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CONCEPTUAL PROBLEMS IN NOBLE GAS AND FLUORINE CHEMISTRY, V:[1]

THE DIFFERENCE IN THE REACTIONS OF THE ISOELECTRONIC $XeOF_4$ and IF_5 WITH KrF^+

JOEL F. LIEBMAN

Department of Chemistry, University of Maryland Baltimore County Baltimore,
Maryland 21228 (USA) and Department of Chemistry, University of Utah,
Salt Lake City, Utah 84112 (USA)[2]

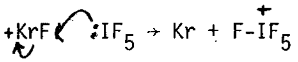
SUMMARY

The isoelectronic $XeOF_4$ and IF_5 show numerous similarities: molecular geometry, formation of complexes with F^- donors and acceptors, complexation with graphite and with XeF_2. However, on reaction with KrF^+, IF_5 forms an expected IF_6^+ ion while $XeOF_4$ forms XeF_5^+ and O_2^+. In this paper we discuss this discordance and present an explanation for it. Nucleophilic displacement on fluorine by IF_5 forms the observed cation while the corresponding reaction with $XeOF_4$ is predicted to form the hypofluorite $(XeF_4\text{-}OF)^+$. Subsequent substitution and elimination reactions of this hypofluorite produce the observed product.

DISCUSSION

The isoelectronic [3] $XeOF_4$ and IF_5 show numerous chemical similarities. Both species are square pyramidal as may be predicted form Nyholm-Gillespie theory [4]. In addition, both form complexes with F^- donors [5,6] and F^-

acceptors [5,6] and intercalate with graphite [6,7]. Stoichiometric complexes are formed by both with XeF_2 [5] and there are octahedral oxides, XeO_2F_4 and IOF_5 [9] corresponding to both species. However, a surprising discordance arises in their reaction with KrF^+ salts. IF_5 is cleanly oxidized to IF_6^+ [10] in what appears to be a type 3, nucleophilic displacement reaction on fluorine [11]:

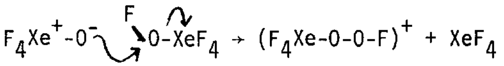


$$+KrF\,:IF_5 \rightarrow Kr + F\text{-}\overset{+}{I}F_5 \qquad (1)$$

$XeOF_4$ reacts with KrF^+ but instead of forming the expected $XeOF_5^+$ ion[10], NMR and Raman evidence showed the formation of O_2^+ and XeF_5^+ [12]. In this paper we wish to discuss this discordance and present an explanation for it.

Let us consider the reaction of IF_5 with KrF^+ first. The most nucleophilic site of the IF_5 molecule is the lone pair on iodine. As such, when these species react, we anticipate formation of an I-F bond to form octahedral IF_6^+. In contrast, consider $XeOF_4$. The xenon is less nucleophilic than the iodine as it has a higher oxidation number. In addition, xenon has a formal positive charge in a major resonance structure of $XeOF_4$, $F_4Xe^+\text{-}O^-$ [13]. Concommitantly, however, the oxygen is increased in nucleophilicity. As such, we would expect formation of $(F_4Xe\text{-}O\text{-}F)^+$, formally analogous to XeF_5^+, but with an apical -O-F group replacing the somewhat more electronegative -F. We may also consider $(F_4Xe\text{-}O\text{-}F)^+$ a hypofluorite [14] with the electronegative (F_4Xe^+)- group attached.

The author had earlier made the suggestion [15] that F_2O is decomposed by aqueous base [16] through the attack of OH^- on the oxygen of a solvent-polarized F_2O molecule. By analogy, we now hypothesize attack of $XeOF_4$ on a $(F_4Xe\text{-}O\text{-}F)^+$ molecule:



$$F_4Xe^+\text{-}O^- \;\; \overset{F}{O}\text{-}XeF_4 \rightarrow (F_4Xe\text{-}O\text{-}O\text{-}F)^+ + XeF_4 \qquad (2)$$

While XeF_4 is not observed among the reaction products of $XeOF_4$ and KrF^+, our intuition suggests it would be fluorinated by either KrF^+ or $(F_4Xe\text{-}O\text{-}F)^+$. Indeed, we may also write a fluorination reaction of XeF_4 with $(F_4Xe\text{-}O\text{-}O\text{-}F)^+$:

$$(F_4Xe\text{-}O\text{-}O\text{-}F)^+ + XeF_4 \rightarrow F_4Xe + O_2 + FXeF_4^+ \qquad (3)$$

Alternatively, $(F_4Xe\text{-}O\text{-}O\text{-}F)^+$ can decompose to $F_4Xe + O_2^+ + F$ by low energy fragmentation reactions analogous to that observed [17] for $(F\text{-}O\text{-}O\text{-}F)^+$, i.e.

$$\begin{aligned} &(X\text{-}O\text{-}\ddot{O}\text{-}F)^+ \rightarrow X + O_2F^+ \\ &\qquad\qquad\qquad\qquad\qquad X = F\text{-},\ XeF_4\text{-} \qquad (4) \\ &(X\text{-}O\text{-}O\text{-}F)^+ \rightarrow X + O_2^+ + F \end{aligned}$$

We parenthetically note that O_2F^+ salts are not formed from O_2F_2 and Lewis Acids but instead O_2^+ salts are formed [18]. We additionally note that our mechanism suggests KrF^+ will react with other nonmetal oxides and oxy fluorides to produce fluorocations [19].

Let us return briefly to reaction (3). It is formally analogous to the β-elimination reactions of the organic chemist [20],

$$(X\text{-}C\text{-}C\text{-}H)^+ + B \rightarrow X + C = C + HB^+ \qquad (5)$$

where X can be numerous electron-withdrawing groups such as substitued ammonio (R_3N^+-). This suggests that the oxygen formed in reaction (13) should be the (excited state) singlet [21]. While we know of no studies of the reaction of singlet oxygen with any fluorocation, nonetheless we are sure that the reaction with KrF^+ and $(F_4Xe\text{-}O\text{-}F)^+$ to form O_2^+, F, and either Kr or $XeOF_4$ would be exothermic [22]. As such, we are not surprised that singlet oxygen (or its concommitant chemiluminescence) has not been reported here, but we emphasize no effort has seemingly been made in looking for it.

In conclusion, we find the seemingly anomalous difference in the reactions of the isoelectronic $XeOF_4$ and IF_5 with KrF^+ is directly explicable in terms of the nucleophilic sites of these hexatomic molecules.

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REFERENCES

1 Paper IV: J. F. Liebman, J. Fluor. Chem. 7 (1976) 531.

2 Permanent Address: University of Maryland Baltimore County

3a H. A. Bent, J. Chem. Ed., 43 (1966) 171.

3b J. F. Liebman, ibid, 48 (1971) 188.

4 R. J. Gillespie, ibid, 40 (1963) 295.

5 N. Bartlett and F. O. Sladky, in "Comprehensive Inorganic Chemistry", J. C. Bailar, H. J. Emeléus, Sir R. Nyholm and A. F. Trotman - Dickenson (editors) Pergamon Press Ltd., Oxford, 2nd Ed., (1973)p.213-350.

6 A. J. Downs and C. J. Adams, "Comprehensive Inorganic Chemistry", op. cit. Vol. 2, Chapter 26, p. 1476 (section 4C).

7 H. Selig and O. Gani, Inorg. Nucl. Chem. Lett., 11 (1975) 75.

8 J. L. Huston, J. Amer. Chem. Soc., 93 (1971) 5255.

9 L. S. Bartell, F. B. Clippard and E. J. Jacob, Acta Cryst., A28 (1972) S 58, and personal communication from Profs. Bartell and Jacobs.

10 D. E. McKee, C. J. Adams, A. Zalkin and N. Bartlett, J. Chem. Soc. Chem. Commun., 26 (1973).

11 J. F. Liebman and B. B. Jarvis, J. Fluor. Chem., 5, (1975) 41.

12 J. H. Holloway and G. J. Schrobilgen, J. Chem. Soc. Chem. Commun., 623 (1975).

13 T. X. Carroll, R. W. Shaw, Jr., T. D. Thomas, C. Kindle and N. Bartlett, J. Amerc. Chem. Soc., 96, (1974) 1989.

14 M. Lustig and J. M. Shreeve, in Adv. Fluor. Chem., Vol. 17, J. C. Tatlow, R. D. Peacock and H. H. Hyman, (Editors) CRC Press, Cleveland, 1973) p. 175.

15 J. F. Liebman and T. H. Vanderspurt, J. Fluor. Chem., 2, (1972/3) 413.

16 "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Supplement I, Wiley, New York, (1956) p. 188.

17 T. J. Malone and H. A. McGee, Jr., J. Phys. Chem., 70, (1966) 316, 71 (1967) 3060.

18 J. N. Keith, I. J. Solomon, I. Sheft and H. H. Hyman, Inorg. Chem., 7 (1968) 230.

19 G. J. Schrobilgen, personal communication.

20a F. C. Bordwell, Accounts Chem. Res., 5 (1972) 374.

20b W. H. Saunders, ibid, 9 (1976) 19.

21 C. S. Foote, ibid, 1, (1968) 104.

22 Since KrF^+ oxidizes ground state O_2 to $O_2{}^+$, (see ref. [12], we expect the excited singlet state of O_2 to be likewise ionized.)