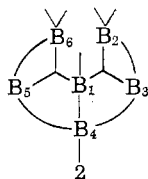


may be expected to be somewhat less stable because of probable interference between hydrogens on borons 2 and 6. This structure would make it necessary to postulate accidental overlap of the n.m.r. signals from borons 1 and 4 to account for the upfield doublet. Furthermore, the high-field doublet occurs at too low a field by some 15 p.p.m. or more for a typical apical boron such as is found in pentaborane-9 or hexaborane-10.<sup>17</sup>



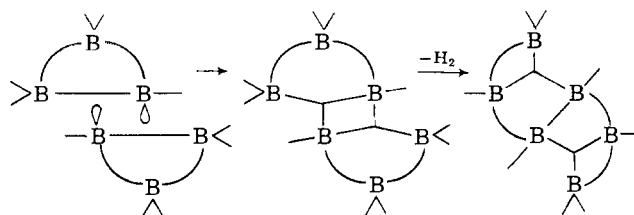
It has been suggested that decomposition of triborohydride-8 salts by anhydrous protonic acids may occur by attack of a proton on triborohydride-8 ion to form a mixture of hydrogen, diborane, and triborane-7 (perhaps through triborane-9 as an intermediate).<sup>9</sup> Tetraborane-10 may then form by reaction of diborane with triborane-7.<sup>9, 19, 20</sup>

The formation of hexaborane-12 with the unusual open structure could be envisioned as occurring through combination of two triborane-7 units to yield hexaborane-14, which then loses hydrogen and rearranges to hexaborane-12. Alternatively, triborane-7 may react with tetraborane-10 or another higher hydride present in relatively substantial concentration. Although there is no experimental evidence to support such a simple process, it seems highly likely that tri-

(19) R. Schaeffer, *J. Inorg. Nucl. Chem.*, **15**, 190 (1960).

(20) R. E. Enriore and R. Schaeffer, *ibid.*, **18**, 103 (1961).

borane-7 is involved since the product is not obtained from other sources.



It is interesting to note that this is the first example of a boron hydride in which the structure is based not upon the most compact icosahedral fragment possible, but rather upon a more open form. Since isomeric forms of lower boranes are unknown, such a structure could be produced either directly as a result of a favorable mechanism or indirectly by rearrangement to the more thermodynamically stable form.

Using bond energies of Gunn and Green,<sup>21</sup> the heat of atomization of hexaborane-12 (formulated as a 4212 structure in terms of the semitopological theory of Lipscomb)<sup>18</sup> is calculated as 1411.7 kcal./mole and the standard heat of formation is then +14.7 kcal./mole.

The degradation of hexaborane-12 to pentaborane-9 in the presence of dimethyl ether can be thought of as occurring through base-catalyzed elimination of a borane group to give a B<sub>5</sub>H<sub>9</sub> fragment (perhaps solvated) which rearranges to the stable pentaborane-9 framework.

Further chemical studies of hexaborane-12 are in progress.

**Acknowledgment.**—This work was supported by a grant from the National Science Foundation.

(21) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 2173 (1961).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
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## Iodine Cations and Oxyocations. I. Solutions of Iodic Acid in Sulfuric Acid

By R. J. GILLESPIE AND J. B. SENIOR

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Solutions of iodic acid in sulfuric acid have been studied by means of cryoscopic and conductometric measurements. No evidence was obtained for the formation of the iodyl cation IO<sub>2</sub><sup>+</sup> or the iodic acidium ion H<sub>2</sub>IO<sub>3</sub><sup>+</sup>, and it appears that iodic acid is converted to solvated and polymerized forms of iodyl hydrogen sulfate, IO<sub>2</sub>·HSO<sub>4</sub>.

### Introduction

Of the four common halogens iodine is the most electropositive and thus is the most likely to form compounds in which it is present as a cation or as a cationic radical. A few classes of compounds are known in which iodine is apparently present in the form of a cation and in many other compounds the presence of cations or oxyocations containing iodine has been suggested.<sup>1</sup> The participation of iodine cations or

oxyocations as transient intermediates in many reactions of iodine compounds in aqueous solution has also been postulated.<sup>2</sup> In very few cases, however, has definite information been obtained on the exact nature of these ions. Arotzky and Symons have recently summarized the evidence for the iodine cation I<sup>+</sup>.<sup>3</sup>

Sulfuric acid has proved to be a useful solvent for the stabilization of many cations which are too electrophilic to exist in more basic solvents. The even

(1) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, London, 1950, p. 1239.

(2) K. J. Morgan, *Quart. Rev.* (London), **8**, 123 (1954).

(3) J. Arotzky and M. C. R. Symons, *ibid.*, **14**, 282 (1962).

stronger acid, fluorosulfuric acid, is also potentially useful in this respect.<sup>4,5</sup> It was the main purpose of the work described in this and following papers to study the ionization of suitable solutes in these two solvents and thus to determine whether, and under what conditions, ions such as  $\text{IO}_2^+$ ,  $\text{IO}^+$ ,  $\text{I}^+$ , and  $\text{I}_3^+$  could exist in solution. Since this work was completed, the results of some similar work have been published by Arotzky, Mishra, and Symons.<sup>6</sup> Some of our experimental results and a number of our conclusions differ substantially from those of these authors. The first paper of this series deals with possible cation formation by iodic acid in solution in sulfuric acid.

**Previous Work on Cationic Forms of Pentavalent Iodine.**—The compounds  $\text{I}_2\text{O}_5 \cdot 2\text{SO}_3$  and  $\text{I}_2\text{O}_4 \cdot 3\text{SO}_3$  prepared by Muir<sup>7</sup> and recently re-examined by Lehmann and Hesselbarth<sup>8</sup> were formulated by the latter authors as iodyl disulfate,  $(\text{IO}_2^+)_2\text{S}_2\text{O}_7^{-2}$ , and as iodyl-iodosyl trisulfate,  $(\text{IO}_2^+)(\text{IO}^+)\text{S}_3\text{O}_{10}^{-2}$ , although no structural evidence was cited. The compound having the empirical formula  $\text{IOF}_3$ , prepared by Aynsley, Nichols, and Robinson,<sup>9</sup> was considered by them to be  $\text{IO}_2^+\text{IF}_6^-$ . However, in view of the general reluctance of iodyl fluoride to form complexes with Lewis acids, Aynsley and Sampath<sup>10</sup> have suggested that the compound  $\text{IO}_2\text{F} \cdot \text{AsF}_5$  obtained by Schmeisser and Lang<sup>11</sup> and formulated by them as  $\text{IO}_2^+\text{AsF}_6^-$  is more likely to be  $\text{AsF}_4^+\text{IO}_2\text{F}_2^-$ . The existence of the ion  $\text{IO}_2^+$  in solutions of iodic acid in liquid hydrogen fluoride has been proposed to explain the solubility of iodic acid in this solvent without apparent decomposition, and Schmeisser and Lang<sup>11</sup> have also suggested that iodine pentoxide is ionized in liquid HF to give  $\text{IO}_2^+$  and  $\text{IO}_3^-$ . Myers and Kennedy<sup>12</sup> postulated the existence of  $\text{IO}_2^+$  as an intermediate in the exchange of iodine between  $\text{I}_2$  and  $\text{IO}_3^-$  in aqueous solution and state that iodic acid forms a "double compound" with concentrated perchloric or sulfuric acid. Masson<sup>13</sup> reported that iodine pentoxide reacts with fuming sulfuric acid to form a white solid of unknown composition. Lamb and Phillips<sup>14</sup> studied the solubility of iodic acid in aqueous sulfuric acid and in oleum. They obtained evidence for the existence of three different solid phases in equilibrium with the saturated solutions which they considered to be  $\text{HIO}_3$  (<77%  $\text{H}_2\text{SO}_4$ ),  $\text{HI}_3\text{O}_8$  (77–85%  $\text{H}_2\text{SO}_4$ ), and  $\text{I}_2\text{O}_5$  (85%  $\text{H}_2\text{SO}_4$ –29% free  $\text{SO}_3$ ). Very recently, Arotzky, Mishra, and Symons<sup>6</sup> have claimed on the basis of ultraviolet spectra and cryoscopic and conductometric data that iodic acid exists in solution

in 100% sulfuric acid as the protonated species  $\text{H}_2\text{IO}_3^+$  and in strong oleum as  $\text{IO}_2^+$  or  $\text{IO}(\text{HS}_2\text{O}_7)_2^+$ .

## Results and Discussion

Iodic acid is only sparingly soluble in 100% sulfuric acid at room temperature, but by heating to about 60° solutions of concentrations up to about 0.045 *m* can be obtained. These solutions deposit a white solid on long standing. The results of the cryoscopic experiments are shown in Table I and the conductivity data are presented in Table II. The results of two conductometric titrations of disulfuric acid with iodic acid are shown in Fig. 1.

TABLE I  
FREEZING-POINTS OF SOLUTIONS OF IODIC ACID IN SULFURIC ACID

$10^2m^a$	F.p., °C.	$10^2m$	F.p., °C.
0.403	10.336	3.292	10.023
0.780	10.302	3.489	9.996
1.148	10.272	3.593	9.998
1.269	10.261	3.673	9.988
1.586	10.228	4.357	9.928
1.964	10.192	4.398	9.886
2.873	10.093		
3.154	10.055		

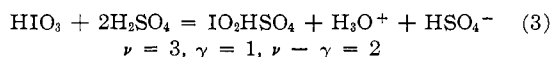
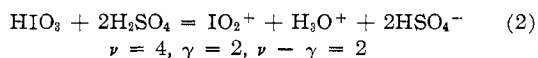
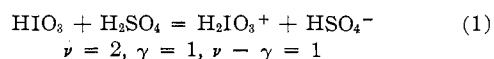
<sup>a</sup> Molality, *i.e.*, moles of solute per 1000 g. of solvent.

TABLE II  
CONDUCTIVITIES OF SOLUTIONS OF IODIC ACID IN SULFURIC ACID

$10^2w^a$	$10^2\kappa$ , ohm <sup>-1</sup> cm. <sup>-1</sup>	$10^2w$	$10^2\kappa$ , ohm <sup>-1</sup> cm. <sup>-1</sup>
0.317	1.0481	1.843	1.1322
0.427	1.0511	1.847	1.1400
0.681	1.0593	2.216	1.1754
0.808	1.0648	2.375	1.1945
0.976	1.0719	2.655	1.2115
1.006	1.0755	2.917	1.2550
1.030	1.0759	2.991	1.2681
1.175	1.0868	3.192	1.2922
1.301	1.0947	3.612	1.3483
1.513	1.1100	3.959	1.3868
1.568	1.1144	4.251	1.4322

<sup>a</sup> Molality (R. J. Gillespie and C. Solomons, *J. Chem. Educ.*, **37**, 202 (1960)), *i.e.*, moles of solute per 1000 g. of solution.

The following possible modes of ionization are considered first.



In each case the appropriate value of  $\nu$ , the number of moles of particles (molecules or ions) produced in solution by one mole of iodic acid, and  $\gamma$ , the number of moles of hydrogen sulfate ion produced in solution by one mole of iodic acid, are given. Experimental values of  $\nu$  and  $\gamma$  calculated from the data in Tables I and II are given in Table III. In considering ionization according to eq. 1,  $\gamma$  values have been calculated from the data in Table II by comparison with the conduc-

(4) J. Barr, R. J. Gillespie, and E. A. Robinson, *Can. J. Chem.*, **39**, 1266 (1961).

(5) J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, in press.

(6) J. Arotzky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 2582 (1962).

(7) M. P. P. Muir, *ibid.*, **95**, 856 (1909).

(8) H. A. Lehmann and H. Hesselbarth, *Z. anorg. allgem. Chem.*, **299**, 51 (1959).

(9) E. E. Aynsley, R. Nichols, and P. L. Robinson, *J. Chem. Soc.*, 623 (1953).

(10) E. E. Aynsley and S. Sampath, *ibid.*, 3099 (1959).

(11) M. Schmeisser and K. Lang, *Angew. Chem.*, **67**, 156 (1955).

(12) O. E. Myers and J. W. Kennedy, *J. Am. Chem. Soc.*, **72**, 897 (1950).

(13) I. Masson, *J. Chem. Soc.*, 1708 (1938).

(14) A. B. Lamb and J. W. Phillips, *J. Am. Chem. Soc.*, **45**, 108 (1923).

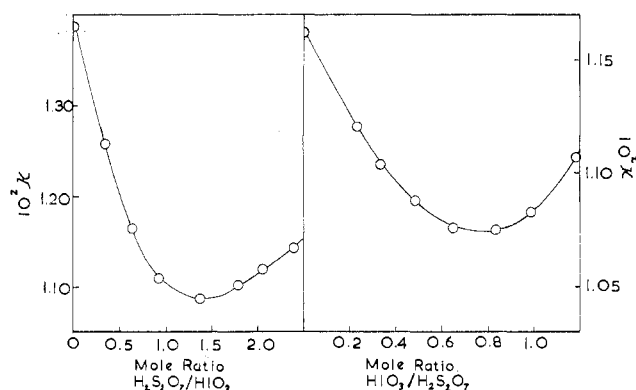


Fig. 1.—Conductometric titrations.

tivity curve for potassium hydrogen sulfate,<sup>15,16</sup> and the values of  $\nu$  have been corrected for the repression of solvent autoprotolysis only (B columns in Table III).<sup>17</sup> Values of  $\gamma$  appropriate to reactions such as 2 and 3 have been calculated by comparison with the conductivity curve for water,<sup>15</sup> and the values of  $\nu$  have been corrected for repression of both the ionic self-dehydration reaction and the autoprotolysis reaction of the solvent (A columns in Table III).<sup>17</sup>

TABLE III

SOLUTIONS OF IODIC ACID IN SULFURIC ACID: VALUES OF  $\nu$  AND  $\gamma$ 

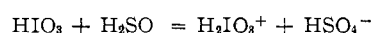
$m$	A <sup>a</sup>			B <sup>b</sup>		
	$\nu$	$\gamma$	$\nu - \gamma$	$\nu$	$\gamma$	$\nu - \gamma$
0.010	3.07	1.41	1.66	2.15	1.14	1.01
0.015	2.86	1.28	1.58	2.15	1.08	1.07
0.020	2.70	1.23	1.47	2.14	1.08	1.06
0.025	2.63	1.17	1.46	2.17	1.08	1.09
0.030	2.57	1.15	1.42	2.17	1.08	1.09
0.035	2.54	1.13	1.41	2.20	1.08	1.12
0.040	2.54	1.12	1.42	2.23	1.08	1.15
0.045	2.53	1.10	1.43	2.27	1.08	1.19

<sup>a</sup> Self-dissociation corrections to  $\nu$  calculated assuming ionization according to



$\gamma$  obtained by comparison with conductivity curve for  $\text{H}_2\text{O}$ .

<sup>b</sup> Self-dissociation corrections to  $\nu$  calculated assuming ionization according to



$\gamma$  obtained by comparison with conductivity curve for  $\text{KHSO}_4$ .

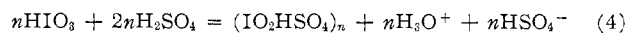
The almost constant value of  $\gamma = 1.08$  is reasonably consistent with ionization according to eq. 1 although the observed values are a little larger than would be expected. Our results agree approximately with those of Arotzky, Mishra, and Symons,<sup>6</sup> who report without detail that one mole of  $\text{HIO}_3$  gives rise to one mole of  $\text{HSO}_4^-$ . However, the values of  $\nu$  which range from 2.15 to 2.27 are substantially larger than the predicted 2.0. Arotzky, *et al.*,<sup>6</sup> report two  $\nu$  values of 2.1 and 2.3 but, ignoring the difference from the expected value of 2.0, conclude that they support the ionization (1).

(15) S. J. Bass, R. J. Gillespie, R. H. Flowers, E. A. Robinson, and C. Solomons, *J. Chem. Soc.*, 4320 (1960).

(16) R. J. Gillespie and C. Solomons, *ibid.*, 1796 (1957).

(17) S. J. Bass, R. J. Gillespie, and E. A. Robinson, *ibid.*, 821 (1960).

The values of  $\nu$  and  $\gamma$  (A columns) are consistent with neither complete ionization to give  $\text{IO}_2^+$  according to eq. 2, nor reaction according to eq. 3 to give un-ionized iodyl hydrogen sulfate,  $\text{IO}_2\text{HSO}_4$ . They are, however, consistent with ionization according to a scheme similar to (3) but involving polymeric forms of iodyl hydrogen sulfate  $(\text{IO}_2\text{HSO}_4)_n$ , which may be partially ionized. For the general reactions



the values of  $\nu$  would be in the range  $2 + 1/n$  to  $2 + 2/n$  and values of  $\gamma$  in the range 1 to  $1 + 1/n$  with  $\nu - \gamma$  equal to  $1 + 1/n$  independently of the position of equilibrium 5. For  $n = 2$ ,  $\nu - \gamma = 1.5$  and for  $n = 3$ ,  $\nu - \gamma = 1.33$ . Experimentally  $\nu - \gamma$  is greater than 1.5 at low concentrations and becomes less than 1.5 at higher concentrations. This suggests an equilibrium involving monomeric, dimeric, and trimeric forms of iodyl hydrogen sulfate, accompanied by small amounts of their ionized forms, and possibly some higher polymeric forms.

Several further reasons may be advanced for preferring an ionization scheme involving the formation of polymeric forms of iodyl hydrogen sulfate rather than that of eq. 1. When a solution of disulfuric acid was titrated conductometrically with iodic acid, a minimum conductivity was obtained at the mole ratio  $\text{HIO}_3/\text{H}_2\text{S}_2\text{O}_7 = 0.75$ , and when a solution of iodic acid was titrated with disulfuric acid, a minimum conductivity was obtained at the mole ratio  $\text{H}_2\text{S}_2\text{O}_7/\text{HIO}_3 = 1.32$ , *i.e.*,  $\text{HIO}_3/\text{H}_2\text{S}_2\text{O}_7 = 0.76$  (Fig. 1). If iodic acid behaved as a fully ionized base as required by eq. 1 the conductivity minimum would occur at the mole ratio  $\text{HIO}_3/\text{H}_2\text{S}_2\text{O}_7 = 0.60-0.63$  with the concentrations used in these experiments,<sup>18</sup> which is in poor agreement with the observed values. The observed values could be explained if iodic acid were a weak base with  $K_b = [\text{H}_2\text{IO}_3^+][\text{HSO}_4^-]/[\text{HIO}_3] = 0.07-0.10$  mole  $\text{kg.}^{-1}$ .<sup>18</sup> This would, however, lead to a value of  $\gamma$  for a 0.05  $m$  solution of 0.65, compared with the observed value of 1.08. Evidently the results of the conductometric titrations are not in agreement with ionization according to eq. 1. If iodic acid forms iodyl hydrogen sulfate according to eq. 4, then the reaction taking place on the titration of this solution with disulfuric acid is simply the formation of sulfuric acid



After the mole ratio  $\text{H}_2\text{S}_2\text{O}_7/\text{HIO}_3 = 1.0$  has been reached, the further reaction may be the titration of the weak base  $(\text{IO}_2\text{HSO}_4)_n$  or the formation of more highly sulfated species as occurs, for example, in the case of arsenic(III) oxide.<sup>19</sup>

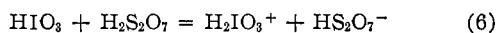
Arotzky, Mishra, and Symons<sup>6</sup> also report the results of a conductometric titration. They obtained a minimum conductivity at the mole ratio  $\text{HIO}_3/\text{H}_2\text{S}_2\text{O}_7 = 0.08$ . We have no explanation for this serious

(18) R. H. Flowers, R. J. Gillespie, and E. A. Robinson, *Can. J. Chem.*, **38**, 1363 (1960).

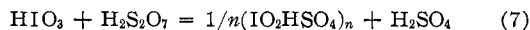
(19) R. J. Gillespie and E. A. Robinson, *ibid.*, **41**, 450 (1963).

difference from our result, and indeed this result seems most unlikely since even a strong base such as  $\text{KHSO}_4$  gives a minimum conductivity at the mole ratio  $\text{KHSO}_4/\text{H}_2\text{S}_2\text{O}_7 = 0.6$ ; a minimum at a mole ratio of 0.08 implies that one mole of iodic acid can neutralize over six times as much disulfuric acid as the strong base  $\text{KHSO}_4$ . Further doubt is thrown on the reliability of these results by the fact that these authors quote the results of a titration of oleum with  $\text{KHSO}_4$  which gives a minimum conductivity at  $\text{KHSO}_4/\text{H}_2\text{S}_2\text{O}_7 = 0.20$ , which is again in serious disagreement with a previous well-established and theoretically justified result that all strong bases give a minimum conductivity in titrations of  $\text{H}_2\text{S}_2\text{O}_7$  at approximately the mole ratio  $\text{B}/\text{H}_2\text{S}_2\text{O}_7 = 0.6$ .<sup>18</sup>

When iodic acid was added to an oleum to give a 0.1933 *m* solution, the freezing point was found to increase from 9.682 to 9.762°. This increase in the freezing point of the solution is clearly not in agreement with simple protonation according to eq. 6, for which



$\Delta\nu = 2.00 - 1.33 = +0.67$  assuming that  $\nu(\text{H}_2\text{S}_2\text{O}_7) = 1.33$ ,<sup>19</sup> since this would give a decrease in the freezing point. The experimental observation is, however, consistent with the formation of un-ionized iodyl hydrogen sulfate, for which  $\Delta\nu$  is clearly negative



As mentioned above, a white solid was precipitated in the course of a few days from the more concentrated solutions of iodic acid in sulfuric acid. The separation of a fairly large amount of this solid caused only a very small decrease in the conductivity of the solution. For example, in one experiment, the specific conductivities before and after separation of the solid were  $1.433 \times 10^{-2}$  and  $1.419 \times 10^{-2}$  ohm<sup>-1</sup> cm.<sup>-1</sup>, respectively. If reaction 1 were occurring the only solid that could separate out would be  $\text{HIO}_3$  or a solvated form, e.g.,  $\text{HIO}_3 \cdot \text{H}_2\text{SO}_4$  ( $\text{H}_2\text{IO}_3^+ \cdot \text{HSO}_4^-$ ), and in this case a large decrease in conductivity would be expected. However, if the solid is a higher polymeric form of the weakly ionized iodyl hydrogen sulfate, the conductivity would not be expected to change very much. Analysis of the white solid gave the results: iodate (as  $\text{I}_2\text{O}_5$ ), 78.8, 77.8, 78.6%. This may be compared with the calculated values  $\text{IO}_2 \cdot \text{HSO}_4$ , 65.2%;  $(\text{IO}_2)_2\text{SO}_4$ , 80.7%;  $\text{HIO}_3 \cdot \text{H}_2\text{SO}_4$ , 60.9%.

We conclude then that iodic acid is not simply protonated in solution in sulfuric acid but forms iodyl hydrogen sulfate,  $\text{IO}_2\text{HSO}_4$ , which probably exists in the monomeric form only in very dilute solution in sulfuric acid but readily polymerizes with increasing concentration to dimeric and trimeric forms and eventually separates from solution, presumably in a highly polymeric form. By analogy with the structures proposed by Gillespie and Robinson<sup>19</sup> for the species present in solutions of arsenic(III) oxide in sulfuric acid and oleums we consider that the monomer of iodyl hydrogen sulfate probably exists in the solvated form  $\text{IO}_2\text{HSO}_4 \cdot \text{H}_2\text{SO}_4$  having the structure I.

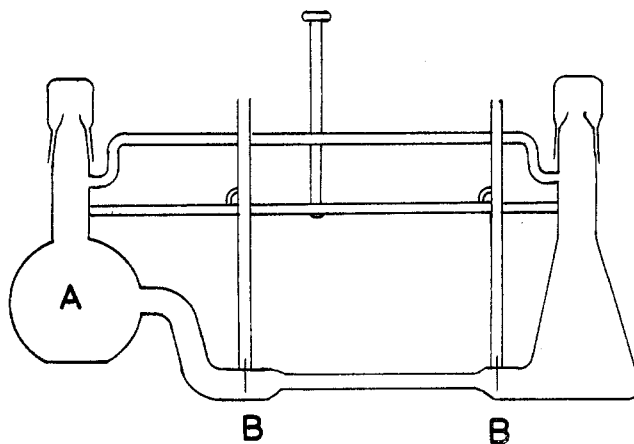
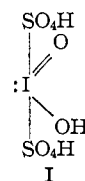
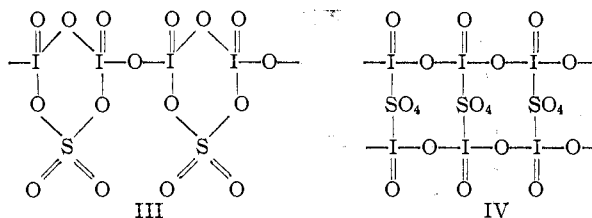
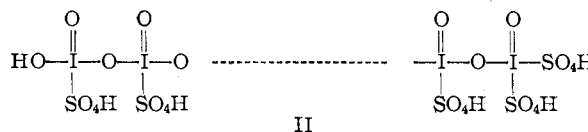


Fig. 2.—Conductivity cell: A, mixing flask; B, electrodes.



Polymeric forms of I can be built up by elimination of solvent molecules (II). The repeating unit in such a polymer is  $\text{IO}_2\text{HSO}_4$  and the chain ending groups are obtained from a solvent molecule. By further elimination of sulfuric acid between adjacent hydrogen sulfate groups on the same chain to give a structure containing six-membered rings (III) or between hydrogen sulfate groups on different chains to give a cross-linked structure (IV), a polymer with the repeating unit  $(\text{IO}_2)_2\text{SO}_4$  or  $\text{I}_2\text{O}_5 \cdot \text{SO}_3$  can be built up.



The structure of the white solid which separates from solution is probably related to III or IV. This, rather than  $\text{I}_2\text{O}_5$ , is presumably the solid phase found by Lamb and Phillips<sup>14</sup> to be in equilibrium with solutions of iodic acid in sulfuric acid stronger than 85% and is also presumably identical with the iodic acid-sulfuric acid complexes reported by Masson<sup>13</sup> and by Myers and Kennedy.<sup>12</sup>

Arotsky, Mishra, and Symons<sup>6</sup> found that the absorption spectrum of iodic acid in 65% oleum is different from that in 100%  $\text{H}_2\text{SO}_4$ , and they conclude that a different species is present in oleum which they suggest could be  $\text{IO}_2^+$  or, more probably,  $\text{IO}(\text{HS}_2\text{O}_7)^+$ . The spectral results do not, in fact, provide any evidence as to the nature of the new species that is formed, al-

though by comparison, for example, with the behavior of  $\text{As}_2\text{O}_3$  in oleum<sup>19</sup> it seems probable that more sulfated species such as  $\text{IO}(\text{HSO}_4)_3$  and possibly  $\text{I}(\text{HSO}_4)_5$  are likely to be formed.

### Experimental

The apparatus for the cryoscopic measurements was a slightly modified form of that described previously.<sup>20</sup> The concentrations of the solutions were varied by dilution of a relatively concentrated solution by addition of successive weighed quantities of the solvent rather than by successive additions of weighed quantities of solute. This experimental procedure was adopted because of the slow rate of solution of iodic acid in sulfuric acid even at 100°. Freezing points were measured as previously described<sup>20</sup> using a calibrated resistance thermometer in conjunction with a Mueller bridge.

The conductivity cell was a slightly modified version of that

(20) R. J. Gillespie, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2473 (1950).

described by Gillespie, Oubridge, and Solomons<sup>21</sup> (Fig. 2). In order to prepare solutions the bulk of the solvent was transferred to the flask A, which contained a Teflon-covered stirring bar and could be placed on a hot-plate magnetic stirrer to hasten the dissolution of the iodic acid. The resistance of a solution in the conductivity cell was measured by means of a Jones bridge (Leeds and Northrup) used in conjunction with a Hewlett-Packard Model 201C oscillator, operated at 1000 c.p.s., and a General Radio Type 1231-B amplifier and null-detector. Conductivity cells were immersed in an oil thermostat maintained at  $25 \pm 0.002^\circ$ , the temperature of which was checked periodically with a calibrated resistance thermometer.

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## Chemistry of Boranes. VIII.<sup>1</sup> Salts and Acids of $\text{B}_{10}\text{H}_{10}^{-2}$ and $\text{B}_{12}\text{H}_{12}^{-2}$

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A kinetic stability unique for boranes toward thermolysis, hydrolysis, and oxidation has been found for the  $\text{B}_{10}\text{H}_{10}^{-2}$  and  $\text{B}_{12}\text{H}_{12}^{-2}$  anions.

We have found the stability of the  $\text{B}_{10}\text{H}_{10}^{-2}$ <sup>2-4</sup> and  $\text{B}_{12}\text{H}_{12}^{-2}$ <sup>2,5,6</sup> anions toward heat, acids and bases, and oxidizing agents to be truly surprising when contrasted with that of other boron hydrides. Since both  $\text{B}_{10}\text{H}_{10}^{-2}$  and  $\text{B}_{12}\text{H}_{12}^{-2}$  are thermodynamically<sup>7</sup> unstable with reference to boric oxide or boric acid, much of the observed stability, particularly the hydrolytic and oxidative stability, must be kinetic in nature.

**Properties of the Polyhedral Borane Anions in Water.**—There is no evidence of reaction between  $\text{B}_{10}\text{H}_{10}^{-2}$  or  $\text{B}_{12}\text{H}_{12}^{-2}$  and strong aqueous sodium hydroxide even at 95°. Since these boranes bear a dinegative charge, this resistance to the thermodynamically favored hydrolysis is at least in part a reflection of a coulombic repulsion effect.

In 3 *N* hydrochloric acid  $\text{B}_{12}\text{H}_{12}^{-2}$  is stable at 95° while  $\text{B}_{10}\text{H}_{10}^{-2}$  reacts only slowly. There is rapid proton exchange between water and the anions under acidic conditions. This latter effect is evidenced by

rapid changes in the characteristic  $\text{B}^{11}$  n.m.r. spectra when solutions of the anions in  $\text{D}_2\text{O}$  are acidified. Thus, the doublet  $\text{B}^{11}$  spectrum of  $\text{B}_{12}\text{H}_{12}^{-2}$  collapses to a single peak due to conversion to  $\text{B}_{12}\text{D}_{12}^{-2}$ , and the two doublets of  $\text{B}_{10}\text{H}_{10}^{-2}$  yield two singlets. By following rates of  $\text{B}^{11}$  doublet collapse, rough estimates for the rate of deuteration were obtained. With a relative rate of 1 for  $\text{B}_{12}\text{H}_{12}^{-2}$ , the values for  $\text{B}_{10}\text{H}_{10}^{-2}$  are 68 for equatorial positions and 330 for apical positions. We find that the greater reactivity of  $\text{B}_{10}\text{H}_{10}^{-2}$  toward an electrophilic reagent is maintained in the derivative chemistry of the polyhedral anions to be detailed in succeeding papers.

With but few exceptions,<sup>8</sup> anionic boron hydrides are rapidly degraded by acids, and the kinetic stability of the  $\text{B}_{10}\text{H}_{10}^{-2}$  and  $\text{B}_{12}\text{H}_{12}^{-2}$  anions is unexpected. Passage of salts of these anions through a column of strongly acidic ion-exchange resin yields stable solutions of the acids. The solutions may be concentrated at room temperature to give crystalline hydrates of the acids. Free-flowing but still somewhat wet-looking crystals of the  $\text{B}_{12}$  acid with as many as 20 moles of water have been obtained. The  $\text{B}_{10}$  acid, however, becomes crystalline only at much lower degrees of hydration. Both acids are strong, comparable to sulfuric acid, and there

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(8)  $\text{B}_{10}\text{H}_{12}\text{P}(\text{C}_6\text{H}_5)_2^-$  is rather resistant to acid degradation: E. L. Muetterties and V. D. Aftandilian, *Inorg. Chem.*, **1**, 731 (1962).