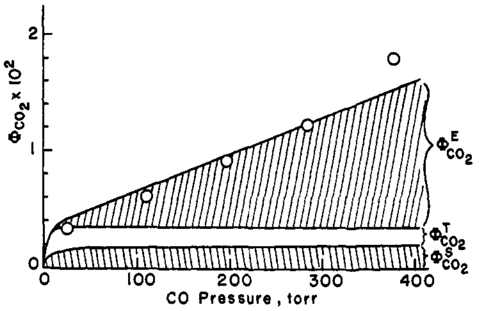

Figure 9. Plot of the theoretical curves for the quantum yields of CO_2 from excited $^1SO_2$ ($\Phi_{CO_2}{}^S$ of relation G), $^3SO_2$ from the low-pressure mechansim ($\Phi_{CO_2}{}^T$ of relation F), and the "excess" triplet ($\Phi_{CO_2}{}^E$ of relation M) *vs.* the pressure of carbon monoxide; calculated for the 3130-Å photolyses of SO_2–CO mixtures at $P_{SO_2} = 2.0$ Torr; the open circles represent the experimentally measured quantum yields of carbon dioxide.

at sufficiently low $[SO_2]/[CO]$ ratio we expect the function $(\Phi_{CO_2}{}^E)\{([SO_2]/[CO]) + 0.35\}$ to be a linear function of [CO]. A test of this dependence is shown in Figure 8 using all data for runs in Table IV for $[SO_2]/[CO] < 0.1$. The expected linear form is at least qualitatively consistent with these data. The slope of the line, 1.12×10^{-5} Torr^{-1}, may be taken as equal to the constant terms on the right side of relation M and equation N may be used to calculate the approximate

$$\Phi_{CO_2}{}^E = 1.12 \times 10^{-5} P_{CO}\ (\text{Torr})/(0.35 + [SO_2]/[CO]) \quad (\text{N}$$

values of $\Phi_{CO_2}{}^E$. It is instructive to test the compatibility of all the Φ_{CO_2} data with the values of the total quantum yields calculated from relations F, G, and N. This has been done for runs at $P_{SO_2} = 2.0$ Torr and varied P_{CO}, and the data are plotted in Figure 9. The experimentally measured values of Φ_{CO_2} appear as circles on the plot. It is seen that the theoretical functions F and G account for most of the CO_2 in runs below CO pressures of about 5 Torr, but the dominant source at high CO pressures is the $^3SO_2$ formed in the high-pressure mechanism. The total quantum yields of CO_2 calculated for each of the runs are shown in Table IV. In general the data are reproduced quite well for all the runs. The largest deviations occur at the high $[SO_2]/[CO]$ ratios where the function M does not reduce accurately to the approximate function N. Obviously a more judicious choice (within the error limits of the experimental rate constant estimates) could be made in the values used for the rate constants in the theoretical functions F and G, and a more complete form of the function N could be employed to fit the experimental data more precisely. There is no point in this exercise at this stage of our knowledge in these systems.

The present work confirms the interesting observations of Cehelnik, *et al.*, that the simple low-pressure mechanism of $^3SO_2$ formation cannot alone account for CO_2 formation in 2400–3200-Å irradiated mixtures of SO_2 and CO at high pressures of the reactants. However, all of our results favor the conclusion that the only reactive SO_2 states in these systems are the fluorescent singlet and the phosphorescent triplet. The significant participation of two new nonemitting singlet and triplet states of SO_2 in CO_2 formation seems unlikely to us. Our results favor the involvement of some undefined intermediate excited state or unstable isomer of SO_2 (X), not as a reactant with CO to form CO_2 directly, but as a new source of phosphorescent triplet in experiments at high reactant pressures. We are continuing tests of these systems to check the alternative hypotheses further.

Acknowledgment. The authors gratefully acknowledge the support of this work through a research grant from the Environmental Protection Agency, Office of Air Pollution Control, U. S. Department of Health, Education and Welfare, Arlington, Va. We also thank Drs. E. Cehelnik, A. Fatta, Silvia Braslavsky, C. W. Spicer, and Professor J. Heicklen of Pennsylvania State University and Dr. C. Hellner, National Bureau of Standards, for their helpful discussions with the authors and the use of reports of their work before publication.

Kinetics of Proton-Transfer Reactions. V.
A Linear Free Energy, Enthalpy, and Entropy System

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received September 16, 1971

Abstract: Rate and equilibrium data as a function of temperature are reported for the deprotonation of a series of seven closely related internally hydrogen-bonded weak acids by means of hydroxide ions. The compounds studied all had an ortho azo or salicylate internal hydrogen bond. Not only are the free energies of activation linearly related to the free energies of reaction ($\alpha_G = 1.1$), but the enthalpies and entropies of activation are linearly related to the enthalpies and entropies of reaction, respectively (slopes 1.0 and 1.4). The consequences of these results are discussed in relation to the origin of the Brønsted relationship for these compounds.

In earlier papers,[1,2] we presented rate and equilibrium data for the reaction of a series of internally hydrogen-bonded acids with OH^-. A graph of log k_f, the forward (deprotonation) rate constant, *vs.* pK_a gen-

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(1) M. C. Rose and J. E. Stuehr, *J. Amer. Chem. Soc.*, **90**, 7205 (1968).

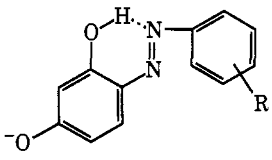
(2) M. C. Rose and J. E. Stuehr, *ibid.*, **93**, 4350 (1971).

erated a series of linear free energy curves, each with a Brønsted slope $\alpha = -\mathrm{d}\log k_f/\mathrm{dp}K_a$, of approximately unity except when the reactions approached the diffusion controlled limit.

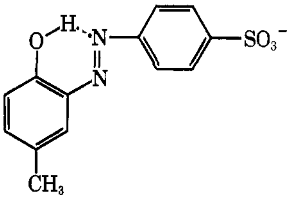
A fundamental question is that dealing with the basis of the linear free energy relationship itself; *i.e.*, is it more meaningful to consider free energies or enthalpies in "deriving" the Brønsted relation. We pointed out that the linear free energy relationship represented by our data and those of others could result from a linear relationship between the enthalpies of activation and reaction ($\mathrm{d}\Delta H^{\ddagger} = \alpha_H \mathrm{d}\Delta H^{\circ}$, where α_H is a proportionality constant for the enthalpies), provided certain restrictions were put on the entropy changes within the series.

It was the purpose of this paper to investigate in detail this question by measuring the temperature dependencies of the rate and equilibrium constants for a series of closely related compounds all possessing an internal hydrogen bond. They had been previously shown to lie on a smooth curve of log k *vs.* pK.[1,2]

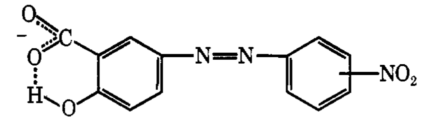
The compounds studied were I, phenylazoresorcinol; II, 4-(*p*-nitrophenylazo)resorcinol; III, 4-(*m*-nitrophenylazo)resorcinol; IV, 2,4-dihydroxy-4′-sulfonateazobenzene; V, 2-hydroxy-4-methyl-4′-sulfonateazobenzene; VI, 4-(*p*-nitrophenylazo)salicylate; VII, 4-(*m*-nitrophenylazo)salicylate. For each of these compounds kinetic and thermodynamic data were obtained over a temperature range of 5–30°. Common names for the compounds are given in Table II.



I, H
II, p-NO_2
III, m-NO_2
IV, p-SO_3^-



V



VI, p-NO_2
VII, m-NO_2

Experimental Section

Purification and synthesis of the compounds, where necessary, were carried out as described previously.[2] pK_a values as a function of temperature were measured spectrophotometrically by means of absorbance measurements (Gilford-Beckman spectrophotometer) as a function of pH (Beckman Expandomatic or Sargent Digital meters). Microcombination pH electrodes were standardized at a minimum of three pH values with buffers prepared from Natonal Bureau of Standards buffer chemicals. The electrodes utilized (Thomas 4858-L60 or Corning 476050) were chosen because of their ability to operate reliably over the 0–14 pH range and a wide temperature range. For measurements of pH at temperatures outside the range 20–25° the electrodes were immersed in buffers at the desired temperature for 1–3 hr prior to taking readings, and frequently overnight. Careful calibration of the electrodes was necessary, since even an error of ±0.02 pH yielded an error of about 7% in a_H. At pH values above 12, the concentration of ions due to added KOH begins to contribute significantly to the ionic strength. In such instances compensation was effected by decreasing the amount of KNO_3 added so that the ionic strength remained 0.1. The solution cell, containing about 10 cc, was glass through which water, thermostated to ±0.02° by means of a Lauda water circulator, was circulated. All solutions were degassed prior to use, and all pH measurements were carried out with slow bubbling of water-saturated N_2, which also served as a source of mild stirring. In this way we feel that our pH measurements are precise and meaningful to the degree specified[3] by the NBS for these conditions, ±0.005–0.01 unit.

Precision optical absorbance measurements were made on a Gilford-Beckman spectrophotometer equipped with linear digital readout and thermostated at the desired temperature to ±0.1°.

All kinetic measurements were carried out on a temperature-jump (T-jump) spectrometer obtained from Messanlagen Studiengesellschaft.[4] Since it was essential to accurately know the final temperature following the T-jump in order to carry out rate studies as a function of temperature, it was necessary to carefully calibrate the magnitude of the T-jump. This was accomplished as follows. A system whose equilibrium was known to be temperature dependent and which had an absorbance peak in the visible region was selected and a solution was made up and thermostated in the T-jump cell. The light current and photomultiplier voltage were adjusted until a deflection of 1 V was observed on the oscilloscope when the lens shutter of the optical system was closed. After temperature equilibrium had been established, as indicated by a steady readout signal, a base line was set on the oscilloscope, and the change in oscilloscope deflection was measured as a function of the thermostated temperature in the cell. The oscilloscope deflections in millivolts, corresponding to changes in light intensity as a function of temperature, were linear with temperature over 5–8° temperature ranges between 5 and 30° and were independent of whether the temperature was slowly increased or decreased. The temperature was then set to known values, the discharge capacitor set to a known voltage and discharged, and the changes in oscilloscope deflection were measured. Enough jumps were made, using base lines that had been steady for at least 15 min and varying the input voltage on the discharge capacitor, to make a graph of oscilloscope deflection *vs.* (kV)^2. This experiment was repeated at several initial temperatures. In this manner, a calibration of temperature rise as a function of the square of the initial discharge voltage was obtained. For example, the temperature rise following a discharge at 35 kV was 5.1 ± 0.1°; for 25 kV, 2.5 ± 0.05°. A 0.09 M $Co(NH_3)_6Cl_3$ solution was found to be suitable for these calibrations. The calibration so obtained was checked independently[5] with the use of 0.1 M Tris buffer and Cresol Red indicator. The agreement between the two calibrations was good.

The procedure used in the T-jump experiment was to prepare a stock solution of each compound ($\sim 10^{-4}$ M) in Stokes distilled water, which had been degassed to reduce possible cavitation effects. Aliquots were then diluted to the desired concentrations using sufficient KNO_3 to maintain an ionic strength of 0.1 and the pH was measured. The T-jump cell was thermostated by a Lauda Ultra Kyromat TK-30D refrigerated water circulator. A stream of dry nitrogen was passed through the cell block to prevent condensation on the cell windows. Prior to making a jump the temperature of the solution in the cell was measured. The voltage of the capacitor was adjusted so that sufficient energy was released on discharge of the capacitor to attain the desired final temperature. The resultant relaxation curves were photographed with a Polaroid camera system. The solution that had been jumped was transferred to a vial which was then immersed in a water bath whose temperature was that of the experiment, and the pH immediately measured after *each* discharge experiment. Relaxation times were evaluated from enlarged copies of Polaroid photographs.

Results

Thermodynamic. Mixed pK_a^m values, defined as $-\log a_H C_A/C_{HA}$, were determined spectrophotometrically. In most instances measurements were taken at five or six temperatures over the range 5–35°. Graphs of pK_a^m *vs.* $1/T$ were linear. The pK_a^m values at 25° and $\Delta H^{\circ}{}_a{}'$ for the ionization process are given in Table I. The use of the prime on these, and other, thermo-

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(3) R. G. Bates, "Determination of pH," Wiley, New York, N. Y., 1964, p 88.

(4) Göttingen, W. Germany.

(5) J. L. Banyasz, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1970.

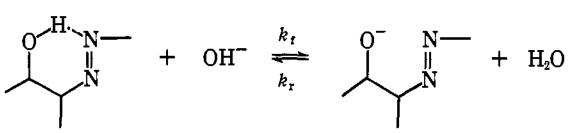
Table I. Spectrophotometric[a] pK_a^m and $\Delta H^{\circ\prime}$ Values at 25° at $I = 0.1$

	pK_a^m	$\Delta H^\circ{}_a{}'$,[b] kcal/mol
I	11.98 ± 0.03	8.69
II	11.67 ± 0.03	6.86
III	11.51 ± 0.03	7.15
IV	11.95 ± 0.01	6.23
V	9.20 ± 0.01	4.96
VI	10.76 ± 0.01	5.85
VII	11.00 ± 0.02	6.71

[a] K_a^m values are "mixed" ionization constants $= a_HC_A/C_{HA}$. [b] $\Delta H^{\circ\prime}$ values are for the ionization reaction; the prime refers to a standard state of $I = 0.1\ M$.

dynamic quantities indicates the use of a standard state defined as $I = 0.1\ M$. As the pK_a increases, the enthalpy of ionization also increases, although not linearly.

While K_a^m refers to the ionization reaction of the weak acid, it is the deprotonation reaction 1 that is



(1)

kinetically observed at pH > 8 (z is the charge on the protonated acid in the pH region studied). The equilibrium constant for reaction 1 as written is

$$K^{0\prime} = K_a^m\gamma_{OH}/K^0{}_w \tag{2}$$

where $K^0{}_w$ is the ion activity product of water at a specified temperature, and γ_{OH} is the activity coefficient of the hydroxyl ion ($\cong 0.75$) at $I = 0.1$.

The enthalpy of reaction $\Delta H^{\circ\prime}$ was calculated from the relation $\Delta H^{\circ\prime} = \Delta H^\circ{}_a{}' - \Delta H^\circ{}_w{}'$. $\Delta H^\circ{}_w{}'$, the enthalpy of water ionization at a finite ionic strength, is somewhat dependent upon temperature.[6] We used the average value for the temperature range utilized, 13.91 kcal/mol. The enthalpies obtained for reaction 1 ranged from −5.2 to −9.0 kcal/mol.

It is interesting to note that enthalpies of reaction can also, in principle, be obtained from the amplitudes of the optical density (or transmittance) changes for the relaxation process.[7] For a single step process coupled to an optical detection, the relative change in light intensity (as measured by appropriately calibrating the voltage axis of the oscilloscope) is given, for a small temperature change, by

$$\delta I/I = -2.303\Gamma b\Delta H^{\circ\prime}(\epsilon_A - \epsilon_{HA})\Delta T/RT^2 \tag{3}$$

where ϵ_i is the indicated extinction coefficient, b the cell path length, ΔT the temperature rise, and Γ a concentration function

$$\Gamma = (\Sigma\nu_i{}^2/C_i)^{-1} = [1/C_H + 1/C_A + 1/C_{HA}]^{-1} \tag{4}$$

where ν_i is the stoichiometric number. Since all quantities except $\Delta H^{\circ\prime}$ are measurable or known, it is possible to obtain $\Delta H^{\circ\prime}$ independently by this method. We tested eq 3 for some of the compounds and obtained the following results. For compound VI (Alizarine Yellow R) at $C^0 = 3.5 \times 10^{-5}\ M$, pH = 10.40 at 20°, we measured $\delta I/I = 0.024$ for a 4.1° temperature jump. At 495 mμ, $\Delta\epsilon = 2 \times 10^4$. With $\Gamma = 6.6 \times 10^{-6}$, we calculate $\Delta H^{\circ\prime} = -7.6$ kcal/mol. Analogous measurements yielded for compound II, $\Delta H^{\circ\prime} = -6.0$ kcal/mol; for VII, −6.1 kcal/mol. The errors on these numbers are ±20% (±1.5 kcal/mol), thus precluding their use in any accurate computations, but they are within their errors in agreement with the values measured from the dependence of pK upon temperature (Table II). The largest source of error is the determination of the extinction coefficient ϵ, which must be determined independently for two species at each temperature. The value of amplitude jumps in obtaining information on reaction enthalpies has been recognized for some time, but few actual applications have been made.[8-10]

Table II. Thermodynamic and Activation Parameters[a] for the Reaction

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

Compd	$-\Delta G^{\circ b}$ kcal/mol	$\Delta G^{\ddagger}{}_f{}^b$ kcal/mol	$-\Delta H^{\circ\prime}$ kcal/mol	$\Delta H^{\ddagger}{}_f$ kcal/mol	$-\Delta S^\circ$ cal/(deg mol)	$-\Delta S^{\ddagger}{}_f$ cal/(deg mol)
I	2.57	8.92	5.22	5.68	8.9	10.9
II	3.01	9.14	7.05	4.29	13.5	16.3
III	3.23	8.71	6.76	4.70	11.8	13.5
IV	2.62	9.16	7.68	2.88	16.9	21.1
V	6.38	4.73	8.95	2.38	8.6	7.9
VI	4.24	7.25	8.06	3.23	12.8	13.5
VII	3.93	7.39	7.20	3.67	11.0	12.5

[a] The digits have been given beyond significant figures to avoid accumulation of roundout errors. The enthalpies are estimated at 5-10%, with resultant average error of ±2-4 cal/(deg mol) in the entropies. [b] Free energy values are given for 25°.

Kinetic. A single relaxation time was observed for each system, ranging from approximately 7 to 200 μsec for the series of compounds investigated (Table III). In all instances the concentration and pH dependences of the inverse relaxation time were consistent with the deprotonation reaction (see equation 1 above) or, for compounds VI and VII, for the analogous reaction of OH⁻ with O–H···O. The reciprocal relaxation time for this reaction is given by (omitting charges)

$$1/\tau = k_f(\bar{C}_{OH} + \bar{C}_{HA}) + k_r \tag{5}$$

where the bar indicates equilibrium values. At each temperature graphs of τ^{-1} *vs.* the sum of the two concentrations were linear, yielding k_f and k_r as the slope and intercept, respectively. The ratio of these values was consistent, as it must be, with the value of $K^{0\prime}$ as obtained from the thermodynamic measurements (eq 2). Rather than let k_f and k_r vary independently of $K^{0\prime}$, we imposed the constraint on the data that the best values of the forward and reverse rate constants were those which returned the equilibrium constant. This constraint reduced the probable error in the rate constants, since the equilibrium constants are known to within a few per cent at any temperature. In all instances, the lines drawn through the data points *via* this constraint were completely consistent with the data.

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(6) H. S. Harned and W. J. Hamer, *J. Amer. Chem. Soc.*, **55**, 4496 (1933).

(7) M. Eigen and L. DeMaeyer in "Technique of Organic Chemistry," 2nd ed, Vol. VIII, Part 2, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Wiley, New York, N. Y., 1963, p 910.

(8) G. H. Czerlinski and J. Malkewitz, *Biochemistry*, 4, 1127 (1965).

(9) R. Winkler, Ph.D. Thesis, Göttingen, 1969.

(10) F. Guillain and D. Thusius, *J. Amer. Chem. Soc.*, **92**, 5534 (1970).

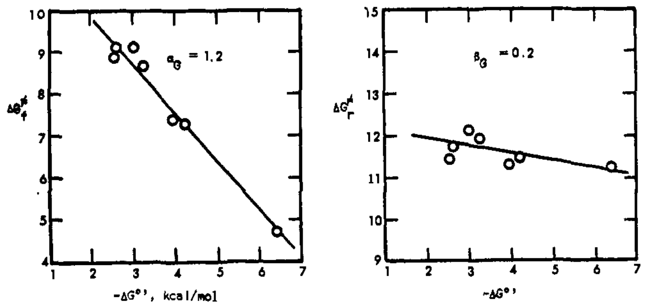

Figure 1. The linear free energy relationship for the forward and reverse directions for reaction 1 at 25° (kcal/mol).

The observed forward rate constants varied from 10^6 to 10^9 M^{-1} sec^{-1} at 25°, *i.e.*, from one to four orders of magnitude slower than diffusion controlled (Table III). The acids with the highest pK_a's (and hence the strongest internal hydrogen bond) had the smallest second-order rate constants. The reverse rate constants clustered for the most part around 10^4 sec^{-1}. Rate constants and p$K_a{}^m$ values reported here are in excellent agreement with measurements reported in an earlier study[11] of compounds I–IV at the single temperature of 25°.

Activation enthalpies ($\Delta H^{\ddagger}$) were obtained from graphs of ln k/T *vs.* $1/T$, consisting of five to seven points over the temperature range 5–30°. The activation enthalpies so measured ranged from 2.4 to 5.7 kcal/mol for the forward direction. We estimate the errors in these values to be no greater than ±10% (±0.2–0.6 kcal/mol), based on a statistical analysis of the graphs, in conjunction with the constraint that the difference $\Delta H^{\ddagger}{}_f - \Delta H^{\ddagger}{}_r$ must equal $\Delta H°'$, the overall enthalpy change for reaction 1 which was measured separately.

There has already been in the literature considerable discussion[1,2,11] of the relative strengths of the various types of internal hydrogen bond (OH···N, NH···N, *etc.*). We provide here some information on the effect of the location of a ring substituent (meta *vs.* para) on the strength of the hydrogen bond. Attention is called in particular to the $\Delta H°'$ and $\Delta H^{\ddagger}{}_f$ values for the following meta–para comparisons. For the two diazoviolet compounds (N···HO), the meta isomer (III) has a $\Delta H°'$ value of −6.8 kcal/mol and $\Delta H^{\ddagger}{}_f = 4.7$ kcal; the corresponding values for the para compound (II) are −7.1 and 4.3 kcal/mol. Analogous comparison for the two Alizarine Yellows (O···HO) is for VII (meta), $\Delta H° = -7.2$, $\Delta H^{\ddagger}{}_f = 3.7$ kcal/mol; for VI (para), $\Delta H° = -8.1$, $\Delta H^{\ddagger}{}_f \approx 3.2$ kcal/mol. That is, in both instances the activation energies are *larger* for the meta isomer, and the heats liberated are smaller, indicating the stronger internal hydrogen bond. These observations are in accord with the prediction,[11] based on electrostatic considerations, that the *p*-nitro group should be more effective than the meta in drawing charge away from the azo-nitrogen proton acceptor, thus decreasing the strength of the hydrogen bond. It is interesting to note that if one compares just the pK_a and k_f values at 25°, he would come to opposing conclusions for the two comparisons made above. It is worth emphasizing, but not surprising, that rate and pK comparisons at a single temperature can be grossly misleading.

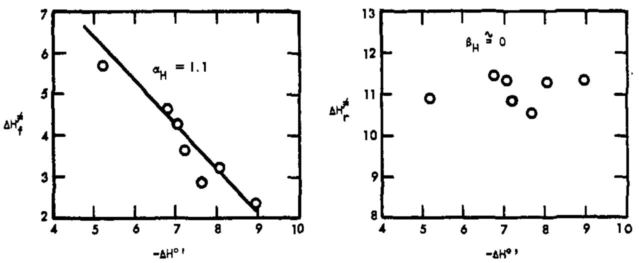

Figure 2. The linear enthalpy relationship for the forward and reverse directions for reaction 1 (units, kcal/mol).

Although all reactions were found to be consistent with the simple deprotonation reaction 1, other processes coupled to it were considered as possible complications. The possibility of tautomerism (O–H···N ↔ O···H–N) for the *o*-hydroxyazobenzene compounds was rejected because the solvent-independent absorption spectrum,[12] nmr data, and the absence of luminescence[13] have shown that *o*-hydroxyazobenzene exists only as the azo species in aqueous solution. The coupling of rapid proton transfer preequilibria for these di- or triprotic acids arising from prior ionizations was demonstrated to be negligible.

Graphs of $\Delta G^{\ddagger}$ *vs.* $\Delta G°'$ at 25° are shown in Figure 1, demonstrating the linear free energy relationship for these compounds. The Brønsted coefficient for the forward direction is $\alpha_G = 1.2$; for the reverse direction, $\beta_G = -0.2$. The slopes are indeed statistically *not* 1.0 and 0 for α and β. We have shown[2] that the value of $\alpha >$ unity which we observe is consistent with Marcus' theory[14] in which there is a "within the series" contribution to α of approximately 0.45 and a contribution of approximately 0.75 due to changes in the intrinsic properties of the compounds due to changes in structure and hence in energy.

The analogous graph of $\Delta H^{\ddagger}$ *vs.* $\Delta H°'$ is shown in Figure 2, demonstrating the existence of a linear enthalpy relationship, $d\Delta H^{\ddagger} = \alpha_H d\Delta H°'$. The value of α_H is 1.1 for the forward direction. The points are more uniformly distributed than those for the free energy. For the reverse direction, the values of $\Delta H^{\ddagger}{}_r$ show no significant trend with $\Delta H°'$; they appear to scatter uniformly around 11.2 kcal/mol as $\Delta H°'$ varies from −5 to −9 kcal/mol.

Discussion

As pointed out in the introduction, linear free energy relationships can result from linear enthalpy relationships if certain conditions regarding entropies are fulfilled. On the other hand, the more common practice has been to derive a linear free energy relationship, $d\Delta G^{\ddagger} = \alpha_G d\Delta G°'$, from "intersecting free energy profiles." While the basis of any molecular interpretation of the Brønsted relation is potential energy,[15,16] it is argued[17] that, at temperatures well

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(11) W. H. Innskeep, D. L. Jones, W. T. Silfvast, and E. M. Eyring, *Proc. Nat. Acad. Sci. U. S.*, **59**, 1027 (1968).

(12) A. Buroway, A. G. Salem, and H. R. Thompson, *J. Chem. Soc.*, 4973 (1952).

(13) G. Gabor, Y. Frei, D. Gegiou, M. Kaganowitch, and E. Fischer, *Isr. J. Chem.*, **5**, 193 (1967).

(14) (a) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968); (b) A. O. Cohen and R. A. Marcus, *ibid.*, **72**, 4249 (1968); (c) R. A. Marcus, *J. Amer. Chem. Soc.*, **91**, 7224 (1969).

Table III. Kinetic Data as a Function of Temperature[a]

T, °C	10^5C^0, M	pH	$10^{-4}\tau^{-1}$, sec^{-1}
I, 4-(Phenylazo)resorcinol			
5°	8.1	12.24	1.33
	12	12.54	1.41
	1.9	12.74	1.54
		12.81	1.68
$k_f = 8.5 \times 10^5\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 6.0 \times 10^3\ \text{sec}^{-1}$			
10°	8.1	11.84	2.04
		11.99	2.04
		12.29	1.56
		12.41	2.09
		12.50	2.08
	8.6	12.21	1.91
		12.65	2.36
$k_f = 1.1 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 9.2 \times 10^3\ \text{sec}^{-1}$			
15°	4.9	12.36	2.57
	4.3	12.39	2.84
	8.6	11.99	1.28
		12.38	2.48
		12.49	3.20
$k_f = 1.2 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.1 \times 10^4\ \text{sec}^{-1}$			
20°	18	11.78	3.24
		12.37	4.08
	9.0	12.09	3.73
	8.6	12.29	3.94
$k_f = 1.5 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.7 \times 10^4\ \text{sec}^{-1}$			
25°	4.9	11.65	3.96
	4.9	12.00	4.75
	4.7	11.99	4.62
	6.3	12.29	7.29
	6.3	12.24	5.13
$k_f = 1.8 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 2.4 \times 10^4\ \text{sec}^{-1}$			
II, *p*-(Nitrophenylazo)resorcinol (*p*-Diazoviolet)			
5°	4.6	12.32	0.56
		12.54	0.84
	3.2	12.15	0.51
		12.61	0.99
$k_f = 7.0 \times 10^5\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.8 \times 10^3\ \text{sec}^{-1}$			
10°	4.6	11.70	0.43
		11.74	0.46
		12.14	0.71
		12.30	0.87
		12.42	0.96
$k_f = 7.5 \times 10^5\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 2.5 \times 10^3\ \text{sec}^{-1}$			
15°	4.3	11.82	0.77
	5.2	12.00	0.83
	7.9	12.14	1.12
$k_f = 9.1 \times 10^5\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 3.7 \times 10^3\ \text{sec}^{-1}$			
20°	4.3	11.68	0.94
	4.6	11.80	1.03
		12.00	1.18
		12.10	1.36
		12.13	1.84
$k_f = 1.0 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 4.9 \times 10^3\ \text{sec}^{-1}$			
25°	1.6	11.22	1.29
		12.17	2.95
	3.2	11.33	1.07
		11.51	1.26
		11.75	1.73
$k_f = 1.2 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 7.8 \times 10^3\ \text{sec}^{-1}$			
28°	3.1	11.49	1.61
	4.6	11.40	1.39
		11.71	2.03
$k_f = 1.3 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 8.6 \times 10^3\ \text{sec}^{-1}$			
III, *m*-(Nitrophenylazo)-resorcinol (*m*-Diazoviolet)			
5°	2.5	12.19	0.88
	4.4	11.74	0.55
	5.9	12.17	0.79
		12.36	1.00
		12.52	1.32
		12.63	1.65
$k_f = 1.4 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 2.6 \times 10^3\ \text{sec}^{-1}$			
10°	2.5	11.56	0.87
		11.72	0.87
		11.90	0.96
		12.40	2.18
$k_f = 1.7 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 4.0 \times 10^3\ \text{sec}^{-1}$			
15°	4.5	11.05	1.05
		11.75	1.26
		12.10	1.65
		12.30	2.34
III (Continued)			
$k_f = 1.9 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 5.5 \times 10^3\ \text{sec}^{-1}$			
20°	5.3	11.68	1.65
	3.9	11.76	2.10
		12.01	2.67
		11.15	1.51
$k_f = 2.4 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 8.6 \times 10^3\ \text{sec}^{-1}$			
25°	2.5	11.31	2.13
		11.39	2.10
		11.62	2.45
		11.97	3.69
$k_f = 2.6 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.1 \times 10^4\ \text{sec}^{-1}$			
30°	5.3	11.02	3.15
		11.33	2.93
		11.39	3.17
		11.86	7.53
$k_f = 3.8 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.9 \times 10^4\ \text{sec}^{-1}$			
IV, 2,4-Dihydroxy-4′-sulfonateazobenzene (Tropaeolin O)			
6°	12	11.99	0.87
		12.25	0.85
		12.71	1.52
	7.3	12.18	0.85
	14	12.08	0.87
$k_f = 8.5 \times 10^5\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 4.2 \times 10^3\ \text{sec}^{-1}$			
7.5°	3.0	12.20	0.87
		12.23	0.84
		12.61	1.16
		12.74	1.41
$k_f = 8.7 \times 10^5\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 4.6 \times 10^3\ \text{sec}^{-1}$			
10°	12	11.81	0.87
		11.97	0.85
		12.30	1.16
		12.76	1.31
	4.9	11.63	0.87
$k_f = 9.4 \times 10^5\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 5.7 \times 10^3\ \text{sec}^{-1}$			
15°	5.6	11.97	1.26
		12.23	1.68
		12.36	1.73
		12.43	1.79
		12.67	2.67
IV (Continued)			
$k_f = 8.8 \times 10^5\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 6.5 \times 10^3\ \text{sec}^{-1}$			
20°	9.8	11.73	1.65
		11.93	1.74
		12.43	2.98
$k_f = 1.0 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 9.5 \times 10^3\ \text{sec}^{-1}$			
25°	4.9	11.21	2.18
		11.63	2.72
		11.72	2.15
		11.89	2.35
$k_f = 1.2 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.5 \times 10^4\ \text{sec}^{-1}$			
28°	5.1	11.53	2.84
		11.86	2.89
	10	11.84	2.62
	3.1	11.91	3.11
$k_f = 1.3 \times 10^6\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.7 \times 10^4\ \text{sec}^{-1}$			
V, *p*-Cresol-4′-sulfonateazobenzene			
5°	2.1	9.71	3.96
	4.2	10.01	5.70
	6.3	10.08	6.20
$k_f = 1.5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.0 \times 10^4\ \text{sec}^{-1}$			
7.5°	2.7	9.33	4.00
	2.7	9.71	6.93
	5.3	10.21	10.66
$k_f = 1.6 \times 10^9\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.3 \times 10^4\ \text{sec}^{-1}$			
10°	6.2	8.41	11.09
	4.1	8.75	7.70
		9.27	6.30
	2.0	9.20	8.40
$k_f = 1.7 \times 10^9\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.6 \times 10^4\ \text{sec}^{-1}$			
15°	1.8	9.18	8.53
	3.6	8.82	5.77
	3.7	9.64	10.46
	7.1	9.16	12.00
	7.1	8.83	13.86
	5.8	9.85	13.40
$k_f = 1.9 \times 10^9\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 2.4 \times 10^4\ \text{sec}^{-1}$			
20°	2.1	9.18	8.66
	4.2	9.27	9.63
	4.2	8.75	9.63
	6.3	8.41	13.86
$k_f = 2.0 \times 10^9\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 3.2 \times 10^4\ \text{sec}^{-1}$			
25°	1.2	9.02	9.12
	1.2	9.34	7.53
	5.3	8.86	14.43
$k_f = 2.1 \times 10^9\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 4.0 \times 10^4\ \text{sec}^{-1}$			
VI, *p*-Nitrophenylazosalicylate (Alizarine Yellow R)			
5.7°	28	10.21	1.18
		11.17	1.32
	17	11.05	1.63
		11.37	1.79
$k_f = 1.8 \times 10^7\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 5.5 \times 10^3\ \text{sec}^{-1}$			
10°	28	10.20	1.63
		10.68	1.69
		10.92	1.93
		11.03	2.38
$k_f = 2.1 \times 10^7\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 8.5 \times 10^3\ \text{sec}^{-1}$			
15°	20	10.76	2.17
		10.96	2.79
		11.20	3.41
		11.30	3.79
		11.34	4.68
$k_f = 2.4 \times 10^7\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.2 \times 10^4\ \text{sec}^{-1}$			
19.5°	30	10.14	2.36
		10.45	2.69
		10.77	3.31
		10.86	3.55
$k_f = 2.5 \times 10^7\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.5 \times 10^4\ \text{sec}^{-1}$			
25°	11	10.13	3.01
		10.27	3.54
		10.61	4.33
		10.76	4.68
$k_f = 3.0 \times 10^7\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 2.3 \times 10^4\ \text{sec}^{-1}$			
30°	65	10.28	4.95
		10.38	5.13
		10.71	5.44
$k_f = 3.2 \times 10^7\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 3.1 \times 10^4\ \text{sec}^{-1}$			

Table III (*Continued*)

T, °C	10^5C, M	pH	$10^{-4}\tau^{-1}$, sec^{-1}	T, °C	10^5C^0, M	pH	$10^{-4}\tau^{-1}$, sec^{-1}
VII, *m*-Nitrophenylazosalicylate (Alizarine Yellow G)							
6.2°	38	11.15	2.31	16.2°	5.6	11.41	6.19
	25	11.49	2.73		2.8	11.58	8.51
	29	11.71	3.15				
	29	11.89	4.92				
$k_f = 1.6 \times 10^7\ M^{-1}\ \text{sec}^{-1}$				$k_f = 2.2 \times 10^7\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.0 \times 10^4\ \text{sec}^{-1}$				$k_r = 2.2 \times 10^4\ \text{sec}^{-1}$			
10.3°	20	10.69	2.31	21.2°	4.7	11.04	4.64
		11.17	2.62		5.0	11.27	7.53
		11.37	3.09		5.0	11.36	7.22
		11.17	6.66		2.5	11.37	9.12
$k_f = 1.8 \times 10^7\ M^{-1}\ \text{sec}^{-1}$				$k_f = 2.4 \times 10^7\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.3 \times 10^4\ \text{sec}^{-1}$				$k_r = 2.8 \times 10^4\ \text{sec}^{-1}$			
14.3°	20	11.20	4.33	25.3°	6.7	10.40	4.13
		11.50	5.61		6.7	10.90	5.45
	30	11.17	3.92		4.5	10.76	4.48
					8.9	11.18	7.37
$k_f = 2.1 \times 10^7\ M^{-1}\ \text{sec}^{-1}$				$k_f = 2.4 \times 10^7\ M^{-1}\ \text{sec}^{-1}$			
$k_r = 1.8 \times 10^4\ \text{sec}^{-1}$				$k_r = 3.3 \times 10^4\ \text{sec}^{-1}$			
				28.3°	27	10.32	5.78
						10.44	6.19
						10.58	6.12
				$k_f = 2.6 \times 10^7\ M^{-1}\ \text{sec}^{-1}$			
				$k_r = 4.0 \times 10^4\ \text{sec}^{-1}$			

[a] All data at $I = 0.1$ (KNO_3).

above 0°K, free energies better represent molecular models in solution than do enthalpies or internal energies. This is because potential energy diagrams typically depict energies of molecules *in vacuo* at absolute zero, where there is no difference between enthalpy and free energy. The influence of both a finite temperature and a solvent changes the energy levels, which are supposed to be taken into account by $\Delta G°$, but not by $\Delta H°$. Therefore, the argument goes, $\alpha_G = d\Delta G^{\neq}/d\Delta G°'$ should be more closely related to the equation $\alpha = d\Delta E^{\neq}/d\Delta E$, which is derived from intersecting Morse potential energy curves for a reaction series, than is $\alpha_H = d\Delta H^{\neq}/d\Delta H°'$. On the other hand, potential energy may be more closely related to enthalpy since in condensed systems at atmospheric pressure the distinction between energy and enthalpy changes is usually quite small.

One wonders if the main reason for preferring free energies to enthalpies is that most kinetic and equilibrium data are available at only one temperature, which allows no comparison of $\Delta H^{\neq}$ and $\Delta H°'$. This is in fact implied by Bell.[18]

Inasmuch as we report here kinetic and thermodynamic data over a 25° temperature range, the question can be examined for this hydrogen-bonded reaction series. An examination of Figure 2 shows that a graph of $\Delta H^{\neq}$ *vs.* $\Delta H°'$ is linear and that $\alpha_H = 1.1 \pm 0.1$. Thus, not only are the free energies linearly related ($\alpha_G = 1.2 \pm 0.1$, Figure 1), but the enthalpies are also, and $\alpha_H = \alpha_G$ within experimental error. Thus, the relation $\alpha_G = d\Delta H^{\neq}/d\Delta H°'$ is a valid starting point for the derivation of the Brønsted relation for this reaction series. With this assumption and the usual equations for the free energies of reaction and activation, one obtains[19]

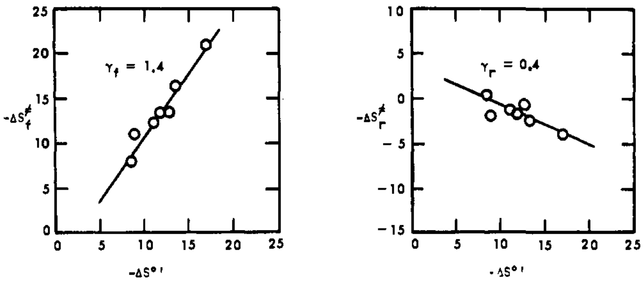

Figure 3. Demonstration of the linear relationship between the entropies of activation and entropies of reaction for reaction 1 (units, cal deg^{-1} mol^{-1}).

$$d\Delta G^{\neq} = \alpha_H d\Delta G°' - T(d\Delta S^{\neq} - \alpha_H d\Delta S°) \quad (6)$$

It is evident that a LFER results if any one of three conditions[20] is fulfilled: (1) if the variations in entropies themselves are both zero, *i.e.*, $d\Delta S/d\Delta G°' = 0$; (2) if a compensation effect between enthalpy and entropy changes exists; *e.g.*, if $d\Delta H° = -aTd\Delta S°$, $d\Delta H^{\neq} = -bTd\Delta S^{\neq}$ where a and b are constants; or (3) if $d\Delta S^{\neq} \cong \alpha_H d\Delta S°'$.

Examination of Table II shows that the entropy changes are not independent of the system, thus eliminating the first possibility. The second can be tested by graphing ΔH *vs.* $-T\Delta S$ for both rate and equilibrium data. Upon so doing it is found that the data points scatter in a random fashion, *i.e.*, no consistent enthalpy–entropy compensation exists for this series. There remains only the third possibility.

A graph of $\Delta S^{\neq}_f$ *vs.* $\Delta S°'$ is given in Figure 3, showing that the activation entropies are linearly related to the reaction entropy changes. The slopes are 1.4 and -0.4 for the forward and reverse directions, respectively. If we now substitute the relation obtained from the Figure 3 plot, *i.e.*, $d\Delta S^{\neq} = \gamma d\Delta S°'$, into eq 6 we obtain

$$d\Delta G^{\neq}_f/d\Delta G°' = \alpha_H - (\gamma - \alpha_H)Td\Delta S°'/d\Delta G°' \quad (7)$$

For the forward reaction, $\alpha_H = 1.1 \pm 0.1$ and $\gamma = 1.4 \pm 0.1$. The quantity $Td\Delta S°'/d\Delta G°'$ is only approximately constant at -0.27. Substitution of these values into eq 7 yields $d\Delta G^{\neq}_f/d\Delta G°' = 1.1 + 0.1 = 1.2$, which is the result obtained from Figure 1.

Thus, it is shown that for this reaction series, a linear free energy and a linear enthalpy relation are interchangeable because the term $d\Delta S^{\neq} - \alpha_H d\Delta S°'$ is small. As a consequence, if one begins with the definition $\alpha_H = d\Delta H^{\neq}/d\Delta H°'$, a linear free energy relation necessarily results. If on the other hand, the Brønsted coefficient is defined as $\alpha_G = d\Delta G^{\neq}/d\Delta G°'$, the linearity between enthalpies necessarily results. It is not possible to determine which is the more fundamental relationship[21] (*i.e.*, the "beginning point" of a molecular interpretation of the Brønsted relation). But we wish to raise the question: are potential energy curves indeed more closely approximated by enthalpy or are the present results simply a special case? A

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detailed examination of this question will require data as a function of temperature so that comparisons similar to those made here can be made. Other work involving LFE relationships has been done[22] as a function of temperature, but the investigators apparently did not address themselves to this question, nor do their data readily lend themselves to analysis in this manner.

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Homogeneous Electron-Transfer Reactions of Several Aromatic Anion and Cation Radicals

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Abstract: The homogeneous electron-transfer reaction between aromatic molecules and their anion or cation radicals represents one of the simplest possible cases of electron transfer. Although this reaction results in no net chemical change, the rate may be measured by magnetic resonance techniques. This study reports the development of a technique which utilizes *in situ* radical ion generation by electrochemical methods in order to produce radical ion–parent mixtures which may be studied by electron spin resonance techniques in the fast exchange limit. This technique permitted the first large-scale study of the homogeneous exchange rates of radical cations, and reports rate constants for the exchange reactions of phenothiazine, 10-methylphenothiazine, phenoxazine, phenoxathiin, *N*,*N*-dimethyl-*p*-phenylenediamine, and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine. The effects of substituents upon the exchange rates of several aromatic nitriles were studied; and the effect of solvent variation upon the exchange rate of benzonitrile was determined.

Exchange reactions of all types have long held a fascination for kineticists,[1] and of these electron-exchange reactions have been of especial interest since these processes represent the simplest sort of electron transfer. The publication by Ward and Weissman[2,3] of an electron spin resonance (esr) study of the rate of electron exchange for the naphthalene–sodium naphthalenide system was significant because it presented a measurement technique which did not rely on radioactive tracers and which was applicable to a large number of organic molecules.

The electron-transfer reactions of aromatic anion radicals have been the most extensively studied group since the early work of Ward and Weissman. They have been shown to be influenced by a variety of factors including solvent,[4–6] identity of counterion,[5,6] and the degree of ion pairing between the anion radical and the counterion.[5,6]

Neutral radicals occur far less frequently but rate constants for the electron-transfer reactions of two systems have been obtained. Lown[7a] studied the triphenylmethyl, triphenylmethyl cation electron transfer while Jones and Weissman[7b] examined the effect of counterion and solvent on the reaction of the tris-*p*-nitrophenylmethyl radical with the tris-*p*-nitrophenyl methide anion.

In spite of the large number of cation radicals that have been observed with esr, it is surprising that so few electron-transfer reactions involving this important class of radicals have been reported. Cross reactions between various aromatic hydrocarbons and their cation radicals have been observed by pulse radiolysis.[8] For the well-known stable cation of tetramethyl-*p*-phenylenediamine (Wurster's Blue cation) three separate investigations[9–11] revealed that the electron transfer occurs primarily between the radical and free amine, even if protonated species are also present. Romans, *et al.*,[12] observed the electron-transfer reaction of the tetramethylhydrazine cation radical complexed with the singly charged anion of molecular iodine with parent tetramethylhydrazine.

The reason for the small number of investigations of cation radicals becomes evident if the requirements for the determination of electron-transfer rate constants using esr are examined. Knowledge of both the parent and radical concentration is a necessity, since the rate constant is determined from the change in line shape of the esr spectrum as the parent-to-radical concentration ratio is varied. The radical concentration must also be kept small enough to prevent spin exchange from becoming an appreciable source of spin

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