

## Nonexistent Compounds: Two Case Histories<sup>1</sup>

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Received August 28, 1972

Nonexistent compounds may be fitted roughly into three categories. The first contains compounds that represent such logical extensions of existing knowledge that no one has bothered to synthesize them. The second also contains compounds that are extensions of existing knowledge, but in this case the syntheses have been attempted without success. The reasons for failure may or may not be understood. In the third category we find whole areas of chemistry that for one reason or another have not been studied or have been written off as unfruitful for synthetic work.

Examples of the first category are new salts made by interchanging similar ions, or new organic compounds made by simple replacement of substituents. This is obviously a trivial category that does not warrant further discussion.

A striking example of the third category is provided by the history of the chemical compounds of the noble gases. The story of the dramatic discovery of these "nonexistent" compounds is well known, however, and we shall not repeat it here.

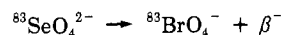
In this account we shall be concerned with some compounds that fall into the second category: the perbromates and hypofluorous acid. The former are homologs of the well-known perchlorates and periodates; the latter can be similarly related to HOCl, HOBr, and HOI. Yet both have until recently defied synthesis.

### The Perbromates

In 1816 von Stadion<sup>2</sup> first synthesized perchlorates by the oxidation of chlorates with sulfuric acid. In 1833 Ammermüller and Magnus<sup>3</sup> prepared trisodium paraperiodate, Na<sub>3</sub>H<sub>2</sub>IO<sub>6</sub>, by passing chlorine through an alkaline solution of sodium iodate. In 1863 Kämmerer<sup>4</sup> claimed the synthesis of perbro-

mates by the reaction of bromine with perchloric acid, but all subsequent efforts to confirm his work were entirely unsuccessful.<sup>5</sup> Equally unsuccessful were a number of other attempts to make perbromates around the turn of the century.<sup>6</sup> As late as 1953 DeCoursey<sup>7</sup> undertook a very systematic effort to prepare perbromates by a variety of methods, with results that once more were uniformly negative.

The first successful synthesis of perbromates in 1968 resulted from a hot-atom process, the  $\beta$  decay of radioactive <sup>83</sup>Se incorporated into a selenate.<sup>8</sup>



The <sup>83</sup>Br is itself radioactive, and its coprecipitation with RbClO<sub>4</sub> was taken to indicate that it was present in the form of BrO<sub>4</sub><sup>-</sup>. A surprising observation was that the perbromate could only be reduced by relatively powerful reductants, such as iodide in 6 M HCl. The half-life of <sup>83</sup>Se is only 24 min, while that of <sup>83</sup>Br is 2.4 hr. Hence the hot-atom synthesis did not provide a feasible method for preparing weighable amounts of perbromates. The results did, however, indicate that perbromates could be made, and they further implied that, once made, the compounds might be relatively inert to reduction.

These results led directly to the first macroscale preparation of perbromates by electrolytic oxidation of a neutral LiBrO<sub>3</sub> solution.<sup>8</sup> A partitioned cell was used, with a platinum anode and an anodic current density of 10 A/cm<sup>2</sup>. Under these formidable conditions perbromate was produced with a rousing 1% current yield. The preparation was analyzed by a method that took advantage of the inertness displayed in the hot atom experiments. First the excess bromate

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) F. von Stadion, *Gilbert's Ann.*, 52, 197, 339 (1816).

(3) F. Ammermüller and G. Magnus, *Pogg. Ann.*, 28, 514 (1833).

(4) H. Kämmerer, *J. Prakt. Chem.*, 90, 190 (1863).

(5) E. MacIvor, *Chem. News*, 33, 35 (1876); 55, 203 (1887); M. M. P. Muir, *J. Chem. Soc.*, 30, 469 (1876); G. Wolfram, *Liebig's Ann.* 198, 95 (1879).

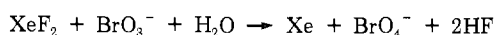
(6) E. H. Cook, *J. Chem. Soc.*, 65, 811 (1894); A. Michael and W. T. Conn, *Amer. Chem. J.*, 23, 89 (1901); P. W. Robertson, *Chem. News*, 106, 50 (1912).

(7) W. F. DeCoursey, Ph. D. Thesis, Iowa State College, Ames, Iowa, 1953.

(8) E. H. Appelman, *J. Amer. Chem. Soc.*, 90, 1900 (1968).

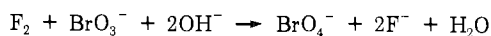
was reduced to  $\text{Br}_2$  by 1 *M*  $\text{HBr}$ , and the  $\text{Br}_2$  was removed by bubbling argon through the solution. Then the solution was made 12 *M* in  $\text{HBr}$ , causing the perbromate to be reduced to  $\text{Br}_3^-$ . Reaction with iodide converted this to  $\text{I}_3^-$ , which was titrated with thio-sulfate.

The electrolytic oxidation of bromate was found to be rather inconvenient, however, and a more practical synthetic method was sought. At this point one "nonexistent" compound came to the rescue of another. The noble gas compound xenon difluoride dissolves in water to form a powerfully oxidizing solution ( $E^0 \cong 2.64$  V).<sup>9</sup> The solutions are not stable, and the  $\text{XeF}_2$  oxidizes the water to  $\text{O}_2$  with a *ca.* 27-min half-time at 25°. If these solutions contain bromate ion in high concentration, perbromate can be formed in yields around 10%, figured on the basis of the reaction



Precipitation of this perbromate as  $\text{RbBrO}_4$  led to the first isolation of a perbromate salt.<sup>8</sup> The oxidation state of the bromine in this compound was confirmed by independent determination of the oxidizing power and total bromine content.

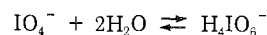
Although somewhat more convenient than electrolysis, oxidation with xenon difluoride is still a rather exotic way to make perbromates. A much more satisfactory method was found to be oxidation of bromate with molecular fluorine in alkaline solution.<sup>10</sup> When  $\text{F}_2$  is bubbled through an alkaline bromate solution, perbromate is formed in yields as great as 20%, based on the reaction



In practice, the fluorine is added until the solution is neutral, excess bromate is precipitated as  $\text{AgBrO}_3$ , and excess fluoride is precipitated as  $\text{CaF}_2$ .<sup>11</sup> Passage of the solution through a cation-exchange column in the hydrogen form yields a dilute solution of perbromic acid. The procedure may be scaled up more or less indefinitely to prepare whatever quantities of perbromate are needed.<sup>12</sup>

The crystal structure<sup>13</sup> and the Raman and infrared spectra<sup>10</sup> of solid  $\text{KBrO}_4$  show it to contain tetrahedral  $\text{BrO}_4^-$  ions and to be isomorphous with  $\text{KClO}_4$ . The Raman spectra of aqueous perbromic acid and neutral aqueous perbromate solutions indicate that these also contain the tetrahedral  $\text{BrO}_4^-$  ions. There is no rapid exchange of oxygen between the perbromate ion and water, indicating the absence of even a small amount of a more highly hydrated ion in equilibrium with the  $\text{BrO}_4^-$ . Thus perbromate resembles perchlorate more than periodate,

inasmuch as the latter often shows octahedral coordination and exchanges oxygen rapidly with water *via* such equilibria as



The X-ray crystallographic measurements on  $\text{KBrO}_4$  indicate a Br-O bond length of 1.61 Å.<sup>13</sup> This is intermediate between the 1.45-Å Cl-O bond length in  $\text{ClO}_4^-$  and the 1.79-Å I-O bond length in  $\text{IO}_4^-$ . On the other hand, the infrared and Raman spectra of the perbromates show that the Br-O stretching frequencies in  $\text{BrO}_4^-$  are almost identical with the I-O stretching frequencies in  $\text{IO}_4^-$ , but are some 20% less than the Cl-O stretching frequencies in  $\text{ClO}_4^-$ .<sup>10</sup> From this we may conclude that the Br-O bond in  $\text{BrO}_4^-$  is comparable in strength to the I-O bond in  $\text{IO}_4^-$ , but is considerably weaker than the Cl-O bond in  $\text{ClO}_4^-$ .

As we have already intimated, the perbromates are rather unreactive compounds. Pure potassium perbromate is stable to about 275°, at which temperature it decomposes smoothly to the bromate and oxygen. Impurities appear to bring about partial decomposition at somewhat lower temperature. Perbromic acid itself is stable to about 6 *M* (55%  $\text{HBrO}_4$ ), even at 100°. At higher concentrations an autocatalytic decomposition to  $\text{Br}_2$  and  $\text{O}_2$  usually takes place. This decomposition also seems to be accelerated by impurities. An azeotropic mixture can be prepared by careful evaporation under vacuum. It is about 12 *M* and approximates the composition of the dihydrate,  $\text{H}_5\text{O}_2^+\text{BrO}_4^-$ . Its stability, however, is very limited, resembling that of anhydrous perchloric acid. If heated rapidly in high vacuum, the azeotrope can be distilled over a short "line-of-sight" path with little decomposition.

The acid fluoride of perbromic acid, perbromyl fluoride,  $\text{BrO}_3\text{F}$ , has been prepared by the reaction of  $\text{KBrO}_4$  with  $\text{SbF}_5$  in anhydrous  $\text{HF}$ .<sup>14</sup> It is much more reactive than the homologous  $\text{ClO}_3\text{F}$ , but it is nevertheless the most stable and best characterized oxyfluoride of bromine.<sup>15</sup>

In dilute solution at room temperature perbromates show little oxidizing power. Even iodide ion is only very slowly oxidized by perbromate in dilute acid. At 100°, 6 *M* perbromic acid is a powerful oxidizing agent, while the 12 *M* acid is a vigorous oxidant at room temperature.<sup>10</sup> In general the reactivity of the perbromates lies between that of the chlorates and that of the perchlorates, which means that next to the perchlorates the perbromates are the least reactive of the known oxyhalogen compounds. This inertness suggests the interesting possibility that earlier investigators may actually have made perbromates, but overlooked them because they were expecting a reactive product instead of an inert one.

The sluggish chemical reactions of the perbromates cannot give us much information about the thermodynamic stability of these compounds. How-

(9) J. G. Malm and E. H. Appelman, *At. Energy Rev.*, 7, 21 (1969).

(10) E. H. Appelman, *Inorg. Chem.*, 8, 223 (1969).

(11) In large-scale preparations a preliminary precipitation of the bulk of the fluoride and bromate may be effected by the addition of barium hydroxide (see ref 12).

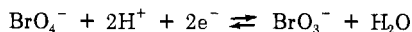
(12) E. H. Appelman, *Inorg. Syn.*, 13, 1 (1972).

(13) S. Siegel, B. Tani, and E. H. Appelman, *Inorg. Chem.*, 8, 1190 (1969).

(14) E. H. Appelman and M. H. Studier, *J. Amer. Chem. Soc.*, 91, 4561 (1969).

(15) H. H. Claassen and E. H. Appelman, *Inorg. Chem.*, 9, 622 (1970); G. K. Johnson, P. A. G. O'Hare, and E. H. Appelman, *ibid.*, 11, 800 (1972).

ever, the results of thermochemical measurements do allow us to assign a free energy to the aqueous perbromate ion and to evaluate its electrode potentials.<sup>16</sup> For the half-reaction



we have  $E^0 = 1.74$  V. The analogous reactions involving  $\text{ClO}_4^-$  and  $\text{IO}_4^-$  have  $E^0$  values of 1.23 and 1.64 V, respectively. (If the periodate half-reaction is written in terms of  $\text{H}_5\text{IO}_6$ , its  $E^0$  becomes 1.59 V.)

It can be seen, therefore, that perbromate is a somewhat more powerful oxidant than periodate, and a much more powerful oxidant than perchlorate. This is not very different from the situation that prevails among the elements of the fifth and sixth periodic groups, as is shown in Table I. Of course, the compounds become less oxidizing as we move toward the left in the periodic table, but it is clear that in all three groups there is a sharp increase in oxidizing power as we descend from the last short period (P, S, Cl) to the first long period (As, Se, Br), whereas only relatively inconsequential changes occur between the next two periods. Or, to phrase it differently, the four-coordinated oxy acids and ions in the last short period are substantially more stable to reduction than are their heavier homologs. Compared to this gross effect, the fact that selenate and perbromate are somewhat stronger oxidants than tellurate and periodate, respectively, appears to be of only secondary importance.

Although 1.74 V is indeed a healthy potential for the bromate-perbromate couple, it would not in itself lead us to anticipate as much difficulty as we actually encounter in trying to oxidize bromate to perbromate. For example, we might expect hot persulfate to bring about the oxidation, which it does not. In order to understand why perbromates are so difficult to make, we must take into account the high degree of inertness that these compounds possess. This, of course, implies a high activation barrier that inhibits *reduction of perbromate*. If, however, we invoke the law of microscopic reversibility, we conclude that the activation barrier to *oxidation of bromate* is the sum of the activation barrier to reduction of perbromate *plus* the overall free energy of the reaction, which is reflected in the electrode potential. Thus the combination of a fairly high electrode potential *and* a high degree of inertness leads to a formidable activation barrier to the synthesis of perbromates.

### Theoretical Aspects of the Perbromate Problem

The apparent nonexistence of perbromates could not but challenge the imagination of chemical theorists. Among the explanations offered for the anomaly were inner-sphere electron repulsions,<sup>17</sup> a high  $s \rightarrow p$  promotion energy making  $sp^3$  hybridization unfavorable,<sup>18</sup> and the presence of a node in the bro-

Table I  
Standard Electrode Potentials (in Acid) Between Highest Oxidation States of Nonmetals<sup>a</sup>

		Periodic group			
		V	VI	VII	
		Species involved			
		$\text{H}_3\text{XO}_3 \rightarrow \text{H}_3\text{XO}_4$	$\text{H}_2\text{XO}_3 \rightarrow \text{HXO}_4^-$	$\text{XO}_3^- \rightarrow \text{XO}_4^-$	
P	-0.28	S	0.10	Cl	1.23
As	0.57	Se	1.09	Br	1.74
Sb	0.72 <sup>b</sup>	Te	0.90 <sup>c</sup>	I	1.64

<sup>a</sup> All potentials are given in volts and are in accordance with the IUPAC sign convention. The chlorine and iodine potentials are taken from ref 16a, and the bromine potential is taken from ref 16b. The phosphorus and tellurium potentials are taken from W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., New York, N. Y., 1952. All other potentials are derived from data in D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Nat. Bur. Stand. Techn. Note*, No. 270-3 (U. S.), (1968). Except where indicated otherwise, potentials apply to species in aqueous solution. <sup>b</sup>  $\text{Sb}_4\text{O}_6(\text{c}) \rightarrow \text{Sb}_2\text{O}_5(\text{c})$ . <sup>c</sup>  $\text{H}_2\text{TeO}_3(\text{c}) \rightarrow \text{H}_6\text{TeO}_6(\text{c})$ .

mine 4d orbital in the region most favorable for bonding.<sup>19</sup> The relatively greater stability of periodate was rationalized in terms of expanded coordination, ionic character,<sup>17</sup> or f-orbital bonding.<sup>20</sup> The arguments were necessarily qualitative or, at best, semiquantitative, and each theorist tended to discount the proposals put forth by others.

Shortly after the successful preparation of perbromates, Cox and Moore<sup>21</sup> published the results of calculations that purported to refute *all* the earlier theoretical arguments and to show that there was no theoretical reason why perbromates should not exist. Their results, however, are unable to account for the most salient characteristic of perhalate energetics, namely, the fact that both perbromates and periodates are very much less stable to reduction than are perchlorates.

We must conclude, therefore, that chemical theory has been notably unsuccessful in its attempt to shed light on the "perbromate problem" and that there is to date no entirely satisfactory explanation for the sharp decrease in the stability of four-coordinated oxy acids and ions to reduction that occurs when we go from the last short period to the first long period. The changes in stability that we find between the first and second long periods are much smaller, and will presumably be even more resistant to theoretical interpretation.

### Hypofluorous Acid

The history of the oxy acids of fluorine is much shorter than that of the perhalates, because it is only in relatively recent times that chemists have learned to work comfortably with fluorine. Although Moissan<sup>22</sup> and Ruff<sup>23</sup> both observed that the reaction of fluorine with water produced small amounts of a

(16) (a) G. K. Johnson, P. N. Smith, E. H. Appelman, and W. N. Hubbard, *Inorg. Chem.*, **9**, 119 (1970); (b) F. Schreiner, D. W. Osborne, A. V. Pocius, and E. H. Appelman, *ibid.*, **9**, 2320 (1970).

(17) R. C. Ferreira, *Bull. Soc. Chim. Fr.*, 135 (1950).

(18) R. S. Nyholm, *Proc. Chem. Soc., London*, 273 (1961).

(19) D. S. Urch, *J. Inorg. Nucl. Chem.*, **25**, 771 (1963).

(20) Z. Z. Hugus, Jr., *J. Amer. Chem. Soc.*, **74**, 1076 (1952).

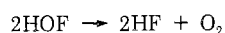
(21) M. M. Cox and J. W. Moore, *J. Phys. Chem.*, **74**, 627 (1970).

(22) H. Moissan, "Le Fluor et ces Composés," Paris, 1900, pp 129-132.

(23) O. Ruff, *Z. Angew. Chem.*, **41**, 1291 (1928).

strongly oxidizing substance, no definite claims for the formation of fluorine oxy acids were put forth until 1932, when Dennis and Rochow<sup>24</sup> reported that they had made solutions of oxy salts of fluorine by passing gaseous F<sub>2</sub> into aqueous alkali. They further stated that they could neutralize the excess alkali and obtain solutions of the corresponding fluorine oxy acids. Dennis and Rochow claimed that in this way they could make both HOF and HFO<sub>3</sub>. In 1934 Cady<sup>25</sup> wrote that he had been unable to confirm the compounds reported by Dennis and Rochow, and he suggested that their observations were most likely the result of chlorine impurity in their fluorine. The matter appears not to have been pursued further, and today it seems virtually certain that Cady's interpretation was correct.

In any case no further report of a fluorine oxy acid transpired until 1968. In that year Noble and Pimentel<sup>26</sup> photolyzed a mixture of fluorine and water that was frozen into a solid N<sub>2</sub> matrix at 14–20°K and examined the products by infrared spectrophotometry. They were able to assign some of the bands that they observed to the new compound HOF. Noble and Pimentel did not, however, think it very likely that this compound could be prepared other than in a low-temperature matrix. In fact, by this time chemists had pretty well convinced themselves that no oxy acids of fluorine were ever likely to be isolated. This conclusion was based primarily on straightforward thermodynamic arguments, which Noble and Pimentel stated explicitly for the case of HOF. If we assume that the O–H and O–F bonds in HOF have about the same energy as those in H<sub>2</sub>O and OF<sub>2</sub>, respectively, we may estimate that HOF should have a standard heat of formation of about –31 kcal/mol. We then conclude that the reaction



should be exothermic by some 68 kcal/mol, and we may also expect it to have a positive  $\Delta S$ . Hence only a substantial kinetic barrier to this simple reaction will permit the isolation of HOF.

Our first inkling that hypofluorous acid could be isolated under ordinary conditions came in the course of a very simple experiment in which a drop of water was placed in a Kel-F (polychlorotrifluoroethylene) tube with about 100 Torr of F<sub>2</sub> gas.<sup>27</sup> When portions of the gas phase were sampled with a time-of-flight mass spectrometer, a small HOF peak at mass 36 was seen on the shoulder of the F<sub>2</sub> peak at mass 38. If the reaction vessel was chilled with liquid nitrogen, the unreacted fluorine could be pumped away, and then, on gradual warming, the HOF could be distilled from the vessel.

If the reaction was allowed to proceed at room temperature until all of the fluorine was consumed,

no HOF was found. This implied that the HOF was present as a steady-state intermediate, which probably reacted much faster with water than did the fluorine itself. The development of a method for isolating substantial quantities of HOF depended upon recognition of this fact. If any product was to be isolated, it had to be removed rapidly from the reaction zone, but if this was accomplished through the use of a rapid fluorine flow, most of the fluorine would pass through the reaction zone unaltered. Hence a recirculating system was called for, and in the successful procedure fluorine was rapidly circulated in a Kel-F apparatus consisting of a reaction vessel, U-tubes cooled to –50 and –79° to remove water and HF, and a U-tube cooled to –183° to trap the HOF. The reaction vessel itself was a Kel-F U-tube filled with Räschig rings cut from Teflon "spaghetti" tubing. The rings were wetted by the simple expedient of filling the vessel with water and then draining it. It was found advantageous to cool the reaction vessel to ca. –40°. Apparently this resulted in the HOF being formed at local "hot spots" in a cool environment, and further reaction of the product was minimized. After the reaction was complete, the by-products OF<sub>2</sub> and O<sub>2</sub>, which are volatile at –183°, were pumped off. In this way 50–200 mg quantities of HOF have been prepared, with yields approaching 50% on the basis of the reaction



We may note that if the heat of formation of HOF is around –30 kcal/mol, as we suggested earlier, equilibrium in this reaction will be far to the right, unlike the analogous reactions of chlorine, bromine, and iodine, in which equilibrium lies to the left.

It is interesting to consider that the preparative procedure described here is rather similar to the techniques used by Cady in the 1930's to study the fluorine–water reaction.<sup>28</sup> Two small but significant modifications stand out: The use of a –50° trap is critical, because without it virtually all of the HOF is trapped with the water in the –79° trap. Pumping away the volatiles is also essential, because OF<sub>2</sub> is formed in amounts comparable to the HOF, and only by pumping can it be removed.

At low temperature HOF is a white solid, melting at –117° to a pale yellow liquid. The compound has a vapor pressure less than 1 Torr at –79° and a normal boiling point somewhat below room temperature. Its volatility is thus comparable to that of HF, with which it is always contaminated. The vapor appears colorless, significant light absorption beginning in the ultraviolet below 400 nm.

Structural parameters of the HOF molecule have been determined from its rotational spectrum.<sup>29</sup> The O–H bond distance is 0.96<sub>4</sub> Å, the O–F bond distance is 1.442 Å, and the bond angle is 97°. This is the smallest known oxygen bond angle. Although it can be rationalized in terms of the character of the bond,

(24) L. M. Dennis and E. G. Rochow, *J. Amer. Chem. Soc.*, **54**, 832 (1932); **55**, 2431 (1933).

(25) G. H. Cady, *J. Amer. Chem. Soc.*, **56**, 1647 (1934).

(26) P. N. Noble and G. C. Pimentel, *Spectrochim. Acta, Part A*, **24**, 797 (1968).

(27) M. H. Studier and E. H. Appelman, *J. Amer. Chem. Soc.*, **93**, 2349 (1971).

(28) G. H. Cady, *J. Amer. Chem. Soc.*, **57**, 246 (1935).

(29) H. Kim, E. F. Pearson, and E. H. Appelman, *J. Chem. Phys.*, **56**, 1 (1972).

a more intuitively satisfying explanation comes from the results of nmr studies on the molecule,<sup>30</sup> which show the fluorine to have a charge of about  $-0.5 e$  and the hydrogen to have a charge of about  $+0.5 e$ . Hence the reduced bond angle can be understood in terms of electrostatic attraction between the two ends of the molecule.

It is perhaps worth emphasizing that with this charge distribution the concept of a  $+1$  valence for the fluorine in HOF is strictly a formalism. The negative charge on the HOF fluorine is intermediate between that on the fluorines in  $OF_2$  and that on the fluorine in HF.

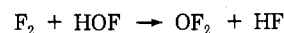
The drawing of negative charge to the fluorine end of the HOF molecule suggests that the O-H bond should be weakened and the O-F bond strengthened. Evidence in support of this notion comes from analysis of the infrared spectrum of HOF, which has now been measured in the gas phase<sup>31</sup> as well as in a solid  $N_2$  matrix.<sup>26,32</sup> The more recent results<sup>31,32</sup> are generally consistent with the earlier matrix work of Noble and Pimentel,<sup>26</sup> if one takes into account the fact that the HOF produced by Noble and Pimentel was hydrogen bonded to HF, whereas the more recent studies were carried out on relatively pure HOF. The force constant for the O-H stretch in HOF ( $7.1 \text{ mdyn}/\text{\AA}$ )<sup>31</sup> is in fact somewhat weaker than the analogous constant for water ( $7.68 \text{ mdyn}/\text{\AA}$ ),<sup>33</sup> whereas the force constant for the O-F stretch in HOF ( $4.27 \text{ mdyn}/\text{\AA}$ )<sup>31</sup> is somewhat stronger than the analogous constant for  $OF_2$  ( $4.05 \text{ mdyn}/\text{\AA}$ ).<sup>34</sup> Although the fractional change is about the same for the two vibrations, the fact that an O-H bond is much stronger than an O-F bond would lead us to expect an overall reduction in the stability of the HOF molecule. This expectation is confirmed by the results of photoionization studies of HOF,<sup>35</sup> which lead to a value of  $-23.5 \text{ kcal/mol}$  for the standard heat of formation of the molecule. This is  $7.5 \text{ kcal/mol}$  less negative than the value estimated by assuming the O-H and O-F bonds in HOF to have the same energy as those in  $H_2O$  and  $OF_2$ , respectively.

The most prominent chemical property of HOF is its instability. It does, indeed, decompose to HF and  $O_2$ . In Kel-F or Teflon apparatus at room temperature and at pressures around 100 Torr, the compound shows a half-life around 30 min. It appears to be less stable in metal vessels and at higher pressure.

Decomposition is accelerated by light and by molecular fluorine. It is inhibited by  $CO$ ,  $H_2$ , and, to a lesser extent, HF. The reaction appears to be complex. It is probably a free-radical process, and most likely also involves surface catalysis. Under certain rather poorly defined conditions, HOF samples can decompose explosively.

Hypofluorous acid reacts rapidly with water to produce HF,  $H_2O_2$ , and  $O_2$ . In weakly acidic solutions the water is usually oxidized primarily to  $H_2O_2$ , while in alkaline solutions  $O_2$  is the principal oxygen-containing product. Hypofluorous acid displays a powerful oxidizing action toward many aqueous substrates. For example, it oxidizes silver(I) to silver(II), and in alkaline solution it oxidizes bromate to perbromate. The reactions of HOF with water and with aqueous substrates generally parallel those of  $F_2$  itself. Thus fluorine also oxidizes water primarily to  $H_2O_2$  in acidic solutions, but primarily to  $O_2$  in alkaline ones,<sup>29</sup> and fluorine, like HOF, can oxidize bromate to perbromate in alkaline solution but not in acid.<sup>10</sup> It therefore seems likely that HOF is the reactive species produced when fluorine reacts with water.

One remaining puzzle is the role that HOF plays in the formation of  $OF_2$  from the reaction of fluorine with water or base. HOF does not dehydrate to  $OF_2$  either spontaneously or in the presence of water or base, nor, for that matter, does  $OF_2$  react with water to give HOF. There is evidence, however, that the reaction



may proceed in the presence of water, although it does not take place in the gas phase.

### The Moral of the Tale

It is interesting to speculate why certain compounds have resisted discovery for long periods of time, only to be synthesized quite painlessly once the initial breakthrough has been made.<sup>36</sup> Although reasons can be given that are peculiar to each system, the general pattern seems to be an initial unsuccessful effort to make a compound, followed by detailed rationalization of the failure. Thereafter the rationalization tends to be accepted, and little or no effort is made to refute it. If there is a lesson to be learned from all this, it would seem to be that it does not pay to be too categorical as to what is or is not a promising line of experiment. Such an admonition may not be entirely superfluous in the present era of tight research budgets and conservative research aspirations.

(36) In the course of a discussion of another group of "nonexistent" compounds, the seven-valent actinide ions, this question was posed to Soviet Academician V. I. Spitzyn. His explanation: "Autohypnosis!"

(30) J. C. Hindman, A. Svirnickas, and E. H. Appelman, *J. Chem. Phys.*, **57**, 4542 (1972).

(31) E. H. Appelman and H. Kim, *J. Chem. Phys.*, **57**, 3272 (1972).

(32) J. A. Goleb, H. H. Claassen, M. H. Studier, and E. H. Appelman, *Spectrochim. Acta, Part A*, **24**, 797 (1968).

(33) T. Shimanouchi and I. Suzuki, *J. Chem. Phys.*, **42**, 296 (1965).

(34) L. Pierce, R. Jackson, and N. DiCianni, *J. Chem. Phys.*, **35**, 2240 (1961).

(35) J. Berkowitz, E. H. Appelman, and W. A. Chupka, *J. Chem. Phys.*, in press.