

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON, EUGENE, ORE.]

## Some Predicted Chemistry of Group VIII Elements; the Aerogens

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The generic term aerogen is proposed for the elements of group VIII of the periodic table. The much greater ease with which the heavier aerogens form polyfluorides than polychlorides is more easily explained by the 3-center-4-electron description than by hybridization with d-orbitals. A search for the hypothetical hydrides  $\text{PH}_5$  and  $\text{ClH}_3$  might provide evidence bearing on which bonding description of the aerogen polyhalides is more satisfactory. Aerogen oxides could be prepared by photolysis with ozone in condensed media. The aerogens may also react with  $^1\text{D}$  sulfur atoms and form gaseous complexes with the polyatomic Lewis acids  $\text{BF}_3$  and  $\text{SO}_3$ . The diatomic radical species  $\text{NeF}$  should be present in equilibrium concentration of the order of a per cent in gas mixtures at a few atmospheres. With the possible exception of  $\text{HeH}$ , other diatomic radical species should be formed less easily. The aerogens might accept protons from strong gaseous Brønsted acids and form crystalline solids. Necessary proton affinity data are not available, but it seems doubtful that such solids will form with the hydrogen halides. They may form with stronger gaseous proton acids.

## Introduction

The heavier elements of group VIII have recently been shown to form ionic solids like  $\text{XePtF}_6$  by electron transfer,<sup>1</sup> to form solid polyhalides like  $\text{XeF}_4$  by direct reaction of the elements,<sup>2</sup> and to form oxides like  $\text{XeO}_3$  by hydrolysis of fluorides.<sup>3,4</sup>

The present paper shows how bond energies for compounds of other elements suggest the bonding in the polyhalides. It also proposes experimental procedures for the preparation of oxides and other Lewis salts and considers the possible formation of diatomic radicals and proton transfer compounds with the group VIII elements.

The preparation of the manuscript has indicated the need for a generic term for these elements now that the designation "inert gas" is no longer appropriate. The name "halogens" for elements of group VII reflects their preparation from the salt of the sea. Since most of the elements of group VIII are derived from the atmosphere, it seems appropriate to call them "aerogens" from the Greek  $\alpha\epsilon\rho\theta\sigma$ .

## Bonding in Polyhalides

Bonding in the aerogen polyhalides is presumably similar to that in other compounds of elements in groups IV to VII that cannot be described by two-center bonds with s- and p-orbitals. Pauling<sup>5</sup> has described these compounds by hybridization involving promoted d-orbitals. Pimentel<sup>6</sup> and Rundle<sup>7</sup> have used 3-center-4-electron combinations of  $p\sigma$ -orbitals.

Table I lists the minimum ionization energies for the aerogens and also the minimum energies to promote an outer p-electron to a d-orbital. Electronegativities in the table are calculated by the method of Mulliken<sup>8</sup> as reported by Rundle.<sup>7</sup> If a compound  $\text{EF}_2$  is barely energetically stable with respect to the elements, the  $B$  entry in the last column is the minimum energy per bond to atomize the compound with formation of an aerogen having one promoted electron. Minimum energies to atomize barely stable  $\text{ECl}_2$  compounds would be about 11 kcal./mole greater.

If hybridized d-orbitals are used in forming the aerogen polyfluorides, the bonds should not differ greatly in polarity from those using only s- and p-

orbitals. Since the more electronegative elements form p-orbital bonds to fluorine and to chlorine that differ by only about 10 kcal./mole in strength,<sup>9</sup> it seems hard to accommodate the promoted orbital description to the observation that krypton forms a polyfluoride while xenon and radon do not easily form polychlorides.

TABLE I

## SOME PROPERTIES OF AEROGENS

Element	Ionization energy, $I$ , kcal./mole	Promotional energy, $P$ , kcal./mole	Electronegativity	Minimum $B$ for $\text{EF}_2$ , kcal./mole
He	566.6	...	4.53	...
Ne	497.0	...	3.98	...
Ar	363.2	319.1	2.91	177.9
Kr	322.6	276.6	2.58	156.6
Xe	279.6	228.0	2.24	132.3
Rn	247.7	194.1	1.98	115.3

The 3c-4e description requires that the outer atoms in the bond be much more electronegative than the central one. Since krypton and radon differ in electronegativity by only 0.6 units while fluorine and chlorine differ by 1.0, the difficulty in forming aerogen polychlorides is more readily explained.

Additional evidence might be provided by a search for higher hydrides of elements of groups V to VII. The atomization of  $\text{PCl}_3$  requires 78.48 kcal./mole per bond broken, while  $\text{PH}_3$  requires 76.41 kcal./mole. The two additional bonds in  $\text{PCl}_5$  average 40.08 kcal./mole. If d-orbital promotion is involved in forming  $\text{PCl}_5$ , the hypothetical  $\text{PH}_5$  would presumably have bonds of comparable strength. Although it would be thermodynamically unstable with respect to  $\text{PH}_3 + \text{H}_2$ , it should be observable as a metastable species.

Similarly, although the bond dissociation energy of  $\text{ClF}$  is much less than that of  $\text{HCl}$ ,  $\text{ClF}_3$  is well known while  $\text{ClH}_3$  is not.

Metastable hydride species like  $\text{PH}_5$  and  $\text{ClH}_3$  could hardly be described except in terms of promoted orbitals. Repeated failure to prepare such compounds would argue for the 3c-4e description of binding in known compounds with the more electronegative halogens.

## Lewis Salts

**General Considerations.**—The aerogen polyhalides bond two groups to a central atom with the use of only one p-orbital of that atom. If an aerogen is to form a more conventional 2-center electron bond without d-orbital promotion, it must contribute *both* of the electrons to that bond. Hence the aerogen behaves as a Lewis base, and the species to which it is bound is a Lewis acid.

(9) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Academic Press, Inc., New York, N. Y., 1958.

(1) N. Bartlett, *Proc. Chem. Soc.*, 218 (1962).

(2) C. L. Chernick, H. H. Claassen, P. R. Fields, H. H. Hyman, J. G. Malm, W. M. Manning, M. S. Matheson, L. A. Quarterman, F. Schreiner, H. H. Selig, I. Sheft, S. Siegel, E. N. Sloth, L. Stein, M. H. Studier, J. L. Weeks and M. H. Zirin, *Science*, **138**, 136 (1962).

(3) D. F. Smith, *J. Am. Chem. Soc.*, **85**, 816 (1963).

(4) D. H. Templeton, A. Zalkin, J. D. Forrester and S. M. Williamson, *ibid.*, **85**, 817 (1963).

(5) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 177.

(6) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

(7) R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963).

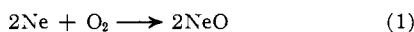
(8) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934); **3**, 573 (1935).

**Positive Salts.**—The aerogens are well known<sup>10</sup> to react with protons forming metastable positive ions of general formula  $\text{EH}^+$ . They could presumably react with other gaseous cations. Since the energy necessary to separate  $\text{LiF}$  into ions differs little from that needed to separate charged conducting spheres initially at the internuclear distance in  $\text{LiF}$ , the bonding in the isoelectronic  $\text{LiNe}^+$  may be quite weak. Because of its greater polarizability, xenon should form such compounds more easily than the lighter aerogens.

**Oxides.**—The  $^1\text{D}$  oxygen atom is one of the strongest neutral Lewis acids, and several laboratories have prepared compounds having xenon-oxygen bonds. Oxides of the lighter aerogens are not known but would be isoelectronic with diatomic halogen fluorides.

Isoelectronic oxides and fluorides usually have very similar bond dissociation energies even though the fluorides dissociate with separation of the bonding electrons while the oxides dissociate heterolytically with the oxygen atom rearranging to a  $^3\text{P}$  state and retaining neither of the bonding electrons.<sup>9</sup>

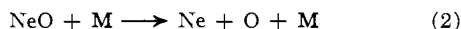
This argument implies that  $\text{NeO}$  should have a bond dissociation energy similar to the isoelectronic  $\text{F}_2$  or about 40 kcal./mole. Then for the reaction



$K = 10^{-32}$  at  $25^\circ$  if standard states are 1 atmosphere fugacity.

Obviously  $\text{NeO}$  cannot be prepared at ambient temperatures by reaction of the elements. Nitric oxide,  $\text{NO}$ , is almost equally unstable with respect to the elements; yet generations of freshmen have prepared it and observed its properties. The possible observability of  $\text{NeO}$  depends upon its inertness to decomposition rather than its stability.

Only two decomposition mechanisms seem plausible. One is



where  $\text{M}$  is a molecule providing the necessary energy. If that energy is indeed 40 kcal./mole for dissociation to  $\text{O}(^3\text{P})$ , it is 85 kcal./mole for reaction without change of multiplicity. No matter how great the rate constant for reaction 3, decomposition by this two-step mechanism should be immeasurably slow at room temperature.

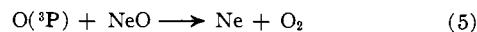
The only other plausible mechanism is the single step reversal of reaction 1. No completely analogous reactions are known, but a paper to be submitted in the near future will indicate that the activation energy may well be of the order of 20 kcal./mole. Since the reversal of reaction 1 also requires a change of multiplicity if the oxygen molecule is produced in its triplet ground state, it appears that  $\text{NeO}$  should be inert to decomposition at room temperature and below provided it did not react with the walls of its container.

Aerogen oxides might be prepared by producing  $^1\text{D}$  oxygen atoms in a medium sufficiently dense to provide third bodies for energy removal in the process



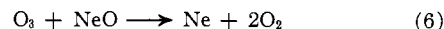
A plausible procedure is to photolyze ozone in liquid neon at wave lengths below 3000 Å. Such a procedure in liquid nitrogen was recently described by DeMore and Raper.<sup>11</sup> These authors did not observe any effect of dilution by argon on the quantum yield for  $\text{N}_2\text{O}$  formation, but this may merely mean that argon does not compete efficiently with nitrogen for  $^1\text{D}$  oxygen

atoms. Since  $^3\text{P}$  atoms may react very efficiently with product by the process



the photochemical steady state concentration of  $\text{NeO}$  may be low but should not be negligible.

The only other possible interfering reaction would seem to be



Interference from this reaction could be overcome by a flash photolysis procedure that dissociated virtually all of the ozone before significant formation of  $\text{NeO}$  had occurred.

Of course the above procedure need not be restricted to preparation of monoxides, and up to four oxygen atoms might combine with a single aerogen atom. Formation of oxides will probably be easier with the larger and more polarizable aerogens.

Although  $\text{HF}$  has one of the strongest bonds involving a single pair of electrons, dissociation of the isoelectronic  $\text{HeO}$  would leave both of the bonding electrons with the more electronegative element. Such a bond might be very weak. The properties of  $\text{HeO}$  are not easily predicted, but the compound would be of considerable interest if it could be prepared.

**Other Neutral Salts.**—If aerogens can form metastable oxides, they should also form sulfides with  $^1\text{D}$  sulfur atoms in dense media. Strausz and Gunning<sup>12</sup> have recently shown that these atoms can be generated by photolysis of  $\text{OCS}$  at wave lengths shorter than about 2500 Å.

The planar gas molecules  $\text{BF}_3$  and  $\text{SO}_3$  are also strong Lewis acids that might form adducts with the basic aerogens. Even if the adducts did not form solids, their presence might be demonstrated by gas law deviations and by absorption spectra. Since  $\text{BF}_3$  and trimethylamine apparently react without activation energy,<sup>13</sup> the rate of formation of aerogen adducts probably would depend little on temperature. Equilibrium concentrations of adducts would be increased at high pressures and low temperatures.

### Diatomic Radicals

Elements of the first row of the periodic table form well characterized neutral and singly charged species having odd numbers of electrons. Examples are  $\text{CN}$ ,  $\text{NO}$ ,  $\text{N}_2^+$ ,  $\text{O}_2^+$ ,  $\text{O}_2^-$ , and  $\text{F}_2^+$ . Since isoelectronic species in this group have very comparable dissociation energies, the hypothetical  $\text{NeF}$  should have a bond strength about equal to the known  $\text{Ne}_2^+$ .

Mason and Vanderslice<sup>14</sup> report binding energies of 50 kcal./mole for  $\text{H}_2^+$  and of 7–23 kcal./mole for  $\text{Ne}_2^+$ . These are about half the dissociation energies of  $\text{H}_2$  and  $\text{F}_2$ , respectively. This argument suggests that  $\text{HeH}$  and  $\text{NeF}$  should form from the elements in reactions that are approximately thermoneutral.

Unlike the oxides discussed above, these radicals would probably be labile. They could only be observed in equilibrium or photostationary concentrations. If their formations are indeed thermoneutral, they should be present in concentrations of the order of a per cent in gas mixtures under pressures of a few atmospheres. Such concentrations could easily be detected by spectroscopic or spin resonance techniques. With the hydrogen radicals, it might be necessary to use photochemical, thermal, or discharge techniques to ensure that equilibrium was attained.

(12) P. O. Strausz and H. E. Gunning, *J. Am. Chem. Soc.*, **84**, 4080 (1962).

(13) D. Garvin and G. B. Kistiakowsky, *J. Chem. Phys.*, **20**, 105 (1952).

(14) E. A. Mason and J. T. Vanderslice, *ibid.*, **29**, 361 (1958); **30**, 599 (1959).

(10) For a review, see G. A. Cook, "Argon, Helium, and the Rare Gases" Volume I, History, Occurrence, and Properties," Interscience Publishers, Inc., New York, N. Y., 1961, p. 161.

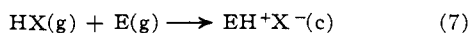
(11) W. DeMore and O. F. Raper, *J. Chem. Phys.*, **37**, 2048 (1962).

Compounds with 3-electron bonds are most stable when the bound elements have comparable electronegativities, and they do not form easily with heavy elements where  $\pi$ -bonds are weaker. Probably NeF is the diatomic aerogen radical that will be formed in greatest concentration, and species like NeH, KrCl, XeF, etc., will be much harder to detect.

### Proton Transfer Compounds

If a gaseous molecule is a Brønsted acid, it can transfer a proton to a basic species to form ions that condense to a crystalline solid similar to the electron transfer reaction forming  $\text{Xe}^+\text{PtF}_6^-$ . A familiar example is the reaction of the gaseous molecules HCl and  $\text{NH}_3$  to form crystalline  $\text{NH}_4^+\text{Cl}^-$ .

Since the aerogens have significant proton affinities, they might in principle react



If it is assumed that the lattice energy of crystalline EHX is the same as that of the isoelectronic alkali salt, it is possible to calculate the proton affinity of E necessary to make reaction 7 thermoneutral. Since considerable entropy is lost in this reaction, larger proton affinities are necessary if the reaction is to take place. These minimum proton affinities for formation of a halide salt are presented in Table II. The value quoted for He is that necessary to get HeHF. The values for the other elements are for iodide formation; values for bromide and chloride formation are the same within about 3 kcal./mole, and values for fluoride formation are somewhat higher.

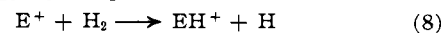
TABLE II

MINIMUM PROTON AFFINITIES (IN KCAL./MOLE) FOR IONIC LATTICE FORMATION WITH A HYDROGEN HALIDE

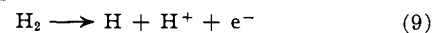
He	Ne	Ar	Kr	Xe
122	144	159	164	170

The proton affinity of helium is calculable with moderate confidence from quantum mechanics. Evett<sup>15</sup> assigns a value between 40 and 47 kcal./mole. It is clear that helium will not react with a hydrogen halide to form a crystalline salt.

The proton affinities of the other aerogens are not known. Stevenson and Schissler<sup>16</sup> observed that neon, argon, and krypton positive ions all reacted without activation energy by the process



Since the process



requires 419 kcal./mole, this observation and the data in Table I indicate that the proton affinity of krypton is at least 96 kcal./mole and may of course be much more. Apparently the proton affinities of the heavier aerogens are greater than that of helium, and xenon and radon are the most apt to undergo reactions like eq. 7.

Even if hydrogen halides do not react to form stable solids, heavy aerogens may react with stronger Brønsted acids. The proton affinity of gaseous perchlorate ion is undoubtedly less than that of any halide, but perchlorate lattice energies are also less than those of halides.

Since ionic lattice energies can be calculated with moderate confidence, measurements of gaseous proton affinities would permit very reliable predictions as to which systems, if any, could produce crystalline EHX compounds. The data presently available are not very encouraging for their preparation.

**Acknowledgment.**—The preparation of this manuscript was supported in part by the Army Research Office under Grant DA-ARO(D)-31-124-G333. I am indebted to Professor Nancy P. Helmbold of the University of Oregon for suggesting the term aerogen.

(15) A. A. Evett, *J. Chem. Phys.*, **24**, 150 (1956).

(16) D. P. Stevenson and D. O. Schissler, *ibid.*, **23**, 1353 (1955); **24**, 926 (1956).

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## The Temperature Dependence of the Steady State Kinetic Parameters of the Fumarase Reaction<sup>1</sup>

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The steady state kinetics of the hydration of fumarate and dehydration of L-malate by pig heart fumarase have been investigated from pH 5.5 to 8.5 and from 5 to 37° in tris-(hydroxymethyl)-aminomethane-acetic acid buffers of 0.01 ionic strength. The pH dependences of the Michaelis constants and maximum initial velocities can be represented by the equations used earlier which contain ten pH-independent kinetic parameters. The temperature dependence has been determined for each of these parameters. The results are discussed in terms of a general mechanism. The apparent activation energies for the lower limits to the bimolecular rate constants for combination of enzyme and substrate are both approximately 6 kcal. mole<sup>-1</sup>, which is in accord with the fact that these lower limits approach the theoretical values for diffusion-controlled reactions.

### Introduction

The steady state kinetics of the reaction catalyzed by fumarase have been thoroughly studied in tris-(hydroxymethyl)-aminomethane-acetic acid buffers.<sup>4,5</sup> In these studies the pH dependences of the maximum initial velocities and Michaelis constants for fumarate

and L-malate have been determined over the pH range from about 5.0 to 8.5 and for a series of ionic strengths. From the effect of hydrogen ion concentration on these four kinetic parameters under given conditions of temperature and ionic strength a total of ten experimental parameters may be evaluated. In the present research the temperature dependence of each of these ten experimental parameters has been determined. An earlier study of the temperature dependence of fumarase kinetics was carried out by Massey<sup>6</sup> using phosphate buffers. Analysis of the effects of pH and temperature on fumarase kinetics cannot be made in as great detail

(1) Taken in part from the Ph.D. Thesis of D. A. Brant, University of Wisconsin, 1962. Presented in part at the 142nd National Meeting of the American Chemical Society, September 9-14, 1962, Atlantic City, N. J.

(2) National Science Foundation Predoctoral Fellow, 1958-1962.

(3) National Science Foundation Postdoctoral Fellow, 1959-1960.

(4) C. Frieden and R. A. Alberty, *J. Biol. Chem.*, **212**, 859 (1955).

(5) C. Frieden, R. G. Wolfe, Jr., and R. A. Alberty, *J. Am. Chem. Soc.*, **79**, 1523 (1957).

(6) V. Massey, *Biochem. J.*, **53**, 72 (1953).