Triple ion formation in these complexes of **2a**,**b**, which is favored by the glymes and HMPT, is not in general dependent on the strength of complexation of lithium with ligand. It is interesting that, except for diethyl ether, oxygen ligands favor triple ions while tertiary amines with **2b** give rise to tight ion paired species. This difference in complexation behavior could be connected with the fact that a tertiary amine has three organic groups bonded to nitrogen while an ether has two.[34,35]

Experimental Section

The origin, preparation, and manipulation of all compounds used in this work is as described by us previously.[9] NMR equipment was also described before.[9]

Preparation of Solutions of 2b with THF. The reaction vessel consisted of a 10-mL 14/20 round bottom flask with side arm protected by a 2-mm straight bore stopcock. The entire system was dried in a current of argon with flaming. A mixture of triene **1** (1.84 g, 10.4 mmol) with THF-d_8 (2.5 g, 31.3 mmol) was syringed in via the stopcock. The apparatus was cooled to 0 °C and a solution of *tert*-butyllithium in cyclopentane (4.25 mL, 11.48 mmol, 2.7 M) added to **1** over a period of 6 min. The reaction mixture was allowed to warm to room temperature and then stirred for another 10 min. Total volume of the reaction mixture was 8.75 mL, measured by syringe. A 0.4-mL aliquot of the reaction mixture was hydrolyzed with O_2-free water in a test tube protected with a serum cap. Gas chromatography (150 °C) using an Aerograph model 700-A instrument with a column (5ft × 0.25 in.) packed with SE-30 on glass beads showed >99.8% conversion of **1** to **4** + **5**. The stock solution just described was concentrated to 1.19 M by evaporating excess solvent in a current of argon. Final concentration of **2b** was 1.19 M. A 2.0-mL aliquot of this solution was introduced into each of three 10-mm o.d. NMR tubes under argon. These tubes were protected with 2-mm straight bore stopcocks. For 3 equiv of THF per equiv of **2b**, the solution was made up to 3.5 mL with cyclopentane. For samples to contain 4.5 and 6 equiv THF for 1 equiv of **2b**, 0.18, 0.36, and 0.54 mL of THF-d_8, respectively, were added, individually, to the 2.0-mL aliquots of stock solution in three NMR tubes and each sample made up to 3.5 mL with cyclopentane. This produced four samples 0.68 M in **2b** containing 3,4,5, and 6 equiv of THF. NMR samples were degassed using the freeze–thaw cycle and sealed off under vacuum.

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(34) Similar results have been observed for fluorenyllithium: Sinyk, R. M.Sc. Thesis, College of Forestry, Syracuse, NY, 1968.

(35) A referee has suggested that the high concentrations of **2b**·THF used in this work favor the loose ion-pair dimer; dilution would tend to dissociate the latter.

Structure of Moderately Strong Acids in Aqueous Solution

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Abstract: A general hypothesis is made that the undissociated forms of moderately strong acids exist in aqueous solution as ion-pair complexes in equilibrium with covalently bonded structures. This suggestion has been made earlier by others for the specific cases of trifluoroacetic, trichloroacetic, and hydrofluoric acids and the present paper offers photometric evidence that squaric, butynedioic, di- and monochloroacetic, and difluoroacetic acids also exist partly as ion pairs. The general hypothesis is supported by ^{13}C NMR and thermodynamic data in the form of a correlation between the carboxylate carbon-13 resonance displacement and the standard entropy change ΔS°_a accompanying acid dissociation. This correlation is interpreted in terms of a model featuring enhanced solvent structuring around highly polar undissociated ion pairs. The observed correlation parameters predict that those acids with ΔS°_a near −13 and −5 cal mol^{-1} K^{-1} have approximately 50% and 90%, respectively, of their undissociated forms as ion pairs.

Nearly a decade ago we reported[1] the rather surprising result that the undissociated form of squaric acid (1,2-dihydroxycyclobutenedione) formed complexes with two unprotonated acid–base colorimetric indicators, cresol red and 4-phenylazodiphenylamine (PDPA), which are anionic and neutral species, respectively. Each of the complexes had a visible spectrum virtually indistinguishable from that of the protonated indicator species and the affinities of the unprotonated indicators for hydronium and undissociated squaric acid were similar. This discovery had important ramifications for acid–base colorimetry which relies on the assumption that spectral differences between protonated and unprotonated indicator depend solely on the solution pH so that the spectral difference serves as a measure of pH. For squaric acid solutions sufficiently concentrated to contain a significant amount of undissociated squaric acid, the indicator spectrum depends on the concentration of molecular acid as well as on the pH. Since then we have found similar complexes in several other systems and these discoveries have important implications not only for the practice of acid–base colorimetry but also for an understanding of the nature and structure of solute species in aqueous solutions of moderately strong acids.

Each system studied consists of two acid–base conjugate pairs. One pair is to be called the controlling acid or pair because its relatively high analytical concentration controls the solution pH, and the other pair, which is present at much lower concentration, is termed photometric because its UV-visible absorbance is measured and used to monitor the presence of complex species. The complex is between the acidic form of the controlling pair and the basic form of the photometric pair and will be referenced in this paper by the term "acid–base complex". If B and Φ denote general controlling and photometric species, respectively, with electric charge on Φ not designated, then the aqueous equilibria are

$$HB + H_2O = B^- + H_3O^+$$

$$H\Phi + H_2O = \Phi + H_3O^+$$

and an acid–base complex has the nominal formula BHΦ. In ref 1, squaric and oxalic acids were the controlling species while the two colorimetric indicators were the photometric species. Both controlling and photometric acids are moderately strong in the sense suggested by others[2] of having aqueous acid dissociation

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(1) Gelb, R. I.; Schwartz, L. M. *Anal. Chem.* 1972, *44*, 554–559.

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constants in the range $-2 < pK_a < 2$. The presence of an acid–base complex in solution is manifested in either of two equivalent ways. Either (a) the pH as measured colorimetrically with the photometric acid appears lower than that calculated from the controlling acid pK_a determined by some other technique such a pH potentiometry or conductance, or (b) the pK_a of the controlling acid appears to be lower when measured colorimetrically than by other methods. Since these discrepancies do not occur when the controlling acid is weak ($pK_a > 2$), the complexes appear to form only in solutions of moderately strong acids and can be detected only under conditions such that the concentration of controlling conjugate acid is significant relative to the hydronium ion concentration. Discrepancies between results of aqueous pK_a determinations by alternative methods have been noted previously for other moderately strong acids such as trifluoroacetic acid (TFA),[2] trichloroacetic acid (TCA),[2,3] and aromatic sulfonic acids.[3] The authors of these reports have hypothesized the existence of ion pairs formed between the anion and hydronium ion to explain those discrepancies. Also, recent spectroscopic work by Giguère and Turrell[4] provides strong evidence for the existence of the complex $H_3O^+{\cdot}F^-$ as a predominant species in aqueous hydrofluoric acid.[35] In the present article we wish to put forward the idea that a logical connection exists between these ion pairs and acid–base complexes. If the UV–visible spectrum of a complex $BH\Phi$ is virtually indistinguishable from the spectrum of $H\Phi$ where both HB and $H\Phi$ are moderately strong acids, and if moderately strong acids can exist partly as $H_3O^+{\cdot}B^-$ ion pairs in aqueous solution, then it is reasonable to hypothesize that the protonated forms HB and $H\Phi$ exist in solution as $H_3O^+{\cdot}B^-$ and $H_3O^+{\cdot}\Phi$, respectively, and that the acid–base complex has the structure $B{\cdot}H_3O^+{\cdot}\Phi$, which would be a triple ion in cases where Φ as well as B were charged. The similarity of the uv-visible spectrum of $H_3O^+{\cdot}\Phi$ and $B{\cdot}H_3O^+{\cdot}\Phi$ follows because the electronic structure of the Φ moiety is not likely to be perturbed significantly by the presence of B^- "on the other side of" the intervening H_3O^+.

We will support this hypothesis by appeals to structural arguments based both on thermodynamic data and on ^{13}C NMR studies of these acids and other model systems. It is important to note that moderately strong acids have dissociation $\Delta S°$ values abnormally positive compared to $\Delta S°$ values of weak acids. The dissociations of most uncharged weak acids have $\Delta S°$ near -20 to -25 cal mol^{-1} K^{-1} and these substantially negative values can be ascribed primarily to enhanced solvent ordering in the vicinities of H_3O^+ and acid anions.[5] On the other hand, stronger acids have less negative dissociation $\Delta S°$ values and these occasionally approach zero.[6] The extent of solvent ordering around the common dissociated H_3O^+ is certainly the same for both weak and stronger acids and it is unlikely that lesser anion solvation of the stronger acid species accounts for the large differences in observed $\Delta S°$ values. It has been suggested elsewhere repeatedly[5,7] that the anomalously positive entropy changes for stronger acids are a manifestation of enhanced solvation of the undissociated acid species and the existence of ion-pair structures is consistent with this suggestion. Furthermore, independent evidence for the solvation properties of the moderately strong acids can be expected to be found from ^{13}C NMR spectrometry because of the likely sensitivity of the ^{13}C NMR chemical shift to changes in solvation.[8] We anticipated and will demonstrate a correlation between $\Delta S°$ values and chemical shift changes upon acid dissociation.

Photometric Experiments

The technique of colorimetric analysis involves prior estimation of the acidity constant (or proton complexation constant) and species absorptivities of a photometric acid–base system designed to be detectable at low concentration levels so that the presence of this system has negligible effect on the solution pH. Such estimation is generally made from absorbance measurements of solutions containing fixed amounts of the photometric pair and various known concentrations or activities of hydronium ion provided either by a buffer system or a controlling acid. Then absorbance measurements of the photometric pair in other solutions yield the unknown pH values. Inherent in this treatment is the assumption that only free hydronium ions may complex with the basic form of the photometric acid, i.e., that no complexation occurs between this base and any species of controlling acid. When this assumption is violated by the existence of such a complex, colorimetry fails as a method to determine solution pH but appropriate absorbance measurements can yield information about the interfering complex. Although we have described these procedures earlier,[1] we feel that a reiteration here is in order for several reasons. Firstly, while the nomenclature in ref 1 is specific for squaric acid as a controlling acid, we report here experiments using several others and so need a more general formulation. Secondly, our earlier derivation failed to account for the existence of the acid ion pairs hypothesized by Covington et al.[2] and we now feel that these exist and play a crucial role in understanding the nature of moderately strong aqueous acids. Thirdly, in the intervening years we have gained experience with data treatment associated with systems described by complicated model equations and are now able to analyze the experimental data from these photometric experiments with more statistical rigor than previously.

The photometric species consist of the $H\Phi$, Φ conjugate pair, and the acid–base complex. If the analytical concentration is F_Φ, the conservation relationship is

$$F_\Phi = [H\Phi] + [\Phi] + [B{\cdot}H_3O^+{\cdot}\Phi] \tag{1}$$

where, as above, we omit possible charge signs on Φ and on B within the complex. Each species is assumed to have a distinctive molar absorptivity ϵ at a given wavelength. Application of Beer's law to a solution of absorption path length b and containing both controlling and photometric species predicts an absorbance

$$A = \epsilon_{H\Phi}b[H\Phi] + \epsilon_\Phi b[\Phi] + \epsilon_c b[B{\cdot}H_3O^+{\cdot}\Phi] \tag{2}$$

where the subscript c denotes the acid–base complex. A solution containing both controlling and photometric species will be called a complexing solution. The photometric pair is characterized by an acid dissociation constant $K_{a\Phi}$ or by a protonation constant $K_{H\Phi}$

$$K_{a\Phi} = K_{H\Phi}^{-1} = a_H\gamma_\Phi[\Phi]/\gamma_{H\Phi}[H\Phi] \tag{3}$$

where a_H is the hydronium ion activity and γ represent molar activity coefficients. Following Covington et al.,[2] we assume that the dissociation of the controlling acid HB occurs in two equilibrium stages: (a) ionization of covalently bonded HB into the ion pair $H_3O^+{\cdot}B^-$ characterized by the partition constant K_{iB}, and (b) dissociation of the ion pair to free ions characterized by K_{dB}

$$HB + H_2O \overset{K_{iB}}{=} H_3O^+{\cdot}B^- \overset{K_{dB}}{=} H_3O^+ + B^-$$

$$K_{iB} = [H_3O^+{\cdot}B^-]/[HB] \tag{4}$$

Equation 4 assumes equal activity coefficients for the two undissociated forms.

This formulation will assume that the dissociation constant K_{aB} for the controlling acid is measured by pH potentiometry or by some other method that does not distinguish between the undissociated forms and so we write

$$K_{aB} = \frac{\gamma_H\gamma_B[H_3O^+][B^-]}{\gamma_{HB}[HB]_{total}} \tag{5}$$

where

$$[HB]_{total} = [H_3O^+{\cdot}B^-] + [HB] \tag{6}$$

We assume that the acid–base complex forms between the pho-

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Table I. Comparative Results of Three Alternative Calculational Methods Based on Squaric Acid Data of Reference 1

parameter	calculational method	series 1[a]	series 2[a]	series 4[b]
$K_{a\Phi}$	1[c]	0.0563 (±3%)	0.0540 (±3%)	0.144 (±3%)
	2[d]	0.0568 ± 0.0014	0.0541 ± 0.0008	0.168 ± 0.009
	3[d]	0.0569 ± 0.0015	0.0542 ± 0.0008	0.168 ± 0.007
K_c	1	31.8 (±42%)	31.2 (±42%)	10.0 (±42%)
	2	29 ± 7	29.9 ± 3.1	11.9 ± 1.3
	3	29 ± 7	30.2 ± 2.7	11.9 ± 2.8
C_c	1	0.399 (±4%)	0.747 (±4%)	1.171 (±4%)
	2	0.427 ± 0.022	0.795 ± 0.013	1.064 ± 0.054
	3	0.426 ± 0.020	0.795 ± 0.011	1.062 ± 0.115
$C_{H\Phi}$	1	0.534 (±1%)	1.079 (±1%)	1.315 (±1%)
	2	0.545 ± 0.004	1.097 ± 0.006	1.498 ± 0.045
	3	0.545 ± 0.005	1.097 ± 0.006	1.499 ± 0.032
C_Φ	1	0.019 (±0.005)	0.039 (±0.005)	0.014 (±0.005)
	2	0.018 ± 0.002	0.038 (±0.002)	0.014 ± 0.045
	3	0.018 ± 0.002	0.038 (±0.002)	0.014 ± 0.032

[a] Φ = cresol red. [b] Φ = 4-phenylazodiphenylamine. [c] Method 1 uncertainties in parentheses are estimated maximum probable errors detailed in ref 1. [d] The uncertainties of methods 2 and 3 are standard error estimates from nonlinear regression calculations.

tometric base and the ion pair so that the complex formation constant is

$$K_{fc} = \frac{\gamma_c[B\cdot H_3O^+\cdot\Phi]}{\gamma_\Phi\gamma_{HB}[\Phi][H_3O^+\cdot B^-]} \qquad (7)$$

In these equations we are particularly interested in evaluating the parameters K_{fc} and ϵ_c which are characteristic of the acid–base complex and these will be extracted from absorbance measurements made of solutions having known but varying analytical concentrations of controlling acid and fixed, negligibly small, yet unknown F_Φ concentration. We begin to arrange these equations into suitable form for data analysis by combining eq 4 and 6 to express $[H_3O^+\cdot B^-] = K_{iB}[HB]_{total}/(1 + K_{iB})$ and substitute this into eq 7 yielding

$$\frac{K_{fc}K_{iB}}{1 + K_{iB}} = \frac{\gamma_c[B\cdot H_3O^+\cdot\Phi]}{\gamma_\Phi\gamma_{HB}[\Phi][HB]_{total}} \equiv K_c \qquad (8)$$

We notice that K_{iB} and K_{fc} appear only together on the left side of eq 8 which means that colorimetric experiments alone are incapable of determining values for these parameters separately. Ion pair/HB partition and acid–base complex strength have equivalent effects on absorbance behavior. Therefore, we define the pseudo-equilibrium constant K_c which characterizes this combined effect. This K_c is formally the same as that defined in ref 1.

Eliminating $[\Phi]$ and $[B\cdot H_3O^+\cdot\Phi]$ from eq 1 and 2 with the use of eq 3 and 8 and then dividing eq 1 and 2 yields

$$A = \frac{C_{H\Phi} + \dfrac{K_{a\Phi}\gamma_{H\Phi}}{a_H\gamma_\Phi}\left(C_\Phi + \dfrac{K_c\gamma_\Phi\gamma_{HB}}{\gamma_c}C_c[HB]_{total}\right)}{1 + \dfrac{K_{a\Phi}\gamma_{H\Phi}}{a_H\gamma_\Phi}\left(1 + \dfrac{K_c\gamma_\Phi\gamma_{HB}}{\gamma_c}[HB]_{total}\right)} \qquad (9a)$$

where we have replaced the constant products $\epsilon_{H\Phi}bF_\Phi$, $\epsilon_\Phi bF_\Phi$, and $\epsilon_c bF_\Phi$ by $C_{H\Phi}$, C_Φ and C_c, respectively. Further rearrangement then yields the linearization

$$G \equiv \frac{A - C_\Phi + (A - C_H)[a_H\gamma_\Phi/K_{a\Phi}\gamma_{H\Phi}]}{[\gamma_{HB}\gamma_\Phi/\gamma_c][HB]_{total}} = C_cK_c - AK_c \qquad (9b)$$

Except for minor differences in symbolism, eq 9b is the same as the combination of eq 7 and 11 of ref 1 where it is explained how plots of G vs. A data yield straight lines from which K_c and C_c are calculated.

Besides absorbance measurements, eq 9a or 9b requires a number of other quantities: a_H, $K_{a\Phi}$, $C_{H\Phi}$, C_Φ, $[HB]_{total}$, and various activity coefficients. Except for the activity coefficients which are estimated from solute specie dimensions and semiempirical correlations, and a_H and $[HB]_{total}$ which are calculated from F_B, the analytical concentration of controlling species, and from eq 5, these other quantities are determined by means of a calibrating set of measurements made on solutions containing only HCl at various concentrations and the photometric pair at the same fixed analytical concentration F_Φ used above. Absorbance measurements from these calibrating solutions are denoted by A_{cal}. The equations relevant to the calibrating solutions are similar to eq 1 and 2, i.e.,

$$F_\Phi = [H\Phi] + [\Phi]$$

$$A_{cal} = \epsilon_{H\Phi}b[H\Phi] + \epsilon_\Phi b[\Phi]$$

When these are combined with eq 3 to eliminate all species concentrations, the result is

$$A_{cal} = \frac{C_{H\Phi} + [K_{a\Phi}\gamma_{H\Phi}/a_H\gamma_\Phi]C_\Phi}{1 + [K_{a\Phi}\gamma_{H\Phi}/a_H\gamma_\Phi]} \qquad (10a)$$

or, equivalently,

$$(A_{cal} - C_\Phi)^{-1} = ([K_{a\Phi}\gamma_{H\Phi}/a_H\gamma_\Phi] + 1)/(C_{H\Phi} - C_\Phi) \qquad (10b)$$

Equation 10b is the same as the combination of eq 3 and 9 of ref 1.

The parameters K_c and C_c of the acid-base complex of squaric acid with cresol red and PDPA were previously found[1] from the slopes and intercepts of G vs. A least-squares lines according to eq 9b to be called Method 1. Each such calculation required a corresponding calibration line in the form of eq 10b from which the parameters $C_{H\Phi}$ and $K_{a\Phi}$ were evaluated and then substituted into the G expression. In those experiments, the parameter C_Φ was determined from a single absorbance measurement. In the more recent work to be reported here, we abandon this method of data treatment in favor of a nonlinear regression approach. The nonlinear model equations describing absorbance A as a function of the concentration F_B are the set of eq 5, 8, and 9a and activity coefficient correlations. Those describing absorbance A_{cal} vs. F_{HCl} are eq 10a and activity coefficient correlations. The five adjustable parameters to be determined are K_c, C_c, $K_{a\Phi}$, $C_{H\Phi}$, and C_Φ. We notice that all five appear in the A vs. F_B model equations so that it is possible in principle to evaluate these from complexing solution data alone and without the need of calibrating measurements. However, we have decided that all five parameters are insufficiently sensitive to complexing solution data alone and that calibrating measurements serve to establish firm values for $K_{a\Phi}$, $C_{H\Phi}$, and C_Φ. Having made this decision, the question arises whether (a) to determine these three parameters from the calibrating data exclusively and then to regard these as fixed constants when evaluating the remaining K_c and C_c from complexing solution data, Method 2, or (b) to determine all five parameters simultaneously from the collection of both types of data, Method 3. Method 2 carries the intuitive appeal of a calibration procedure

Table II. Summary of Results of Photometric Experiments at 25 °C

		controlling acid			parameter values and standard error estimates[a] by nonlinear regression				
controlling acid, HB	photometric pair, Φ, HΦ	pK_{aB}	method	ref	$K_{a\Phi}$	K_c	C_c	$C_{H\Phi}$	C_Φ
squaric (series 1)[1]	cresol red	0.54	cond.	10, 11	0.569 ± 0.0015	28.8 ± 6.6	0.426 ± 0.020	0.545 ± 0.005	0.018 ± 0.002
squaric (series 2)[1]	cresol red	0.54	cond.	10, 11	0.0542 ± 0.008	30.2 ± 2.7	0.795 ± 0.011	1.097 ± 0.006	0.038 ± 0.002
squaric (series 4)[1][b]	PDPA[b]	0.67	cond.	1	0.169 ± 0.007	11.9 ± 2.8	1.062 ± 0.115	1.499 ± 0.032	0.014 ± 0.004
butynedioic[c]	cresol red[c]	0.459,[d] 1.788[d]	pot.	this work	0.0881 ± 0.0063	6.6*	138*	1.370 ± 0.024	0.073 ± 0.004
trifluoroacetic	cresol red	0.40			0.0561 ± 0.0009	9.6 ± 1.5	1.330 ± 0.047	1.381 ± 0.007	0.046 ± 0.002
		0.50			0.0561 ± 0.0009	10.0 ± 1.3	1.328 ± 0.038	1.381 ± 0.007	0.046 ± 0.002
		0.60			0.0561 ± 0.0009	10.5 ± 1.1	1.326 ± 0.032	1.382 ± 0.007	0.046 ± 0.002
trifluoroacetic	squaric acid	0.40			0.266 ± 0.042	1.6*	0.62*	0.698 ± 0.051	1.342 ± 0.007
		0.50			0.268 ± 0.043	1.8*	0.66*	0.696 ± 0.053	1.341 ± 0.007
		0.60			0.270 ± 0.044	1.9*	0.69*	0.694 ± 0.054	1.341 ± 0.007
trifluoroacetic	picric acid[e]	0.40			0.525 ± 0.012	0.66 ± 0.06	0.0	0.0	1.467 ± 0.005
		0.50			0.525 ± 0.012	0.71 ± 0.05	0.0	0.0	1.467 ± 0.005
		0.60			0.525 ± 0.012	0.75 ± 0.0	0.0	0.0	1.467 ± 0.005
trichloroacetic	cresol red	0.40			0.0561 ± 0.0007	16.2 ± 1.2	1.290 ± 0.019	1.381 ± 0.005	0.050 ± 0.002
		0.50			0.0561 ± 0.0007	15.6 ± 1.1	1.297 ± 0.017	1.381 ± 0.005	0.050 ± 0.002
		0.60			0.0561 ± 0.0007	15.1 ± 0.09	1.303 ± 0.016	1.381 ± 0.005	0.050 ± 0.002
dichloroacetic	cresol red	1.320	pot.	this work	0.0516 ± 0.0013	0.86*	1.48*	1.347 ± 0.015	0.051 ± 0.002
dichloroacetic[f]	cresol red[f]	1.073[g]	pot.	this work	0.0741 ± 0.0013	0.82*	1.40*	1.443 ± 0.011	0.047 ± 0.002
difluoroacetic[h]	cresol red[h]	1.325	pot.	this work	0.0512 ± 0.0006	0.7	(1.286)	1.286 ± 0.006	0.052 ± 0.002
chloroacetic	cresol red	2.865	pot.	12	0.0535 ± 0.0009	0.20*	0.8*	1.145 ± 0.007	0.045 ± 0.002
maleic	cresol red	1.895	pot.	this work	0.0534 ± 0.0011	0.08*	4*	1.145 ± 0.009	0.045 ± 0.003

[a] Entries marked with an asterisk indicate that reliable standard error estimates could not be made. Reliability requires that the residual sum-of-squares approximate a quadratic function of the parameters at the minimum.[13] In these cases this approximation failed at appreciable distances from the minimum and this precluded accurate standard error estimates. [b] All solutions in 17.8% acetone–H_2O in order to dissolve sufficient photometric species. [c] All solutions made up to 0.50 ± 0.07 M ionic strength with KCl. [d] Entries are primary and secondary conditional acid dissociation constants in 0.05 M ionic strength medium. [e] Absorptivities of both picric acid and its acid–base complex are assumed to be zero at 400 nm. [f] All solutions made up to 1.07 ± 0.02 M ionic strength with KCl. [g] Conditional dissociation constants in 1.07 M ionic strength medium. [h] Parameter values estimated from a single solution composition. C_c assumed equal to $C_{H\Phi}$. See Experimental Section.

while Method 3 is statistically preferable because it permits free transmittal of information from each data point to all the parameters. The digital computer program for nonlinear regression described elsewhere[9] offers the convenient option of making the calculations either way and we show in Table I the results obtained both ways, using Series 1, 2, and 4 data reported in ref 1. Method 1 results are also shown for comparison. Clearly, the two nonlinear regressions yield virtually identical results for all parameters in all series. This indicates that $K_{a\Phi}$, $C_{H\Phi}$, and C_Φ have very little dependence on the complexing solution data. Their values are essentially set by the calibrating data. Also we see that the nonlinear regression results agree within the quoted uncertainties with those derived from linear plots. Some differences are expected because different correlations were used for the controlling acid ionic activity coefficients. We conclude that the essential results of these experiments are not dependent on the calculation method and so will, henceforth, report only the results from Method 3 calculations.

Table II summarizes the results of the recent as well as the older experiments. Each experimental series involved photometric measurements of 3–8 calibrating solutions and 3–8 complexing solutions, typically five of each. We have added two photometric pairs, picric acid–picrate and squaric acid–hydrogen squarate, to the others used previously.[1] Each photometric pair was monitored at a particular wavelength so chosen to maximize the absorptivity difference between acidic and basic forms and these were 518, 537, 265, and 400 nm for cresol red, PDPA, squaric acid, and picric acid, respectively. The ion-size parameters used in the Debye–Hückel correlations were taken as follows: 1.2 nm for cresol red anion, PDPA cation, and acid–base complexes formed with cresol red, 0.6 nm for picrate, hydrogen squarate, and haloacetate ions, and 0.9 nm for acid–base complexes of these ions and also for hydronium ion. Two experimental series were done in constant ionic strength media, using specially measured conditional acid dissociation constants and activity coefficients of unity. The thermodynamic dissociation constants of all the controlling acids, except chloroacetic, were remeasured in our laboratory by conductimetry or pH potentiometry. Because our values for the trihaloacetic acids differed somewhat from previous determinations,[2,6] we repeated each calculation over a range of 0.2 pK_{aB} units about our values. These repetitions shown in four series in Table II serve to demonstrate the insensitivity of K_c and C_c to a reasonable uncertainty in pK_{aB}.

We note from Table II that acid–base complexes with cresol red are not only detectable with squaric and butynedioic acids ($K_c \sim 30$ and 12, respectively) but also with tri-, di-, and monochloroacetic acids ($K_c \sim 16$, 0.8, and 0.2, respectively) and with tri- and difluoroacetic acids ($K_c \sim 10$ and 0.7, respectively). Thus, formation of these complexes is not uniquely associated with oxocarbon acids,[14] diprotic acids, or any particular structural feature. Furthermore, the phenomenon is not unique to cresol red as our results show that the other photometric species PDPA, picrate ion, and hydrogen squarate ion also participate in acid–base complexes with moderately strong acids. By comparing the three K_c values of the three photometric bases of cresol red, squaric acid, and picric acid with the common controlling trifluoroacetic acid, we see that these are observed in the ratios of about 10:1.8:0.7, respectively. Referring to eq 8 where K_c is defined, we see that the acid–base complex formation constants K_{fc} involving these three photometric bases must exist in the same approximate ratios. In other words, the affinity of trifluoroacetic acid for the basic form of cresol red is about 5.5 times greater than that of trifluoracetic acid for hydrogen squarate ion which affinity is itself about 2.5 times greater than that of trifluoroacetic acid for picrate ion. If we make the same comparisons of the affinities of hydronium ion for each of these three bases, we note that these are

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Table III. ^{13}C NMR Resonances,[a] C–F Coupling Constants,[b] and Their Uncertainties[c] of Fluoro- and Chloroacetic Acids and Their Conjugate Bases at 30 °C

acid	pK_a	ref	$\delta_0^{(1)}$	$\delta_0^{(2)}$	$\delta_1^{(2)d}$	$\delta_1^{(2)d}$	$^2J_0^{(1)}$	$^1J_0^{(2)}$	$^2J_1^{(1)}$	$^1J_1^{(2)}$
FCH_2CO_2H	2.60	5	173.53 ± 0.02	78.87 ± 0.02	177.22	80.55	22 ± 3	177 ± 3	19 ± 3	179 ± 3
F_2CHCO_2H	1.40	6	167.23 ± 0.03	108.06 ± 0.03	170.80	110.09	28 ± 4	239 ± 4	24 ± 3	246 ± 3
F_3CCO_2H	0.51	6	162.16 ± 0.07	116.17 ± 0.07	163.94	117.45	38 ± 10	287 ± 10	36 ± 3	292 ± 3
$ClCH_2CO_2H$	2.87	5	172.73 ± 0.02	42.22 ± 0.02	175.87	44.98				
Cl_2CHCO_2H	1.25	6	168.98 ± 0.04	65.73 ± 0.04	171.84	65.59				
Cl_3CCO_2H	0.51	6	166.21 ± 0.07	93.07 ± 0.07	167.58	96.21				

[a] Relative to external Me_4Si in ppm. [b] In Hz. [c] Standard error estimates by propagation of variance techniques assuming 0.02 ppm standard deviation in each resonance measurement. [d] ±0.02 ppm estimated standard deviation.

proportional to $K_{a\Phi}^{-1}$ values and observe that the affinity of H_3O^+ for cresol red is 4.8 times greater than that of H_3O^+ for hydrogen squarate ion which is 2.0 times greater than that of H_3O^+ for picrate ion. We believe that these sets of ratios are in remarkable agreement considering the rather substantial experimental uncertainties of the K_c determination. This observation is further evidence that the interactions between photometric bases and undissociated moderately strong acids are similar to those between these bases and hydronium ion. This helps to substantiate the hypothesis[2] that undissociated moderately strong acids exist largely as hydronium–conjugate base ion pairs.

We also notice in Table II that the two parameters C_c and $C_{H\Phi}$, which are proportional to the molar absorptivities of the acid–base complex and photometric acid, respectively, are similar in all experiments except for the dubious case of maleic acid where the existence of the complex is in doubt. Apparently, the absorptivity of the photometric moiety is virtually the same when complexed with the undissociated controlling acid or with H_3O^+. This conclusion is even more apparent when the UV–visible spectra of photometric pairs in HCl solution are compared to the spectra in other controlling acids and found to be virtually indistinguishable as was shown in Figure 1 of ref 1.

Finally, we notice in Table II by observing all the complexes involving cresol red that the pseudoequilibrium constant K_c tends to decrease as the controlling acid strength decreases. The detectability limit for K_c by these experiments seems to occur with controlling acids having pK_a values near 2 or 3. This trend will be interpreted in the Discussion section.

^{13}C NMR Investigations

Reasoning that the complex formation of moderately strong acids might be related to some structural or environmental factors, we made ^{13}C NMR measurements of aqueous solutions of these acids and their anions, as well as of weaker acids which apparently do not undergo complexations. This latter class of acids will serve as a standard of comparison. Another reason for making NMR studies is to investigate the recent suggestion of Bonner et al.[3] that aqueous ion pairs exist between hydronium and trichloroacetate ions with the hydronium situated proximate to the electronegative chlorine atoms. On the other hand, we would expect the hydronium in this complex to be closer to the carboxylate. In any case, ^{13}C NMR resonance displacements of Cl_3CCOOH and related acids upon dissociation should be sensitive to the ion pair structure.

Our experimental and calculational strategies are as follows. The intrinsic chemical shifts for parent acid species will be denoted by the symbol $\delta_0^{(n)}$, where the superscript indicates the nth carbon of the parent acid. Corresponding intrinsic shifts for anionic species are indicated by numerical subscripts. For example, symbols for the intrinsic chemical shifts of carbon 1 of a diprotic acid, monoanion, and dianion are $\delta_0^{(1)}$, $\delta_1^{(1)}$, and $\delta_2^{(1)}$, respectively. These intrinsic shifts are calculated from observed shifts $\delta_{obsd}^{(n)}$ obtained by measuring the ^{13}C NMR spectra of solutions (5% $D_2O–H_2O$) at 30 °C of mono- and diprotic acids (0.2–0.9 F) upon addition of portions of NaOH solutions (0.2–0.9 F) also prepared in 5% D_2O/H_2O. In some cases we also made additions of up to 0.4 F HCl in order to enhance the relative concentrations of protonated species of the stronger acids.

At the rapid exchange limit an observed chemical shift of the nth carbon $\delta_{obsd}^{(n)}$ is the mole-weighted average of the various equilibrating B acid species. In the case of a monoprotic haloacetic acid, only HB and anionic B^- species are present so that $\delta_{obsd}^{(n)}$ is given by

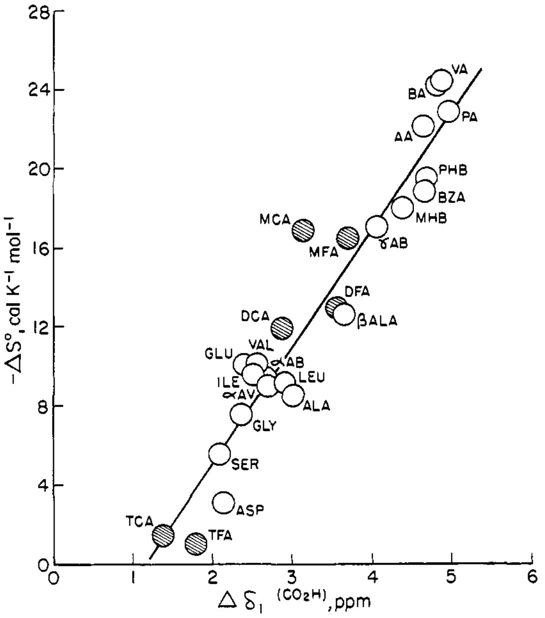

Figure 1. Correlation of entropy changes ($\Delta S°_a$, ordinate) and $^{13}CO_2H$ NMR chemical shift displacements ($\Delta\delta_1^{(1)}$, abscissa) of carboxylic acids undergoing dissociation in aqueous solution (eq 16). Abbreviations of acids' names are defined in Tables V and VI.

$$\delta_{obsd}^{(n)} = (\delta_0^{(n)}[HB] + \delta_1^{(n)}[B^-])/F_B \qquad (11)$$

$\delta_1^{(n)}$ values are obtained directly from measurements of completely neutralized solutions of the acid in which $\delta_{obsd}^{(n)} = \delta_1^{(n)}$. Then $\delta_0^{(n)}$ are obtained from $\delta_{obsd}^{(n)}$ measurements of partially neutralized acid solutions after calculation of HB and B^- species concentrations in these solutions. These calculations are based on the usual conservation and charge balance equations and an equilibrium constant expression

$$K_{aB} = \frac{\gamma_\pm^2[H^+][B^-]}{\gamma_0[HB]} \qquad (12)$$

In spite of the unreliability of the correlation toward higher ionic strengths, we assumed that the mean ionic activity coefficients were given by the Debye–Hückel correlation[12] with temperature-dependent parameters found in the Robinson and Stokes tabulation[12] and a mean ionic radius of 0.7 nm assumed for the ion-size parameter. γ_0 for the uncharged species HB is assumed to be unity. K_{aB} values at 30 °C were taken from references listed in Table III. The calculation requires an iteration beginning with an initial estimate of the solution ionic strength, calculation of the mean ionic activity coefficient from the Debye–Hückel equation, and calculation of species concentrations from eq 12. These concentrations lead to refined estimates of the ionic strengths and thus another iteration. Convergence of this scheme is very rapid. Finally, substitution of species concentrations into eq 11 along with the available $\delta_{obsd}^{(n)}$ and $\delta_1^{(n)}$ values yields $\delta_0^{(n)}$. The results of these calculations and our estimates of the standard

Table IV. ^{13}C NMR Resonances and Their Uncertainties of Diprotic Acids and Their Anions at 30 °C

acid	pK_{a1B}	pK_{a2B}	ref	$\delta_0^{(1)}$, $\delta_0^{(2)}$, $\delta_0^{(3)}$ ^{a,b}	$\Delta\delta_1^{(1)}$, $\Delta\delta_1^{(2)}$, $\Delta\delta_1^{(3)}$ ^{c}	$\Delta\delta_2^{(1)}$, $\Delta\delta_2^{(2)}$, $\Delta\delta_2^{(3)}$ ^{d}	ref
HO_2CCO_2H	1.27	4.28	5	161.80 ± 0.03	4.89 ± 0.04	13.06 ± 0.05	
$HO_2CCH_2CO_2H$	2.86	5.71	5	172.10 ± 0.03, 42.19 ± 0.03	3.92 ± 0.04, −0.45 ± 0.05	6.36 ± 0.05, 6.98 ± 0.05	
				172.13, 42.35		6.36, 6.69	26
$HO_2CCH_2CH_2CO_2H$	4.20	5.64	5	178.09 ± 0.03, 29.95 ± 0.03	2.73 ± 0.04, 2.33 ± 0.04	5.58 ± 0.05, 5.10 ± 0.05	
				178.15, 30.07		5.39, 5.19	26
$HO_2CCH_2CH_2CH_2CO_2H$	4.35	5.42	5	179.02 ± 0.03, 33.91 ± 0.03, 20.69 ± 0.03	2.76 ± 0.04, 2.42 ± 0.04, 1.84 ± 0.04	5.22 ± 0.05, 4.59 ± 0.05, 3.39 ± 0.05	
				179.12, 34.05, 20.80		5.19, 4.46, 3.34	26
$HO_2CCH_2CH_2CH_2CH_2CO_2H$	4.43	5.28	5	179.65 ± 0.03, 34.45 ± 0.03, 24.70 ± 0.03	2.64 ± 0.04, 2.12 ± 0.04, 1.18 ± 0.04	5.21 ± 0.05, 4.13 ± 0.05, 2.27 ± 0.05	
$HO_2CC(H)=C(H)CO_2H$	3.03	4.50	5	169.62 ± 0.03, 135.22 ± 0.03	2.99 ± 0.04, 0.44 ± 0.04	6.12 ± 0.05, 1.01 ± 0.05	
$HO_2CC(H)=C(H)CO_2H$	1.92	6.35	5	170.51 ± 0.03, 131.43 ± 0.03	1.41 ± 0.04, 4.58 ± 0.02	5.95 ± 0.05, 0.02 ± 0.05	
$HO_2CC{\equiv}CCO_2H^e$	0.55	1.78	27	155.87 ± 0.05, 76.56 ± 0.05	1.99 ± 0.08, 0.40 ± 0.08	5.04 ± 0.07, 0.35 ± 0.07	
C(OH)=C(OH)C(=O)C(=O)	0.54	3.48	14	192.81 ± 0.09	4.16 ± 0.09	9.56 ± 0.11	

[a] Resonances are given in ppm relative to external Me_4Si. [b] Standard error estimates are derived assuming standard deviation of 0.02 ppm in each measured resonance. [c] $\Delta\delta_2^{(n)} \equiv \delta_1^{(n)} - \delta_0^{(n)}$. Positive values indicate dowfield displacements upon dissociation of the parent acid to the monoanion. [d] $\Delta\delta_2^{(n)} \equiv \delta_2^{(n)} - \delta_2^{(n)}$. Positive numbers represent the total downfield displacement upon dissociation of the parent acid to the dianion. [e] Both acid dissociation equilibria and ^{13}C NMR measurements were made in 0.5 M ionic strength solutions, using additional KCl.

errors are given in Table III. There we also list the fluorine–carbon coupling constants determined for the series of fluoracetic acids. These are derived by the same calculational procedure described above but with eq 11 replaced by

$$ {}^{m}J_{\text{obsd}}^{(n)} = ({}^{m}J_0^{(n)}[\text{HB}] + {}^{m}J_1^{(n)}[\text{B}^-])/F_{\text{B}} $$

${}^{m}J^{(n)}$ is the m-bond coupling constant of fluorine with the nth carbon atom as derived from splitting of the carbon resonances and the numerical subscripts on J carry the same significance as those on δ.

Intrinsic ^{13}C chemical shift values were determined for a number of dicarboxylic acids by an approach similar to the monocarboxylic acids. The relevant equations are more complicated because of the additional solute species and equilibria. These equations are

$$ \delta_{\text{obsd}}^{(n)} = (\delta_0^{(n)}[\text{H}_2\text{B}] + \delta_1^{(n)}[\text{HB}^-] + \delta_2^{(n)}[\text{B}^{2-}])/F_{\text{B}} \quad (13) $$

$$ K_{\text{a1B}} = \frac{\gamma_\pm^2}{\gamma_0}\frac{[\text{H}^+][\text{HB}^-]}{[\text{H}_2\text{B}]} \quad (14) $$

$$ K_{\text{a2B}} = \frac{\gamma_+\gamma_{2-}}{\gamma_-}\frac{[\text{H}^+][\text{B}^{2-}]}{[\text{HB}^-]} \quad (15) $$

Species concentrations are calculated from eq 14 and 15 together with conservation and charge balance equations, ionic activity coefficient correlations, known values of K_{a1B} and K_{a2B}, and known solution compositions. The intrinsic shifts are then calculated from eq 13 from these concentration $\delta_{\text{obsd}}^{(n)}$ data, using a multiple regression analysis which provides standard error estimates as well. These results are shown in Table IV where in addition to $\delta_0^{(n)}$, the resonance displacements $\Delta\delta_1^{(n)} \equiv \delta_1^{(n)} - \delta_0^{(n)}$ and $\Delta\delta_2^{(n)} \equiv \delta_2^{(n)} - \delta_0^{(n)}$ are listed which result from dissociation of the parent acids to monanions and dianions, respectively. Positive values indicate downfield displacements upon dissociation.

Monocarboxylic Acids. We begin discussion of these results by noting that the general downfield displacement of the carboxylate ion relative to the carboxylic acid carbon resonance found here and elsewhere[15–18] has been the subject of considerable discussion in the past. Hagen and Roberts[15] point to an apparent inconsistency between the deshielding displacement and a decreased carbon electronegativity in the anion compared to the parent acid but they reject an explanation involving an overriding contribution from the second order paramagnetic effect[19] because of the similarities between UV spectra of aqueous acetic acid and acetate anion. Horseley and Sternlicht[16] attribute the downfield displacements of carboxylic and aminocarboxylic acid Cl resonances to polarizations of the neighboring C–H bonds. Quirt et al.[17] suggest on the basis of CNDO/2 calculations that the observed deprotonation deshieldings may be the result of a decrease of the excitation energy of carboxylic carbons which overrides a corresponding increase in electron density via the second-order paramagnetic effect. However, these explanations are based on species charge density calculations in vacuo and as pointed out by Quirt et al.[17] and London et al.[18] the poor agreement between observed and calculated ^{13}C parameters of CO_2H/CO_2^- species results from neglect of solvation changes inherent in the aqueous dissociation process. An alternative explanation for the downfield displacement of $^{13}CO_2H$ resonance with dissociation relies on increased interaction of the solvent water with the carboxylate ion relative to the neutral acid. Increased solvation would serve to disperse electron density toward the solvation sphere and away from the carbon atom and this interaction would cause the observed downfield displacements.

Table V lists the $^{13}CO_2H$ dissociation displacements for a number of alkanoic and benzoic acids at 30 °C as well as the thermodynamic functions $\Delta H°$ and $-T\Delta S°$ for the acid dissociations at 298 K. The small temperature difference here will have no effect on our conclusions because both $\Delta\delta$ and $\Delta S°$ values have very small temperature dependencies in this range. We note that $\Delta\delta_1^{(1)}$ is essentially the same value for these seven acids and also for the nine α,β-unsaturated carboxylic acids reported by Wenkert et al.[20] We attribute this invariancy to the essentially similar

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Table V. Thermodynamic Parameters and ^{13}C NMR Displacements upon Dissociation of Monocarboxylic and Aminocarboxylic Acids

acid						
name	abbrev	$\Delta H^{\circ\,a}$	$-T\Delta S^{\circ\,a}$	ref	$\Delta\delta_1^{(1)\,b}$	ref
monocarboxylic acids	HB^c					
acetic acid	AA	−0.10	6.59	5	4.5	15
					4.66	26
					4.64	28
propionic acid	PA	−0.16	6.82	5	4.7	15
					4.95	26
butyric acid	BA	−0.68	7.24	5	4.7	15
					4.80	26
valeric acid	VA	−0.72	7.30	5	4.7	15
					4.86	26
benzoic acid	BZA	0.10	5.63	5	4.65	28
p-hydroxybenzoic acid	PHB	0.4	5.84	5	4.69	29
m-hydroxybenzoic acid	MHB	0.16	5.39	5	4.64	29
aminocarboxylic acids	$^+H_3NRCO_2H^d$					
glycine	GLY	0.94	2.26	5	2.37	26
		0.98	2.24	30	2.52	17
alanine	ALA	0.62	2.56	5	3.01	26
		0.75	2.44	30	3.15	17
leucine	LEU	0.42	2.74	5	2.9	17
isoleucine	ILE	0.30	2.86	5	2.52	26
valine	VAL	0.08	3.04	5	2.57	26
					2.5	17
serine	SER	1.32	1.67	5	2.1	17
aspartic acid	ASP	1.78	0.92	5	2.14	18
glutamic acid	GLU	−0.06	3.01	5	2.41	18
					2.57	17
α-aminobutyric acid	αAB	0.31	2.80	5	2.67	26
					2.6	18
α-aminovaleric acid	αAV	0.55	2.62	5	2.69	26
β-alanine	βALA	1.06	3.78		3.64	26
γ-aminobutyric acid	γAB	0.40	5.10		4.07	26

[a] kcal mol^{-1} at 298 °K. [b] $\Delta\delta_1^{(1)} \equiv \delta_1^{(1)} - \delta_0^{(1)}$. Positive values indicate downfield displacement. ^{13}C NMR measurements were done at 303 °K. [c] $HB\ (aq) + H_2O(l) = B^-\ (aq) + H_3O^+\ (aq)$. [d] $^+H_3NRCO_2H\ (aq) + H_2O\ (l) = {}^+H_3NRCO_2^-\ (aq) + H_3O^+\ (aq)$.

difference in carboxylate environment due to increased solvation of the anion vs. the neutral acid in all these cases. It appears that resonance, magnetic anisotropy, and polarizing interactions which differ widely among the acids listed in Table V have little or no effect on $\Delta\delta_1^{(1)}$ values. This interpretation is supported by several other observations of deshielding of nuclei at or near the site of ion-forming reactions. These deshielding displacements are 23.6 ppm for ^{17}O in CH_3CO_2H,[21] 20.5 ppm for ^{19}F in HF,[22] about 3 ppm for ^{31}P in H_3PO_4,[23] and about 10 ppm for ^1H in H_2O.[24] Also, the protonation of $CH_3CH_2NH_2$ results in a deshielding displacement of 15 ± 3 ppm[25] in ^{14}N reflecting the increased solvation at the cationic site.

The logical linkage of $\Delta\delta_1^{(1)}$ values with solvation changes leads inescapably to the existence of a correlation between these values and dissociation entropy changes. It has been noted many times[5] that both aqueous acid strengths and ΔS° values reflect primarily the solvent ordering changes induced by ion formation. To further emphasize this fact we have listed ΔH° and $-T\Delta S^\circ$ values in Table V. It is clear that the entropy terms dominate smaller enthalpic differences between the acids. For example, glycinium ion is a stronger acid (ΔG° = 3.20 kcal mol^{-1}) than acetic acid (ΔG° = 6.49 kcal mol^{-1}). The difference in ΔG° of these two disociations is 3.29 kcal mol^{-1} and since the entropic component of this difference is 4.33 kcal mol^{-1} while the enthalpic difference is −1.04 kcal mol^{-1}, it is obvious that the glycinium ion is stronger because of entropy effects. The dissociation of the cationic glycinium ion to H_3O^+ and the strongly dipolar zwitterion results in relatively little net solvent ordering ($-T\Delta S^\circ$ = 2.26 kcal mol^{-1}) in contrast to the greater solvation change accompanying the dissociation of the poorly solvated neutral acetic acid to H_3O^+ and acetate ion ($-T\Delta S^\circ$ = 6.59 kcal mol^{-1}). For the same mechanistic reason, the α-CO_2H group of the glycinium ion is deshielded by only 2.37 ppm upon dissociation compared to 4.6 ppm for acetic acid. Furthermore, it seems that the proximity of the two opposite charges in the aminocarboxylic acid zwitterion influences the solvation environment also. In the series α-glycine, β-alanine, and γ-aminobutyric acid these charges become increasingly separated and the solvent interaction increases accordingly from essentially that of a polar solute toward two separate ionic solutes. Therefore, $-T\Delta S^\circ$ and $\Delta\delta_1^{(1)}$ progressively increase in this series as seen in Table V. A similar trend has been noted for ^{17}O dissociation displacements reported by Valentine et al.[21]

The anticipated correlation between ΔS° vs. $\Delta\delta_1^{(1)}$ reflecting these solvation effects is shown in Figure 1 where 19 entries from Table V are illustrated. The correlation appears to be linear and a least-squares fit is

$$-\Delta S^\circ = (6.0 \pm 0.40)\Delta\delta_1^{(1)} - (7.1 \pm 1.5)\ \text{cal mol}^{-1}\ \text{K}^{-1} \tag{16}$$

where the parameter uncertainties are standard error estimates. The standard deviation of the scatter of the points about the fitted line is about 1.8 cal mol^{-1} K^{-1} which is comparable to the uncertainties in most of the ΔS° measurements. In summary, we conclude that this correlation confirms our hypothesis that $\Delta\delta_1^{(1)}$ and ΔS° values primarily represent manifestations of a common physical phenomenon, the solvation differences between reactants and products in acid dissociation reactions.

We may now analyze the ^{13}C NMR and thermodynamic properties of the haloacetic acids which are of particular interest here. The relevant data appear in Table VI. The well-known trend of increasing acid strength with further halogenation may be attributed primarily to solvation properties which stem from

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Table VI. Thermodynamic Parameters and ^{13}C NMR Resonance Displacements for Aqueous Haloacetic Acid Dissociations

acid					
formula	abbrev	$\Delta H^{\circ a}$	$-T\Delta S^{\circ a}$	ref	$\Delta\delta_1^{(1)b,c}$
FCH_2CO_2H	MFA	−1.39	4.92	5	3.69 ± 0.04
F_2CHCO_2H	DFA	−2.0	3.9	6	3.57 ± 0.04
F_3CCO_2H	TFA	0.4	0.3	6	1.78 ± 0.09
$ClCH_2CO_2H$	MCA	−1.14	5.04	5	3.14 ± 0.04
Cl_2CHCO_2H	DCA	−1.9	3.6	6	2.86 ± 0.06
Cl_3CCO_2H	TCA	0.28	0.42	6	1.37 ± 0.09

[a] kcal mol^{-1} at 298 °K. [b] $\Delta\delta_1^{(1)} \equiv \delta_1^{(1)} - \delta_0^{(1)}$. Positive values indicate downfield displacements. Measurements done at 303 °K. [c] Uncertainties are standard error estimates based on 0.02 ppm standard deviation of the resonance measurements.

the dominance of the $-T\Delta S°$ terms. Furthermore, the relationship of $\Delta S°$ to $\Delta\delta_1^{(1)}$ for these acids appears to conform to the correlation of Figure 1 (corresponding data points are denoted by shaded circles) and so we conclude that both $\Delta S°$ and $\Delta\delta_1^{(1)}$ values reflect the extent of differential solvation between parent acids and anionic species in these systems. Thus, the relatively small values of $-T\Delta S°$ and $\Delta\delta_1^{(1)}$ observed for the trihalo acids reflect either increased solvation of the parent acids or decreased solvation of the anions. This latter effect is conceivably due to dispersion of the carboxylate negative charge to the halogen atoms. However, we believe that anion solvation differences alone cannot account for these observations and ascribe the trends to substantially increased solvation of the parent acids with increasing halogenation. This view is supported by the fact that F–C coupling constants in the fluoroacetic acids are essentially identical in the parent acids and anions. Any substantial change in charge delocalization by fluorine atoms in the anions relative to the neutral acids would be expected to cause corresponding changes in the one- and two-bond coupling constants upon dissociation. These changes are not observed in the measurements shown in Table III.

Bonner et al.[3] have recently suggested that aqueous molecular trichloroacetic acid exists as an ionized yet undissociated structure. Their hypothesized ion pair has the form $H_3O^+{\cdot}Cl_3CCO_2^-$ with direct proximal interaction between the three chloro substituents and the hydronium ion. In view of the marked similarities of both $\Delta S°$ and $\Delta\delta_1^{(1)}$ values of chloro- and fluoroacetic acids and the nearly identical F–C coupling constants in the fluoroacetic acids and their anions, it is unlikely that either of these haloacetic acid series features direct hydronium–halogen interactions. It is noteworthy, however, that the ionized yet associated form of trichloroacetic acid suggested by Bonner et al.[3] would be highly solvated, thus accounting for the observed small values of $-T\Delta S°$ and $\Delta\delta_1^{(1)}$ for the trisubstituted acids. In the following discussion it will be shown that the phenomenon of enhanced solvation of undissociated acid solutes is not unique to the haloacetic acids and occurs for structures incapable of forming complexes analogous to the hydronium–trichloromethyl adduct.

Diprotic Acids. Table VII compares $\Delta\delta_1^{(1)}$, $\Delta\delta_2^{(1)}$, and entropy changes for the dissociation of nine diprotic acids. The analysis of these data is complicated by a number of factors which seem to preclude simple correlations. These are a consequence of the chemical equivalence of two carboxylic acid groups per molecule so that $\Delta\delta_1^{(1)}$ is an average displacement of two $^{13}CO_2H$ groups upon dissociation of a single proton. Thus, a given $\Delta\delta_1^{(1)}$ measurement represents both one $^{13}CO_2H$ displacement due to dissociation and a second $^{13}CO_2H$ displacement due to interaction with the newly formed carboxylate. Similarly, a given $\Delta\delta_2^{(1)}$ value represents both displacement due to dissociation of two protons and to the interaction between the carboxylates formed. In spite of these complications, a qualitative discussion is possible based on the fact that carboxylic acid groups in the series of *n*-alkanedioic acids become essentially isolated from each other with increasing chain length and interactions between carboxylic groups on the same molecule become negligible. From Table V the displacement due to dissociation of long-chain alkanoic acids appears to be approaching 5 ppm and thus for an *n*-alkanedioic acid of sufficient length, $\Delta\delta_1^{(1)}$ is expected to be near 2.5 ppm, the average of one dissociating group and one group not dissociating. $\Delta\delta_2^{(1)}$ for this same acid reflects both groups dissociating and so should be near 5 ppm. The net ^{13}C NMR resonance displacement due to the secondary dissociation is $\delta_2 - \delta_1$ and it is convenient to define the ratio $r_\delta \equiv (\delta_1 - \delta_0)/(\delta_2 - \delta_1) = \Delta\delta_1/(\Delta\delta_2 - \Delta\delta_1)$ which is the ratio of net displacement upon primary dissociation to net displacement upon secondary dissociation. This ratio is unity both when there is negligible interaction between carboxylic acid groups and when the interaction between these groups changes equally with each dissociation. Those diprotic acids for which the ratio r_δ is near unity will be called "normal" and those acids which exhibit r_δ deviating from unity will be termed "abnormal" in the sense that the relevant carbon interaction changes are unequal for the two dissociations.

The entropy changes $\Delta S°_1$ and $\Delta S°_2$ for the primary and secondary dissociations, respectively, have two principal components. Each $\Delta S°$ reflects solvent structural changes about a dissociating carboxylic acid group and also the symmetry changes of the solute species due to dissociation. For a sufficiently lengthy dicarboxylic acid, the solvent structural changes about essentially isolated carboxylic groups become equal but the symmetry component of $\Delta S°$ of the primary dissociation differs from that of the secondary dissociation by the well-known $R \ln 4 = 2.8$ cal mol^{-1} K^{-1}. Thus, as the chain length increases, $\Delta S°_1$ approaches a fixed value characteristic of the solvent structural change about a single carboxylic group, and $\Delta S°_2$ approaches that same value less 2.8 cal mol^{-1} K^{-1}.

In Table VII we see that succinic, glutaric, adipic, and fumaric acids have r_δ ratios within experimental uncertainty of unity. The occurrence of the unsaturated fumaric acid in this list of "normal" acids suggests that the *trans*-vinylene group does not complicate the interactions between the carboxylate terminals and so the primary and secondary dissociation displacements are approximately equal. However, we see that oxalic, malonic, and maleic acids are "abnormal" and this is consistent with well-known chemical factors. Oxalic and maleic acids both feature proximal CO_2H groups capable of strong intramolecular hydrogen bonding in both molecular and monoanionic forms and there is no reason

Table VII. Standard Entropy Changes and ^{13}C NMR Displacements for Dissociations of Aqueous Dicarboxylic Acids

acid	$-\Delta S°_1{}^a$	$-\Delta S°_2{}^a$	ref	$\Delta\delta_1^{(1)b}$	$\Delta\delta_2^{(1)b}$	$r_\delta{}^c$	ref
oxalic acid	9.2	24.8	5	4.89 ± 0.04	13.06 ± 0.05	0.60 ± 0.01	
malonic acid	13.0	29.1	5	3.02 ± 0.04	6.36 ± 0.05	1.61 ± 0.03	
					6.36		26
succinic acid	16.7	25.7	5	2.73 ± 0.04	5.58 ± 0.05	0.96 ± 0.02	
					5.39		26
glutaric acid	20.3	26.7	5	2.76 ± 0.04	5.22 ± 0.05	1.12 ± 0.03	
					5.19		26
adipic acid	21.5	26.9	5	2.64 ± 0.04	5.21 ± 0.05	1.03 ± 0.03	
fumaric acid	13.8	23.3	5	2.99 ± 0.04	6.12 ± 0.05	0.95 ± 0.02	
maleic acid	8.5	31.8	5	1.41 ± 0.04	5.95 ± 0.05	0.31 ± 0.01	
butynedioic acid	−0.6	19.3	27	1.99 ± 0.08	5.04 ± 0.07	0.65 ± 0.04	
squaric acid	7.5	26	14	4.16 ± 0.09	9.56 ± 0.11	0.77 ± 0.03	

[a] cal mol^{-1} K^{-1} at 298 °K. [b] Uncertainties are standard error estimates. [c] $r_\delta \equiv (\delta_1 - \delta_0)/(\delta_2 - \delta_1)$.

to expect the changes in intramolecular bonding to be the same for each dissociation. Malonic acid may also form an internally bonded structure in the monoanion but seems unlikely to do so in the parent acid. The involvement of both carboxylic groups in a cyclic monoanion is probably responsible for the large value observed for $\Delta\delta_1^{(1)}$ relative to the other longer chain dicarboxylic acids. We have observed a negative value $\Delta\delta_1^{(2)} = -0.45$ ppm for the resonance displacement of the methylene carbon upon primary dissociation of malonic acid, and this supports the hypothesis of a cyclic monoanion since methylene carbons are generally shielded upon cyclization.[31]

Another "abnormal" acid, butynedioic acid, with $r_\delta = 0.65$ does not seem capable of intramolecular hydrogen bonding in the molecular or anionic forms. Neither is the abnormal interaction likely to be a resonance interaction because fumaric acid, which is structurally similar, has a normal r_δ value. The observed small $r_\delta = 0.65$ and the very positive $\Delta S°_1 = 0.6$ cal mol^{-1} K^{-1} [27] lead us to the conclusion that the loss of a proton from the neutral butynedioic acid molecule causes little environmental change for the CO_2H groups and in turn that this stems from a neutral acid molecule which is highly solvated even before loss of a proton.

Squaric acid also is "abnormal" with $r_\delta = 0.77$ but the observed displacements are difficult to interpret because four equivalent carbons are involved in all squaric acid species and both the parent acid and the monoanion are capable of intramolecular hydrogen bonding. However, it appears likely that the small R_δ value is related to a high degree of solvation in the neutral squaric acid species.

Discussion

The spectrophotometric study of acid–base complexes and ^{13}C NMR measurements of moderately strong acid systems reported here serve to strengthen the hypothesis that ion-pair forms exist in aqueous solution between hydronium ion and the conjugate bases. This work, therefore, complements the vibrational spectroscopic evidence presented earlier by Covington et al.,[2] Bonner and Prichard,[3] and Giguère and Turrell[4] in support of the ion-pairing hypothesis in several particular acid systems.[35] We can summarize our results by the general observation that moderately strong conjugate acids tend to form acid–base complexes with conjugate bases of other moderately strong acids and these complexes can be readily detected photometrically when absorption spectral differences are favorable.

The measured spectral properties of these complexes are remarkably similar to those of the protonated forms of the conjugate bases. Furthermore, we have observed that moderately strong acids exhibit abnormally small ^{13}C NMR $\Delta\delta_1^{(1)}$ values and these correlate well with abnormally small negative values of $\Delta S°_1$. All these factors strongly suggest that the undissociated forms of these acids exist largely as ion pairs. Compared to weaker acids, the dissociation of these ion pairs causes a minimal change in the environment of ^{13}C nuclei and in the structuring of solvent molecules around the solute species, thus explaining the observed correlation.

The hypothesis of aqueous acid ion pairing would be significantly strengthened if direct measurement could be made of the equilibrium constants K_i and K_d of the two-step dissociation process

$$HB + H_2O \overset{K_i}{=} H_3O^+\cdot B^- \qquad (17)$$

$$H_3O^+\cdot B^- \overset{K_d}{=} H_3O^+ + B^- \qquad (18)$$

But we note, as did the earlier proponents of aqueous acid ion pairing, that these parameters are difficult to measure. Any technique which cannot distinguish between undissociated forms HB and $H_3O^+\cdot B^-$ yields an apparent acidity constant[2]

$$K_a = K_d K_i/(1 + K_i) \qquad (19)$$

Thus, a measurement of either K_i or K_d suffices to determine both if K_a is also known.

Because of the partition described by eq 4, the apparent dissociation of moderately strong acids is a composite reaction involving $1/(1 + K_i)$ moles of HB and $K_i/(1 + K_i)$ moles of $H_3O^+\cdot B^-$ producing 1 mol each of B^- and H_3O^+. Thus any intensive property X having changes ΔX_i, ΔX_d, and ΔX_a associated with eq 17, 18, and the composite reaction, respectively, can be shown by stoichiometry to yield the relationship $\Delta X_a = [1/(1 + K_i)]\Delta X_i + \Delta X_d$. In particular, where X is regarded as $\delta_1^{(1)}$, the chemical shift of a ^{13}C NMR resonance of the carboxylate carbon, this becomes

$$\Delta\delta_1^{(1)} = \left(\frac{1}{1 + K_i}\right)\Delta\delta_i^{(1)} + \Delta\delta_d^{(1)} \qquad (20)$$

and when X is the standard entropy change

$$\Delta S°_a = \left(\frac{1}{1 + K_i}\right)\Delta S°_i + \Delta S°_d \qquad (21)$$

Equation 21 and the corresponding expression for enthalpy also follow by applying van't Hoff-type transformations to eq 19.

We will now show that by making reasonable assumptions about the two-step dissociation we can arrive at a roughly quantitative confirmation of the observed correlation between $\Delta S°$ and $\Delta\delta_1^{(1)}$ embodied in eq 16. These assumptions are (i) that the values of $\Delta S°_d$ and $\Delta\delta_d^{(1)}$ are constants, i.e., independent of the structure of B^-, (ii) that $\Delta S°_d$ may be approximately evaluated by using Bjerrum's electrostatic theory of ionic association,[32] (iii) that those weak acids with $\Delta S°_a$ in the range $22 < -\Delta S°_a < 24$ cal mol K^{-1} have K_i essentially zero, and (iv) that the value of $\Delta\delta_d^{(1)}$ is a small part of $\Delta\delta_1^{(1)}$. The latter assumption seems reasonable since dissociation of a solvated ion pair would be expected to cause only a minor fraction of the total change in the environment of the Cl nucleus upon complete dissociation of a covalent bond.

We begin by solving eq 20 for the coefficient $1/(1 + K_i)$. Substituting this into eq 21 yields

$$\Delta S°_a = \left(\frac{\Delta S°_i}{\Delta\delta_i^{(1)}}\right)(\Delta\delta_1^{(1)} - \Delta\delta_d^{(1)}) + \Delta S°_d \qquad (22)$$

which implies a linear relationship between $\Delta S°_a$ and $\Delta\delta_1^{(1)}$ if $\Delta S°_i/\Delta\delta_i^{(1)}$ is uncorrelated with $\Delta\delta_1^{(1)}$ and if $\Delta\delta_d^{(1)}$ and $\Delta S°_d$ are also uncorrelated with $\Delta\delta_1^{(1)}$ or are small. With the aid of our assumptions we will make approximate estimates of the parameters in this equation. Firstly, we employ assumptions i, iii, and iv along with the data for a typical weak acid to estimate $\Delta\delta_i^{(1)}$. A typical weak acid, propionic acid, has $\Delta\delta_1^{(1)} = 4.7$ ppm,[15] and utilizing eq 20 and assumption iii we arrive at $\Delta\delta_i^{(1)} \simeq 4.7 - \Delta\delta_d^{(1)}$. Assumption iv implies $\Delta\delta_d^{(1)} < \sim 2$ ppm or, equivalently, $\Delta\delta_d^{(1)} \simeq 1 \pm 1$ ppm. Hence, we estimate $\Delta\delta_i^{(1)}$ to be 4 ± 1 ppm. Assumption iii again leads to $\Delta S°_i \simeq -23 - \Delta S°_d$ for this same weak acid. Our theoretical prediction of $\Delta S°_d$ based on Bjerrum's[32] electrostatic model is $\Delta S°_d = -19.3/a$ cal mol^{-1} K^{-1}, where a is an effective distance in angstroms between ionic charges in the ion pair. Since all ion pairs here involve hydronium ions and carboxylate ions with diameters in the range 5–7 Å, we will assume $a \simeq 7$ Å, which value is a typical "distance of closest approach" used in the Debye–Hückel ionic activity coefficient correlation. This assumption implies $\Delta S°_d \simeq -3$ cal mol^{-1} K^{-1} and $\Delta S°_i \simeq -20$ cal mol^{-1} K^{-1}. Consequently, with $\Delta\delta_i^{(1)} \simeq 4 \pm 1$ ppm we estimate the ratio $\Delta S°_i/\Delta\delta_i^{(1)}$ in eq 22 to be in the range 4–5 cal mol^{-1} K^{-1} ppm^{-1}. This estimate is in satisfactory agreement with the observed slope of 6.0 ± 0.4 cal mol^{-1} K^{-1} ppm^{-1} in eq 16. The

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observed linearity of the plot in Figure 1 is evidence that the ratio $\Delta S^\circ_i/\Delta\delta_i^{(1)}$ is, indeed, uncorrelated with $\Delta\delta_1^{(1)}$ or ΔS°_a. This is not unreasonable since both ΔS°_i and $\Delta\delta_i^{(1)}$ depend largely on the enhanced solvation of the ion pair over the covalently bonded acid species and approximate proportionality of both ΔS°_i and $\Delta\delta_i^{(1)}$ to this enhancement is possible.

An important ramification of the exercise of the previous paragraph is that the two-step dissociation process provides a meaningful mechanism for understanding the ^{13}C NMR and entropy of dissociation data for weak as well as moderately strong acids in aqueous solution. This is not meant to imply that a significant proportion of undissociated weak acid exists as the $H_3O^+{\cdot}B^-$ species, but that the two-step dissociation serves as a useful framework for all acidic dissociations. Thus, $H_3O^+{\cdot}B^-$ is a real species for moderately strong acids but must be regarded as a virtual intermediate state for weaker acids. If our rough estimates of ΔS°_i and ΔS°_d, about −20 and −3 cal mol^{-1} K^{-1}, respectively, are correct, then eq 21 implies that those moderately strong acids with small $|\Delta S^\circ_a|$ are likely to exist primarily as $H_3O^+{\cdot}B^-$. For example, $\Delta S^\circ_a = -13$ cal mol^{-1} K^{-1} implies $K_i \simeq 1$, half the undissociated acid as ion pairs, and $\Delta S^\circ_a = -5$ cal mol^{-1} K^{-1} implies $K_i \simeq 9$, 90% of the undissociated acid as ion pairs. Small $|\Delta S^\circ_a|$ values such as these reflect the fact that little solvent reorganization occurs upon dissociation of acid species which are largely solvated ion pairs. In particular, this class of acids includes not only trifluoro- and trichloroacetic acids but also the photometric acids squaric acid ($\Delta S^\circ_1 = -7.5$ cal mol^{-1} K^{-1}),[14] picric acid ($\Delta S^\circ_a = -6$ cal mol^{-1} K^{-1}),[5] and cresol red ($\Delta S^\circ_a = -2.3 \pm 0.4$ cal mol^{-1} K^{-1} and $\Delta H^\circ_a = 1.1 \pm 0.1$ kcal mol^{-1}, measured in this laboratory by temperature dependence of K_a between 15 and 35 °C). That these photometric acids exist primarily as ion pairs helps explain the observations made earlier in the section on Photometric Experiments where it was shown that the ratios of K_c and K_{fc} with trifluoroacetic acid paralleled the ratios of $K_{a\Phi}^{-1}$. The constants $K_{a\Phi}$ are related to the microscopic constants $K_{i\Phi}$ and $K_{d\Phi}$ by eq 19 and if $K_{i\Phi}$ are large, then it must follow that $K_{a\Phi}^{-1} \simeq K_{d\Phi}^{-1}$. Thus $K_{a\Phi}^{-1}$ essentially represent ion association equilibria between a given Φ^- and H_3O^+ and these values would be expected to parallel K_{fc} which represents an ion pairing of Φ^- with $H_3O^+{\cdot}B^-$, itself consisting of hydrated proton with a B^- in the outer solvation sphere.

Extension of these arguments helps explain the observed trend of decreasing K_c with decreasing controlling acid strength and why acid–base complexes are not observed with weak controlling acids. Weaker acids are characterized by more negative ΔS°_a and smaller K_{iB} values and so, according to eq 8, K_c vanishes as K_{iB} vanishes. In other words, weak controlling acids which do not form ion pairs do not form acid–base complexes with photometric bases.

In conclusion, we mention one further logical extension of the phenomenon of ion pairing in moderately strong acids. If $H_3O^+{\cdot}B^-$ forms acid–base complexes with the conjugate base Φ^- of another moderately strong acid, then it must follow that $H_3O^+{\cdot}B^-$ is capable of forming an acid–base complex with its own conjugate base B^-. The resulting triple ion would be expected to be observable only in solutions of moderately strong acids which are sufficiently concentrated to contain significant amounts of both the anion and the undissociated acid. Experiments are underway in this laboratory to search for this species in squaric acid.

Experimental Section

All materials were of the best reagent grade available and were used without further purification. Solutions of acids were standardized with NaOH to a phenolphthalein end point at least with duplicate and usually with triplicate samples. The results of these assays were always reproducible to ±0.5% or better, and in the case of solid acids where samples could be readily weighed, experimental equivalent weights agreed with theory to within 0.5% or less.

pH potentiometric experiments employed an Orion Model 801 pH meter equipped with conventional glass and reference electrodes and believed reproducible to ±0.002 pH units. The meter was standardized prior to each use with a 0.1 F HCl solution. The pH value of this standard was taken as 1.084 at 25 °C, a value which is consistent with the hydrogen ion activity calculated by an extended form of the Debye–Hückel correlation with $a = 0.9$ nm for the H_3O^+ species.[33] All solutions were thermostated to within ±0.1 °C of the set temperature.

^{13}C NMR measurements employed a Varian CFT 20 Fourier transform nuclear magnetic resonance spectrometer equipped with a 10 mm sample tube. The sample compartment was maintained at 30 ± 2 °C. Sample solutions which contained 5% D_2O (v/v) were allowed to equilibrate for a few minutes before data acquisition (typically 10 000 transients, 30° tip angle, and a 1–2 s repetition rate). The system resolution was 0.02 ppm. Measurements of fluoroacetic acid solutions were made with a Bruker HX-270 spectrometer operating at 67.89 MHz for ^{13}C observation. Sample solutions contained 5% v/v D_2O and were maintained at 30 ± 1 °C. Instrument settings were similar to those reported in an earlier publication.[34] Spectrophotometric measurements employed a Beckman Acta CIII UV–visible spectrometer with thermostated sample holder. Slits were adjusted for a 1 nm band pass. The same matched 1.00 cm reference and sample cuvettes were employed for each series of measurements and a distilled water blank was used throughout.

Solutions of controlling acids at the appropriate concentrations were checked for residual absorbance and these were uniformly negligible (≤0.001) except in the case of trichloroacetic acid where a slight turbidity gave an absorbance of 0.01 in the most concentrated solution. Subsequent data were appropriately corrected for the blank.

In one series of experiments, the pH value of a difluoroacetic acid solution containing a small amount of cresol red was determined by direct potentiometric measurement. A second solution of HCl and identical cresol red concentration was prepared to match the measured pH. Repeated measurement with portions of the two solutions indicated that no pH difference could be detected by pH potentiometry. Measurements of the absorbances indicated that the difluoroacetic acid solution had an apparent H_3O^+ activity about 10% larger than that of the HCl solution. This discrepancy along with the assumption that $C_c = C_{H\Phi}$ allowed estimation of K_c. Similar experiments with $HClO_4$ and HCl showed no detectable discrepancy between potentiometric and spectrophotometric results.

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