicator. The purity of the sample, determined by titration, was 99.9%.

Stock solutions of each indicator were made up in degassed distilled water. Aliquots were diluted to the desired concentrations using sufficient KNO$_3$ to maintain an ionic strength of 0.1.

Instrumentation. pH measurements were made on a Sargent Digital or Beckman Expandomatic meter standardized at several pH values with National Bureau of Standards or Sargent buffers. Visible spectra were measured on a Bausch and Lomb 505 spectrophotometer in order to locate the optimum wavelengths for maximum changes in transmittance. For each acid investigated, a "mixed" ionization constant, K_a^M, was determined. It is defined as $K_a^M = a_H C_{A^-}/C_{HA}$, where a_H is the hydrogen ion activity as measured by the pH meter. K_a^M is related to the ionization constant at finite ionic strength (K_a') by $K_a' = K_a^M/\gamma_H$, where γ_H, the activity coefficient of the proton, may be estimated as 0.83 at $I = 0.1$ from the Debye-Hückel extended theory. The advantage of using a mixed constant is that its numerical value, as well as the ratio C_A/C_{HA}, is independent of any assumption of the value of γ_H. The pK_a^M values were determined optically[17] at 15° and 0.1 ionic strength on a Beckman DU spectrophotometer modified with a Gilford direct reading absorbance indicator unit. The pH of each solution was measured in the cuvette using a miniature combination electrode. The cuvette assembly was thermostated by a Lauda circulating water bath. Absorbance and pH readings were taken when the temperature was 15.0° as indicated by a thermocouple–potentiometer assembly. Absorbance readings were determined well above and well below the approximate pK_a in order to establish A_A and A_{HA} (absorbances of the anionic and protonated forms of acid, respectively). Then several readings were made at intermediate pH values, from which pK_a^M was calculated using the relation pK_a^M = pH + log $(A_A - A)/(A - A_{HA})$. In most instances the pK_a^M values so measured had a total uncertainty of ±0.03 log unit (±7% in K_a) or less.

All kinetic runs were carried out on a temperature-jump relaxation spectrometer[4,18] obtained from Messanlagen Studiengesellschaft.[19] The cell was thermostated with a Lauda Ultra Kryomat TK-30D such that the temperature following the jump was 15.0 ± 0.5°. The magnitude of the temperature jump as a function of the voltage stored in the capacitor had previously been calibrated. The pH in the temperature-jump cell was measured at 15° before and after each temperature-jump experiment. The pH varied by no more than 0.02 unit. The relaxation curves were photographed with a Polaroid camera system. Relaxation times were evaluated from an enlarged copy.

Results

The pK_a's of the seven compounds investigated ranged from approximately 9 to 12 at 15° and $I = 0.1$ (Table I). The four substituted resorcinol compounds (I–IV) had pK_a values around 12, in agreement with measurements[15] at 25°; the modifications shown in compound V were necessary to substantially lower the pK to 9. Compounds VI and VII were intermediate.

A single relaxation time was observed for each system, ranging from approximately 7 to 140 μsec for the series of compounds investigated (Table II). In all instances the concentration and/or pH dependences of the inverse relaxation time were consistent with the de-

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Table I. pK_a' values[a,b] at 15° and I = 0.1

Compound	R	pK_a'
I	H	12.13 ± 0.01
II	p-NO_2	11.74 ± 0.01
III	m-NO_2	11.63 ± 0.03
IV	p-SO_3^-	12.00 ± 0.05
V		9.24 ± 0.02
VI	p-NO_2	10.86 ± 0.03
VII	m-NO_2	11.09 ± 0.03

[a] Determined spectrophotometrically as the "mixed" pK_a^M and corrected to the concentration pK_a' at I = 0.1 by pK_a' = pK_a^M + log γ_H (see text). [b] Uncertainties are maximum values obtained, *i.e.*, one-half the range for each compound.

Table II. Kinetic Data for Compounds I–VII at 15° and I = 0.1

C^0, M	pH[a]	τ^{-1} × 10^{-4} sec^{-1}
I. 4-(Phenylazo)resorcinol		
4.9 × 10^{-5}	12.36	2.6
4.3 × 10^{-5}	12.39	2.8
8.6 × 10^{-5}	11.99	1.3
	12.38	2.5
	12.49	3.2
II. p-(Nitrophenylazo)-resorcinol		
4.3 × 10^{-5}	11.82	0.77
5.2 × 10^{-5}	12.00	0.83
7.9 × 10^{-5}	12.14	1.1
III. m-(Nitrophenylazo)-resorcinol		
4.5 × 10^{-5}	11.06	1.1
	11.75	1.3
	12.10	1.7
	12.30	2.3
IV. 2,4-Dihydroxy-4′-sulfonatazobenzene		
5.6 × 10^{-5}	11.97	1.3
	12.23	1.7
	12.36	1.7
	12.43	1.8
	12.67	2.7
V. 2-Hydroxy-4-methyl-4′-sulfonatazobenzene		
1.8 × 10^{-5}	9.18	8.5
3.6 × 10^{-5}	8.82	5.8
3.7 × 10^{-5}	9.64	10.5
5.8 × 10^{-5}	9.85	13.4
7.1 × 10^{-5}	9.16	12.0
	8.83	13.9
VI. Alizarin Yellow R		
2.0 × 10^{-4}	10.76	2.2
	10.96	2.8
	11.20	3.4
	11.30	3.8
	11.34	4.7
VII. Alizarin Yellow G		
2.0 × 10^{-4}	11.20	4.3
	11.50	5.6
3.0 × 10^{-4}	11.17	3.9

[a] Hydroxyl ion concentrations calculated by dividing the hydroxyl ion activity by γ_{OH} (~0.75).

protonation reaction

$$\mathrm{OH^- + HA^z \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A^{z-1} + H_2O} \tag{a}$$

where z is the charge on the protonated acid in the pH region studied and k_f and k_r are the forward and reverse rate constants. The proton being removed from HA is the one which is shown internally hydrogen bonded in structures I–VII. The relaxation time for (a) is given by eq 1 (charges omitted), where the bar indicates

$$\tau^{-1} = k_f(\bar{C}_{OH} + \bar{C}_{HA}) + k_r \tag{1}$$

equilibrium values. The values of k_f and k_r were determined from the slope and intercept, respectively, of graphs of τ^{-1} *vs.* the sum of the two equilibrium concentrations. For all systems except V, the OH^- concentration was much larger than that of the acid as given by the summation in eq 1. As a result, the values of k_f and k_r are in principle independent of accurate knowledge of C_{HA} (*i.e.*, of the pK_a'). In graphing the data in Table II, the constraint was employed that the ratio k_r/k_f was numerically equal to K_h', the hydrolysis equilibrium constant given by $K_h' = K_w'/K_a'$, where K_w' is the ion product of water at 15° and I = 0.1. The use of this constraint allowed accurate values of k_f and k_r to be obtained from relatively few data points, since K_a' is known to within a few per cent. In all instances the line fixed by this constraint was one of the best lines representing the data points. We estimate the rate constants to be accurate to ±10% or better.

The observed forward rate constants ranged from 10^6 to 10^9 M^{-1} sec^{-1} for the series investigated (Table III). Rate constants were generally smaller than the values at 25°, where comparisons could be made. The values of the forward rate constants decreased regularly as the pK increased, *i.e.*, as the strength of the internal hydrogen bond increased. The reverse rate constants were in the vicinity of 10^4 sec^{-1}.

Table III. Kinetic and Thermodynamic Results for the Deprotonation of Internally Hydrogen-Bonded Weak Acids by Hydroxide Ion at 15°

	k_f, M^{-1} sec^{-1}	k_r, sec^{-1}	$K_h' = K_w^0/(K_a^M\gamma_{OH})$[a]
I	1.2 × 10^6	1.1 × 10^4	9.8 × 10^{-3}
II	9.1 × 10^5	3.7 × 10^3	4.1 × 10^{-3}
III	1.9 × 10^6	5.5 × 10^3	2.9 × 10^{-3}
IV	8.8 × 10^5	6.5 × 10^3	7.4 × 10^{-3}
V	1.9 × 10^9	2.4 × 10^4	1.3 × 10^{-5}
VI	2.4 × 10^7	1.2 × 10^4	5.0 × 10^{-4}
VII	2.1 × 10^7	1.9 × 10^4	9.0 × 10^{-4}

[a] K_w^0 = 4.51 × 10^{-15} at 15°.

Graphs of log k *vs.* pK_a' for the forward and reverse reaction of the compounds studied are shown in Figure 1. The Brønsted coefficient for the forward reaction is α = 1.2 and for the reverse reaction is β = −0.2.

Discussion

The experimental Brønsted slopes can be compared to those predicted by Marcus' theory.[10,12] The important quantities in his theoretical treatment have been mentioned earlier and include $\Delta G^{\circ\prime}$, the free energy of reaction under prevailing experimental conditions (*i.e.*, = $-RT \ln K'$ for reaction a at I = 0.1 and 15°). ΔG^*, the "free energy barrier" to reaction, is related to a rate constant k by

$$\Delta G^* = -RT \ln (k/Z) = \Delta G^{\ddagger} - RT \ln \left(\frac{\mathrm{k}T}{hZ}\right) \tag{2}$$

where $\Delta G^{\ddagger}$ is the usual free energy of activation, Z is a collision number for solution reactions (~10^{11} M^{-1} sec^{-1}), and the other symbols have their usual meanings. ΔG^* is related to $\Delta G^{\circ\prime}$ by

$$\Delta G^* = \Lambda[1 + (\Delta G^{\circ\prime}/4\Lambda)]^2 \tag{3}$$

where Λ is the "intrinsic" barrier for the reaction, *i.e.*, the value of ΔG^* at $\Delta G^{\circ\prime}$ = 0. The quantity Λ is the sum of the reorganizational energies that occur in the outer (solvent) and inner (ligand) coordination spheres and is a reflection of the structural reorganization due to conjugation, resonance, or solvational effects. Equations exist for calculating Λ from physical constants for the case of weak-overlap electron-transfer

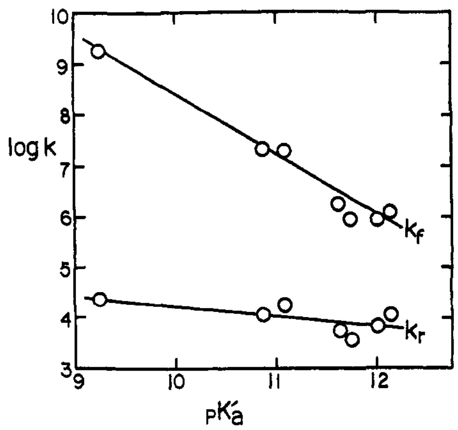

Figure 1. Brønsted graph of the forward and reverse rate constants for reaction a *vs.* pK_a'.

reactions,[20] but these have not yet been extended to proton-transfer reactions. Steric and work terms have been neglected in eq 3, as they contribute only negligibly to the reactions examined.

The Brønsted coefficient from eq 3 is

$$\alpha = \mathrm{d}\Delta G^*/\mathrm{d}\Delta G^{\circ\prime} = 0.5(1 + x) + (1 - x^2)\alpha_1 \quad (4)$$

where $x = \Delta G^{\circ\prime}/4\Lambda$ and $\alpha_1 = \mathrm{d}\Lambda/\mathrm{d}\Delta G^{\circ\prime}$, *i.e.*, the variation of the intrinsic barrier with $\Delta G^{\circ\prime}$. The significance of α_1 can be seen by writing it as $\alpha_1 = (\mathrm{d}\Lambda/\mathrm{d}[\mathrm{R}])\cdot(\mathrm{d}[\mathrm{R}]/\mathrm{d}\Delta G^{\circ\prime})$, where R is the varied substituent in proton-transfer reactions of the type $\mathrm{RAH} + \mathrm{B} \rightleftharpoons \mathrm{BH} + \mathrm{RA}$. When the intrinsic barrier Λ is constant within a series of compounds ($\mathrm{d}\Lambda/\mathrm{d}[\mathrm{R}] = 0$), eq 4 reduces to $\alpha = 0.5(1 + x)$. This would be the equation which applied if, for example, a single acid had been studied with a series of "normal" bases. However, where the base is maintained constant and the acids are varied by the substituent R, the possibility of Λ varying must be considered. It should be noted that if $\alpha_1 = 0$ (Λ constant), eq 4 will predict α values of around 0.5 for small values of x. If, however, the intrinsic barrier varies, larger values of α may result, even exceeding unity. The data of Bordwell, *et al.*,[21] and Gregory and Bruice,[22] for example, for deprotonation of the carbon acid series $\mathrm{RNO_2}$ (R = $\mathrm{CH_3}$, $\mathrm{C_2H_5}$, i-$\mathrm{C_3H_7}$) by $\mathrm{OH^-}$, indicated the unusual value $\alpha = 1.7$. Marcus[12] showed that these results were consistent with a major contribution from the second term of eq 4, with the first term contributing approximately 0.6 to the total coefficient.

The intrinsic barrier Λ for each compound was calculated from eq 3 and listed in Table IV. This quantity is the same for the forward and reverse reactions and varies from 5 to 8 kcal/mol for the compounds studied. While the intrinsic barriers for compounds I to IV are essentially constant, changing the resorcinol substituent of an arylazo group to the *p*-cresol substituent in V changed the intrinsic barrier substantially.

The Brønsted coefficient can be calculated from eq 4 using the quantities given in Table IV. The quantity α_1, the slope of a graph of Λ *vs.* $\Delta G^{\circ\prime}$ (Figure 2) is 0.83 ± 0.07 for the forward reaction. Substitution of these values into eq 4 yields a predicted value of $\alpha = 1.2 \pm 0.1$ for the forward reaction, in agreement with the experimental value. Similar calculations for the reverse reaction yield $\beta = -0.2 \pm 0.1$. This agrees with the value from the Brønsted plot (Figure 1b) where $\beta = \mathrm{d}\log k_r/\mathrm{dp}K_a$ and a value of $\beta = -0.2$ fits the data. The condition that the Brønsted coefficients for the forward and reverse reaction must sum to unity is fulfilled. The kinetic and thermodynamic studies presented in this paper are, to the best of the authors' knowledge, the first application of Marcus' theory to oxygen and nitrogen acids, for a series where the substituent R is varied and the base is maintained constant.

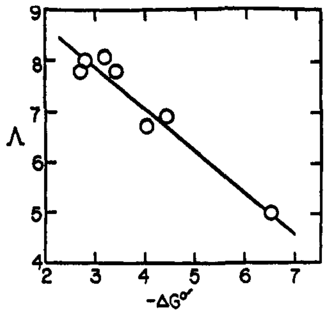

Figure 2. Variation of intrinsic barrier with $\Delta G^{\circ\prime}$.

Table IV. Parameters at 15° Relating to Marcus' Theory of the Brønsted Slope

	$\Delta G^{\circ\prime}$,[a] kcal/mol	ΔG_f^*,[b] kcal/mol	ΔG_r^*, kcal/mol	Λ,[c] kcal/mol	$0.5\cdot(1 + x)_f$[d]	$0.5\cdot(1 + x)_r$[d]
I	−2.68	6.49	9.17	7.8	0.46	0.54
II	−3.15	6.65	9.80	8.1	0.45	0.55
III	−3.35	6.22	9.57	7.8	0.45	0.55
IV	−2.81	6.67	9.48	8.0	0.46	0.54
V	−6.46	2.27	8.73	5.0	0.34	0.66
VI	−4.35	4.77	9.12	6.9	0.42	0.58
VII	−4.02	4.85	8.86	6.7	0.43	0.57

[a] $\Delta G^{\circ\prime}$ is negative for reaction a as written. [b] Calculated from eq 2. [c] Calculated from eq 3. [d] The subscripts f and r indicate forward and reverse directions.

According to Marcus, the Brønsted coefficient is a measure of the position of the transition state along the reaction coordinate only when eq 5 is applicable.[10]

$$\alpha = 0.5(1 + \Delta G^{\circ\prime}/4\Lambda) \quad (5)$$

Thus, for the reactions studied here, where the intrinsic barrier Λ is not constant, the measured Brønsted coefficient must be corrected for this variation. It is interesting to note that the "within-a-series" part of the Brønsted coefficient [*i.e.*, that given by eq 5] is approximately 0.45 (Table IV) for all except the lowest pK_a compound (V). The conclusion, then, is that, *within the framework of the Marcus treatment*, the position of the transition state is almost halfway along the reaction coordinate; *i.e.*, the activated complex resembles the reactants more than the products. This is opposite to the conclusion reached when the variations of Λ within a series were not considered. It is important to realize that the results presented here are consistent with, but do not represent a verification of, the Marcus treatment. The reason is that, owing to mathematical identities, the agreement between experimental and theoretical values is a necessary consequence of the theory.

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Since each of the parallel curves plotted in Figure 2 of ref 13 constitutes a reaction series with HA varying and the hydroxide base remaining constant, it might be expected that α_l contributes to the total Brønsted coefficient. It should be noted that if the weak acid were maintained constant and the base varied, eq 5 predicts that if $\Delta G^{\circ\prime} \ll 4\Lambda$, the limits on α are 0–0.5 for the reaction in one direction and 0.5–1 for the reaction in the opposite direction, since the sign of $\Delta G^{\circ\prime}$ determines whether the term in parentheses is greater or less than unity. It is only when $\Delta G^{\circ\prime} \sim 4\Lambda$ that α can approach the limits of 0 or 1 in the case of constant Λ.

Marcus' theory has, to date, been shown to be consistent with a large number of experimental results for both normal and carbon acids, both when the base is varied and when the acid is varied. This does not, however, constitute a critical test of the theory, since the parameters involved (Λ, ΔG^*, $d\Lambda/d\Delta G^{\circ\prime}$) are themselves calculated from the experimental data. It would be particularly desirable to be able to calculate Λ from other data. Since Λ in eq 3 is assumed to be the arithmetic mean of the intrinsic barriers for the two exchange reactions[10]

$$\mathrm{RAH} + \mathrm{RA}^- \rightleftharpoons \mathrm{RA}^- + \mathrm{RAH} \qquad \text{(b)}$$

$$\mathrm{BH} + \mathrm{B}^- \rightleftharpoons \mathrm{B}^- + \mathrm{BH} \qquad \text{(c)}$$

determination of the exchange rates *via* nmr would allow Λ to be calculated for reaction a. Λ is also the sum of the reorganizational energies for the outer (Λ_o) and inner (Λ_i) coordination spheres. The Λ_o and Λ_i values for the exchange reaction (a) are assumed also to be the arithmetic mean of the cross-reaction terms.[20] Since Marcus has derived equations for these terms, Λ_o and Λ_i could conceivably be calculated for each exchange reaction, if the equilibrium values of the bond coordinates and reduced force constants were known. Unfortunately, such calculations apparently cannot be readily performed at the present time.

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Photodissociation of the CH_3Cl^+ and N_2O^+ Cations

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Abstract: The ion cyclotron resonance technique was used to observe the photodissociation of the cations CH_3Cl^+ and N_2O^+ in the gas phase. Ions were trapped in the icr cell for periods of the order of seconds, which permitted the photodissociation process to be observed with wavelength-selected light. A cyclotron resonance ejection technique was employed to show that CH_3Cl^+ ions were being dissociated rather than the CH_3ClH^+ ions which were also present. The photodissociation cross section for N_2O^+ was found to be roughly 0.25×10^{-18} cm² without strong wavelength dependence between 4000 and 6500 Å. The cross section for CH_3Cl^+ showed a large peak at 3150 Å, having a value at that wavelength of 7.8×10^{-18} cm². Possible assignments of this peak are considered, and it is suggested that photodissociation occurs through an ion excitation involving a change in occupation of the bonding or antibonding orbitals of the C–Cl bond.

The dissociation of positive ions by photon impact, apart from its intrinsic interest as a basic photochemical process, has potential importance to several areas of interest. (1) Approximate theoretical calculations can be made of photodissociation cross sections in simple systems, and such studies would benefit from having experimental data for comparison. (2) In the event that a well-defined threshold were observed, the energy of the photodissociation threshold would provide bond dissociation energies of a precision far greater than is presently available for most ions. (3) The possibility of depositing a precisely known quantum of energy in an ion and observing the subsequent competitive unimolecular dissociation processes offers a stringent test of unimolecular dissociation theories. (4) If the photodissociation process could be observed at sufficiently high resolution, the assignment of vibrational structure could provide new information on the symmetries and bonds of simple ions. (5) As the results of the present study suggest, the determination even of the broad features of the wavelength dependence of the dissociation process can give interesting information about the upper electronic levels of ionic species.

In view of the potential interest which such processes have in terms of characterizing ions, the almost total absence of experimental data must be attributed to the lack of a sensitive and convenient means of observing them. The present study is intended to show that ion cyclotron resonance spectroscopy (icr) may provide such a technique, and also that the photodissociation cross sections of some simple cations are sufficiently large to make such investigations quite feasible.

Several other experimental techniques provide information about cation dissociation, of which the most important are uv optical spectroscopy, electron impact mass spectroscopy, and photoionization mass spectroscopy.[1] All of these methods examine processes in

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(1) See, for example, V. H. Dibeler, J. A. Walker, and K. E. McCulloh, *J. Chem. Phys.*, 51, 4230 (1969); T. A. Walter, C. Lifshitz, W. A. Chupka, and J. Berkowitz, *ibid.*, 51, 3531 (1969).