

enzyme was not created. One particularly active catalyst was tested, but the mode of catalysis is not yet understood.

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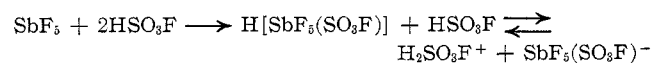
## The Fluorosulfuric Acid Solvent System. VI. Solutions of Phosphorus, Arsenic, Bismuth, and Niobium Pentafluorides and Titanium Tetrafluoride

By R. J. GILLESPIE, K. OUCHI, AND G. P. PEZ

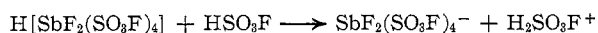
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Conductivity measurements on solutions of  $\text{PF}_5$ ,  $\text{AsF}_5$ ,  $\text{BiF}_5$ ,  $\text{NbF}_5$ ,  $\text{PF}_5\text{-SO}_3$ ,  $\text{NbF}_5\text{-SO}_3$ , and  $\text{AsF}_5\text{-SO}_3$  are reported. Conductometric titrations have been carried out on solutions of  $\text{AsF}_5$ ,  $\text{BiF}_5$ , and  $\text{AsF}_5\text{-SO}_3$ . The results are compared with those obtained previously for  $\text{SbF}_5$  and  $\text{SbF}_5\text{-SO}_3$ . It is concluded that acid strength increases in the order:  $\text{PF}_5 \sim \text{NbF}_5 < \text{TiF}_4 \sim \text{AsF}_5 < \text{BiF}_5 < \text{AsF}_4(\text{SO}_3\text{F}) < \text{SbF}_5 < \text{AsF}_2(\text{SO}_3\text{F})_3 < \text{SbF}_2(\text{SO}_3\text{F})_3$ .

It was shown in part II<sup>1</sup> of this series that antimony pentafluoride is a rather weak acid of the fluorosulfuric acid solvent system ionizing according to the equation



the acid  $\text{H}[\text{SbF}_5(\text{SO}_3\text{F})]$  having a dissociation constant  $K = 3.7 \times 10^{-8} \text{ mol kg}^{-1}$ . Although antimony pentafluoride is not fully ionized, these solutions have an extremely high acidity because of the rather high concentration of the fluorosulfuric acidium ion  $\text{H}_2\text{SO}_3\text{F}^+$  and they have been extensively employed for studies of the protonation of very weak bases and for the formation of stable solutions of carbonium ions.<sup>2</sup> Because of the great utility of this medium for the production of new cationic species, it has been termed "magic acid" by Olah and his coworkers.<sup>3</sup> It was also shown in part II<sup>1</sup> that addition of sulfur trioxide to this system still further increases the acidity as  $\text{SbF}_5$  is replaced by the fluorosulfates  $\text{SbF}_4(\text{SO}_3\text{F})$ ,  $\text{SbF}_3(\text{SO}_3\text{F})_2$ , and  $\text{SbF}_2(\text{SO}_3\text{F})_3$  which increase in acid strength with increasing number of fluorosulfate groups. Indeed the trifluorosulfate  $\text{SbF}_2(\text{SO}_3\text{F})_3$  forms the strong acid  $\text{H}[\text{SbF}_2(\text{SO}_3\text{F})_3]$  in solution in fluorosulfuric acid which is fully ionized according to the equation



Although this  $\text{HSO}_3\text{F}\text{-SbF}_5\text{-SO}_3$  medium has not been nearly so extensively exploited as the "magic acid" ( $\text{HSO}_3\text{F}\text{-SbF}_5$ ) it is certainly considerably more acidic, at least at low  $\text{SbF}_5$  concentrations (0–0.3 *m*  $\text{SbF}_5$ ). The object of the work described in this paper was to investigate the behavior of other fluorides, primarily pentafluorides, in fluorosulfuric acid, to see if they exhibit acid behavior and, in particular, to ascertain if

any of them are stronger acids than  $\text{SbF}_5$ . The effect of sulfur trioxide on the acidity of some of the systems was also studied.

### Experimental Section

**Niobium Pentafluoride.**—Technical grade Ozark-Mahoning material was purified by triple distillation under vacuum at 100–110°, mp 79–81°.

**Bismuth Pentafluoride.**—Bismuth trifluoride was fluorinated in a flow system at 500°. The crude  $\text{BiF}_5$  was purified by sublimation under vacuum in an apparatus made entirely of Vycor glass which is not attacked by  $\text{BiF}_5$  at ~100°.

**Phosphorus Pentafluoride.**—Dry diazonium hexafluorophosphate (Phosfluogen A, Ozark Mahoning Co.) was thermally decomposed at 130° and the resulting  $\text{PF}_5$  was purified by trap-to-trap distillation on a vacuum line.

**Arsenic Pentafluoride.**—The material obtained from a cylinder supplied by the Allied Chemical Co. was purified by trap-to-trap distillation on a vacuum line.

**Titanium Tetrafluoride.**—Pure material obtained from the Allied Chemical Co. and the Titanium Alloy Manufacturing Co. was used after rigorous drying.

Fluorosulfuric acid and sulfur trioxide were purified as described previously.<sup>1,5</sup> Conductivity measurements were made with the apparatus and technique described previously.<sup>5</sup>

### Results and Discussion

The results of conductivity measurements on solutions of phosphorus, arsenic, bismuth, and niobium pentafluorides and titanium tetrafluoride are given in Table I and Figure 1. It may be seen in the figure that all of the fluorides give much smaller conductivities than  $\text{SbF}_5$ , and, therefore, if they behave as acids at all, they are clearly considerably weaker than antimony pentafluoride. Niobium and phosphorus pentafluorides give an almost negligible increase in the conductivity and must therefore be essentially nonelectrolytes. Arsenic and bismuth pentafluorides and titanium tetrafluoride all cause a rather similar small increase in the

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TABLE I  
 CONDUCTIVITIES OF SOLUTIONS IN FLUOROSULFURIC ACID<sup>a</sup>

10 <sup>2</sup> <i>m</i>	10 <sup>4</sup> <i>k</i> , ohm <sup>-1</sup> cm <sup>-1</sup>	10 <sup>2</sup> <i>m</i>	10 <sup>4</sup> <i>k</i> , ohm <sup>-1</sup> cm <sup>-1</sup>
BiF <sub>5</sub>		AsF <sub>5</sub>	
0.5842	2.911	2.27	5.092
1.832	5.861	5.09	6.60
2.893	7.569	6.17	10.06
5.542	11.00	9.29	10.79
10.92	16.60	11.56	14.24
17.82	20.44	13.48	14.72
26.83	26.58	25.87	17.68
NbF <sub>5</sub>		PF <sub>5</sub>	
2.30	3.081	5.19	2.22
3.20	2.915	6.11	4.02
5.46	3.350	TiF <sub>4</sub>	
6.9	3.72	0.392	2.039
11.1	4.72	1.375	4.332
AsF <sub>5</sub> ·SO <sub>3</sub>		2.546	5.562
1.09	47.45	3.803	7.032
AsF <sub>5</sub> · <i>n</i> SO <sub>3</sub> ( <i>n</i> ≥ 3)			
5.98	65.34		
9.15	90.48		
12.22	110.4		
14.77	124.8		
19.04	148.7		

<sup>a</sup> Conductivities of the HSO<sub>3</sub>F solvent ranged from 1.5 to 2.2 × 10<sup>-4</sup> ohm<sup>-1</sup> cm<sup>-1</sup>.

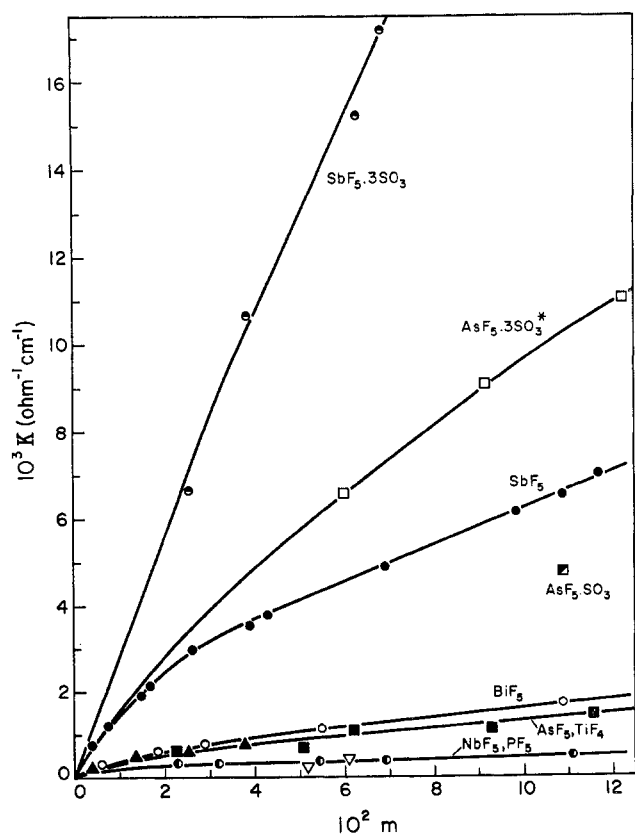
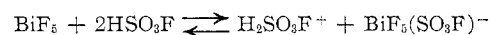
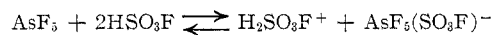
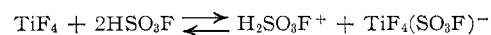


Figure 1.—Conductivities in fluorosulfuric acid: ▲, TiF<sub>4</sub>; ■, AsF<sub>5</sub>; ▽, PF<sub>5</sub>; ●, NbF<sub>5</sub>. The asterisk signifies that these solutions had the composition AsF<sub>5</sub>·*n*SO<sub>3</sub>, *n* > 3, but excess SO<sub>3</sub> over the composition AsF<sub>5</sub>·3SO<sub>3</sub> has very little effect on the conductivity.

conductivity. The conductivity of the bismuth pentafluoride solutions is slightly greater than that of the arsenic pentafluoride solutions and it is presumably a slightly stronger acid but both are considerably weaker than antimony pentafluoride. By analogy with the established behavior of SbF<sub>5</sub>, we presume that AsF<sub>5</sub> and BiF<sub>5</sub> ionize as acids according to the equations



The mode of ionization of TiF<sub>4</sub> cannot be predicted with such certainty; possibly it ionizes as



In any case its solubility appears to be quite small (4 × 10<sup>-2</sup> *m* at 25°).

The proposed acid behavior of BiF<sub>5</sub> and AsF<sub>5</sub> was confirmed by conductometric titration with the base KSO<sub>3</sub>F (Figure 2).<sup>1</sup> In such a titration a strong acid,

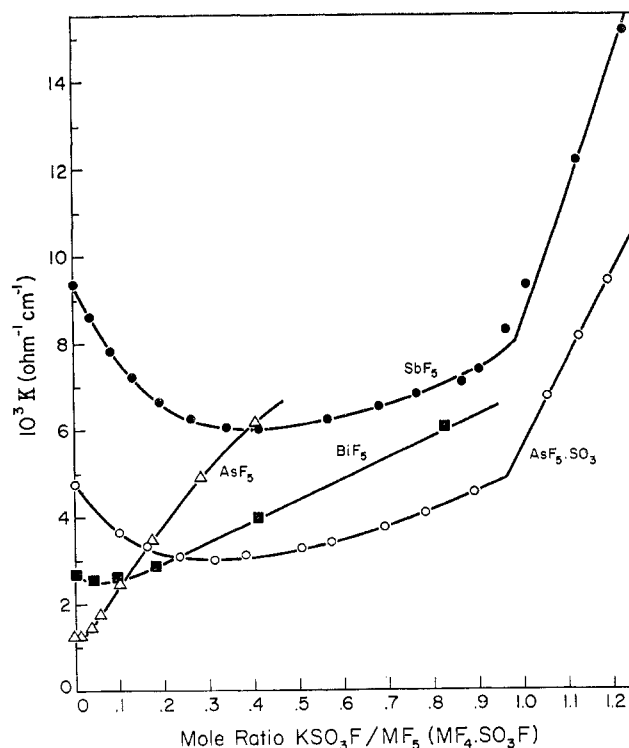


Figure 2.—Conductometric titrations of some acids with KSO<sub>3</sub>F in fluorosulfuric acid.

e.g., H[SbF<sub>2</sub>(SO<sub>3</sub>F)<sub>4</sub>], gives a minimum conductivity at the mole ratio KSO<sub>3</sub>F/acid = 1. Weaker acids give a minimum at mole ratio KSO<sub>3</sub>F/acid < 1. For BiF<sub>5</sub> a minimum conductivity was obtained at a mole ratio KSO<sub>3</sub>F/BiF<sub>5</sub> = 0.06 while for AsF<sub>5</sub> the minimum was not very clear but appeared to be approximately at the very small mole ratio KSO<sub>3</sub>F/AsF<sub>5</sub> = 0.01. Thus the acid behavior of BiF<sub>5</sub> and AsF<sub>5</sub> is confirmed as is also the fact that BiF<sub>5</sub> is a slightly stronger acid than AsF<sub>5</sub>. No conductometric titrations could be carried out with PF<sub>5</sub> and NbF<sub>5</sub>.

Since the addition of sulfur trioxide has a marked effect on the acidity of a solution of SbF<sub>5</sub> in fluorosul-

furic acid, the effect of sulfur trioxide on some of these acid systems was also investigated. Sulfur trioxide was found to have no effect on the conductivities of solutions of  $\text{NbF}_5$  and  $\text{PF}_5$  both of which have negligible acidic properties, but it was found to have a considerable effect on the conductivities of  $\text{AsF}_5$  solutions. For example, at a concentration of 0.11 *m*, addition of sulfur trioxide to give the mole ratio  $\text{SO}_3/\text{AsF}_5 = 1$  increased the conductivity by more than three times and further addition of sulfur trioxide to give the mole ratio  $\text{SO}_3/\text{AsF}_5 = 3$  increased the conductivity by more than seven times (Figure 2). The conductivity was not much affected by larger amounts of sulfur trioxide, and we presume that, as for  $\text{SbF}_5$ , arsenic pentafluoride combines with a maximum of 3 mol of sulfur trioxide to give  $\text{AsF}_2(\text{SO}_3\text{F})_3$ . Thus  $\text{AsF}_5 \cdot \text{SO}_3$  which we presume to be  $\text{AsF}_4 \cdot \text{SO}_3\text{F}$  is a somewhat weaker acid than  $\text{SbF}_5$ , but  $\text{AsF}_5 \cdot 3\text{SO}_3$  which we presume to be  $\text{AsF}_2(\text{SO}_3\text{F})_3$  is a rather stronger acid than  $\text{SbF}_5$  although not as strong as the acid  $\text{H}[\text{SbF}_2(\text{SO}_3\text{F})_4]$ . The rather high acidity of  $\text{AsF}_4(\text{SO}_3\text{F})$  was confirmed by a conductometric titration with  $\text{KSO}_3\text{F}$  which gave a minimum conductivity at  $\text{KSO}_3\text{F}/\text{AsF}_4(\text{SO}_3\text{F}) = 0.31$  compared with the minimum of  $\text{KSO}_3\text{F}/\text{SbF}_5 = 0.41$  observed in the titration of  $\text{SbF}_5$  (Figure 2). Solutions of  $\text{SO}_3$  in  $\text{HSO}_3\text{F}-\text{BiF}_5$  are unstable and deposit a white precipitate on standing.

We conclude therefore that the order of increasing acid strength of the fluorides in fluorosulfuric acid is:  $\text{PF}_5 \sim \text{NbF}_5 < \text{TiF}_4 \sim \text{AsF}_5 < \text{BiF}_5 < \text{AsF}_4(\text{SO}_3\text{F}) < \text{SbF}_5 < \text{AsF}_2(\text{SO}_3\text{F})_3 < \text{SbF}_2(\text{SO}_3\text{F})_3$ . It is interesting to note that, in the series of pentafluorides  $\text{PF}_5$ ,  $\text{AsF}_5$ ,  $\text{SbF}_5$ , and  $\text{BiF}_5$ , antimony pentafluoride is the strongest acceptor for fluorosulfate and presumably the strongest Lewis acid in general. Replacement of fluorine by the fluoro-

sulfate group appears generally to cause an increase in the acceptor strength, but unfortunately the maximum acidity that is, in principle, possible cannot be obtained as the pentafluorosulfates do not appear to be stable. At the present time therefore it appears that  $\text{SbF}_2(\text{SO}_3\text{F})_3$  is the strongest known acceptor for fluorosulfate ion and that  $\text{HSO}_3\text{F}-\text{SbF}_5-n\text{SO}_3$ , where  $n \geq 3$ , is the strongest proton-donating medium, *i.e.*, the strongest acid in the Brønsted sense. The increase in acidity on replacing fluoride by fluorosulfate may be reasonably attributed to the greater dispersal of negative charge that is made possible by the introduction of fluorosulfate groups.

It should be emphasized that the above conclusions concerning the acidity of the  $\text{HSO}_3\text{F}-\text{SbF}_5-n\text{SO}_3$  and  $\text{HSO}_3\text{F}-\text{AsF}_5-n\text{SO}_3$  systems refer only to rather dilute solutions of  $\text{SbF}_5$ . The effect of sulfur trioxide on the acidity of the very concentrated solutions of  $\text{SbF}_5$  in  $\text{HSO}_3\text{F}$  that have been referred to as "magic acid" by Olah, *et al.*,<sup>8</sup> has not yet been determined. In such concentrated solutions conductometric measurements cannot be interpreted with any certainty and other methods must be used to determine relative acidities, *e.g.*, the measurement of the Hammett acidity function. Such an investigation is in progress in our laboratories. There seems to be no reason to think that the system  $\text{HSO}_3\text{F}-\text{SbF}_5$  has any unique acid properties that would justify the use of the term "magic acid." It would seem more satisfactory to use the term superacid<sup>2</sup> to describe all those systems that have higher acidities than anhydrous sulfuric or fluorosulfuric acid.

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## Line Broadening of the Proton Magnetic Resonance of Nonaqueous Solvents by Vanadyl Ion

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The solvent proton line broadening caused by solvated vanadyl ion has been measured in the solvents acetonitrile, dimethyl sulfoxide, trimethyl phosphate, and trimethyl phosphite. Chemical exchange control of the line broadening was observed only in acetonitrile, from which  $k_{ex} = 2.85 \times 10^8 \text{ sec}^{-1}$  (25°, assuming four exchanging solvent molecules in the coordination sphere of the vanadyl ion),  $\Delta H^\ddagger = 7.05 \text{ kcal mol}^{-1}$ , and  $\Delta S^\ddagger = -20 \text{ cal mol}^{-1} \text{ deg}^{-1}$ . Comparison of the calculated and observed dipolar broadening indicates that only a lower limit can be placed on the exchange rates of dimethyl sulfoxide and trimethyl phosphate while an upper limit is obtained for the trimethyl phosphite system.

### Introduction

The nmr line-broadening technique has been applied to a number of systems to determine ligand exchange rates on metal ion complexes. This report describes the application of this technique to the solvated vanadyl ion in several nonaqueous solvents. The results are considered in relation to previous work on the water,<sup>1,2</sup> methanol,<sup>3</sup> and N,N-dimethylformamide<sup>4</sup>

exchange rates on vanadyl ion and the rates for several nonaqueous solvents on cobalt(II) and nickel(II).<sup>5-7</sup>

In the vanadyl-acetonitrile system the solvent ex-

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