794. *The Conductometric Determination of Basic Dissociation Constants of Weak Bases in Sulphuric Acid. Part II.*[1] *The Basicities of Monochloro-, Dichloro-, and Trichloro-acetic Acid*

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The basic ionisation constants at 10° and 25° of the three chlorosubstituted acetic acids have been determined from the conductivities of their solutions in 100% sulphuric acid. The values obtained, recalculated to the pK_{AH^+} of the conjugate acids, have been plotted against the pK_A of the acids in water. The linear relationship obtained embraces also existing data for acetic, propionic, and benzoic acids. The slope of the line is >1. The thermodynamic functions for the basic ionisation of dichloroacetic acid have been calculated and found to be similar to those for the basic ionisation of nitrobenzene.

Cryoscopic investigations by Hantzsch [2] of the solutions of the three chloroacetic acids in sulphuric acid have shown monochloroacetic acid to be fully ionised as a base, dichloroacetic acid only partly so, and trichloroacetic acid not at all. His conductance measurements confirmed these conclusions regarding dichloro- and trichloro-acetic acids. Recent, accurate, conductance measurements [3] on solutions of these two acids in sulphuric acid at 25° are in general agreement with these earlier findings. These data were not used, however, to evaluate the basic dissociation constants of these bases by the conductometric method which was developed somewhat later.[4] This would not have been possible for trichloroacetic acid in any case, since this solute depresses the conductivity of pure sulphuric acid, and the conductometric method developed by Gillespie and Solomons [4] is not applicable to such solutes. It has been suggested, however, that trichloroacetic acid is almost certainly slightly ionised in sulphuric acid.[5] Since the conductometric method for the evaluation of basic dissociation constants of weak bases in sulphuric acid has been modified [1] and made applicable also to solutes which depress the conductivity of the pure solvent, work was undertaken to obtain more reliable information about the basic ionisation of the three chloroacetic acids in sulphuric acid. Conductance measurements at 10° and 25° have been made and analysed to give basic ionisation constants of these acids in sulphuric acid. The results obtained correlate very well with the pK_A values of these acids in water.

Results

Measurements of electrical conductivity at 10° and 25° are reported in Table 1. Earlier measurements [3] on solutions of dichloro- and trichloro-acetic acids at 25° involve an error [6] of ~1%, reflected in the lower value of the conductance of the pure solvent given there,

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[1] Part I, M. Liler, *J.*, 1962, 4272.

[2] A. Hantzsch, *Z. physikal. Chem.*, 1908, **61**, 257.

[3] R. J. Gillespie and S. Wasif, *J.*, 1953, 221.

[4] R. J. Gillespie and C. Solomons, *J.*, 1957, 1796.

[5] R. J. Gillespie, E. D. Hughes, and C. K. Ingold, *J.*, 1950, 2473.

[6] R. J. Gillespie, J. V. Oubridge, and C. Solomons, *J.*, 1957, 1804.

TABLE 1

Specific conductivities of chloroacetic acids in sulphuric acid at 10° and 25°

Concn. (mole kg.$^{-1}$ soln.)	$10^2\kappa_{10}$ (ohm^{-1} cm.$^{-1}$)	$10^2\kappa_{25}$ (ohm^{-1} cm.$^{-1}$)	Concn. (mole kg.$^{-1}$ soln.)	$10^2\kappa_{10}$ (ohm^{-1} cm.$^{-1}$)	$10^2\kappa_{25}$ (ohm^{-1} cm.$^{-1}$)
		Monochloroacetic acid			
0·0583	1·004	1·592	0·142	1·679	2·554
0·0685	1·085	1·713	0·168	1·882	2·851
0·0855	1·233	1·920	0·175	1·927	2·919
0·114	1·470	2·254	0·194	2·029	3·062
		Dichloroacetic acid			
0·0232	0·6051	1·083	0·119	0·7890	1·312
0·0424	0·6392	1·122	0·162	0·8683	1·420
0·0637	0·6820	1·176	0·192	—	1·498
0·107	0·7678	1·286			
		Trichloroacetic acid			
0·0588	0·5723	1·034	0·244	0·5529	0·988
0·110	0·5684	1·024	0·301	0·5438	0·971
0·137	0·5630	1·012	0·379	0·5308	0·946
0·189	0·5585	1·001			

$\kappa_{25} = 1\cdot033 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$. If earlier measurements are corrected by that amount (*i.e.*, made consistent with the conductance of the pure solvent of $1\cdot044 \times 10^{-2}$ ohm^{-1} cm.$^{-2}$ at 25°), the agreement with the present data for dichloroacetic acid is very good, and it is reasonable for trichloroacetic acid. Density values can be expressed as before [1] in terms of the slope of the plot of density *vs.* concentration, $s = (d - d_0)/\omega$, where d is the density of the solution, d_0 density of the pure solvent (1·8420 at 10° and 1·8269 at 25°), and ω the concentration of the solution in moles per kg. of solution (molon units). The values of s are as follows for 10° (the values in parentheses are for 25°): monochloroacetic acid, $-0\cdot018$ ($-0\cdot021$), dichloroacetic acid, $-0\cdot031$ ($-0\cdot033$), and trichloroacetic acid, $-0\cdot031$ ($-0\cdot033$).

DISCUSSION

Treatment of Results.—Optimum conditions for the application of the conductometric method of estimating basic ionisation constants of weak bases in 100% sulphuric acid obtain when the base is 30—70% ionised in the useful concentration range of 0·05—0·25 mole l.$^{-1}$. This was the case for nitro-compounds,[1] for which the method was shown to be as reliable as the spectrophotometric and cryoscopic methods. The results for the ionisation of dichloroacetic acid fall in the same optimum range, and the basic ionisation constants for this base are therefore probably equally reliable.

For bases more than 70% ionised, the uncertainties of the determination increase with increasing basic strength. This is not due only to the increased uncertainty of the ratio $\alpha/(1 - \alpha)$ in the expression for the ionisation constant, but also to a greater effect on the estimates of α of the differences in the viscosity of the solution of the "mean" strong electrolyte ($KHSO_4$) and the solutions of the fairly strong base studied. Gillespie and Wasif [3] have shown that the products $\kappa(\eta/\eta_0)^{\frac{1}{2}}$, rather than the conductivities, of the solutions of all strong bases in sulphuric acid coincide. Therefore, conductivities corrected for the effect of viscosity should be used in estimating the degrees of dissociation of fairly strong bases. Viscosity data for the solutions of monochloroacetic acid in sulphuric acid at 50° are available in the literature.[7] If η/η_0 values for these solutions at 25° are assumed to be the same as the values at 50°, these can be compared with the values for the solutions of potassium hydrogen sulphate in sulphuric acid [8] at 25°. The comparison shows that the relative viscosities of the solutions of these two solutes at equal concentrations are practically identical, which means that the viscosity correction in this case would not alter the estimate of the basic ionisation constants from conductivities.

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[7] N. Pushin and D. Stanojevich, *Bull. Soc. chim. Beograd*, 1940—1946, **11**, 33.

[8] R. J. Gillespie and S. Wasif, *J.*, 1953, 215.

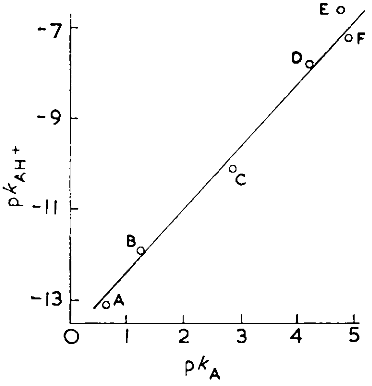
The basic ionisation constants for trichloroacetic acid were obtained on the assumption that sulphuryl chloride is a good " mean " reference non-electrolyte for comparison with this base. They are probably as reliable as those for the very weakly basic nitro-compounds.[1] All basic ionisation constants are given in Table 2.

TABLE 2

Basic ionisation constants of the three chloroacetic acids in sulphuric acid at 10° and 25°

Base	K_b^{10}	K_b^{25}	$pK_{AH^+}^{25}$
Monochloroacetic acid	$1{\cdot}1 \times 10^{-1}$	$1{\cdot}1 \times 10^{-1}$	$-10{\cdot}1$
Dichloroacetic acid	$1{\cdot}6 \times 10^{-3}$	$1{\cdot}9 \times 10^{-3}$	$-11{\cdot}9$
Trichloroacetic acid	$1{\cdot}1 \times 10^{-4}$	$1{\cdot}2 \times 10^{-4}$	$-13{\cdot}1$

The Calculation of the pK_{AH^+} *of the Conjugate Acids.*—In order to recalculate these basic ionisation constants to pK_{AH^+} values based on the acidity function of sulphuric acid, the procedure developed for nitro-compounds [1] was followed. However, the most recent values for the acidity function for sulphuric acid–water mixtures [9] were used, instead of the earlier data of Paul and Long; [10] the value thus obtained for dichloroacetic acid at 25° is 11·93. The values for the other two acids were calculated similarly by using appropriate ΔpK_b^{25} values. The $pK_{AH^+}^{25}$ values thus obtained are also given in Table 2.



A plot of the pK_{AH^+} of the conjugate cation acids in sulphuric acid against the pK_A of the carboxylic acids in water

A, Trichloroacetic acid. B, Dichloroacetic acid. C, Monochloroacetic acid. D, Benzoic acid. E, Acetic acid. F, Propionic acid.

Correlation with the pK_A *Values of the Acids in Water.*—The most reliable values for the dissociation constants in aqueous solution at 25° of monochloroacetic ($1{\cdot}36 \times 10^{-3}$), dichloroacetic ($5{\cdot}53 \times 10^{-2}$), and trichloroacetic acid (0·232), as selected by Kortüm, Vogel, and Andrussow,[11] were used in calculating pK_A values. A plot of the pK_{AH^+} of the conjugate acids in sulphuric acid against the pK_A of the carboxylic acids in aqueous solution is shown in the Figure. Existing data for benzoic,[12] propionic,[13] and acetic acid [14] (all corrected to the acidity-function scale of Jorgenson and Hartter [9]) are included in the plot. As can be seen, a good linear relationship is obtained over a wide range of acidities. The point for acetic acid deviates most, but the spectrophotometric determination of the pK_{AH^+} for this acid [14] is not very reliable, owing to low absorption. The slope of the line is 1·4, and is comparable to the slope ($\rho = 1{\cdot}30$) obtained by Ross Stewart and Yates [12] in an analogous plot for substituted benzoic acids (the original ρ value of 1·09 is increased, when the acidity function scale of Jorgensen and Hartter is used). A plot of pK_1 *vs.* pK_2 for a number of dibasic inorganic acids [15] also has a similar slope.

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[9] M. J. Jorgenson and D. H. Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878.

[10] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1.

[11] G. Kortüm, W. Vogel, and K. Andrussow, " Dissociation Constants of Organic Acids in Aqueous Solution," Butterworths, London, 1961.

[12] Ross Stewart and K. Yates, *J. Amer. Chem. Soc.*, 1960, **82**, 4059.

[13] J. T. Edward and I. C. Wang, *Canad. J. Chem.*, 1962, **40**, 966.

[14] A. R. Goldfarb, A. Mele, and N. Gutstein, *J. Amer. Chem. Soc.*, 1955, **77**, 6194.

[15] Ross Stewart and J. P. O'Donnell, *Canad. J. Chem.*, 1964, **42**, 1694.

Thermodynamic Functions for Basic Ionisation.—The only experimental values in this work which are accurate enough to justify a calculation of thermodynamic functions for basic ionisation are those for dichloroacetic acid. The two basic ionisation constants given in Table 2 for this base are both accurate to probably ±6%. If the same errors account for the variations of the K_b values at the two temperatures, their ratio might be more accurate than suggested by the accuracies of the two K_b values. Assuming that it is probably no less accurate than ±5%, one obtains the standard heat of ionisation, $\Delta H^\circ = 1{\cdot}8 \pm 0{\cdot}6$ kcal. mole^{-1}. The standard entropy of ionisation, $\Delta S^\circ_{298\cdot1} = -6$ cal. deg.$^{-1}$ mole^{-1}, is of the same order of magnitude as the value obtained for the basic ionisation of nitrobenzene [1] and is also probably due mainly to the ordering of the solvent by the anion.

EXPERIMENTAL

Sulphuric acid was prepared as previously described.[1] It had a conductivity of $1{\cdot}044 \times 10^{-2}$ ohm^{-1} cm.$^{-1}$ at 25°.

The three chloroacetic acids were all B.D.H. laboratory reagents, and were purified by vacuum distillation. The distilled sample of trichloroacetic acid was, in addition, purified by fractional crystallisation.

Solutions of dichloroacetic acid were prepared by adding the solute from a dropper to a weighed amount of the solvent, taking precautions to avoid contamination of the solutions by atmospheric moisture. The most concentrated solutions of mono- and tri-chloroacetic acids were prepared by weighing the solute first and then adding the solvent in flasks, from which the solution could be transferred into other vessels by means of a siphon arrangement. The more dilute solutions were prepared by diluting the most concentrated solutions by weight with the pure solvent, kept also in a flask with a siphon arrangement. Although the solutions are quite stable, measurements were carried out within 24 hr. of their preparation.

The conductance bridge and the cells used were described before.[1] Density measurements were carried out by means of a specific-gravity bottle and are not accurate to more than 1 part in 10^5.

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