Journal of Fluorine Chemistry, 20 (1982) 65–74

Received: May 13, 1981

SPONTANEOUS REACTIONS OF XENON, FLUORINE AND ANTIMONY PENTAFLUORIDE[†]

L. STEIN

Chemistry Division, Argonne National Laboratory,
Argonne, Ill. 60439 (U.S.A.)

SUMMARY

Mixtures of xenon and fluorine gases react spontaneously with liquid antimony pentafluoride in the dark to form solutions of $XeF^+Sb_2F_{11}^-$. Dixenon cation, Xe_2^+, is formed as a labile intermediate product and is oxidized by the fluorine to XeF^+ cation. The rate of the overall reaction is proportional to the partial pressure of xenon and the partial pressure of fluorine. This direct combination of reagents provides a simple method for the preparation of $XeF^+Sb_2F_{11}^-$.

INTRODUCTION

Many fluorine-containing compounds and ions are capable of spontaneously oxidizing xenon. These include the metal hexafluorides PtF_6, RhF_6, RuF_6, and PuF_6 [1-3]; dioxygenyl and fluoronitrogen salts $O_2^+SbF_6^-$, $O_2^+Sb_2F_{11}^-$, and $N_2F^+SbF_6^-$ [4,5]; complex ions NiF_6^{2-}, CoF_6^{2-}, and CuF_6^{3-} [6]; halogen fluoride complexes $Cl_2F^+AsF_6^-$ and $BrF_6^+AsF_6^-$ [7,8]; chromium pentafluoride complex $CrF_4^+Sb_2F_{11}^-$ [9]; and krypton fluoride complexes $KrF^+AuF_6^-$ and $KrF^+AsF_6^-$ [10,11]. In contrast, molecular fluorine does not oxidize xenon at room temperature in the absence of photochemical, electric-discharge, or other types of activation. The present study shows that molecular fluorine has enhanced oxidizing power in antimony pentafluoride, a strong Lewis acid, and is able to combine directly with xenon in this medium.

[†] This paper was presented at the Fifth Winter Fluorine Conference held at Daytona Beach, Fla., U.S.A., February 1-6, 1981.

0022-1139/82/0000-0000/$02.75

EXPERIMENTAL

In a typical experiment, a mixture of Xe and F_2 in a 1:1, 1:2, or 2:1 molar ratio was added to 24.7 to 61.1 mmol of degassed antimony pentafluoride in a vessel attached to a metal vacuum line. The total pressure was measured with a 0-1000 or 0-4000 torr bourdon gauge at 5-minute intervals as the gases reacted with the liquid at room temperature, 21 ± 1°C. The volume of the system was determined beforehand by PVT measurements. The most satisfactory results were obtained with a vessel made of Teflon PFA, which completely resisted attack by the reagents. This vessel contained a Teflon-coated stirring bar and was covered with black tape on the outside to exclude light. Reactors made of Monel metal, Pyrex glass, and Kel-F plastic were also used. Kel-F rapidly developed cracks at molding stress points, and Pyrex liberated silicon tetrafluoride, which interfered with the measurements. Monel was satisfactory but showed some evidence of corrosion. The volumes of the systems, including gauges, ranged from 36.3 to 120.0 ml. Xenon (Matheson, 99.995%) and fluorine (Linde, 98.0%) were used as received; antimony pentafluoride (Ozark-Mahoning) was redistilled prior to use. U.V.-visible spectra of solutions were obtained with a Cary 14 spectrophotometer, using 1 mm and 1 cm path-length quartz cells. Raman spectra were obtained with a Spex Ramalog 1403 spectrometer and Scamp computer, using quartz or Pyrex cells and the 514.5 nm wavelength exciting line of a Spectra-Physics Model 165 argon-ion laser. The solubility of xenon in antimony pentafluoride at 21° was determined by weighing 14-20 g amounts of the degassed solvent in Pyrex or metal flasks (24.63 to 54.46 ml volumes), stirring the solvent with xenon at pressures of 100-2000 torr, and reweighing the total contents of the flasks (gas + liquid). The amounts of xenon in the gas phase were calculated from the free volumes, using the Ideal Gas Law and the value 2.99 g/ml for the density of the liquid; the amounts in solution were then obtained by difference. A correction of 2.0 torr was applied for the vapor pressure of the liquid. The solubility of fluorine in antimony pentafluoride could not be measured by this method because of its low magnitude. It was measured approximately by saturating the solvent with fluorine at pressures of 250-1000 torr at 21°, degassing known volumes of the solutions, and determining the amounts of fluorine that were liberated (PVT measurements).

RESULTS AND DISCUSSION

Equimolar mixtures of xenon and fluorine reacted smoothly with liquid antimony pentafluoride to form solutions of xenon (II).

$$Xe + F_2 + 2SbF_5 \rightarrow XeF^+Sb_2F_{11}^- \qquad (1)$$

The solutions acquired first a yellow color, characteristic of monofluoroxenon cation, XeF^+, then a green color, characteristic of dixenon cation, Xe_2^+ [12]. The latter species was formed by a reversible reaction of elemental xenon with xenon (II) [13] and was removed by oxidation by fluorine.

$$3Xe + 3XeF^+Sb_2F_{11}^- + 2SbF_5 \rightleftarrows 2Xe_2^+Sb_2F_{11}^- \cdot XeF^+Sb_2F_{11}^- \qquad (2)$$

$$Xe_2^+Sb_2F_{11}^- \cdot XeF^+Sb_2F_{11}^- + 3/2F_2 + 2SbF_5 \rightarrow 3XeF^+Sb_2F_{11}^- \qquad (3)$$

Upon depletion of the gas mixtures or removal of the mixtures by pumping, the solutions reverted to their original yellow color; upon evaporation to dryness, they yielded solid $XeF^+Sb_2F_{11}^-$ which was identical to that prepared from xenon difluoride and antimony pentafluoride [14-16].

Figure 1 shows the Raman spectrum of a solution that was prepared by reactions 1-3 and pressurized to 1000 torr with xenon alone; bands of Xe_2^+ and XeF^+ can be seen at 123 cm^{-1} and 619 cm^{-1}, respectively. Figure 2 shows the Raman spectrum of the same solution after pressurization to 2000 torr with xenon; the band of Xe_2^+ is now much stronger. During the course of reactions (1-3), the band of Xe_2^+ rose to a maximum intensity and then declined, whereas that of XeF^+ increased continuously. The spectra revealed that Xe_2^+ is able to coexist with fluorine in the solutions in a state of transient equilibrium. In U.V.-visible spectra, a band of XeF^+ at 287 nm and bands of Xe_2^+ at 335 and 720 nm [12,13] were observed.

Some typical curves of the change of pressure with time for reactions of 1:2, 2:1, and 1:1 molar mixtures of xenon and fluorine with well-stirred liquid antimony pentafluoride in the

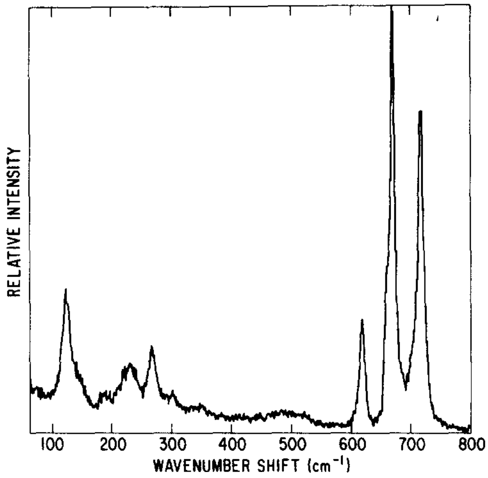

Fig. 1. Raman spectrum of a solution of $XeF^+Sb_2F_{11}^-$ in equilibrium with xeno at 1000 torr.

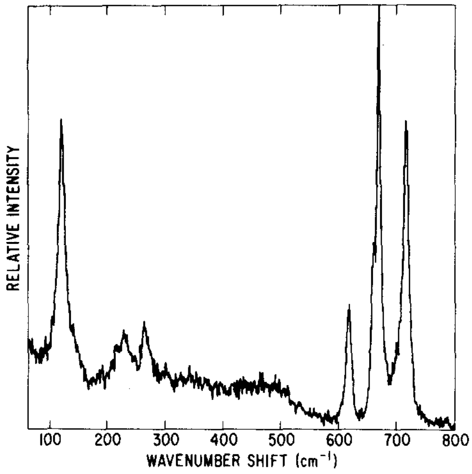

Fig. 2. Raman spectrum of the same solution after establishment of a new equilibrium with xenon at 2000 torr.

Teflon reactor are shown in Figure 3. The rate of reaction, indicated by the slope, fell off sharply for both a 1:2 mixture (A) and 2:1 mixture (B) after about 25% of the gas had been consumed but declined very gradually for a 1:1 mixture (C). The reduction in rate for the first two mixtures was probably caused in part by the accumulation of excess xenon or excess fluorine (i.e., whichever gas was present in excess) at the gas-liquid interface, since this accumulation would slow the diffusion of the second gas to the liquid phase. The composition of the gas phase remained constant for the 1:1 mixture, which was uniformly consumed.

The change of pressure with time for an equimolar mixture obeyed a second-order rate equation.

$$\frac{dP}{dt} = -k_{gas}P^2 \tag{4}$$

The integrated form of this equation is

$$\frac{1}{P} = k_{gas}t + \frac{1}{P_0} , \tag{5}$$

where P is the total pressure and P_0 is the initial pressure. By plotting the reciprocal of pressure vs time, as shown in Figure 4, it was possible to determine the value of k_{gas} from the slope. (In the section below it is shown that k_{gas} is invariant only for a fixed ratio of gas volume to liquid volume; this ratio changed in different experiments.)

The relationship between the empirical rate constant, k_{gas}, for the disappearance of the gas and the solution rate constant, k, for the reaction in the liquid phase was derived as follows from the mass balance for xenon in the gas phase and liquid phase. In this derivation the following symbols are used: V_{gas}, gas volume; V_{liq}, liquid volume; C_{Xe}, concentration of xenon; C_{F_2}, concentration of fluorine; C_{prod}, concentration of $XeF^+Sb_2F_{11}^-$; C_{SbF_5}, concentration of antimony pentafluoride; P, total pressure; P_{Xe}, partial pressure of xenon; P_{F_2}, partial pressure of fluorine; R, gas constant; T, absolute temperature; K_{Xe}, Henry's Law constant for xenon; K_{F_2}, Henry's Law constant for fluorine; and t, time. The derivation is for an equimolar mixture of gases in which $P_{Xe} = P_{F_2} = 1/2P$.

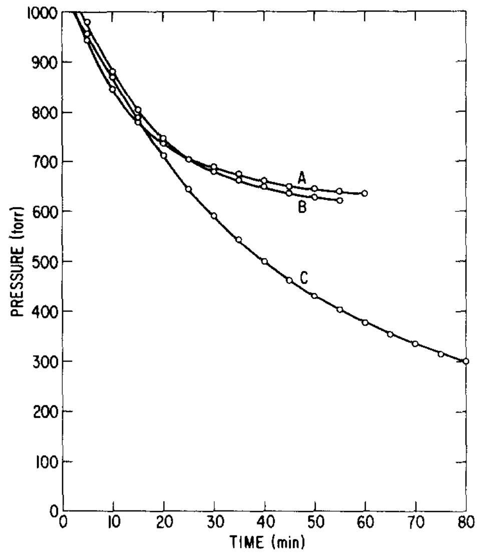

Fig. 3. Change of pressure with time for reactions of xenon-fluorine gas mixtures with liquid SbF_5. $Xe:F_2$ molar ratios: A, 1:2; B, 2:1; C, 1:1.

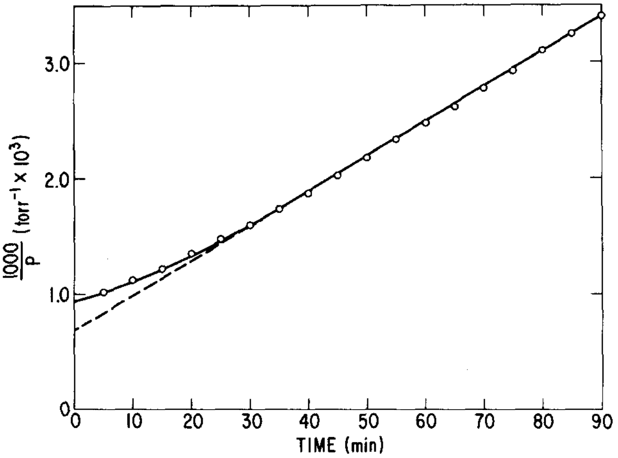

Fig. 4. Change of the reciprocal of pressure x 1000 with time for the reaction of an equimolar mixture of xenon and fluorine with liquid SbF_5.

Rate of loss of xenon = Rate of appearance of xenon
from gas phase in liquid phase

$$-V_{gas}\left(\frac{dC_{Xe}}{dt}\right)_{gas} = V_{liq}\left[\frac{dC_{Xe}}{dt} + \frac{dC_{prod}}{dt}\right]_{liq} \tag{6a}$$

$$= V_{liq}\left[K_{Xe}\left(\frac{dP_{Xe}}{dt}\right) + \frac{dC_{prod}}{dt}\right]_{liq} \tag{6b}$$

$$-V_{gas}\left(\frac{1}{2RT}\right)\left(\frac{dP}{dt}\right) = V_{liq}\left[\frac{K_{Xe}}{2}\left(\frac{dP}{dt}\right) + \frac{dC_{prod}}{dt}\right]_{liq} \tag{6c}$$

Rearranging terms,

$$-\left(\frac{dC_{prod}}{dt}\right)_{liq} = \left[\frac{K_{Xe}}{2} + \frac{V_{gas}}{V_{liq}}\left(\frac{1}{2RT}\right)\right]\left(\frac{dP}{dt}\right) \tag{6d}$$

$$= \left[\frac{K_{Xe}}{2} + \frac{V_{gas}}{V_{liq}}\left(\frac{1}{2RT}\right)\right]\left(-k_{gas}P^2\right) \tag{6e}$$

The rate equation for reaction 1 might be expected to have a dependence upon antimony pentafluoride as well as upon xenon and fluorine. However, the concentration of antimony pentafluoride is nearly constant and can be combined with the rate constant to give a second-order equation.

$$\frac{dC_{prod}}{dt} = kC_{Xe}C_{F_2} \tag{7a}$$

$$= k(K_{Xe}1/2P)(K_{F_2}1/2P) \tag{7b}$$

$$= \frac{kK_{Xe}K_{F_2}}{4}P^2 \tag{7c}$$

The second-order rate constant for the reaction in solution is related to the empirical rate constant as follows.

$$k = \frac{2k_{gas}}{K_{Xe}K_{F_2}}\left[K_{Xe} + \frac{V_{gas}}{V_{liq}}\frac{1}{RT}\right] \tag{8}$$

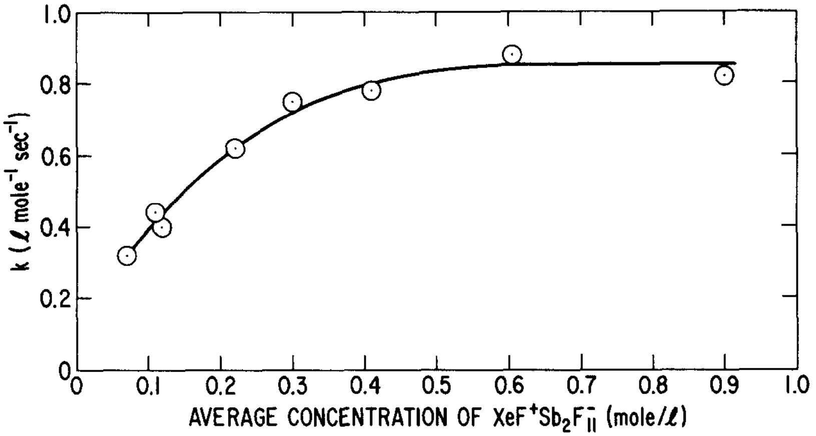

Fig. 5. Change of the second-order rate constant with the concentration of $XeF^+Sb_2F_{11}^-$.

Both xenon and fluorine were found to obey Henry's Law approximately with the concentration of dissolved gas expressed in molar rather than molal units. The value 0.059 mole l^{-1} atmos^{-1} was obtained for K_{Xe} at 21° and the value 0.0081 mole l^{-1} atmos^{-1} for K_{F_2}.

Table 1 shows the rate constants obtained in experiments with equimolar gas mixtures. The second-order rate constant increased by a factor of about 2.5 when the concentration of product rose from 0.1 to 0.4 M (Figure 5). It remained fairly constant (mean value 0.82 l mole^{-1} sec^{-1}) when the concentration of product increased further from 0.4 to 0.9 M. There was a marked change in the viscosity of the solutions as the reaction progressed. The initial antimony pentafluoride was highly viscous and difficult to stir, whereas 0.4 M and more concentrated solutions of $XeF^+Sb_2F_{11}^-$ were very fluid. This change in viscosity is similar to that which has been observed by others [17,18] for antimony pentafluoride solutions and can be ascribed to the disruption of fluorine bridges in the polymeric solvent [19].

The mechanism for the oxidation of xenon in this system is not known, but it seems probable that an interaction between molecular fluorine and very acidic antimony pentafluoride occurs.

$$SbF_5 + F_2 \rightarrow F_5SbF^{\delta^-}\cdots F^{\delta^+} \qquad (9a)$$

$$F_5SbF^{\delta^-}\cdots F^{\delta^+} + SbF_5 + Xe \rightarrow XeF^+Sb_2F_{11}^- \qquad (9b)$$

Molecular oxygen, which has an ionization potential close to that of xenon, might be expected to form the dioxygenyl ion, O_2^+, by a similar reaction; however, no reaction of oxygen, fluorine, and liquid antimony pentafluoride has been observed at room temperature in the absence of photochemical activation.

TABLE 1

Rate constants for the reaction of equimolar mixtures of xenon and fluorine with liquid SbF_5 at 21°C

Initial conc. of $XeF^+Sb_2F_{11}^-$ (mole/l)	Final conc. of $XeF^+Sb_2F_{11}^-$ (mole/l)	$\frac{V_{gas}}{V_{liq}}$	k_{gas} (atmos^{-1} sec^{-1})	k (l mol^{-1} sec^{-1})
0.000	0.220	11.3	2.02×10^{-4}	0.445
0.220	0.381	11.3	3.40×10^{-4}	0.750
0.000	0.252	21.2	1.03×10^{-4}	0.402
0.758	1.043	19.3	2.28×10^{-4}	0.820
0.000	0.140	10.4	1.54×10^{-4}	0.315
0.140	0.307	10.4	3.04×10^{-4}	0.623
0.307	0.507	10.4	3.83×10^{-4}	0.784
0.507	0.704	10.4	4.23×10^{-4}	0.867

ACKNOWLEDGMENT

I thank A. J. Downs and A. Mete for making available their data on the solubility of xenon in antimony pentafluoride; W. W. Henderson for further xenon solubility measurements; and E. H. Appelman, J. G. Malm, and F. Schreiner for stimulating discussions of results. This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under Contract W-31-109-Eng-38.

REFERENCES

1 N. Bartlett, Proc. Chem. Soc., (1962) 218.
2 C. L. Chernick, Record of Chemical Progress, 24 (1963) 139.
3 N. Bartlett and N. K. Jha, in H. H. Hyman (Editor), Noble Gas Compounds, University of Chicago Press, Chicago, 1963, p. 23.
4 L. Stein, Nature, 243 (1973) 30.
5 L. Stein, Chemistry, 47 (1974) 15.
6 T. L. Court and M. F. A. Dove, J. Fluorine Chem., 6 (1975) 491.
7 K. O. Christe and R. D. Wilson, Inorg. Nucl. Chem. Lett., 9 (1973) 845.
8 R. J. Gillespie and G. J. Schrobilgen, Inorg. Chem., 13 (1974) 1230.
9 S. D. Brown, T. M. Loehr, and G. L. Gard, J. Fluorine Chem., 7 (1976) 19.
10 J. H. Holloway and G. J. Schrobilgen, J. Chem. Soc. Chem. Comm., (1975) 623.
11 R. J. Gillespie and G. J. Schrobilgen, Inorg. Chem., 15 (1976) 22.
12 L. Stein, J. R. Norris, A. J. Downs, and A. R. Minihan, J. Chem. Soc. Chem. Comm., (1978) 502.
13 L. Stein and W. W. Henderson, J. Am. Chem. Soc., 102 (1980) 2856.
14 V. M. McRae, R. D. Peacock, and D. R. Russell, Chem. Comm., (1969) 62.
15 F. O. Sladky, P. A. Bulliner, and N. Bartlett, J. Chem. Soc. (A), (1969) 2179.
16 R. J. Gillespie and B. Landa, Inorg. Chem., 12 (1973) 1383.
17 R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, Inorg. Chem., 4 (1965) 1641.
18 R. J. Gillespie and K. C. Moss, J. Chem. Soc. (A), (1966) 1170.
19 C. J. Hoffman, B. E. Holder, and W. L. Jolly, J. Phys. Chem., 62 (1958) 364.