chromatographed on alumina. The appropriate fractions were combined and recrystallized from benzene-methanol to give 50 mg (0.8%) of white crystals, mp 128–133° (lit.[9] mp 140°).

Anal. Calcd for $C_{20}H_{13}Cl$: C, 83.18; H, 4.54. Found: C, 83.26; H, 4.50.

The compound showed in the infrared strong aromatic bands at 738 and 752 cm^{-1} (*ortho*-disubstituted benzene) and 895 cm^{-1} (pentasubstituted benzene). The ring-halogen band appeared at 1054 cm^{-1}. The ultraviolet spectrum matched that reported in the literature.[9]

1-Phenyl-5-methoxynaphthalene (8). In the same manner as that used to prepare 1-(*o*-chlorophenyl)-5-methoxy-3,4-dihydronaphthalene, **1-phenyl-5-methoxy-3,4-dihydronaphthalene**, bp 145–150° (0.05 mm), was prepared in 74% yield from phenylmagnesium bromide and 5-methoxytetralone. Dehydrogenation with sulfur as before followed by recrystallization from methanol gave **1-phenyl-5-methoxynaphthalene,** mp 80–83°, in 68° yield. An analytical sample, mp 82–83°, was prepared by recrystallization from hexane.

Anal. Calcd for $C_{17}H_{14}O$: C, 87.14; H, 6.02. Found: C, 87.04; H, 5.99.

The infrared spectrum showed strong peaks at 706, 766, and 784 cm^{-1} (1,5-disubstituted naphthalene and monosubstituted benzene) and 1086 and 1233 cm^{-1} (aromatic ether). The ultraviolet spectrum in ethanol displayed peaks at 219 $m\mu$ (log ϵ 4.62), 235 (4.52), 299 (3.99), 309 sh (3.94), 314 sh (3.89), and 323 (3.78).

3-Methoxyfluoranthene (9). A solution of 200 mg of **6** in 100 ml of methanol was irradiated with 254-$m\mu$ light for 18 hr. The brilliantly fluorescent solution was evaporated and chromatographed on alumina. The yellow, fluorescent fractions were combined, evaporated, and recrystallized from methanol to give 95 mg of **3-methoxyfluoranthene** as lemon-yellow plates, mp 160–161° (lit.[37] mp 156°). The ultraviolet spectrum in methanol matched that reported in the literature.[37]

5-Methoxy-1-(2-biphenylyl)naphthalene (10). Using the same method as for the preparation of 1-(2-biphenylyl)naphthalene,[11] **5-methoxy-1-(2-biphenylyl)-3,4-dihydronaphthalene** was prepared in 88% yield from 2-biphenylyllithium and 5-methoxynaphthalene. Dehydrogenation with sulfur at 250–280° followed by chromatography on alumina gave a very intractable oil. This finally crystallized from ethanol to give a 55% yield of **5-methoxy-(4-biphenylyl)naphthalene,** mp 98–99°.

Anal. Calcd for $C_{23}H_{18}O$: C, 88.99; H, 5.84. Found: C, 88.82; H, 5.75.

The infrared spectrum showed strong peaks at 702, 746, 766, 787, 1080, and 1255 cm^{-1}. The ultraviolet spectrum in ethanol displayed peaks at 223 $m\mu$ sh (log ϵ 4.70), 234 sh (4.65), 290 sh (3.88), 301 (3.97), 310 sh (3.92), and 324 (3.74).

1-(*o*-Acetoxyphenyl)naphthalene. To 1.4 g of **1-(*o*-hydroxyphenyl)naphthalene**[14] in 1 ml of acetic anhydride was added 1 drop of concentrated sulfuric acid. The solution became warm, and after 5 min, it was heated gently on a steam bath for an additional 5 min. The solution was poured into water and extracted with ether-benzene. The organic layer was dried, concentrated, and distilled at reduced pressure to give 1.1 g (67%) of 1-(*o*-acetoxyphenyl)naphthalene as a thick, uncrystallizable oil, bp 126–135° (0.1 mm).

Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.40; H, 5.35.

The compound showed strong aromatic peaks in the infrared (neat oil) at 758 cm^{-1} (*ortho*-disubstituted benzene) and 780 and 804 cm^{-1} (1-substituted naphthalene). The acetoxy group absorbed at 1765, 1365, and near 1200 cm^{-1}.

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The Entropies of Dissociation of Some Moderately Strong Acids

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Abstract: The dissociation constants of seven moderately strong ($0.5 < \mathrm{p}K_a < 1.4$) uncharged acids have been measured as a function of temperature. The acids were chosen to serve as models for the interpretation of $\Delta S^{\ddagger}$ values derived from rates. A simplified method for the determination of these dissociation constants is shown to give results of more than sufficient accuracy when applied to those few moderately strong acids for which classically determined values exist. The near-zero values of ΔS° measured for the ionization of certain of the acids are discussed from the viewpoints of their implications concerning changes in solvent structure accompanying the activation process in solvolytic reactions and concerning the general use of equilibrium ΔS° values as models for interpreting $\Delta S^{\ddagger}$ values. The parameters found for dissociation at 25° are (given in order for each acid are $\mathrm{p}K_a$, ΔH° in kcal $mole^{-1}$, and ΔS° in cal deg^{-1} $mole^{-1}$): Cl_2FCCO_2H, 0.46, −1.4, −7; F_3CCO_2H, 0.50, 0.4, −1; Cl_3CCO_2H, 0.515, 0.28, −1.4; $^{+}H_3NSO_3^{-}$, 0.998, 0.41, −3.2; $(CO_2H)_2$, 1.30, −0.8, −9; F_2CHCO_2H, 1.34, −2.0, −13; Cl_2CHCO_2H, 1.36, −1.9, −12.

Owing to the difficulties encountered in applying the classical potentiometric, conductometric, and spectrophotometric methods for the precise measurement of $\mathrm{p}K_a$ values to acids with $\mathrm{p}K_a$ less than 2, the standard thermodynamic parameters for ionization of very few such acids have been reported. This is unfortunate in view of the use of acid ionization equilibria as models for the interpretation of thermodynamic parameters for activation, particularly $\Delta S^{\ddagger}$[1–3] and $\Delta C_p^{\ddagger}$.[3] This unavailability of data has required that the values of ΔS° and $\Delta C_p{}^\circ$ for the ionization of weak acids, such as acetic, be compared to values of $\Delta S^{\ddagger}$ and $\Delta C_p^{\ddagger}$ for ionogenic reactions in which the leaving groups are the anions of acids which bear little structural resemblence to the anion of the model acid. Such comparisons invoke the generalization[4] that all ionizations of un-

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(1) L. L. Schaleger and F. A. Long in "Advances in Physical Organic Chemistry," Vol. I, V. Gold, Ed., Academic Press, New York, N. Y., 1963, pp 1–33.

(2) R. E. Robertson, R. L. Heppolette, and J. M. W. Scott, *Can. J. Chem.*, 37, 803 (1959).

(3) K. T. Leffek, R. E. Robertson, and S. Sugamori, *J. Amer. Chem. Soc.*, 87, 2097 (1965).

(4) K. S. Pitzer, *ibid.*, 59, 2365 (1937).

charged acids have standard entropy changes near -22 cal mole^{-1} deg^{-1}; that this generalization may not always be valid is implied by the value of $\Delta S° = -3.9$ cal mole^{-1} deg^{-1} reported[5] for the ionization of HCN at 8°, and by the values of $S°$ tabulated[6] for $H_2Se(aq)$ and $HSe^-(aq)$ which require $\Delta S° = +2$ cal mole^{-1} deg^{-1} for the first ionization of H_2Se at 25°. These values suggest that $\Delta S°$ for the ionization of the structurally similar hydrogen halides may also be significantly less negative than -22 cal mole^{-1} deg^{-1}. (By assuming the entropies of hydration of undissociated hydrogen halides to be similar to those for HCN and H_2S, McCoubrey[7] has estimated the values of $-\Delta S°$ for ionization of HF, HCl, HBr, and HI to be 21, 13, 9, and 3 cal deg^{-1} mole^{-1}.) Of particular interest in relation to the hydrolyses of polyhaloacetate esters which are under investigation in these laboratories is the preliminary report by Jordan[8] that the heats of ionization of trihaloacetic acids are near zero; since estimates of pK_a for these acids lie in the range 0 ± 1, this observation would require that $\Delta S°$ for these ionizations be near zero.

Ambiguities in the extrapolation to infinite dilution from the high ionic strengths required for the measurement of pK_a values in the range 0–2 do prevent the determination of those pK_a's with the same accuracy as is obtainable for weaker acids.[9,10] However, the measurements of King and King[10] on sulfamic acid demonstrate that it is possible to determine the values of pK_a for such acids with sufficient certainty to permit the values of $\Delta H°$ and $\Delta S°$ derived from the temperature dependence of those pK_a's to be used as models for the interpretation of the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ parameters derived from rate data. The present paper reports values of pK_a, $\Delta H°$, and $\Delta S°$ for selected acids whose pK_a values lie between 0.5 and 1.5.

Experimental Section

Reagents. Fisher Certified trichloroacetic acid was used without further purification; samples with two different lot numbers were found to have identical equivalent weights (within 1 ppt) and give identical values for pK_a (within 0.005 pK unit). Mallinckrodt AR oxalic acid·dihydrate was recrystallized twice from deionized water and dried at room temperature *in vacuo*. Fisher Certified sulfamic acid was purified as directed by Butler, Smith, and Audrieth.[11] The best available grades of trifluoroacetic, chlorodifluoroacetic, dichloroacetic, and difluoroacetic acids were purified by fractional distillation through a Nester/Faust annular Teflon spinning band column; the main fraction of each acid had a boiling point range which was less than 0.2°, and the middle half of that fraction was collected for use in the pK_a determinations. Hydrobromic, hydrochloric, nitric, and perchloric acids were Mallinckrodt or B & A reagent grade and were used without further purification. Carbonate-free 0.1 N NaOH was standardized by titration of National Bureau of Standards acid potassium phthalate (sample 84 g). This standard base was used to determine the concentrations of solutions prepared from the acids described above and to check the purity of those acids by equivalent weight determination. Water used in preparing solutions of the acids was ordinary distilled water which had been passed through a strong acid–strong base mixed-bed ion-exchange column. Solutions of sulfamic and trichloroacetic acids (which respectively hydrolyze and decarboxylate slowly in aqueous solution) were prepared and standardized immediately before use; solutions of other acids were standardized within 2 weeks of their use. The acid samples used in the pK_a determinations were found to have the following equivalent weights: trifluoroacetic acid 114.14 (calcd 114.02); trichloroacetic acid, two samples, 164.56, 164.38 (calcd 163.40); chlorodifluoroacetic acid 130.83 (calcd 130.40); dichloroacetic acid 129.02 (calcd 128.95); difluoroacetic acid 95.89 (calcd 96.04); oxalic acid dihydrate 62.95 (calcd 63.04); sulfamic acid 97.15 (calcd 97.10).

Procedure. Measurements of pH were made using a Beckman Model 1019 research pH meter. The solution whose pH was being determined was maintained within ±0.1° of the desired temperature in a cell which was closed except for a small vent to allow the contents to be at atmospheric pressure, and the electrodes were kept at each temperature for at least 12 hr before being used for measurements at that temperature. All four possible combinations of Beckman No. 41263 general purpose glass electrodes and Fisher No. 13-639-1 full range glass electrodes with Beckman No. 39071 carborundum frit junction calomel reference electrodes and Fisher No. 13-639-53 ceramic porous plug silver–silver chloride reference electrodes gave identical (within a range of 0.002 pH unit) values for the difference in pH between solutions of HCl, HBr, HNO_3, and Cl_3CCO_2H whose concentrations were in the range 0.1–0.2 F and were chosen to make the measured pH differences less than 0.05 pH unit. These electrodes were used interchangeably in the pK_a determinations. Neither agreement between reference electrodes nor sufficiently stable pH readings could be obtained for perchloric acid solutions, presumably due to precipitation of $KClO_4$ in the liquid junction. Fiber junction reference electrodes gave grossly nonreproducible and unstable readings (±0.01 pH) in most solutions. To avoid clogging the liquid junction with solid KCl, the internal solutions in the reference electrodes were 2 F in KCl rather than saturated.

For the pK_a determinations, pH readings were taken successively on solutions of HCl and of the acid under investigation. The concentrations of the acids were determined with an uncertainty less than 0.2% by titration; those of the sample acid lay between 0.1 and 0.2 F; those of the HCl were chosen to give readings within 0.03 pH of the samples with which they were paired. Times required for the pH meter reading to reach a constant value (±0.0005 pH) varied from less than 10 min at the higher temperatures up to about 40 min at 15°. Successive duplicate measurements on portions of the same solution consistently agreed within 0.001 pH. The pH of the sample acid solution was calculated from the observed difference in pH between it and its corresponding HCl solution; the pH of the latter was defined by eq 3. The value of the mean molal activity coefficient for the HCl was calculated from the Debye–Hückel eq 1. The values of A and B for each temperature

$$-\log \gamma_{\pm,\mathrm{HCl}} = \frac{AI^{1/2}}{1 + BaI^{1/2}} \qquad (1)$$

were taken from the tabulation given by Robinson and Stokes,[12] and the value of a was chosen to be 6.07 Å at all temperatures. This value of a predicts the observed value of $-\log \gamma_{\pm}$ for 0.1000 m HCl at 25° (0.099)[13] and a value of 0.120 for 0.2000 m HCl at 25° (observed value 0.115).[13] The actual concentrations of the HCl solutions used varied from 0.04 to 0.15 M. The pH differences between solutions of HCl and HNO_3 or HBr which were measured by this procedure were within ±0.002 of the value of $\log (m_{\mathrm{HX}}\gamma_{\pm,\mathrm{HX}}/m_{\mathrm{HCl}}\gamma_{\pm,\mathrm{HCl}})$. Solutions were prepared volumetrically at 25 ± 3° and their molar concentrations at other temperatures calculated assuming the temperature coefficient of their density to be equal to that for pure water. The mean molar activity coefficient, $y_{\pm}$, of each acid was assumed to be equal to the corresponding mean molal activity coefficient. The maximum error in this assumption implied by the densities at 25° was $|\log (y_{\pm}/\gamma_{\pm})| = 0.007$ for 0.2 F trichloroacetic acid; for most solutions, this error was near 0.002. These errors were considered to be smaller than other uncertainties and were ignored.

Results

Determinations of the pH of acidic solutions using conventional pH meters and electrodes are subject to

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(5) R. M. Izatt, J. J. Christensen, R. T. Pack, and R. Bench, *Inorg. Chem.*, **1**, 828 (1962).

(6) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(7) J. C. McCoubrey, *Trans. Faraday Soc.*, **51**, 743 (1955).

(8) J. Jordan, *Rec. Chem. Progr.*, **19**, 193 (1958).

(9) W. J. Hamer in "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley & Sons, New York, N. Y., 1959, pp 236–252.

(10) E. J. King and G. W. King, *J. Amer. Chem. Soc.*, **74**, 1212 (1952).

(11) M. J. Butler, G. F. Smith, and L. F. Audrieth, *Anal. Chem.*, **10**, 690 (1938).

(12) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworth and Co., Ltd., London, 1959, p 468.

(13) See ref 12, p 491.

Table I. Observed Values of pK_a[a]

Acid	Temperature, °C 15	20	25	30	35	40	45	50	55
ClF_2CCO_2H	0.42	0.46	0.46	0.48	0.49	0.51	0.54	0.56	
F_3CCO_2H	0.5_0	0.5_2	0.5_2	0.5_1	0.4_8	0.4_7	0.5_1	0.5_2	
Cl_3CCO_2H	0.53_2	0.51_8	0.51_2	0.51_3	0.51_3	0.51_6	0.52_7	0.52_8	0.53_8
$^+NH_3SO_3^-$	1.02_3	1.00_2	1.00_1	0.99_3	0.99_4	1.00_4	1.01_8	1.03_7	1.04_9
$(CO_2H)_2$			1.30	1.31	1.32	1.33	1.34	1.36	1.36
F_2CHCO_2H	1.29	1.31	1.34	1.37	1.39	1.41	1.43	1.46	
Cl_2CHCO_2H	1.31	1.33	1.35	1.38	1.40	1.42	1.44	1.45	

[a] The reproducibility of replicate determinations was *ca.* ±1 in the last significant figure for those values in which that figure is written normally and *ca.* ±5 in that figure for those values in which it is written as a subscript. Tabulated values are means of two or more determinations.

errors from two sources: nonideal response of the glass electrode to hydrogen ions in strongly acidic media,[14] and changes in the potential of the liquid junction between the sample solution and the KCl bridge to the reference electrode as the pH becomes lower.[15] It has recently been shown[16] that errors of the first kind are not significant in solutions of the acidity range employed in these measurements. The cause of the change in liquid junction potential which accompanies increasing acidity of the sample solution presumably is the very high mobility of hydrogen ion.[15]

It therefore should be possible to make accurate measurements of pH with conventional glass and reference electrodes in solutions at least as acidic as pH 1 if the electrode pair is standardized against a solution whose known pH and ionic strength are essentially identical with those of the sample solution. In this work, HCl solutions were chosen as the standards, and the convention was adopted that for those standards

$$\gamma_{H^+} = \gamma_{Cl^-} = \gamma_{\pm,HCl} \tag{2}$$

so that

$$pH_{HCl} = -\log\,(m_{H^+}\gamma_{\pm,HCl}) \tag{3}$$

To permit calculation of the dissociation constant of an acid, HA, from the measured pH of a solution in which HA is the sole solute and has a formal, stoichiometric concentration, F_{HA}, which is less than 0.2 F, it was assumed that the activity coefficient of the undissociated HA does not deviate from unity and that

$$\gamma_{H^+} = \gamma_{A^-} = \frac{\gamma_{\pm,HA}}{\alpha} \tag{4}$$

where α is the fraction of HA which is dissociated into ions, and $\gamma_{\pm,HA}$ is the mean molal activity coefficient of HA based on its stoichiometric concentration. It was further assumed that if the measured pH of a solution of HA is identical with that of a solution of HCl, then for these two solutions

$$\gamma_{\pm,HA} = \alpha\gamma_{\pm,HCl} \tag{5}$$

These assumptions lead to eq 6 for the dissociation constant of HA. Since solutions of HCl and HA with identical values of pH would have ionic strengths which were very nearly equal even if eq 5 were not exact, any difference between log $\lambda_{\pm,HA}$ and the value predicted by eq 1 and 5 would be approximately linear in ionic strength.[17] Deviations from unity of the quantity, log γ, for undissociated HA molecules should also be linear in ionic strength.[18] The error in K_a resulting from such deviations thus should vary with ionic strength and vanish at zero ionic strength. No variation in pK_a outside of random experimental scatter (range less than 0.02 even at the lowest concentration) was observed for trichloroacetic acid at stoichiometric concentrations ranging from 0.07 to 0.20 F (ionic strengths from 0.06 to 0.15). Determinations of pK_a for other acids were all made using solutions whose stoichiometric concentrations were near 0.1 F; the effect of lowering the ionic strength from 0.1 to 0.06 F was tested for oxalic, dichoroacetic, and difluoroacetic acids and found to produce no significant variation in the measured pK_a. The value of α for all acids always was between 0.3 and 0.7 in the solutions used.

$$K_a = \frac{10^{-2pH}}{F_{HA} - 10^{-pH}/\gamma_{\pm,HCl}} \tag{6}$$

The values of pK_a computed from the observed pH values using eq 6 are given in Table I. These values have been used to determine the parameters in the Harned and Robinson[19] equation written in the form

$$pK_a = \frac{A}{T} + B + CT \tag{7}$$

The data for all acids except sulfamic and trichloroacetic acids may also be represented by the simpler equation,

$$pK_a = \frac{A'}{T} + B' \tag{8}$$

with a fit which is not significantly poorer than that given by eq 7. The least-squares parameters of best fit for both eq 7 and eq 8 are listed for all seven acids in Table II together with the rms deviation of the observed values from those predicted by each equation.

The reproducibility of repeated pK_a determinations for any one acid did not vary with temperature, but was quite different for different acids. For trichloroacetic and sulfamic acids, the reproducibility of pK_a (better than ±0.005) corresponds to a scatter in pH measurements which is less than ±0.001. For trifluoroacetic acid, the scatter is an order of magnitude greater, which may suggest some interference with formation of a stable liquid junction potential similar to that observed for

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(14) M. Dole, "The Glass Electrode," John Wiley & Sons, Inc., New York, N. Y., 1941, Chapter 8.

(15) R. G. Bates, "Determination of pH, Theory and Practice," John Wiley & Sons, Inc., New York, N. Y., 1964, Chapter 3.

(16) A. J. Zielen, *J. Phys. Chem.*, 67, 1474 (1963).

(17) See ref 12, pp 235–238.

(18) M. Randall and C. F. Failey, *Chem. Rev.*, 4, 291 (1927).

(19) H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, 36, 973 (1940).

Table II. Temperature Dependence of pK_a

Acid	From eq 7				From eq 8		
	A	B	C	RMS[a]	A'	B'	RMS'[a]
ClF_2CCO_2H	565.20	−4.3366	0.009733	0.007	−342.80	1.613	0.008
F_3CCO_2H	1542.81	−9.5459	0.016342	0.017	18.19	0.444	0.018
Cl_3CCO_2H	1418.26	−8.7951	0.015273	0.003	−29.57	0.618	0.008
$^+NH_3SO_3^-$	2706.44	−16.8564	0.029439	0.003	−84.23	1.287	0.016
$(CO_2H)_2$	404.27	−1.9789	0.006449	0.003	−209.71	2.003	0.004
F_2CHCO_2H	−386.42	2.4383	0.000663	0.003	−448.27	2.844	0.003
Cl_2CHCO_2H	−723.94	4.8507	−0.003579	0.003	−390.07	2.663	0.004

[a] Root mean square deviation of the observed pK_a values from those predicted by the indicated equation.

Table III. Thermodynamic Parameters for Dissociation at 25° [a]

Acid	pK_a	$\Delta H°$, kcal mole^{-1}	$\Delta S°$, cal deg^{-1} mol^{-1}	$\Delta C_p°$, cal deg^{-1} mol^{-1}
ClF_2CCO_2H	0.46	−1.4	−7	
F_3CCO_2H	0.50	0.4	−1	
	(0.23)[b]			
	(−0.03)[c]			
Cl_3CCO_2H	0.515	0.28	−1.4	−42
	(0.63)[b]	(0 ± 2)[e]	(−2 ± 5)[e]	
$^+H_3NSO_3^-$	0.998	0.41	−3.2	−80
	(0.988)[d]	(0.46, 0.27)[d]	(−3.0, −3.8)[d]	(−110, −85)[d]
$(CO_2H)_2$	1.30	−0.8	−9	
	(1.27)[b]	(−1.02)[f]	(−9.2)[f]	
F_2CHCO_2H	1.34	−2.0	−13	
Cl_2CHCO_2H	1.36	−1.9	−12	
	(1.24)[b]	(−0.17)[g]	(−6.5)[g]	
		(−3.3)[h]	(−17)[h]	

[a] Calculated from the coefficients in eq 7. Values reported by previous investigators are given in parentheses. [b] G. Kortüm, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworth and Co., Ltd., London, 1961. When this source lists more than one reported value, only that indicated to be the most reliable is given above. [c] Reference 13. [d] Reference 10. [e] J. Jordan and W. H. Dumbaugh, Jr., *Anal. Chem.*, **31**, 210 (1959). [f] Reference 20. [g] L. Avedikian, *Bull. Soc. Chim. Fr.*, 2570 (1966). [h] Calculated from the data of N. J. Cleve and E. K. Euranto, *Suomen Kemistilehti*, **B37**, 126 (1964).

perchloric acid solutions. The rms deviation of the observed pK_a values from eq 7 is for each acid consistent with the scatter observed at any one temperature. The thermodynamic parameters for ionization at 25° derived from the constants in eq 7 for each acid are listed in Table III. Values for $\Delta C_p°$ are listed only for those two acids in which the fit of the observed pK_a values to eq 7 is significantly better than that to eq 8 (which implies $\Delta C_p° = 0$). For the other five acids, the $\Delta H°$ and $\Delta S°$ values derived from the parameters of eq 7 for ionization at 25° do not differ from the values derived from the parameters of eq 8 (which are averages over the experimental temperature range) within the number of significant figures reported. Values of pK_a taken from the literature are included in Table III for comparison. Previously reported values of $\Delta H°$, $\Delta S°$, and $\Delta C_p°$, when available, are also given.

The close agreement between the pK_a values determined here for sulfamic acid at various temperatures and those calculated by King and King[10] from their measurements of the emf of cells using hydrogen electrodes and containing no liquid junction suggests that the assumptions used in the derivation of eq 6 are valid. This conclusion is reinforced by the agreement of the values of $\Delta H°$ and $\Delta S°$ found here for oxalic acid with those recently derived from precise calorimetric measurements.[20] An attempt to estimate the maximum error in pK_a, $\Delta H°$, and $\Delta S°$ which might result from the dependence of $\gamma_{\pm,HA}/\alpha$ on the structure of A^-,[21] from the deviation of γ_{HA} from unity,[18,22] from the assumed identity of the molarity and molality bases for standard state,[23] from the difference between the pH scale defined by eq 3 and the Bates–Guggenheim convention adopted by the National Bureau of Standards,[24] from the random scatter in pH measurements, and from the variation in these parameters with the assumed dependence of $\gamma_\pm$ on ionic strength and ionic size (as observed by King and King for sulfamic acid[10]), leads to the conclusion that most of the values reported in Table III should be accurate within 0.1 pK_a, ±0.3 kcal/mole in $\Delta H°$, and ±1 eu in $\Delta S°$. Errors arising from noncancellation of liquid junction potentials should be of similar or smaller magnitude. The values for trifluoroacetic acid may be appreciably less certain than this. Values for some of the acids may be significantly more accurate; for example, the absence of variation in pK_a for trichloroacetic acid over a range of a factor of 2 in ionic strength suggests that errors in the assumed behavior of $\gamma_\pm/\alpha$ and of γ_{HA} for that acid are too small to lead to an error in pK_a which is outside of experimental scatter. Further, Hamer[9] has pointed out that the observations of Davies, Jones, and Monk[25] on cells in which hydrogen ion was the sole cation present (as in the present study) suggest that such cells may yield pK_a values extrapo-

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(20) J. J. Christensen, R. M. Izatt, and L. O. Hansen, *J. Amer. Chem. Soc.*, 89, 213 (1967).

(21) Estimated from the observed range of $\gamma_\pm$ values for alkali metal salts and for strong acids given in ref 11, pp 491–495.

(22) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, pp 536, 737.

(23) This will lead to an error no larger than 0.03 in any pK_a at one temperature and to an error of *ca.* 0.06 kcal in $\Delta H°$ arising from the temperature dependence of the density.

(24) See ref 14, pp 57, 74.

(25) C. W. Davies, H. W. Jones, and C. B. Monk, *Trans. Faraday Soc.*, 48, 921 (1952).

lated to zero ionic strength which are independent of the assumed value of *a*. For each of the acids, the difference between the pK_a values for two temperatures should have a smaller uncertainty than the value at any one temperature.

Discussion

The acidities reported here for the di- and trihaloacetic acids are consistent with those of the corresponding alcohols.[26] If the pK_a values of the carboxylic acids,[27] RCOOH, are plotted against those of the alcohols,[27] RCH_2OH, including all substituents, R, for which both pK_a's are known, only the formic acid–methanol point deviates widely from a linear correlation. The linear least-squares equation of best fit, excluding the latter point, is

$$pK_a(RCOOH) = -14.42 + 1.21pK_a(RCH_2OH) \quad (9)$$

The root mean square of the nine carboxylic acid pK_a's from this equation is 0.19. The root mean square deviation of the four pK_a values for polyhaloacetic acids is 0.20, showing that these low pK_a values are as well correlated as are the higher (and thus more precisely measurable) pK_a's. The slope (1.21 ± 0.05) is in good agreement with the ratio (1.17 ± 0.10) of the ρ^* values for ionization of RCOOH (1.721 ± 0.037)[28] and of RCH_2OH (1.45 ± 0.10);[29] the uncertainties quoted are standard deviations.

The most striking conclusion resulting from these measurements is that the difference in strength between acetic acid and the polyhaloacetic acids is due primarily to a more positive entropy of ionization for the latter. A simple increase in the size of the hydrophobic tail of the acid does not produce such a change in the entropy of ionization. (The values of $\Delta S°$ for ionization of polymethylacetic acids in cal deg^{-1} $mole^{-1}$ are acetic, −22; propionic, −23; isobutyric, −26; pivalic, −25.)[20] If the value of −5.5 cal deg^{-1} $mole^{-1}$ for the absolute standard partial molal entropy of hydrogen ion in aqueous solution at 25°[30,31] is accepted, then the data in Table III require that trifluoracetate and trichloroacetate anions have partial molal entropies which are about 4 cal deg^{-1} $mole^{-1}$ more *positive* than the corresponding uncharged acids. In order for the entropy decrease expected from electrostatic orientation of solvent by the charge on the anion to be so masked, the introduction of halogen substituents into acetic acid must either cause the undissociated acid to be a powerful promoter of solvent structure or cause the anion to be a strong structure breaker. If this effect is to be attributed to an increase in "iceberg"[32] or "flickering cluster"[33] structure around the undissociated acid accompanying an increase in the size or water repellency of the hydrophobic tail, then it is necessary to assume that icebergs induced by hydrocarbon groups are not disrupted by generation of a negative charge on the carboxyl moiety, while those induced by halocarbon groups are disrupted. An alternate possible explanation would be that the field surrounding the highly polar CX_3 group is sufficiently strong to cause the decrease in entropy resulting from the increase in electrostatic solvent orientation brought about by adding a negative charge to the carboxyl moiety to be more than cancelled by the interference of that charge with the structure already induced by the CX_3 group; a zone of disorder analogous to that proposed to exist around a structure-breaking ion[32] might thus result.

The near-zero value of $\Delta V°$ (−2.5 ± 1.5 cm $mole^{-1}$) recently reported[34] for the ionization of trifluoroacetic acid reinforces these conclusions and is in agreement with the known[35] rough proportionality between $\Delta S°$ and $\Delta V°$ for the ionization of carboxylic acids. In contrast, the value found here for $\Delta C_p°$ for the ionization of trichloroacetic acid is within the range[36,37] which is normal for the weaker carboxylic acids; any significant changes in solvent structure occurring in addition to those ascribable to electrostatic orientation would have been expected to produce large changes in $\Delta C_p°$, particularly if they were of the kind commonly described as destruction of "icebergs"[32] or "flickering clusters."[33] However, it is possible that this value of $\Delta C_p°$ may be appreciably in error.

These pK_a values imply that the acid-strengthening effects of the CX_3 and CHX_2 substituents are very nearly independent of whether X is chlorine or fluorine. This is in agreement with the data for the alcohol ionizations,[26] but in conflict with a simple prediction based on group dipole moments. (The dipole moments of the corresponding gaseous halocarbons in Debye units are HCF_3, 1.64; $HCCl_3$, 1.00; H_2CF_2, 1.96; H_2CCl_2, 1.63.)[38] However, the longer C–Cl dipole length and the greater cavity volume corresponding to Cl might lead both to more efficient transmission of the field effect of the dipole and to greater dominance of the effect of the positive end of the dipole[39] when X is Cl than when it is F. Whether this is sufficient to explain the relative pK_a values, or whether specific solvent structure effects are also important, remains an open question.

Large variations in entropies of activation corresponding to those in equilibrium entropy changes seem not to have been observed. For example, the value of $\Delta S^{\ddagger}$ observed for uncatalyzed addition of water to a carbonyl group remains nearly constant as the substrate is varied from acetaldehyde[40] (−38 cal deg^{-1} $mole^{-1}$) through acetic anhydride[41] (−42 cal deg^{-1} $mole^{-1}$) to

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ethyl trifluoroacetate[42] (-38 cal deg^{-1} mole^{-1}) and ethyl trichloroacetate[43] (-43 cal deg^{-1} mole^{-1}). The transition states for these reactions should have appreciable charges located on oxygens bound to the former carbonyl carbon,[40] yet the variation in the value of $\Delta S°$ for generating such charges in the corresponding acids is not reflected in $\Delta S^{\ddagger}$. Whether this results from dominance of the entire solvent structure around the transition state by those features required to produce this very negative $\Delta S^{\ddagger}$,[40] from nonequilibrium solvation of the transition state,[44] or from other factors remains unanswered.

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Kinetic Study of Ring Inversion in 9,10-Disubstituted *cis*-$\Delta^{2,6}$-Hexalins, [4.4.4]Propella-3,8,12-triene, and 3,3-Difluoro[4.4.4]propellane

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Abstract: The kinetic parameters for ring interconversions were measured in three hexalin (I–III) and two propellane derivatives (IV, V). Measurements were performed by the comparison of the calculated and experimental nmr spectra line shapes at various temperatures. The results indicate two characteristic reaction paths, applicable to saturated and unsaturated compounds, respectively. It is suggested that in the saturated compounds the reaction profile has discrete steps involving one ring at a time. On the other hand in the unsaturated compounds the reaction profile seems to contain only one maximum.

The kinetics of the chair–chair interconversion have been studied both experimentally and theoretically in cyclohexane and its derivatives.[1–5]

The ring interconversions have also been studied in *cis*-decalins and substituted *cis*-decalins.[6–9] On the basis of the experimental results and theoretical calculations, an energy profile containing four minima has been suggested for this interconversion.[6,8] The following stepwise mechanism has been assumed. (a) Conversion of a chair into a twist-boat in one ring, with an activation energy close to that of the cyclohexane inversion. This implicitly assumes that the presence of the second ring has a small effect on the conformational change. (b) The second ring undergoes a chair to twist-boat transition with the same activation energy as in step a. (c) Both rings undergo a transition to a new twist-boat conformation related geometrically to the final chair–chair conformation. (d) Repetition of steps b and a give the final chair–chair conformation. The major difficulty in confirming this mechanism lies in the fact that experiment provides the over-all energy change but not values for each step. A logical extension of these systems is [4.4.4]propellane which consists of three condensed saturated rings. In this study we report measurements on the ring interconversions in this system.

Ring interconversion has also been studied in cyclohexene[3,10] and in a substituted cyclohexene.[11] The measured free energy of activation, $\Delta G^{\ddagger}$, for cyclohexene is 5.3 kcal/mole.[10] Beckett, *et al.*,[12] have theoretically derived the value of 2.7 kcal/mole for the difference between the half-chair and boat forms of cyclohexene. By comparing the calculated and experimental results Anet and Haq[10] concluded that the interconversion process in cyclohexene has a similar reaction profile to that of cyclohexane, *i.e.*, that the energy has a minimum in the transition state. Bucourt and Hainaut[3] opposed this view and claimed that not all of the relevant factors had been taken into account by Beckett, *et al.* In a more elaborate calculation, these authors have obtained a value of 6.9 kcal/mole for the energy difference between the boat and half-chair forms in cyclohexene. They have also calculated the energy involved in other steps of the half-chair–half-chair interconversion and concluded that an energy minimum is absent in the neighborhood of the transition state portion of the reaction profile. This presumably shows that the interconversion mechanism in cyclohexene is substantially different from that in cyclohexane, the latter having a minimum

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