p-Acetamidobenzenestibonic Acid.—The clear solution obtained by the reduction of 6.6 g. of p-nitrobenzenestibonic acid, after removal of the catalyst, was shaken with acetic anhydride (25 ml.) for thirty minutes. Sufficient sodium hydroxide was added as necessary to keep the solution just alkaline. The stibonic acid was precipitated by acidification, and washed on a filter with 5% hydrochloric acid.

p-Benzamidobenzenestibonic acid was prepared in a similar manner from p-aminobenzenestibonic acid and benzoyl chloride. The acid was washed with 5% hydrochloric acid followed by alcohol and ether to remove any benzoic acid. The pyridinium salt after one recrystallization from ethanol–hydrochloric acid, gave analytical figures for antimony and chlorine which approached the theoretical values, but the higher analytical data on repeated recrystallization indicated hydrolysis of the benzamide group.

p-(p-Hydroxyphenylazo)-benzenestibonic Acid.—The reduction mixture from 6.6 g. of p-nitrobenzenestibonic acid was acidified with 100 ml. of N hydrochloric acid and diazotized at 0°. The diazo solution was added dropwise to 2 g. of phenol dissolved in 10 ml. of N sodium hydroxide and 50 ml. of water. Sodium hydroxide solution was added when necessary to dissolve the precipitate which formed. The solution was allowed to stand overnight at 10°, filtered, the stibonic acid precipitated by acidification, and purified through the pyridinium salt. The pure stibonic acid was a pale orange powder.

p-Cyanobenzenestibonic Acid.—A solution of diazotized p-aminobenzenestibonic acid (from the reduction of 13.2 g., 0.04 mole of p-nitrobenzenestibonic acid) was neutralized with sodium carbonate at 0°, and added to an excess of freshly prepared cuprous cyanide solution. After all the nitrogen was evolved the mixture was allowed to stand for twenty-four hours, filtered, and the filtrate acidified with dilute hydrochloric acid. The crude stibonic acid which precipitated was converted to the pyridinium salt and recrystallized several times from ethanol–hydrochloric acid. The free acid was then obtained by alkaline hydrolysis.

Table I lists the stibonic acids prepared, together with the corresponding pyridinium salts.

Acknowledgment.—The authors wish to acknowledge the assistance given by David N. Kramer throughout the course of the work.

Summary

The chemical nature of various substituted arylstibonic acids has been modified by reactions which include oxidation of tolyl groups, reduction of nitro groups, esterification, and ammonolysis. The resulting stibonic acids, which are usually contaminated with inorganic antimony compounds, can often be effectively purified by recrystallization of the corresponding pyridinium salts.

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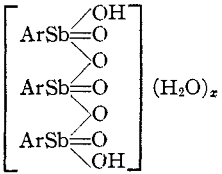
[CONTRIBUTION FROM THE UNITED STATES PUBLIC HEALTH SERVICE VENEREAL DISEASE RESEARCH AND POSTGRADUATE TRAINING CENTER, JOHNS HOPKINS HOSPITAL]

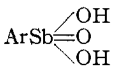
The Structure of Arylstibonic Acids

BY G. O. DOAK

While a large number of arylstibonic acids have been described in the literature, the chemical structure of these compounds has not been established with certainty. On the basis of (1) analytical results, (2) their behavior as pseudo acids, and (3) the differences in weight loss obtained on thermal and vacuum drying, Schmidt[1] concluded that the arylstibonic acids existed in the solid state as trimers (I), but dissociated in alkaline solution to the salt of the orthoantimonic form (II), and that the number of associated water molecules (x in formula I) varied not only with different compounds, but with the same compound prepared by different procedures.



I



II

Further evidence for this hypothesis was advanced by Fargher and Gray[2] who prepared neutral sodium salts of these acids with a sodium: antimony ratio of less than unity.

While Schmidt's conception has been generally accepted, Macallum,[3] on the basis of molecular weight determinations in solution, concluded that these compounds possessed the monomolecular structure (II). The experimental evidence has been summarized by Christiansen[4] and Goddard,[5] both of whom favor Schmidt's conception.

In the two preceding papers[6] new methods for the preparation and purification of arylstibonic acids have been described. By recrystallization of the corresponding pyridinium salts, followed by alkaline hydrolysis, one regularly obtained compounds of fixed composition, independent of the method of preparation or isolation. With compounds which could not be purified through the pyridinium salts, the analytical figures usually showed considerable variation. In general,

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[1] Schmidt, *Ann.*, **421**, 174 (1920); *Ber.*, **55**, 697 (1922).

[2] Fargher and Gray, *J. Pharmacol.*, **18**, 353 (1922).

[3] Macallum, *J. Soc. Chem., Ind.*, **42**, 468 T (1923).

[4] Christiansen, "Organic Derivatives of Antimony," The Chemical Catalog Co., New York, N. Y., 1925. This review, however, contains an error, pp. 60–61, where it is stated that the formula $[3(C_6H_5SbO_2)H_2O]\cdot 3H_2O$ used by Schmidt could be written as $C_6H_5SbO_3H_2\cdot H_2O$ without altering the proportions of the constituents. Internal evidence in Schmidt's paper, however, indicates that the factor 3 was not meant to apply to the following H_2O, and that the formula as postulated by Schmidt should be written $C_6H_5SbO_3H_2\cdot {}^1/_3H_2O$.

[5] Goddard, "A Text-book of Inorganic Chemistry," Vol. XI, part III, Charles Griffin and Co., Ltd., London, England.

[6] Doak and Steinman, THIS JOURNAL, **68**, 1987, 1989 (1946).

the derivatives of benzenestibonic acid substituted by electron-repelling groups possessed the empirical structure $ArSbO_3H_2$; while derivatives with electron-attracting groups, particularly in ortho and para positions, possessed the empirical structure $ArSbO_3H_2 \cdot H_2O$. As these results are inconsistent with Schmidt's data and interpretation, we have repeated and amplified the work of the previous investigators.

Experimental

The Behavior of Arylstibonic Acids in Alkaline Solution.—In order to determine whether arylstibonic acids behaved as pseudo acids, we have followed the progressive change with time in the *p*H of solutions of these acids in less than one equivalent of sodium hydroxide, employing the Beckman *p*H meter with a glass electrode.

To a measured amount of 0.1 *N* sodium hydroxide, diluted with 50 ml. of carbon dioxide-free water, and cooled to 0°, exactly 0.002 mole of the stibonic acid, previously passed through an 80-mesh standard sieve, was added. When the acid had completely dissolved the electrodes were placed in the solution and the *p*H determined at fixed intervals, maintaining the temperature at 0°. A stream of air which had passed through a soda-lime tube, was directed over the surface of the solution throughout the determination, and the solution was stirred mechanically. All the experiments were performed in duplicate.

The resulting change in *p*H plotted against time is shown in Fig. 1. The results obtained clearly show the behavior of arylstibonic acids as pseudo acids and are in conformity with Schmidt's experimental results.

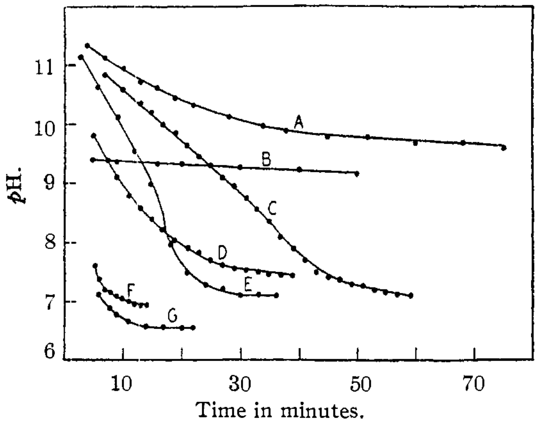

Fig. 1.—The change with time in the *p*H of solutions of stibonic acids dissolved in less than one equivalent of sodium hydroxide. With curves A and G, 0.45 equivalent of sodium hydroxide was used; with the remaining curves, 0.6 equivalent. The letters refer to the following stibonic acids: A, *o*-toluene-; B, *o*-nitro-; C and G, benzene-; D, *p*-toluene-; E, *m*-nitro; F, *p*-nitro-.

Determination of the Weight Loss on Drying Arylstibonic Acids.—Duplicate samples of 0.3 to 0.5 g., previously sieved through a 325 mesh standard sieve, were weighed into dry, tared weighing bottles and the weight loss determined over sulfuric acid at 0.1 mm. pressure. When constant weight had been attained the bottles were placed in an oven at 125 ± 1° and again weighed at intervals. The values obtained by this procedure were neither constant nor reproducible. In every case a large and irregular loss occurred within one week, with further loss for periods up to several months. These weight losses, even after drying for one week, often exceeded the calculated values for the formation of the anhydride, $ArSbO_2$; and the analytical values for antimony obtained with these dried samples regularly exceeded the calculated values for the anhydride. In view of the known lability of the antimony–carbon bond, these results suggest that thermal decomposition has occurred and that the experimental values were the resultant of two factors, water loss and decomposition.

The results obtained in one experiment in which the stibonic acids were dried to constant weight *in vacuo*, and at 125° for one week, together with the theoretical weight loss for the formation of the anhydride, and the calculated and found antimony analyses on the thermally dried samples, are given in Table I. Not only do these latter values exceed the calculated values for the anhydride, but they also exceed the antimony values calculated on the basis of the experimental weight loss. In view of the greater reliability of the analytical figures which strongly suggest thermal decomposition, we feel that the results obtained on thermal drying of arylstibonic acids are of dubious significance in relation to the structure of these compounds.

TABLE I

THE WEIGHT LOSS ON VACUUM AND THERMAL DRYING OF ARYLSTIBONIC ACIDS

Stibonic acid	Loss *in vacuo*, %	Loss at 125°, %	H_2O calcd.	Sb analyses, % $ArSbO_2$ Calcd.	Found
C_6H_5-	3.3	7.8	7.2	52.8	53.0
o-$CH_3C_6H_4$-	2.9	6.8	6.8	49.8	50.0
m-$CH_3C_6H_4$-	3.2	7.1	6.8	49.8	51.3
p-$CH_3C_6H_4$-	2.8	19.8	6.8	49.8	58.0
p-ClC_6H_4-·H_2O	4.1	18.9	11.2	45.9	53.0
p-$CH_3CO_2C_6H_4$-·H_2O	3.6	12.3	11.1	42.2	44.5
p-$C_2H_5CO_2C_6H_4$-·H_2O	3.2	13.0	10.6	40.2	42.5
p-$NO_2C_6H_4$-·H_2O	4.8	11.1	11.5	44.1	47.5

The Apparent Molecular Weight of Stibonic Acids in Benzene.—Among the stibonic acids prepared in this Laboratory, only the three isomeric toluenestibonic acids

TABLE II

THE FREEZING POINT DEPRESSION OF TOLUENESTIBONIC ACIDS IN BENZENE

Acid	Weight, g. in 25 ml. of benzene	Δ° Calcd.	Δ° Found	Poly. no.
o-Toluenestibonic	0.1537	0.136	0.040	3.46
	.1712	.152	.041	3.70
	.2539	.225	.055	4.09
	.3005	.266	.060	4.43
	.3614	.320	.068	4.71
	.4223	.374	.074	5.05
	.4796	.425	.079	5.38
m-Toluenestibonic	.1508	.134	.038	3.53
	.2011	.178	.047	3.78
	.2548	.226	.059	3.83
	.3000	.266	.063	4.22
	.3309	.293	.066	4.44
	.4203	.357	.077	4.63
	.4436	.393	.084	4.68
	.4947	.438	.087	5.03
	.5511	.488	.092	5.30
p-Toluenestibonic	.1524	.135	.039	3.45
	.2012	.178	.050	3.56
	.2508	.222	.060	3.70
	.3353	.297	.073	4.06
	.4050	.359	.089	4.03
	.4574	.405	.090	4.50
	.5106	.453	.098	4.62
	.5643	.500	.105	4.76

were sufficiently soluble in benzene or other non-polar solvents to give even approximate values for the molecular weights.

The customary Beckman freezing-point apparatus was used in the following determinations. The benzene was dried and fractionated before use and exactly 25 ml. were used in each determination. The final concentration in each case represented the limiting solubility of the compound in benzene, at the freezing point.

The found depressions, together with the calculated values based on the monomolecular formula and the polymerization number (calculated depression/found depression) are given in Table II. Not only are the found values less than the values calculated for either Schmidt's or Macallum's structures, but the degree of polymerization increases with increasing concentration. This behavior is typical of organic acids in non-polar solvents and has been successfully interpreted as reflecting polymerization due to hydrogen bond formation.[7] The present experimental data are completely consistent with this interpretation. Figure 2 shows the plot of polymerization number against concentration; and it is seen that polymerization progresses linearly with increasing concentration, within the limits that could be studied.

TABLE III

THE FREEZING POINT DEPRESSION OF STIBONIC ACIDS

Compound	Weight, g., in 25 ml. of solvent	Δ° Calcd.	Δ° Found	% Dissociation	K $\times 10^{-3}$
(A)	In Acetic Acid				
$C_6H_5SbO_3H_2$	0.0748	0.045	0.056	24	0.9
	.1071	.064	.080	25	1.4
	.1519	.091	.111	22	1.5
	.1994	.119	.140	18	1.3
	.2675	.160	.185	16	1.3
o-$CH_3C_6H_4SbO_3H_2$	.1013	.057	.061		
	.1117	.063	.065		
	.1260	.071	.074		
	.1504	.085	.088		
m-$CH_3C_6H_4SbO_3H_2$	.0760	.043	.049	14	0.3
	.1050	.059	.067	14	0.4
	.1130	.064	.071	11	0.2
	.1452	.082	.092	12	0.4
	.1990	.113	.121	7	0.2
p-$CH_3C_6H_4SbO_3H_2$	.1034	.059	.070	19	0.7
	.1212	.069	.087	26	1.7
	.1519	.086	.102	19	1.0
	.2211	.125	.141	13	0.7
	.2600	.147	.167	14	0.9
	.3111	.176	.205	16	1.4
o-$BrC_6H_4SbO_3H_2$	.0616	.028	.049	75	17
	.0804	.036	.061	69	15
	.0951	.043	.072	67	16
	.1183	.054	.085	57	14
p-$ClC_6H_4SbO_3H_2 \cdot H_2O$	.0601	.030	.068	63	0.2
	.0821	.041	.114	89	0.3
	.0992	.049	.105	57	0.3
	.1098	.054	.108	50	0.2
p-$C_2H_5CO_2 \cdot C_6H_4SbO_3H_2 \cdot H_2O$	.1107	.049	.091	43	0.1
	.1677	.074	.136	42	0.2
	.2161	.095	.171	40	0.3
	.2560	.114	.188	33	0.2
	.3149	.138	.221	30	0.2
(B)	In Formic Acid				
m-$CH_3C_6H_4SbO_3H_2$	.2080	.072	.100	39	8
	.2661	.091	.125	37	9
	.2999	.103	.138	34	8
p-$CH_3CO_2 \cdot C_6H_4SbO_3H_2 \cdot H_2O$	.2014	.056	.150	84	9
	.4034	.112	.270	71	12
	.6356	.177	.377	57	11
	.8366	.233	.471	51	11
	1.0394	.289	.564	48	14
p-$C_2H_5CO_2 \cdot C_6H_4SbO_3H_2 \cdot H_2O$	0.2030	.054	.147	86	10
	.3140	.084	.215	78	12
	.4189	.112	.266	69	10
	.6213	.166	.376	63	15
	.8436	.225	.474	55	15
m-$CH_3CO_2 \cdot C_6H_4SbO_3H_2$	.4043	.119	.201	69	81
	.6062	.178	.283	59	67
	.8078	.239	.384	61	99
	1.0094	.297	.446	50	65

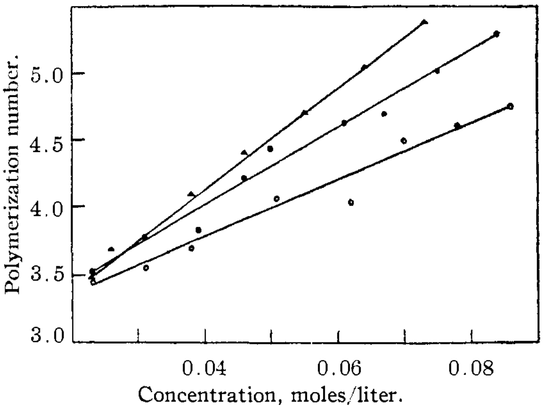

Fig. 2.—The polymerization of toluenestibonic acids in benzene as a function of concentration: Δ, *o*-toluene; ●, *m*-toluene; ○, *p*-toluene.

The Apparent Molecular Weight of Stibonic Acids in Acetic and Formic Acid.

If, as indicated by the above results, stibonic acids are polymerized by hydrogen bond formation, they should dissociate in such polar solvents as water and organic acids to give normal molecular weight values.[7] Qualitative solubility studies indicated that acetic and formic acid were suitable solvents for cryoscopic molecular weight determinations with some of the stibonic acids. Accordingly, C.P. samples of these solvents were dried and fractionated for that purpose. It was also found that the depressions obtained in fresh solutions in these solvents were not constant, but increased rapidly on standing to reach a constant limiting value within one hour. In order to avoid the absorption of atmospheric moisture by acetic acid, the modified Beckman apparatus shown in Fig. 3 was used. The compound was weighed in the thin-walled glass bulb, A, blown on the end of a short length of glass tubing. A pointed glass rod, B, served as a plunger to break the bulb when the compound was to be added to the solvent. This rod made an air-tight seal with the glass tubing by means of a short length

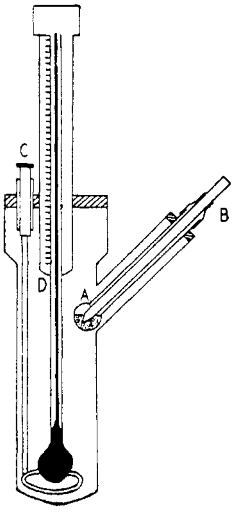

Fig. 3.—Molecular weight apparatus.

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[7] *Cf.* Lassettre, *Chem. Rev.*, **20**, 259 (1937).

of rubber tubing, wired to both the rod and the glass tubing. The stirrer, C, was constructed by removing the tip of a 1 ml. glass tuberculin syringe. The customary glass ring stirrer was then attached to the plunger of the syringe. D is the Beckman thermometer. With this apparatus it was possible to perform the entire operation without exposure to atmospheric moisture. With all compounds tested in acetic acid, and with *m*-toluenestibonic acid in formic acid, the largest concentration studied represents the approximate limiting solubility of that compound in the particular solvent at the freezing point.

The depressions in freezing point obtained with seven stibonic acids in acetic acid solution, and with four in formic acid, together with the calculated values based on the monomolecular formulas, $ArSbO_3H_2$ and $ArSbO_3H_2 \cdot H_2O$, are given in Table III. With the exception of *o*-toluenestibonic acid, which gave the expected values within the limit of experimental error, the found depressions of freezing point were even greater than the theoretical, and the discrepancy was usually larger than could be explained by possible contamination with impurities of low molecular weight.

The most obvious explanation for these results is that, at least in these solvents, stibonic acids dissociate further according to the equations

$$ArSbO_3H_2 \rightleftarrows ArSbO_2 + H_2O \qquad (1)$$

$$ArSbO_3H_2 \cdot H_2O \rightleftarrows ArSbO_2 + 2H_2O \qquad (2)$$

If this dissociation were relatively slow it would account for the initial increase in the freezing-point depression found in freshly prepared solutions (*cf.* p. 1993). Moreover, the experimental data should conform to the postulated hydrolytic reaction, and give constant values for the relationships

$$K_1 = \frac{[ArSbO_2][H_2O]}{[ArSbO_3H_2]} \text{ and } K_2 = \frac{[ArSbO_2][H_2O]^2}{[ArSbO_3H_2]}$$

The calculated per cent. dissociation and values for K are listed in the final two columns of Table III.[8] While the stibonic acids could not be studied in acetic acid over a sufficient range of concentration to establish the constancy of K, the results in formic acid did cover a sufficient range of concentration to suggest that the experimental data do in fact conform to the postulated hydrolytic reaction, and that the anomalous depression of the freezing point does actually reflect the dissociation of the stibonic acids to the anhydride and water. This is strongly supported by the fact that those compounds which analyzed for the structure $ArSbO_3H_2 \cdot H_2O$, gave freezing point depressions reflecting their dissociation into more than 2 moles per mole of stibonic acid, and corresponding quantitatively to the postulated equation (2).

Sodium Salts of Arylstibonic Acids.—While salts of the arylstibonic acids have been described by a number of workers, adequate analytical data have seldom been given. Fargher and Gray,[2] however, prepared sodium salts of several acids by dissolving the free acid in sufficient sodium hydroxide solution to form neutral solutions (presumably *p*H 7) and evaporating to dryness. The molar ratio, sodium:antimony, in the resulting salts varied with the acid studied, but was always less than unity. From these results the authors concluded that the salts consisted of a mixture of the monomolecular and trimolecular forms.[9]

We feel that the conclusions of Fargher and Gray are not justified by their data. In compounds isolated at *e.g.*, *p*H 7, the ratio sodium: antimony will obviously depend upon the *pKa* for the particular stibonic acid, and no values for that constant with stibonic acids have ever been reported. Accordingly, an attempt was made to determine the *pKa* for several stibonic acids by electrometric titration, using the Beckman *p*H meter and a glass electrode.[10] Unfortunately, in every case the free acid precipitated before sufficient data had been obtained to permit the calculation of the *pKa* values. Qualitative evidence, however, strongly suggests that the arylstibonic acids are extremely weak acids. Thus from the data given in Fig. 1, it is apparent that considerably less than one equivalent of sodium hydroxide would be required to bring the stibonic acids to *p*H 7. The precipitation of many stibonic acids from alkaline solution by carbon dioxide is further evidence for this viewpoint. The results obtained by Fargher and Gray could thus be adequately explained by assuming that they were dealing with a mixture of free acid and sodium salt. In order to avoid this difficulty, we have prepared the sodium salts of several stibonic acids by the following procedure.

The free acid (0.02 mole) was finely powdered and shaken at room temperature with 400 ml. of 0.1 *N* sodium hydroxide. A clear solution resulted in each case, but with *p*-toluenestibonic acid, a precipitate developed on standing which was removed by filtration. After one hour, the solution was added to five volumes of alcohol and the mixture cooled to −25°. The crystalline sodium salt slowly precipitated from solution. It was removed by filtration, washed with alcohol, and recrystallized by dissolving in a minimum of water and again precipitating with alcohol.

Three methods for the determination of sodium in these salts were investigated: (1) The weighed sample was dissolved in 150 ml. of water, 10 ml. of 10% hydrochloric acid added, and the mixture heated to boiling. A stream of hydrogen sulfide was passed in for one-half hour and the

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[8] The values for the dissociation with the two types of stibonic acids ($ArSbO_3H_2$ and $ArSbO_3H_2 \cdot H_2O$) were calculated respectively by the formulas % Dissociation$_1$ = [(Δfound − Δcal.)/Δcal.] × 100 and % Dissociation$_2$ = [(1/2(Δfound − Δcal.))/Δcal.] × 100 and the values of K by the formulas K_1 = (dissociation)^2 × molar concentration)/1 − dissociation and k_2 = 4 (dissociation)^3 × (molar concentration)^2/1 − dissociation.

[9] German Patent 267,083 describes the preparation of neutral salts of arylstibonic acids with a molar ratio, sodium: antimony = 0.33. However, no analytical data are presented.

[10] The technique used has been adequately described elsewhere; *cf.* Pressman and Brown, THIS JOURNAL, **65**, 540 (1942); Eagle Hogan, Doak and Steinman, *J. Pharmacol.*, **70**, 221 (1940).

mixture cooled to room temperature. The precipitated sulfide was removed by filtration and thoroughly washed with hydrogen sulfide water. Sodium was determined by evaporating the combined filtrate and washings to dryness and weighing as sodium chloride. (2) The weighed sample was dissolved in water in a volumetric flask, the solution made to volume, and the sodium determined directly by means of the flame photometer.[11] (3) The method of Fargher and Gray,[2] which consists essentially of precipitating the stibonic acid with dilute sulfuric acid, and determining sodium in the filtrate as barium sulfate, after removal of excess sulfuric acid.

Samples of benzene- and *p*-toluenestibonic acids were dissolved in 50 ml. of accurately standardized 0.1 *N* sodium hydroxide and the sodium determined by each of the methods described above. The maximum error with methods (1), (2) and (3) was −3, ±3 and +4%, respectively. Accordingly, sodium in the sodium salts described above was regularly determined by method (1) and the values checked by means of the flame photometer. The analyses of the sodium salts of four stibonic acids are given in Table IV.

TABLE IV

SODIUM SALTS OF THE ARYLSTIBONIC ACIDS

Stibonic acid, sodium salt	Formula	Sb analyses, % Calcd.	Sb analyses, % Found	Na analyses % Calcd.	Na analyses % Found
Benzene-	$[C_6H_5Sb(OH)_5]Na$	39.7	39.8	7.49	7.47
p-Toluene-	$[CH_3C_6H_4Sb(OH)_6]Na$	38.0	38.0	7.17	7.27
p-Bromobenzene-	$[BrC_6H_4Sb(OH)_5]Na$	31.6	31.5	5.96	6.08
p-Nitrobenzene-	$[NO_2C_6H_4Sb(OH)_5]Na$	34.6	34.6	6.54	6.54

The structure of the inorganic antimonate ion has been shown by a number of workers to be $[Sb(OH)_6]^-$.[12] The analysis of the sodium salts of the arylstibonic acids suggests a similar structure for these compounds, $[ArSb(OH)_5]^-Na^+$, with one hydroxyl group of the antimonate ion replaced by an aryl group.

Discussion

The molecular weight determinations described in the present paper are incompatible with either Schmidt's or Macallum's concept of the structure of the arylstibonic acids, and indicate rather that these compounds exist in the solid state as high molecular weight polymers, associated by hydrogen bond formation, with the structures $(ArSbO_3H_2)_x$ and $(ArSbO_3H_2{\cdot}H_2O)_x$. Their colloidal properties and lack of a definite melting point, as well as the analytical data, are in agreement with this concept. In contrast to the free acids, the corresponding ions probably exist in the simple hydrated form $[ArSb(OH)_5]^-$. It is only necessary to explain the behavior of these compounds as pseudo acids to complete the picture.

In the solid state the acidic hydrogens of the stibonic acids are blocked by hydrogen bond formation, and it is possible that the measurable rate of increase in acidity when these compounds are dissolved in alkaline solution represents the rate of dissociation of these hydrogen bonds. This explanation, however, seems improbable. Because of the low energy content of the hydrogen bond, it has always been assumed that compounds associated in this manner would dissociate rapidly when dissolved in solvents such as water,[7] whereas the increase in acidity proceeds at a measurable rate (Fig. 1). However, the present experiments indicate that a second reaction occurs when stibonic acids are dissolved in alkaline solution.

$$[ArSbO_3H]^- + 2H_2O \longrightarrow [ArSb(OH)_5]^-$$

While the relative *pKa* values for the two acids $[ArSbO_3H]H$ and $[ArSb(OH)_5]H$ are not known, it is only necessary to assume that the latter is a somewhat stronger acid to explain the behavior of the arylstibonic acids as pseudo acids in alkaline solution.

Acknowledgment.—The author wishes to thank David N. Kramer for performing the antimony analyses and Harry Eisenberg for performing the sodium analyses by means of the flame photometer.

Summary

Molecular weight determinations of a series of arylstibonic acids in both polar and non-polar solvents indicate that these compounds exist in the solid state as high molecular weight polymers, associated by hydrogen bond formation. This concept is contrary to previous theories of the structure of these compounds. The ions of arylstibonic acids, however, probably exist in the form $[ArSb(OH)_5]^-$. The behavior of the stibonic acids as pseudo acids in alkaline solution has been explained as involving a change from the ion $[ArSbO_3H]^-$ to the ion $[ArSb(OH)_5]$.

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[11] Barnes, Richardson, Berry and Hood, *Ind. Eng. Chem., Anal. Ed.*, **17**, 605 (1945).

[12] Pauling, THIS JOURNAL, **55**, 1895 (1933); Beintema, *Rec. trav. chim.*, **56**, 931 (1937); Schrewelius, *Z. anorg. allgem. chem.*, **238**, 241 (1938).