The Dissociation Constants of Di- and Trichloroacetic Acids Measured by a Distribution Method

Berta Perlmutter-Hayman* and Eliana Tapuhi
Department of Physical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

The acid dissociation constants of dichloro- and trichloroacetic acids have been determined at an ionic strength of 1.0 M and a temperature of 25 °C. The results were obtained by the partition method. This simple method was found very suitable for the moderately strong dichloro acid, but less so for the much stronger trichloro acid. The results are $K_c = 8.0 \times 10^{-2}$ and ~1.0 M, respectively. The agreement with previous findings (at zero ionic strength) is discussed.

A number of reliable methods are available for the determination of the dissociation constants of weak acids (see, for instance, ref 12). The situation is much less satisfactory with respect to strong and moderately strong acids. Different methods give widely differing results.

We have recently carried out a kinetic investigation (*15*) which required a knowledge of the dissociation constants of di- and trichloroacetic acids at an ionic strength of 1 M. For dichloroacetic acid, apart from indirect determinations (*2, 10*), measurements carried out in 1889 (*14*) and 1913 (*11*; see also ref 17) still seem to be the only ones available (*12, 13, 16, 18*; no values are given in the 1971 supplement of ref 18). For trichloroacetic acid the results reported for $I = 0$ vary between 0.23 and 5 M (*2, 4*).

We decided to evaluate the two constants by determining the partition of the acids between water and an organic solvent which dissolves the acid, but does not dissolve the anion (*3, 12*). Di-*n*-butyl ether was found to be a suitable solvent (*16*).

Experimental Section

Known volumes of aqueous solutions and di-*n*-butyl ether were mixed for 20 min with the aid of a magnetic stirrer, transferred into a separating funnel, and kept in a thermostat at 25 °C where they were shaken from time to time. After 1 h the solutions were separated and titrated with sodium hydroxide solution. The organic layer was titrated slowly, under constant stirring.

The ionic strength after the extraction was 1 M throughout, regulated by the addition of sodium perchlorate solution.

Blank experiments showed that no measurable amount of perchloric acid passed into the organic solvent.

Results

The partition coefficient of the acid HA between water and organic solvent is:

$$P = [\mathrm{HA}]_S/[\mathrm{HA}]_W \tag{1}$$

In addition, we define an apparent distribution coefficient (*6*)

$$D = [\mathrm{HA}]_S/([\mathrm{HA}]_W + [\mathrm{A}^-]_W) \tag{2}$$

where $[\mathrm{HA}]_W + [\mathrm{A}^-]_W$ is the total stoichiometric concentration of the acid in water. Introducing K_c, the dissociation constant of HA, combining eq 1 and 2 and rearranging, we get

$$1/D = K_c/P[\mathrm{H}^+]_W + 1/P \tag{3}$$

From a plot of $1/D$ as a function of $1/[\mathrm{H}^+]_W$ we can evaluate $1/P$ and K_c.

For dichloroacetic acid, the results are shown in Table I. For eight experiments in which the stoichiometric concentration before extraction, $[\mathrm{HA}]_0$, was varied between (0.76 and 9.54) $\times 10^{-2}$ M, the values of $[\mathrm{H}^+]_W$ were calculated from $([\mathrm{HA}]_W + [\mathrm{A}^-]_W)$ titrated *after* extraction, using trial values for K_c, until the value used for the calculation coincided with that obtained from a $1/D$ vs. $1/[\mathrm{H}^+]_W$ plot. This was achieved after the fifth iteration. The result is shown in Figure 1. This figure contains two additional points, shown as dots on the graph, representing the experiments where perchloric acid was added. These points correspond to much lower values of $[\mathrm{HA}]_S$ than do their neighbors on the graph. An extension of eq 3 to include the possibility of dimerization in the organic phase shows that, for any given value of $1/[\mathrm{H}^+]_W$, we should find $1/D$ higher the lower the value of $[\mathrm{HA}]_S/D$. From the absence of this effect we conclude that our results are not vitiated by dimerization.

We obtained

$$1/P = (2.12 \pm 0.21) \times 10^{-1} \text{ (standard deviation)}$$

and

$$K_c = 8.0 \times 10^{-2} \text{ M}$$

Neglecting the standard deviation of the slope which is much smaller than that of $1/P$, we find that, within 90% confidence limits, K_c lies between (6.8 and 9.8) $\times 10^{-2}$ M.

For trichloroacetic acid the results were less satisfactory. Since this is a much stronger acid, very little of the undissociated form would be present in solutions as dilute as those used for the dichloro acid, and only a small percentage of the original $[\mathrm{HA}]_0$ would pass into the organic phase. This can be overcome to some extent by adding perchloric acid, but $([\mathrm{HA}]_W + [\mathrm{A}^-]_W)$ must not become much lower than $[\mathrm{HClO_4}]$, since it is obtained as the difference between the titrated acid concentration and the known $[\mathrm{HClO_4}]$. We compromised by employing $[\mathrm{HA}]_0$ between 5×10^{-2} and 5×10^{-1} M; furthermore, in five of the ten determinations, we added perchloric acid, at concentrations between 5×10^{-2} and 3×10^{-1} M. The results were treated as described for the dichloro acid, and became self-consistent after the fourth iteration; they are shown in Table II and Figure 2, where the experiments in the presence of perchloric acid are again represented as dots. From the slope and intercept we obtain

$$1/P = (3.7 \pm 1.5) \times 10^{-2} \text{ (standard deviation)}$$

and

$$K_c = 1.0 \text{ M}$$

We note that P is higher for the trichloro than for the dichloro acid. This is in accordance with theoretical considerations (*6*).

The extremely high standard deviation in the intercept stems from the fact that K_c is now very much higher, and although P is also higher, the line is much steeper than in Figure 1. (This becomes apparent when we consider the difference in the $(1/[\mathrm{H}^+]_W)$ scale of the two graphs!) Within 90% confidence limits, K_c lies in the range of 0.59–4.35 M.

The influence of $[\mathrm{HA}]_S/D$ was again entirely insignificant; this shows that no dimerization occurs in the organic phase.

Table I. Distribution of Dichloroacetic Acid between Water and Di-*n*-butyl Ether at 25 °C and *I* = 1 M

Water layer $10^3([A^-]_W + [HA]_W)$	Water layer $10^3[HClO_4]$	Organic layer $10^2[HA]_S$	$1/D$	$10^{-1}/[H^+]_W$[a]
5.80	—	1.72	3.372	18.410
7.36	—	2.70	2.726	14.740
8.80	—	3.84	2.292	12.500
16.10	—	11.00	1.464	7.278
17.90	—	14.24	1.257	6.639
31.00	—	32.98	0.940	4.189
40.40	—	49.80	0.811	3.388
42.80	—	54.20	0.790	3.238
4.39	8.61	2.96	1.484	8.058
6.83	8.61	5.00	1.367	6.945

[a] After fifth iteration.

Table II. Distribution of Trichloroacetic Acid between Water and Di-*n*-butyl Ether at 25 °C and *I* = 1 M

Water layer $10^2([A^-]_W + [HA]_W)$	Water layer $10^2[HClO_4]$	Organic layer $10^2[HA]_S$	$1/D$	$1/[H^+]$[a]
2.36	—	1.37	1.723	43.314
3.69	—	3.26	1.132	28.030
4.77	—	5.20	0.917	21.885
5.30	—	7.16	0.740	19.785
7.00	—	11.44	0.612	15.190
3.00	5.30	5.99	0.501	12.371
5.00	5.80	12.35	0.405	9.664
6.425	10.50	21.74	0.296	6.225
1.00	21.00	4.58	0.219	4.582
4.00	29.40	22.70	0.176	3.082

[a] After fourth iteration

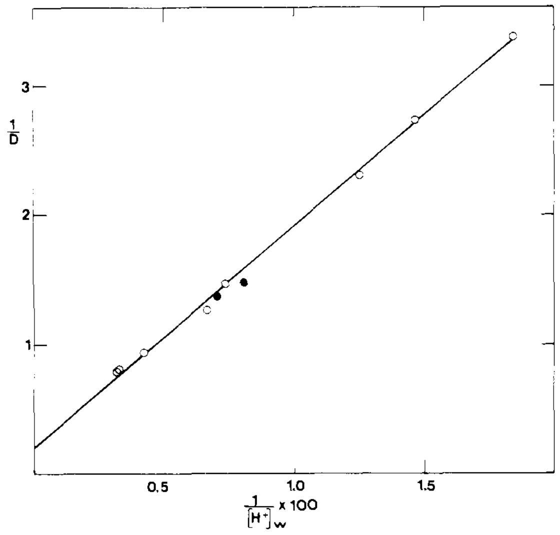

Figure 1. The reciprocal value of the distribution coefficient as a function of $1/[H^+]_W$, for dichloroacetic acid, dots, perchloric acid added.

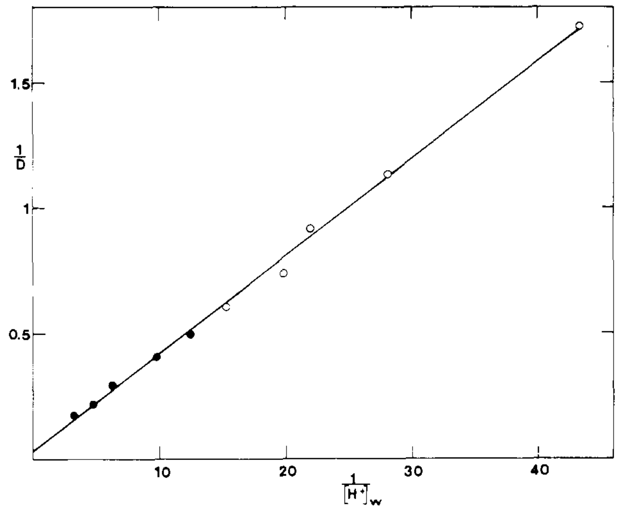

Figure 2. As in Figure 1, for trichloroacetic acid.

Discussion

Our value of K_c for dichloroacetic acid may be compared with $K_a = (4.3 \text{ to } 5.5) \times 10^{-2}$ M given in the literature (*13, 18*) for zero or near zero ionic strength. Using the Davies equation (*5*) to correct our value to zero ionic strength we get 5.0×10^{-2} M. This agreement is rather better than can be expected: on the one hand, the values in the literature are very old, and on the other hand, the Davies equation is not really supposed to be valid (*5*) at an ionic strength as high as 1 M.

Our result for trichloroacetic acid coincides with the older value of 1.0 M obtained from the catalytic influence of trichloroacetic acid (*2, 14*).

Our method cannot nearly compete with the precision claimed in the most recent investigation (*1*), but our value is statistically compatible with its result of 3.3 ± 0.1 M (at 1 M, taken from the author's data) and with the slightly less recent value (*4*) of 2–5 M, both obtained from Raman and NMR spectroscopy. If the difference between our result and these values is considered real, the effect must be attributed to the different experimental conditions. Our aim was to measure K_c under conditions similar to those obtaining in our kinetic experiments, namely, constant ionic strength and the presence of a supporting electrolyte. The NMR and Raman measurements were carried out in solutions where the ionic strength of up to 4.8 M was due entirely to the trichloroacetic acid, and were extrapolated to zero.

There is no doubt that our result contradicts (even within 99% confidence limits!) the value of 0.23 obtained by an indicator method (*9*). This method was pronounced "reliable" as late as 1961 (*13*; see also ref 12); for the somewhat weaker iodic acid, for example, it gave results (*9*) entirely consistent with those obtained by other methods, including distribution methods and Raman spectroscopy (*7*).

The results for trichloroacetic acid thus fall into two distinct groups: $K \geq 1$ M, and $K = 0.23$ M. Covington and co-workers (*4*) speculate on the reason for this discrepancy. They suggest that the low value might represent essentially the dissociation constant, that is to say, the equilibrium between A^- and H^+ on the one hand and the sum of undissociated HA and the ion-pair $H^+ \cdot A^-$ on the other, whereas the Raman and NMR spectroscopy measure the ionization constant, the ion-pair having essentially the same spectroscopic properties as the ions. This explanation would invalidate the elegant method of extrapolation used by Bonner and co-workers (*7*). Furthermore, from the ion-pair formation constant derived on the basis of this explanation (*4*) we find (using the Fuoss equation (*8*)) that two ions as far apart as 9.5 Å are to be considered associated. In addition, the equilibrium constant derived for the ratio between the ion-pairs and covalent acid would make *undissociated* trichloroacetic acid unique among ionogens in *ionizing* in aqueous solutions to ~94%. Therefore the explanation, considered tentative by the authors themselves (*4*), seems to create more problems than it solves.

Literature Cited

(1) Bonner, O. D., Flora, H. B., Aitken, H W., *J. Phys. Chem.*, **75**, 2492 (1971).
(2) Ciapetta, F. G., Kilpatrick, M., *J. Am. Chem. Soc.*, **70**, 639 (1948).
(3) Cookson, R. F., *Chem. Rev.*, **74**, 5 (1974).
(4) Covington, A. K., Freeman, J. G., Lilley, T. H., *J. Phys. Chem.*, **74**, 3773 (1970).
(5) Davies, C. W., "Ion Association", Butterworth, London, 1962, p 41.
(6) Diamond, R. M., Tuck, D. G., *Prog. Inorg. Chem.*, **2**, 109 (1960).
(7) Durig, J. R., Bonner, O. D., Breazeale, W. H., *J. Phys. Chem.*, **69**, 3886 (1965).
(8) Fuoss, R. M., *J. Am. Chem. Soc.*, **80**, 5059 (1958).
(9) v. Halban, H., Brüll, J., *Helv. Chim. Acta*, **27**, 1719 (1944).
(10) Harned, H. S., Hawkins, J. E., *J. Am. Chem. Soc.*, **50**, 85 (1928).
(11) Kendall, J., *Medd. Vetenskapsakad., Nobelinst.*, **2** [38] (1913) (*Chem. Zentralbl.*, **35**/1, 841 (1914)).
(12) King, E. J., "Acid-Base Equilibria", The International Encyclopedia of Physical Chemistry and Chemical Physics, Vol. 15/4, Pergamon, Oxford, 1965, Chapter 6.2.
(13) Kortüm, G., Vogel, W., Andtrussow, K., "Dissociation Constants of Organic Acids in Aqueous Solution", Butterworth, London, 1961, pp 294, 295. (reprinted from: *Pure Appl. Chem.*, **1**, 187 (1961)).
(14) Ostwald, W., *Z. Phys. Chem.*, **3**, 170 (1889).
(15) Perlmutter-Hayman, B., Tapuhi, E., *J. Coord. Chem.*, accepted for publication.
(16) Randall, M., Failey, C. F., *Chem. Rev.*, **4**, 291 (1927).
(17) Schreiner, E., *Z. Anorg. Allg. Chem.*, **122**, 201 (1922).
(18) Sillén, L. G., Martell, A. E., *Chem. Soc., Spec. Publ.*, **No. 17** (1964).

Received for review March 22, 1976. Accepted July 23, 1976.

Derived Thermodynamic Properties of Ethylene

Roland H. Harrison* and Donald R. Douslin
Bartlesville Energy Research Center, Energy Research and Development Administration, Bartlesville, Oklahoma 74003

The real fluid values for enthalpy, entropy, and Gibbs energy in the ranges −35 to +175 °C, 0 to 16 mol dm^{-3}, and 0 to 400 bar were derived for ethylene from experimental P–V–T measurements given in a companion paper (*4*) and published values of the ideal gas properties and a derived value of the enthalpy of sublimation at 0 K.

Although the U.S. production of ethylene ranks fifth in all chemicals and first in petrochemicals, its thermodynamic properties have not been known with high accuracy. A recent comprehensive correlation of the available data for ethylene was undertaken by Angus et al. (*1*), from which they prepared tables of thermodynamic properties, but they concluded that a considerable amount of new experimental measurement was needed. When this study was later presented to a group drawn from government, industry, and universities engaged in a critical assessment (*9*) of the published information on the P–V–T surface of ethylene, there was general agreement with the need for more experiment. Thus, an independent comprehensive set of new data on the P–V–T surface of ethylene was measured with the highest accuracy reasonably accessible to modern P–V–T methods and was presented in a companion paper (*4*). The present work is based on those unsmoothed experimental compressibility values given at even temperatures and densities. The real fluid values for enthalpy, entropy, and Gibbs energy presented here cover a wide range of conditions including the region of the critical point. Since the present values of the thermodynamic properties were calculated from a single set of accurate P–V–T data, they are not subject to the large errors in $(\partial P/\partial T)_\rho$ that result when different sets of compressibility data are combined and averaged. Also, the calculative methods used in the investigation reported in this paper were developed especially for isometric data, and inaccuracies that otherwise would have originated from crossplotting, interpolating, or smoothing of original data were not introduced.

The thermodynamic properties of ethylene have been calculated with a reference to the crystal at 0 K from the data on the compressibility of the real fluid and the heats of vaporization given in the companion paper (*4*) and from published values of the ideal gas properties and a derived value of the enthalpy of sublimation at 0 K. The values are presented in graphical and tabular form and are also compared with published experimental and correlated values.

Calculation Methods

The difference between the real fluid and ideal gas thermodynamic properties of enthalpy, entropy, and Gibbs energy were evaluated from isometric and isothermal data by the following relations, in which T appears on the thermodynamic temperature scale:

$$H - H^\circ = {}_T\!\int_0^\rho \frac{[P - T(\partial P/\partial T)_\rho]\mathrm{d}\rho}{\rho^2} + P/\rho - RT \qquad (1)$$

$$S - S^\circ = {}_T\!\int_0^\rho \frac{[R\rho - (\partial P/\partial T)_\rho]\mathrm{d}\rho}{\rho^2} - R \ln RT\rho \qquad (2)$$

$$G - G^\circ = {}_T\!\int_0^\rho \frac{(P - RT\rho)\mathrm{d}\rho}{\rho^2} + P/\rho - RT + RT \ln RT\rho \qquad (3)$$

The superscript degree mark as in H°, S°, and G° indicates the ideal gas state at 1 atm of pressure. Experimental values of P, ρ, and T were taken only from Tables 1–4 and 7 of ref 4. The slopes, $(\partial P/\partial T)_\rho$, of the isometric lines were derived from the original data (Table 9 of ref 4) by combined analytical and graphical residual correlating techniques that reflect all of the inherent accuracy of the original measurements. Details of the method used and an analysis of the uncertainties involved in the calculation of the thermodynamic functions from P–V–T data have been fully described (*7, 8*). Gibbs energies were calculated at every point of original P–ρ–T data. Enthalpies and entropies were calculated at all points where the slopes, $(\partial P/\partial T)_\rho$, were available. The values of the integrals at zero density were obtained as exact functions of the second virial coefficients and/or their temperature derivatives which were derived from the values given in Table 12 of ref 4. At temperatures below the critical, the path of integration for the enthalpy function (eq 1) passes through the two-phase region and yields the enthalpy of vapor-