CCLXXIV.—*The Titrimetric Determination of Primary Arsinic Acids.*

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THE identification of arsinic acids is a matter of some difficulty, for, although as a rule they are highly crystalline substances, they do not usually possess characteristic sharp melting points. The urgent need for some simple and rapid means of identifying arsinic acids arose during some experiments on the oxidation of *m*- and *p*-xylylarsinic acids to the corresponding *iso*- and tere-phthalic acid arsinic acids.

The analogy between phosphoric and arsenic acid, and the similarity of their first, second, and third dissociation constants, suggested that the methods which are applicable to the titration of phosphoric acid might with suitable modification be adapted to primary arsinic acids. There is no record of the determination of the dissociation constants of any primary phosphinic or arsinic acid, but a comparison of benzenesulphonic acid, for which $K_1 = 2 \times 10^{-1}$, with sulphuric acid ($K_1 = 2 \times 10^{-1}$ and $K_2 = 2 \times 10^{-2}$) suggested that K_1 and K_2 for a primary arsinic acid should be of

the same order as K_1 and K_2 for arsenic acid. This fact is, indeed, familiar to workers on arsenicals, for the monosodium salt of a primary arsinic acid is usually regarded as approximately neutral to litmus and the disodium salt is alkaline to phenolphthalein (Astruc, *Compt. rend.*, 1902, **134**, 660).

Some preliminary results on the titration of *p*-tolylarsinic acid, 3-nitro-*p*-tolylarsinic acid, and benzarsinic acid with 0·1*N*-alkali and phenolphthalein as indicator showed that the end-point was reached too early and the development of a pink colour was gradual. Treadwell (" Quantitative Analyse," 1921, ii, 471, 506) has suggested that, in the titration of phosphoric acid with phenolphthalein, hydrolysis could be avoided by addition of a large excess of sodium chloride, and Kolthoff (*Chem. Weekblad*, 1915, **12**, 644) recommends titration in the presence of an equal volume of saturated sodium chloride solution. The effect, on the titration with phenolphthalein of the above-mentioned arsinic acids, of adding sodium chloride to practically complete saturation is shown by the following table: the volumes are expressed in terms of *M*/1000 of substance titrated.

Acid.	Without NaCl.	With NaCl.	Theory.
p-Tolylarsinic acid	13·53 c.c.	18·86 c.c.	20 c.c.
3-Nitrotolylarsinic acid ...	17·88	19·69	20
p-Benzarsinic acid	25·36	29·49	30

The addition of sodium chloride raises the titre almost to the calculated value and, what is of practical importance, sharpens the end-point, so that maximum colour intensity of the indicator is produced by one or two drops of 0·1*N*-alkali. This is the great advantage gained by titration to the disodium salt rather than to the monosodium salt, and there is no complicating influence of a third dissociating hydrogen ion.

The turning point for phenolphthalein is given by Sørensen (*Biochem. Z.*, 1907, **7**, 51) at a p_H of approximately 8·5, and a trial of other indicators with turning points slightly further on the alkaline side was clearly suggested. For this purpose we chose thymolphthalein with a pronounced colour change at about p_H 9·5 (Sørensen, *loc. cit.*) and thymolsulphonphthalein (thymol-blue) with a p_H range of 8·0—9·6 (Clark and Lubs, *J. Amer. Chem. Soc.*, 1918, **40**, 1443). Trial of these two indicators on a long series of arsinic acids in the presence of excess of solid sodium chloride showed that thymol-blue gave values above those of phenolphthalein but still short of the theoretical values, whilst thymolphthalein gave values slightly above the theoretical. It may be that 1 : 2 : 3-xylenolphthalein (Clark, " Determination of Hydrogen Ions," 1925, 92), with a p_H range of 8·9—10·2, standing between phenolphthalein and thymolphthalein, is the ideal indicator for arsinic acids under such con-

ditions. Before proceeding to synthesise this indicator, which is not available commercially, it seemed desirable to try the effect of half-saturation with sodium chloride on the titration figures with thymolphthalein. This could readily be effected experimentally by first titrating the substance with thymolphthalein and then adding an equal volume of saturated sodium chloride solution (previously neutralised to thymolphthalein) to the titration solution and continuing the titration. This method proved successful, as is shown by the following table, which gives the values obtained with thymol-blue in the presence of solid sodium chloride, and with thymolphthalein in the presence of solid sodium chloride and with half-saturation with this salt. The volumes used (c.c.) are all expressed in terms of $M/1000$ of substance, and the final column gives the error % observed on the half-saturation method. The results were usually correct to within 1% and were, as a rule, determined on about 0·1 g. of substance.

Acid.	Thymol-blue. Satd. NaCl.	Thymolphthalein. Satd. NaCl.	Thymolphthalein. ½-Satd. NaCl.	Error, % (½-satd. NaCl).
Methylarsinic acid	19·3	20·47	20·20	+1·0
Phenylarsinic acid	—	—	20·06	+0·3
p-Tolylarsinic acid	20·14	20·56	19·94	−0·3
m-Xylylarsinic acid	19·54	20·51	19·84	−0·8
p-Xylylarsinic acid	19·89	20·26	19·71	−1·5
3-Nitro-*p*-tolylarsinic acid	20·0	20·80	19·84	−0·8
Benzarsinic acid	29·85	30·83	30·20	+0·7
3-Nitrobenzarsinic acid	29·69	30·49	29·64	−1·2
4-Acetamido-3-benzarsinic acid monohydrate	—	31·07	30·06	+0·2
3-Acetamido-4-benzarsinic acid monohydrate	—	—	30·00	0·0
Hippuroarsinic acid	29·97	30·55	30·03	+0·1
Phenylarsinic acid disulphide	40·01	40·61	40·00	0·0

Many of the values obtained with thymol-blue show as good agreement with the theoretical values as do the values obtained by the half-saturation method using thymolphthalein. Thymol-blue, however, has several disadvantages. The titration solution is coloured yellow by it, the colour change at the turning point is not so clear and brilliant as with thymolphthalein, and certain arsinic acids exert a specific action on the thymol-blue, resulting in an abnormally low titre.

Titration to an end-point at about p_H 9·5 has certain disadvantages. It was found by H. Meyer (*Monatsh.*, 1907, **28**, 1381) that the hydroxyl group in various salicyl derivatives might consume, when titrated with phenolphthalein as indicator, any quantity up to 1 mol. of alkali, depending on the substituents present. This is not surprising, since the dissociation constants of phenolphthalein and of

phenol are of the same order, being respectively $2{\cdot}0 \times 10^{-10}$ and $1{\cdot}3 \times 10^{-10}$. Thymolphthalein is a slightly weaker acid than phenolphthalein and groups of comparable acidity in the compounds titrated will produce an effect. This is distinctly brought out by the following results.

No.	Acid.	Thymol-blue. Satd. NaCl.	Thymolphthalein. Satd. NaCl.	Thymolphthalein. ½-Satd. NaCl.
1	Salicylic acid 5-arsinic acid	31·58 c.c.	34·52 c.c.	32·00 c.c.
2	Salicylic acid 4-arsinic acid	—	—	33·44
3	Salicylamide-5-arsinic acid	25·68	29·98	28·02
4	Salicylamide-4-arsinic acid	—	—	27·52
5	3-Acetamido-4-hydroxyphenylarsinic acid	—	—	29·66
6	Benzamide-*p*-arsinic acid	20·64	21·14	20·53
7	Benzamide-*m*-arsinic acid	20·47	21·09	20·75
8	Benzethylamide-*p*-arsinic acid	19·98	20·15	20·08
9	Benzdiethylamide-*p*-arsinic acid ...	—	—	20·18
10	*N*-Phenylbenzamide-*p*-arsinic acid...	20·23	20·67	20·48
11	*p*-Nitrobenzamidophenylarsinic acid	19·13	21·55	20·82
12	Benzenesulphonamide-*p*-arsinic acid	21·27	27·13	26·83
13	*iso*Phthalamic acid 6-arsinic acid ...	25·94	30·9	29·54
14	Phenylglycineamide-*p*-arsinic acid	—	—	20·09
15	Phenylglycine-*p*-arsinic acid	—	29·92	—
16	Anthranilic acid 5-arsinic acid	—	28·41	—
17	Anthranilic acid 4-arsinic acid	—	23·72	—

The first five compounds show the effect of the hydroxyl group. The values show variations as great as those in Meyer's series. The next seven compounds are of special interest and need further discussion. Benzenesulphonamide-*p*-arsinic acid (No. 12) on titration gives a value 68% above its arsinic acid content. This could be interpreted in one of two ways, but only one interpretation is tenable. *p*-Sulphonamidobenzoic acid is a much stronger acid than benzoic acid, their respective dissociation constants being 26×10^{-5} and $6{\cdot}6 \times 10^{-5}$ (Lucas, *J. Amer. Chem. Soc.*, 1926, **48**, 1832), so when these acids are titrated to the same p_H, as is theoretically done with phenolphthalein or thymolphthalein, the stronger acid will be over-titrated in comparison with the weaker. For two such acids as these, the difference of hydrogen-ion concentration at their half-neutralisation points will be approximately the difference of their dissociation constants and this will correspond to a difference in p_H of about 0·6. The titration curves (p_H plotted against % titrated) for these acids will be approximately parallel, so that the end-points of the two titrations measured electrometrically will differ by about 0·6 unit of p_H. This is practically negligible, as is verified experimentally by titration of *p*-nitrobenzoic acid, a much stronger acid than *p*-sulphonamidobenzoic acid, and benzoic acid to the same p_H, 0·1*N*-alkali being used. Both acids give the correct

equivalent. The only other explanation of the high titration of benzenesulphonamide-*p*-arsinic acid is that its third dissociation constant is sufficiently large to make itself felt (compare Schroeter, *Ber.*, 1907, **40**, 1615), and this will be similar in magnitude to that of the phenolic group. This also we believe is the interpretation of the slightly high titres of benzamide-*m*- and -*p*-arsinic acids (Nos. 7 and 6), the figures for which are significant, and in agreement with this the titres of the monoethyl- and diethyl-amides (Nos. 8 and 9), where a third dissociation of hydrogen is less or impossible, are almost normal. The increased acidity of the amide group is shown, as might be anticipated, in *N*-phenylbenzamide-*p*-arsinic acid (No. 10) and *p*-nitrobenzamidophenylarsinic acid (No. 11). Finally, the effect of basic groups is shown by the last four examples. In Nos. 14 and 15 the secondary amino-group has little effect on the acidity of the compound, whereas in Nos. 16 and 17 the primary amino-group lowers the acidity noticeably.

EXPERIMENTAL.

The following method is recommended for the titration of primary arsinic acids.

About 0·1 g. of the acid is accurately weighed out into a 50-c.c. extraction flask, treated with 2 drops of 0·1% solution of thymolphthalein in alcohol, and titrated with 0·1*N*-sodium hydroxide until a blue colour appears. An approximately equal volume of saturated sodium chloride solution, neutral to thymolphthalein, is then added, and the bleached solution titrated with alkali until a blue colour is again produced. Maximum intensity of blue is usually secured by addition of one or two drops of 0·1*N*-alkali after the first faint blue coloration has developed. The results can then be interpreted either in terms of the number of c.c. of 0·1*N*-alkali required for *M*/1000 of substance, as is done in this paper, or in terms of the equivalent of the acid. The former method is the more convenient where new acidic groups are being produced by oxidation of alkali radicals and some guide as to the progress of the oxidation is required.

Pure sodium chloride of commerce is often acid in reaction, showing a p_H of about 5 with a " universal " indicator. A litre of saturated sodium chloride solution made up from such a salt will require about 1 drop of 50% sodium hydroxide solution to bring its p_H to neutrality to thymolphthalein as judged by a universal indicator.

The 0·1*N*-alkali used in the titrations should be free from carbonate, since the titrations are carried out in cold solution. We have not found any error to be introduced by the use of 0·1*N*-alkali made

up freshly from good stick sodium hydroxide, and control titrations of benzoic acid in cold and in boiling solution with phenolphthalein as indicator showed no difference.

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