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

ANOMALOUS REACTIONS OF THE ISOELECTRONIC F_2O and Cl_2O WITH LEWIS ACIDS

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SUMMARY

The isoelectronic F_2O and Cl_2O are known to react with Lewis acids to produce salts of the unrelated O_2^+ and ClO_2^+ ions. We propose a unifying mechanism entailing formation of $F_3O_2^+$ and $Cl_3O_2^+$ by the simultaneous abstraction of halide ions and attack of a second molecule of the halogen oxide. Logic is presented for nonisostructural arrangements of these ions, F_2O^+-OF and $(ClOClOCl)^+$. Subsequent dehalogenation reactions then produce the observed ions.

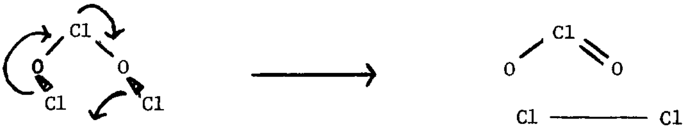
DISCUSSION

The isoelectronic [3] nonmetal oxides F_2O and Cl_2O show no surprises with regard to physical properties [4], both are gases [4] with approximately tetrahedral [5] X-O-X angles. Their chemical properties, however, differ markedly. Cl_2O behaves as the anhydride of hypochlorous acid: it reacts with water to form this acid [6] and with N,N-dimethylaniline [1] and cyclohexene [8] to form products formally derived from positive chlorine. F_2O shows no such anhydride properties [9], reacting with OH^- to form O_2 and F^- [10] and with primary amines to form the corresponding nitroso compound [11]. Both of these reactions have been explained in terms of positive oxygen [12], a result in accord with the relative electronegativities of F, O and Cl. Nonetheless, it is still surprising that F_2O and Cl_2O react so differently with Lewis acids, F_2O to form O_2^+ salts with SbF_5 [13] while Cl_2O forms ClO_2^+ salts with AsF_5 [14]. We would have expected OF^+ and OCl^+ salts to have been formed via abstraction of F^- and Cl^- respectively. Both of these cations are bound, having been seen in the mass spectra of various oxygen and halogen - containing species [15]. (We note quantum chemical calculations that give bond strengths of 74 kcal/mol [16] and 110 kcal/mole [17] for OF^+ and OCl^+ respectively.) This article discusses this difference in the reaction chemistry of F_2O and Cl_2O with Lewis Acids and offers an explanation for the anomalous products.

With regard to the nonreaction of F_2O to form OF^+ salts, one might have thought that the fluorines were insufficiently negative to react. More precisely the low dipole moment of F_2O (.297 D) [18] suggests stringent reaction condition will be required for F^- abstraction from F_2O. This is, in fact, experimentally realized: 200°C, 200 atm for six days in the reaction of F_2O cited above [13]. Analogously, the positive chlorine in Cl_2O might also be expected not to react with Lewis acids. However, let us briefly consider N-Cl compounds, N-chlorinate amines. These species are well known to react with Ag^+ by Cl^- abstraction [19], even though the nitrogen in amines is usually basic enough to form donor-accepto complexes with Ag^+ [20]. We thus conclude both F_2O and Cl_2O should react with Lewis acids to form OF^+ and OCl^+ salts. However, we recall from the above cited calculations [16,17] that OF^+ and OCl^+ are expected to be ground state triplets, and, other studies [21] on OF^+ have given a $^3\Sigma$ - $^1\Delta$ energy difference of 91 kcal This quantity is larger than the correspondingly quantity computed for O_2[21], 55 kcal/mol, and so we may quite safely say that the corresponding energy difference is at least 13 kcal/mol, the experimental quantity for SO [22]. Since F_2O, Cl_2O, the Lewis acids and the halide addition products are all singlets, spin conservation logic [23] suggests that the OF^+ and OCl^+ cations [24] would have to be formed in the energetically exicted singlet state. Accordingly, the reaction of OF_2 and OCl_2 with Lewis acids would be expected to be less energetically favorable and so salts of the OF^+ and OCl^+ cations is unexpected.

However, this does not explain the formation of the observed products from reaction of F_2O and Cl_2O. We suggest that $F_3O_2^+$ and $Cl_3O_2^+$ ions are formed initially by the abstraction of F^- and Cl^-, and the simultaneous attack of a second molecule of the halogen oxide. This reaction is precendented by author's mechanism of amine to nitroso compound interconversion presented in reference [11]: the O-F bond in OF_2 is weakened and the oxygen made positive by an ammonium ion hydrogen bonding with a fluorine, and simultaneously the oxygen is attacked by a molecule of the amine. This suggests that the $F_3O_2^+$ ion would have the $(F_2O\text{-}OF)^+$ structure. While this structure is somewhat unusual, the all hydrogen analog has been suggested in connection with reactions of peroxides with acid [25] and indeed has been observed in gas phase protonation studies of H_2O_2 [26]. Our intuition suggests for $(F_2O\text{-}OF)^+$ a relatively weak O-O bond. This bond would be strengthened by cleavage of the also weak O-F bonds to form a less fluorinated cation and, say atomic fluorine noting that the O-F bond strengths in O_2F^+ and $O_2F_2^+$ are but ca. 18 and 0 kcal/mol [27] in contrast to 63 kcal/mol in OF_2 [16,28]. Indeed, as we expect greater crystal stabilization for salts of O_2^+ than of O_2F^+ or the other fluorinated dioxygen cations, we are not surprised that O_2^+ salts are isolated here as well as in the reaction of Lewis Acids with O_2F_2 [29].

The + charge on the incipient OCl^+ ion is more evenly distributed than on the corresponding OF^+. Cl-Cl and Cl-O bonds are considerably stronger than the F-F and F-O bonds [28]. As such, we anticipate that the $Cl_3O_2^+$ ion will have either the $(Cl\text{-}O\text{-}Cl\text{-}O\text{-}Cl)^+$ or $(Cl\text{-}O\text{-}Cl\text{-}Cl\text{-}O)^+$ structure. These structures are isoelectronic with the trisulfane F_2S_3 [30] and additionally the former is "merely" a chloronium ion [31] with two electronegative -O-Cl substituents. For either compound, (assumed "doubly gauche" [32]) simple "arrow-pushing" results in formation of ClO_2^+ and Cl_2 [33]. These reactions are both symmetry "allowed" [34].



Indeed, we recognize the first reaction as a (3 + 2) cycloreversion, formally analogous to the reverse of the addition of ozone to an alkene to form the 1,2,3,-trioxacyclopentane [35]. The analogous reaction of ozone with C-H bonds to form C-O-O-O-H has recently been discussed[36]. We also note analogous "arrow-pushing" interconverts $(Cl\text{-}O\text{-}Cl\text{-}O\text{-}Cl)^+$ and $(Cl\text{-}O\text{-}Cl\text{-}Cl\text{-}O)^+$ in an "allowed" (3,2) sigmatropic rearrangement [34]. It thus comes as no surprise that Cl_2O reacts with Lewis Acids to form ClO_2^+ salts while F_2O forms O_2^+ salts as noted above.

In conclusion we find the seemingly anomalous difference in the reactions of the isoelectronic F_2O and Cl_2O with Lewis acids is directly applicable in terms of the strengths and polarities of O-F and O-Cl bond.

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