

Acidic Dissociation of Chlorodifluoroacetic Acid: Determination of K° , ΔH° , and ΔS°

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Using pH potentiometric measurements, concentration quotient and thermodynamic acid dissociation constants were determined for chlorodifluoroacetic acid. The determinations were carried out in aqueous media at seven temperatures ranging from 20 °C to 50 °C at an ionic strength of 0.25 mol dm⁻³. Standard enthalpies and entropies of the dissociation reaction were also obtained. At 25 °C, the thermodynamic values of these properties are $K^\circ = 0.495 \pm 0.020$, $\Delta H^\circ = (-5.0 \pm 1.1)$ kJ mol⁻¹, and $\Delta S^\circ = (-23.1 \pm 3.6)$ J K⁻¹ mol⁻¹.

Chlorodifluoroacetic acid (ClF₂CCO₂H), here referred to as HCF, is one of the trihaloacetic acids. Since both trifluoroacetic and trichloroacetic acids are moderately strong, presumably HCF is moderately strong as well. As part of our ongoing study of the properties of moderately strong acids, we require precise values of the dissociation constant of HCF and its uncertainty at various temperatures. Although values of the dissociation constant of HCF at various temperatures have been published (Kurz and Farrar, 1969), this work does not appear to have been confirmed. In addition, the accuracy of the thermodynamic dissociation constants given by Kurz and Farrar depends on accurate estimates of the ionic activity coefficients since the ionic strengths of the solutions used in their experiments varied between 0.1 mol dm⁻³ and 0.2 mol dm⁻³. The *Critical Stability Constants of Metal Complexes Database* (Smith and Martell, 1997) lists no value for the p*K* of HCF. Similarly, a recent paper involving many of the haloacetic acids (Langner and Zundel, 1995) also fails to give a p*K* value for HCF.

This paper reports values of the dissociation constants obtained from pH potentiometric experiments. These constants are reported both in terms of K° , the thermodynamic values based on estimates of the activities of solution species, and in terms of K' , the "concentration quotient" constant based on species concentrations in a solution with ionic strength $I = 0.25$ mol dm⁻³. We also report values of the enthalpy and entropy of dissociation together with their uncertainties.

Experimental Section

Materials. All materials were of reagent grade. Samples of HCF were obtained from the Aldrich Chemical Co. and were used without further purification. Commercial HCl and KOH solutions were restandardized using customary titrimetric methods. Stock solutions of KCF, the potassium salt of HCF, were prepared by titrating weighed portions of the acid with KOH to pH ≈ 5 . The purity of HCF samples was found to be (99.5 \pm 0.2)%. Dichloroacetic acid of purity 99.6%, which is used in this work as a test system, was obtained from the same source. Solutions of its potassium salt were prepared in the same manner as were the corresponding solutions of KCF.

Procedures. Experiments involved the addition of 0.25 mol dm⁻³ HCl to a covered thermostated cell equipped with

conventional glass and saturated Ag, AgCl reference electrodes. Experiments were performed at (20, 25, 30, 35, 40, 45, and 50) °C. In each experiment the temperature was monitored continuously and maintained to within ± 0.05 °C of the set point during a 2–48 h equilibration period before calibrating the Beckman model 71 pH meter. At each temperature, the electrodes were equilibrated for at least 24 h prior to use. Portions of a 0.28 mol dm⁻³ solution of KCF were added with an equilibration time of 10–15 min after each addition. The volumes of KCF solution were chosen so that 10 data points (pH vs volume of KCF) would be obtained at approximately equal intervals over the range in which the molar ratio of KCF to HCl varied from 0 to 1.1. This range corresponds to a 2-fold change in the volume of the titration mixture. The pH values in these experiments ranged from 0.6 to 1.0.

The analysis of the pH vs composition data relies on the estimation of the concentration of H⁺ from the observed pH readings. These estimates are subject to error both because of the high and variable concentration of H⁺ in the mixed electrolyte solutions and because of possible variations in the liquid junction potential at the reference electrode–analyte solution interface. To estimate these possible errors, we performed calibration experiments involving the "titration" of a 0.25 mol dm⁻³ solution of HCl with 0.25 mol dm⁻³ KCl.

These calibration experiments were designed to mimic the titrations of HCl with KCF. Both types of titrations were equilibrated in the same fashion, used the same ionic strength, encompassed the same 2-fold volume change in the titration mixture, and showed a similar range of pH readings, 0.6 to 0.9. The data in the calibration experiments consisted of 10 approximately evenly distributed readings of pH_{obs}. Values of pH_{calc} ($= -\log[H^+]$) were obtained assuming that since the ionic strength of each solution remained constant at 0.25 mol dm⁻³, the activity coefficient of the H⁺ was constant.

Regressions of pH_{calc} vs pH_{obs} had slopes within the interval [-0.99, 1.01] and intercepts within the interval [-0.002, 0.002]. The differences, pH_{calc} - pH_{obs}, appeared to be randomly scattered. Their values were generally less than 0.002 pH and in no case exceeded 0.003 pH. The root-mean-square (rms) scatter about each regression ranged from 0.001 to 0.002 pH.

This result, namely that the electrode response is essentially linear in the narrow range of conditions characterizing our titrations, depends on the assumption that the activity coefficient of H^+ is constant in the mixed electrolyte solutions used in these calibration experiments. This assumption cannot be directly verified by experiments. However, experimental values of γ_{\pm} , the mean ionic activity coefficient of HCl in KCl solutions, are available (Harned and Owen, 1958). These values show an approximately 2% variation in γ_{\pm} in the relevant concentration domain. Assuming that the behavior of γ_H , the activity coefficient of the hydrogen ion, parallels that of γ_{\pm} , the response of the glass electrode should be slightly nonlinear.

Since our experimental results show a linear response to within experimental uncertainty, there must be other factors, also ignored in our analysis, that influence the response so as to cancel the small nonlinearity caused by variations in γ_H . The most important of these factors is probably the liquid junction potential at the reference electrode/electrolyte solution interface. As a result of the fortuitous cancellation of deviations from linearity due to these factors, our experiments indicate that the measured pH values can be equated with $-\log[H^+]$ within an estimated uncertainty of ± 0.002 pH.

At the completion of each titration, we confirmed the meter calibration with a fresh portion of HCl solution. The deviations in pH were generally less than 0.002 pH and never exceeded 0.003 pH.

As a check on our experimental methods and calculational procedures, we performed essentially identical experiments using 0.25 mol dm^{-3} solutions of potassium dichloroacetic acid as the titrant. The values of pK° for dichloroacetic acid at 20 °C, obtained from two experiments, were 1.356 ± 0.005 and 1.353 ± 0.005 . These values are in agreement with the earlier value of 1.33 ± 0.01 (Kurz and Farrar, 1969).

Data Analysis and Results

The experiments provide sets of pH vs composition data at seven different temperatures. The thermodynamic dissociation constant K° and the concentration quotient K' can be obtained from these data using the following relations:

$$v_{KCF} = [HCF](V + v) + [CF^-](V + v) \quad (1)$$

$$V_{HCl} = [H^+](V + v) + [HCF](V + v) \quad (2)$$

$$K^{\circ} = (\gamma_H \gamma_{CF} / \gamma_{HCF}) [H^+] [CF^-] / [HCF] \quad (3)$$

$$pH = \log \gamma_H [H^+] = pH(\text{observed}) - \Delta - \log \gamma_{H,0.25} \quad (4)$$

$$K' = K^{\circ} (\gamma_{HCF} / \gamma_H \gamma_{CF})_{0.25} \quad (5)$$

In these equations c_{KCF} is the concentration of the KCF titrant, v is the volume of titrant added, c_{HCl} is the concentration of the original HCl solution, and V is the volume of that solution. $[HCF]$ and $[CF^-]$ represent the concentrations of the protonated and anionic forms, respectively, of chlorodifluoroacetic acid. We assume that the solution volumes are additive. Δ , in eq 4, represents a meter calibration constant.

The γ 's represent activity coefficients of the various solution species. The subscript 0.25 indicates the activity coefficient evaluated at ionic strength 0.25 mol dm^{-3} . The activity coefficient term, $\gamma_{H,0.25}$, in eq 4 reflects the fact that

Table 1. Concentration Quotient and Thermodynamic Acid Dissociation Constants of Chlorodifluoroacetic Acid at Various Temperatures^{a,b}

$t/^{\circ}C$	K'	K°	$\chi^2/\text{d.f.}$
20	0.805	0.473	1.4
25	0.844	0.495	0.8
30	0.795	0.464	0.2
35	0.804	0.467	0.2
40	0.684	0.396	0.2
45	0.720	0.415	0.3
50	0.722	0.414	0.3

^a The uncertainty in each value of K' and K° is $\pm 4\%$ of its value.

^b The entries at (20, 25, and 45) °C are averages of the values obtained from duplicate experiments.

the meter was calibrated to $pH = 0.602$ using an HCl solution whose ionic strength was 0.25 mol dm^{-3} .

The values of the activity coefficients were obtained from the extended Debye–Huckel equation

$$-\log \gamma = \frac{A\sqrt{\mu}}{1 + Ba\sqrt{\mu}} \quad (6)$$

The values of the temperature-dependent A and B parameters are those suggested by Robinson and Stokes (Robinson and Stokes, 1965). The ion-size parameter, a , of H^+ was set at 0.9 nm (Kielland, 1937), and the corresponding parameter for CF^- was estimated to be 0.6 nm. We take the value of γ_{HCF} as unity.

As noted above, K° is the thermodynamic dissociation constant and K' is the concentration quotient constant at ionic strength 0.25 mol dm^{-3} . Because the ionic strength in all the experimental solutions during the titrations was very close to 0.25 mol dm^{-3} (always within the interval (0.245, 0.250) mol dm^{-3}), the value of K' is essentially independent of the estimates of the activity coefficients.

Optimized values of K° , K' , and Δ were obtained by applying a nonlinear regression analysis to the data using eqs 1–4 and 6 to formulate the model equation. The Levenberg–Marquardt algorithm (Press et al., 1992) was used to minimize χ^2 :

$$\chi^2 = \sum [pH(\text{observed}) - \log \gamma_{H,0.25} - \Delta - pH(\text{calculated})]^2 / \sigma^2 \quad (7)$$

In this equation, $pH(\text{observed})$ denotes the experimental pH value, $pH(\text{calculated})$ is the calculated value obtained from the estimates of K° and Δ using eqs 1–4 and 6, and σ is the standard deviation of the pH readings. As noted above, on the basis of the results of our calibration experiments, we set σ equal to 0.002 pH units.

Values of K° and K' (calculated from eq 5) and their uncertainties expressed as standard errors are listed in Table 1. Two separate determinations were made at 20 °C, 25 °C, and 45 °C as a check on our work. At the three temperatures, the two values of K° (and, thus, also of K') differed by 3.5%, 4%, and 1%, respectively. In particular, at 20 °C, the two values of K° were 0.819 and 0.790; at 25 °C, 0.827 and 0.860; and at 45 °C, 0.717 and 0.724. The values listed in Table 1 for each of the three temperatures are averages of the two determinations. The standard errors were derived by propagation of variance based on $\sigma = 0.002$. The values of the uncertainties of K° and K' were all approximately 4% (3.7%–4.3%) of their respective values. We confirmed these results by means of Monte Carlo simulations and found the calculated uncertainties using the two methods to be essentially identical.

Table 2. Concentration Quotient and Thermodynamic Enthalpies and Entropies of Dissociation of Chlorodifluoroacetic Acid

$\Delta H^\circ/\text{kJ mol}^{-1}$	-5.0 ± 1.1
$\Delta H/\text{kJ mol}^{-1}$	-4.4 ± 1.1
$\Delta S^\circ/\text{J mol}^{-1} \text{K}^{-1}$	-23.1 ± 3.6
$\Delta S/\text{J mol}^{-1} \text{K}^{-1}$	-16.5 ± 3.6

Table 1 also includes values of $X^2/\text{d.f.}$ (d.f. = degrees of freedom) for each regression. Again, the values for 20 °C, 25 °C, and 45 °C are each averages of two determinations. $X^2/\text{d.f.}$ is a goodness-of-fit estimator. X^2 is obtained from the regression procedure, and d.f. is the difference between the number of data points and 2, the number of adjustable parameters. With the single exception of one experiment at 20 °C where $X^2/\text{d.f.} = 1.7$, the values are less than unity and most are less than 0.5.

An alternative view of the quality of fit is provided by the rms value of the difference between observed and calculated pH values. This value is readily calculated from X^2 . We find that the rms deviation in the worst case example at 20 °C is 0.0026 pH units, while the values for the other regressions fall between 0.001 and 0.002 pH units. These results indicate that the model provides an accurate representation of the chemical system.

At this point we note that the data span a wide range of CF^- concentrations, from 0 mol dm^{-3} to about 0.12 mol dm^{-3} . The quality of fit obtained here implies that the formation of "triple ion" species of the type $\text{H}(\text{CF})_2^-$ plays no significant role in these experiments. While it is possible that such solution species exist, their concentrations must be very small compared with $[\text{HCF}]$ and thus contribute negligibly to the acid dissociation equilibria.

We do not tabulate the value of Δ , the meter calibration constant, since it is of no chemical interest. However, we do note that most of the values of Δ lie in the interval $(-0.002, 0.002)$ pH units and that no Δ exceeded 0.003 pH units. These results are consistent with our estimate of $\sigma = 0.002$ for the uncertainty in pH.

The set of model equations as given do not incorporate the thermal expansion of the solutions used in these experiments. The effect of this expansion is easily included by comparing the density of water at the measurement temperature with its value at 25 °C and adjusting the volumes of the solutions accordingly. These calculations gave values of K° and K' nearly identical to the values obtained ignoring thermal expansion. Since the differences are nearly an order of magnitude smaller than the standard error estimates for K° and K' , we do not report the volume corrected values.

Values of the enthalpies and entropies of dissociation were calculated using a van't Hoff analysis. Because the uncertainties in K at the various temperatures had very similar values, an unweighted least-squares analysis could be used to obtain optimized values of the slopes and intercepts of the van't Hoff lines. Plots of both $\ln K^\circ$ vs $1/T$ and $\ln K'$ vs $1/T$ appeared to be linear with random scattering of points about the lines. The values of enthalpies and entropies of dissociation and their uncertainties derived from the plots are given in Table 2. The rms scatter about these 10 point regression lines was approximately 0.04 $\ln(K)$. The most deviate point, found for the value at 40 °C, lies 0.08 $\ln(K)$ from the regression line. This estimate of the uncertainty in the regression lines is consistent with the estimate of 4% for the standard error in the various values of K obtained from the assumption that $\sigma = 0.002$ pH units.

Error Analysis

There are three sources of systematic errors: (1) systematic errors in V , α_{HCl} , and α_{KCF} , (2) errors in the ionic activity coefficients γ_{H} and γ_{CF} , and (3) systematic errors in the pH vs v data.

The effect on the equilibrium constants due to errors in V , α_{HCl} , and α_{KCF} were estimated by a recalculation procedure in which independently perturbed values of V , α_{HCl} , and α_{KCF} were used in the regression analysis. Assuming maximum excursions of 0.3% in V , 0.5% in α_{HCl} , and 0.5% in α_{KCF} , we find the contributions of these excursions to the errors in both K° and K' to be 1.5%, 0.2%, and 0.7%, respectively.

The errors in K° resulting from errors in the ionic activity coefficients were estimated by perturbing the ion-size parameter in the Debye–Huckel equation by 0.1 nm. There is no error in K' due to this source of error since, as mentioned earlier, the ionic strengths of all the measurement solutions were very nearly constant at 0.25 mol dm^{-3} . The errors in K° resulting from errors in the ion sizes of CF^- (0.6 nm to 0.7 nm) and H^+ (0.9 nm to 1.0 nm) were 2.3% and 1.5%, respectively.

Systematic errors in the pH data arise from two sources: (1) the possibility of a nonlinear electrode response and (2) an offset error related to the calibration procedure. The first source was shown to be negligible compared with the measurement uncertainty of 0.002 pH units by means of the calibration experiments described earlier. The second source of error was eliminated by using the meter offset parameters Δ in the regression procedure.

The results of this error analysis indicate that the maximum likely excursion in K' due to systematic errors is about 2.4%, a value about half that of the standard error estimate of this equilibrium constant. Thus, the random error component appears to be the most important source of uncertainty in the values of K' . On the other hand, systematic errors can amount to 6% of the value of K° . For K° , systematic errors, primarily due to the uncertainties in the ionic activity coefficients, are somewhat larger than the random errors resulting from statistical fluctuations in the pH readings.

The effect of systematic errors on the enthalpies and entropies of dissociation were obtained by first noting that the experiments employed a single stock solution of HCl and of KCF. Likewise, the volume of HCl added to the titration cell was always delivered by the same pipet. We assume that the errors in γ_{H} and γ_{CF} are temperature independent and that all the errors are cumulative. Thus we perturb each value of K' (or K°) to its maximum value at each temperature and repeat the van't Hoff regression. Both ΔH , the enthalpy change associated with K' , and ΔH° , the enthalpy change associated with K° , are essentially unaffected by systematic errors. The values of ΔS and ΔS° values are shifted by approximately 0.3 $\text{J K}^{-1} \text{mol}^{-1}$ and 0.7 $\text{J K}^{-1} \text{mol}^{-1}$, values significantly less than the random error uncertainties in these quantities. We conclude that the most important source of uncertainty in the enthalpy and entropy of dissociation is the random error component in K' and K° arising from the uncertainty in the measurements of pH.

Discussion

The values of the enthalpy and entropy of the acidic dissociation of chlorodifluoroacetic acid reported here, $\Delta H^\circ = (-5.0 \pm 1.1) \text{ kJ mol}^{-1}$ and $\Delta S^\circ = (-23.1 \pm 3.6) \text{ J K}^{-1} \text{mol}^{-1}$, are in reasonably good agreement with the previously reported values, -5.8 kJ mol^{-1} and $-29 \text{ J K}^{-1} \text{mol}^{-1}$

(Kurz and Farrar, 1969). However, our value of the acidic dissociation constant at 25 °C, $K^\circ = 0.495$, is significantly different from their value, $K^\circ = 0.35$ at 25 °C. A possible explanation of the discrepancy lies in the treatment of the activity coefficients. In the earlier work, the concentration of the undissociated acid was calculated using the expression $c_{\text{HCF}} = a_{\text{H}}/\gamma_{\pm}$, where c_{HCF} is the analytical concentration of the acid, a_{H} is the activity of free hydrogen ions, and γ_{\pm} is the mean ionic activity coefficient of a chemical model, namely, HCl. Because the experiments involved acid concentrations in the range (0.1–0.2) mol dm⁻³, where the acid is approximately 90% dissociated, a relatively small error in the value of the mean activity coefficient may result in a large error in the concentration of undissociated acid. This error, in turn, results in a large error in K° . For example, an estimate of the activity coefficient that is 3% too high results in a value of the concentration of undissociated acid that is 30% too low.

The experiments described here were designed so that the ionic strength of each solution remains essentially constant (0.25 mol dm⁻³) throughout each titration. As the calibration experiments demonstrate, the activity coefficients also remain constant. Consequently, the concentration quotient dissociation constants are independent of the actual values of the activity coefficients. The thermodynamic dissociation constants do depend on the values of the activity coefficients, but as we have seen, the uncertainties in the activity coefficients result in relatively small errors in the K° 's.

This explanation of the discrepancy in values of the acidic dissociation constant of chlorodifluoroacetic acid may also explain a similar discrepancy (both in direction and magnitude) in reported values for the dissociation constant

of trifluoroacetic acid. Kurz and Farrar (1969) found $K^\circ = 0.32$ at 25 °C while a more recent paper reported $K^\circ = 0.61$ at 22 °C (Strehlow and Hildebrandt, 1990).

As mentioned earlier in this paper, we compared the value of pK° for dichloroacetic acid obtained using the method described here with the value reported by Kurz and Farrar (1969) in order to test the validity of our method. The good agreement between the two values of pK° for this acid is a consequence of the fact that K° for dichloroacetic acid is significantly smaller than K° for KCF. As a result, the approximation $\gamma_{\text{H}} = \gamma_{\pm}$ used by Kurz and Farrar results in a noticeably smaller error in pK° .

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