

## Acidity of Trichloroacetic Acid

HOWARD BURKETT, RICHARD MURPHY and DEAN YARIAN,  
DePauw University

Authors of numerous textbooks state that trichloroacetic acid is a strong acid—comparable to the strong mineral acids. This statement is correct for dilute aqueous solutions. In addition to other evidence measurements of the Hammett acidity function<sup>1</sup> showed that the acidity function,  $H_0$ ,

$$H_0 = pK_a + \log\left(\frac{[B]}{[BH^+]}\right) \quad (1)$$

of trichloroacetic acid was almost identical with that of the strong mineral acids in dilute solutions. At concentrations above about twenty percent, however, the acidity function did not increase further but remained constant with increasing acid concentration. The maximum value of the acidity function was reported to be approximately +0.60.

Two observations would lead one to question this low value for the acidity of trichloroacetic acid. First, comparison of the rates for the hydrolysis of sucrose vs. the acidity function for various acids (2) shows that trichloroacetic acid appears to be a much better catalyst than the mineral acids. If the rate constants vs. molar concentration (rather than vs. acidity function) are plotted, the curve for trichloroacetic acid deviates no more from the mineral acids than the mineral acids deviate from each other. If catalytic action is proportional to acidity function, as was proposed for the mineral acids, it seems likely that the measurements of the acidity functions were in error. That only one indicator was used in this study made this possibility of error more plausible.

Second, cryoscopic measurements (3) show that trichloroacetic acid is unionized (as a base) in pure sulfuric acid. On the other hand, weak to moderately strong acids (acetic, chloroacetic, dichloroacetic, nitric and hydrochloric acids, for example) do ionize as bases in sulfuric acid. The stronger acids ionize less than the weaker ones. Perchloric acid, a very strong acid, does not so ionize. It has been proposed that the greater the acid strength of an acid the lower will be its basicity toward sulfuric acid. If this correlation is valid for all acids, trichloroacetic acid should be approximately as strong as perchloric acid.

The authors considered the possibility that trichloroacetic acid could form a strong dimeric association complex (as does acetic acid) in the more concentrated solutions, which would lower its effectiveness as a proton donor (acid). Gillette (4) concludes, from shifts of the infrared absorption band near 1721  $\text{cm}^{-1}$ , that association is considerably decreased in the series alkylacetic, acetic, chloroacetic, dichloroacetic and trichloroacetic acids. Moreover, dipole moment studies (5) and vapor density measurements (6) indicate the order of decreasing association to be alkylacetic, acetic and chloroacetic acid. Although no

quantitative estimation can be made of the degree of association, these experiments suggest that dimeric association is an unlikely cause for the low acidity of trichloroacetic acid.

In addition, conductimetric measurements (7) of concentrated solutions of acids in acetic acid indicated trifluoroacetic acid to be a stronger acid than nitric acid. It is to be noted, of course, that these studies were for trifluoroacetic acid (not trichloroacetic acid) and in the solvent acetic acid rather than water.

For the reasons indicated above, a reinvestigation of the acidity of concentrated solutions of trichloroacetic acid was considered to be desirable.

### Experimental

**Materials.** The nitrogen indicators, *o*-nitroaniline, *p*-nitroaniline and 2-chloro-4-nitroaniline, were obtained from commercial sources. They were recrystallized from alcohol-water mixtures until no further rise in melting point was obtained, then recrystallized one more time. Final drying was in a desiccator over phosphorous pentoxide. The 2,4,6-trimethoxybenzaldehyde was prepared by a published method (8). It was carefully recrystallized and dried in the same manner as the nitrogen indicators. Concentrations of the acid solutions were determined by titrating weighed samples.

**Procedure.** For each measurement a weighed sample of the indicator was dissolved in the solvent acid in a volumetric flask so that the resulting solution was  $10^{-4}$  to  $10^{-5}$  molar. The ultra violet spectrum was determined using the Beckmann D U instrument. Duplicate measurements were made in every case including the preparation of the solution. The extinction coefficients were calculated and plotted vs. the wavelength. For each indicator the spectrum in water was considered to be the spectrum of the unionized indicator. Since ionization was not complete in any concentration of the trichloroacetic acid solutions, the spectrum in a suitably high concentration of sulfuric or perchloric acid was used for the spectrum of the conjugate acid (complete ionization) of each indicator.

Calculation of the ratio of base to conjugate acid of the base were made at several wavelengths near the absorption maximum of the unionized base, using the equation

$$[B]/[BH^+] = (E_B - E_X)/(E_X - E_{BH^+}),$$

where  $E_B$  is the extinction coefficient of the unionized indicator,  $E_{BH^+}$  is the extinction coefficient of the completely ionized indicator and  $E_X$  is the extinction coefficient of the solution under consideration. By substituting this ratio into equation (1) calculations of the  $pK_a$  of the indicator, using the known acidity functions for the sulfuric acid solutions, and the acidity functions of trichloroacetic acid, using the known  $pK_a$  of each indicator, were readily made.

## Results and Discussion

Data used for the calculation of the  $pK_a$  and the calculated  $pK_a$  for 2-chloro-4-nitroaniline are given in Table I.

TABLE I

Extinction coefficients and  $pK_a$  for 2-chloro-4-nitroaniline ( $E \times 10^{-3}$ ).

$H_2SO_4, \%$	$H_0$	365	370	375	377.5	380	Av. $pK_a$
Water		11.9	12.2	12.3	12.2	11.9	
4.76	+0.25	11.0	11.4	11.5	11.4	11.2	-0.88
9.62	-0.15	9.8	10.0	10.1	10.1	10.0	-0.85
14.72	-0.61	8.0	8.2	8.3	8.3	8.2	-0.93
19.65	-0.87	5.9	6.1	6.2	6.2	6.1	-0.89
28.93	-1.53	2.2	2.3	2.3	2.3	2.2	-0.86
49.55		0.2	0.2	0.2	0.2	0.2	
						Average	-0.88

Using the extinction coefficients for solutions of the three nitrogen indicators in several concentrations of trichloroacetic acid, the acidity functions of trichloroacetic acid solutions were calculated in the same manner indicated above. The resulting acidity functions are listed in Table II. Results obtained recently by Randles and Tedder (9), using a colorimetric method, are given for comparison. In order to obtain figures at the same concentrations used in the present study their data were plotted and the acidity function read from the plot at each desired concentration.

The  $pK_a$  of 2,4,6-trimethoxybenzaldehyde was found to be -2.08. No spectroscopic evidence for the ionization of this indicator was observed at any concentration of trichloroacetic acid, including melted pure trichloroacetic acid. Hence, no data for this indicator are given. From the above observation it is unlikely that the acidity function of pure trichloroacetic acid exceeds -1.25.

The present results for the acidity function of trichloroacetic acid are consistent with those of Randles and Tedder within the usually-acceptable experimental error ( $\pm 0.05$  at lower concentrations and  $\pm 0.10$  at higher concentrations). Both recent studies indicate trichloroacetic acid to be a stronger acid than was indicated by Hammett's results. On the other hand, trichloroacetic acid in the higher concentrations is a weaker acid than the strong mineral acids.

TABLE II

Acidity function of trichloroacetic acid.

Molar conc.	H <sub>0</sub>				
	p-nitroaniline		o-nitroaniline		2-chloro-4-nitroaniline
	Present study	Randles Tedder	Present study	Randles Tedder	
0.197	+0.80	+0.83			
0.394	+0.51	+0.54	+0.48	+0.52	
0.788	+0.32	+0.25			
0.98	+0.12	+0.14	+0.14	+0.14	
1.18	+0.03	+0.05			
1.48					+0.16
1.58	-0.03	+0.03			
3.16	-0.03	+0.03			
4.74			+0.04	+0.03	
4.82	-0.12	-0.05			
6.4			+0.02	+0.01	
7.2				-0.40	-0.51
7.9				-0.78	
8.6					-0.95 to -1.05

The authors have determined the  $pK_a$  of 2-chloro-4-nitroaniline for the first time and have measured the acidity function of trichloroacetic acid at a higher concentration than has previously been reported.

Randles and Tedder suggest a reasonable explanation for the low acidity function for trichloroacetic acid. The more concentrated solutions have a low dielectric constant. Since solvents of low dielectric constant increase the difficulty of forming charged ions, ionization does not occur as readily in concentrated solutions of trichloroacetic acid as one would otherwise expect.

## Literature Cited

- HAMMETT, L. P. and M. A. PAUL. 1934. A Series of Simple Basic Indicators. III. The Zero Point of the Acidity Function Scale. *J. Am. Chem. Soc.* **56**:827.
- HAMMETT, L. P. and M. A. PAUL. 1934. The Relation between the Rates of Some Acid Catalysed Reactions and the Acidity Function,  $H_0$ . *J. Am. Chem. Soc.* **56**:830.
- HAMMETT, L. P. 1940. "Physical Organic Chemistry." McGraw-Hill Book Company, Inc. New York. p. 45 ff.
- GILLETTE, R. H. 1936. The Effect of Substitution on the Infra-red Absorption Spectrum of Acetic Acid. *J. Am. Chem. Soc.* **58**:1143.
- MARYOTT, A. A., M. E. HOBBS and P. M. GROSS. 1949. Electric Polarization of Carboxylic Acids. III. A Study of the Association of Some Additional Carboxylic Acids in Benzene Solution. *J. Am. Chem. Soc.* **71**:1671.

6. JOHNSON, E. W. and L. K. NASH. 1950. The Vapor-Phase Association of Acetic and Trimethylacetic Acids. *J. Am. Chem. Soc.* **72**:547.
7. EMELEUS, H. J., R. N. HASZELDINE and R. C. PAUL. 1954. Organometallic and Organometalloidal Compounds. Part VIII. Properties of Trifluoromethylarsenic Acids and of Other Fluorine-containing Acids. *J. Chem. Soc.* 881.
8. HERZIG, J., F. WENZEL and H. GEHRINGER. 1903. *Monatscheft für Chemie.* **24**:866.
9. RANDLE, J. E. B. and J. M. TEDDER. 1955. The Acidity Function  $H_0$  for Solutions of Trifluoroacetic Acid and Trichloroacetic Acid in Water. *J. Chem. Soc.* 1218.