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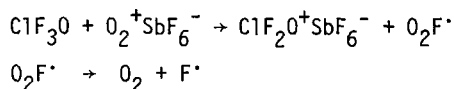
SHORT COMMUNICATION

Some Observations on the Reaction Chemistry of Dioxygenyl Salts and on the Blue and Purple Compounds Believed to be  $\text{ClF}_3\text{O}_2$

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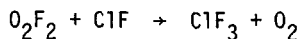
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During our studies of dioxygenyl compounds [1-3] we have also explored the synthetic usefulness of  $\text{O}_2^+$  salts for the generation of F atoms at low temperature. Displacement reactions between  $\text{O}_2^+\text{MF}_6^-$  and suitable amphoteric molecules produces free  $\text{O}_2\text{F}$  radicals which can readily decompose to  $\text{O}_2$  and atomic F [4] as shown by the following typical example



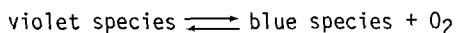
This method of in situ generation of F atoms is superior to uv-photolysis if one of the desired products is unstable towards uv-radiation. Furthermore,  $\text{O}_2^+$  salts can readily be synthesized [5,6] in large quantities and, hence, F atoms can be generated in this way more economically and at lower temperatures than by the thermal decomposition of compounds, such as  $\text{KrF}_2$ . While our study of this method so far has not produced any new high oxidation state compounds, interesting observations were made which provide a better understanding of the nature of the violet and blue unstable compounds, first reported in 1962 by Streng and Grosse [7].

The deep violet compound was obtained [7] by the reaction of  $\text{O}_2\text{F}_2$  with ClF at  $-133$  to  $-154^\circ$ . This compound was a strong oxidizer and was stable at  $-78^\circ$ . It was soluble in anhydrous HF at  $-78^\circ$  and was not an electrolyte. Its thermal decomposition was suppressed by oxygen. Based on the observed stoichiometry of the overall reaction



the violet compound was postulated to have the composition  $(\text{ClF}_3\text{O}_2)_n$ . The same material was also obtained by the interaction of  $\text{O}_2\text{F}_2$  with  $\text{Cl}_2$  or  $\text{HCl}$  or by uv-photolysis of mixtures of  $\text{ClF}_3$  and  $\text{O}_2$  at  $-78^\circ$  [7-9]. The violet compound could be converted into a blue compound by treatment with  $\text{ClF}$  at  $-133^\circ$  or by pumping off the oxygen decomposition product from the violet HF solution at  $-78^\circ$  [8]. Similar violet unstable compounds were also observed in the reactions of  $\text{O}_2\text{F}_2$  with either  $\text{BrF}_3$  or  $\text{SF}_4$  producing  $\text{BrF}_5 + \text{O}_2$  and  $\text{SF}_6 + \text{O}_2$ , respectively [8]. However, no inferences were drawn that the unstable violet intermediate formed in all of these reactions might be identical, and was explained in terms of the compounds  $\text{ClF}_3\text{O}_2$ ,  $\text{BrF}_5\text{O}_2$ , and  $\text{SF}_6\text{O}_2$ , respectively [8].

The nature of these violet and blue compounds was studied by Gardiner and Turner [10,11] by infrared and visible spectroscopy. The violet and the blue compound exhibited an infrared absorption at 1535 and 1527  $\text{cm}^{-1}$ , respectively, and were interpreted in terms of the peroxides  $\text{F}_2\text{ClOOF}$  and  $\text{F}_2\text{ClOOCIF}_2$ , respectively [10]. Evidence was also found [11] for the existence of an oxygen pressure dependent equilibrium between the violet and the blue compound



In the present study it was found that intensely colored species, exhibiting the same characteristics and thermal stability as Streng's violet and blue compounds, could be obtained for example by the reaction of  $\text{O}_2^+\text{SbF}_6^-$  with  $\text{ClF}$ ,  $\text{ClF}_3$ ,  $\text{ClF}_5$ ,  $\text{ClF}_3\text{O}$ ,  $\text{BrF}_5$  or  $\text{HF}$ , the reaction of  $\text{O}_2^+\text{AsF}_6^-$  with  $\text{FClO}_2$  or  $\text{HF}$ , and the reaction of  $\text{O}_2^+\text{GeF}_5^-$  with  $\text{HF}$ . The observed color scheme was similar for all systems. On melting of the amphoteric component an intensely violet colored species, stable below  $-78^\circ$  was formed. Frequently, the violet color was concentrated near the surface of the solid  $\text{O}_2^+$  salt, whereas the solution had a brownish color. On further warm up the colors changed towards brown and then disappeared with gas evolution. The observed colors also depended to some extent on the melting point of the amphoteric reagent. For example, in the case of  $\text{ClF}_3\text{O}$  which has the highest mp ( $-42^\circ$ ) of all the compounds studied, the higher reaction starting temperature resulted in the immediate formation of the brown species.

The nature of the reactions was studied by allowing the reactions to go to completion at room temperature, obtaining material balances, and identifying the solid products by vibrational spectroscopy. It was found that lower oxidation state compounds were fluorinated with  $\text{O}_2$  evolution as

found by Streng [8] for the corresponding  $O_2F_2$  systems. The solids were the  $MF_6^-$  salts of the amphoteric fluorides. For the higher oxidation state compounds, a simple displacement reaction accompanied by  $O_2$  and  $F_2$  evolution occurred as shown above for  $ClF_3O$ . The only exception to this scheme was HF, which on contact with  $O_2^+MF_6^-$  showed initially a violet color. However, on warm up to room temperature a colorless stable solution of  $O_2^+MF_6^-$  in HF was obtained, thus demonstrating that HF does not interact with  $O_2^+MF_6^-$ . The intensity of the initial violet color appeared to vary

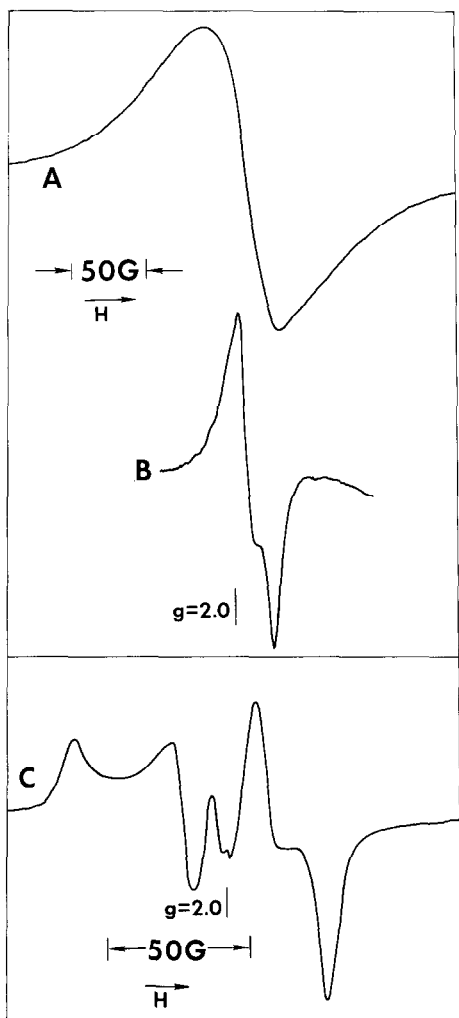
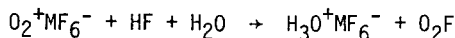


Fig. 1. Typical esr spectra of the colored species produced by the interaction of  $O_2^+SbF_6^-$  with amphoteric molecules. Spectrum A: violet species in high concentration at  $-196^\circ$  formed in the  $O_2^+SbF_6^- - ClF_3$  system. When warmed to  $-78^\circ$  and recooled to  $-196^\circ$ , the intensity of the signal decreased and its linewidth changed from 53 to 33 G. Spectrum B: light violet species in the  $O_2^+SbF_6^- - BrF_5$  system at  $-196^\circ$ . Spectrum C:  $O_2F$  observed at  $-150^\circ$  in the  $O_2^+SbF_6^- - ClF_3O$  system.

with the degree of dryness of the HF and, therefore, the following reaction is most likely responsible for the initial violet color:



The stability of  $\text{O}_2^+\text{MF}_6^-$  in HF solution at room temperature was verified by Raman spectroscopy. The spectrum showed bands at 656, 565, and  $273\text{ cm}^{-1}$ , characteristic [12] for octahedral  $\text{SbF}_6^-$ , and at  $1870\text{ cm}^{-1}$ , characteristic [4] for  $\text{O}_2^+$ .

Since the intense colors observed for the above systems suggest the presence of paramagnetic species, the colored species were generated, then frozen at  $-196^\circ$ , and their esr spectra were recorded. It was found that the intense colors are indeed associated with paramagnetic species and, hence, cannot be due to diamagnetic species such as  $\text{ClF}_3\text{O}_2$ ,  $\text{BrF}_5\text{O}_2$  [7-9],  $\text{ClF}_2\text{OOF}$ , or  $\text{ClF}_2\text{OOCIF}_2$  [10,11]. Recently it was also shown that  $\text{ClF}_3\text{O}_2$ , prepared by a different method, is a colorless stable compound [13,14].

Typical esr spectra of the colored species are shown in Figure 1. Spectrum C of Figure 1 is in excellent agreement with the known [15,16] anisotropic esr spectrum of  $\text{O}_2\text{F}$ . Previous studies [15-17] on  $\text{O}_2\text{F}$  have furthermore shown that the observed spectra are extremely sensitive to experimental conditions. Thus, Spectrum A of Figure 1 closely resembles the spectrum ascribed to  $\text{O}_2\text{F}$  in solid  $\text{O}_4\text{F}_2$  [17]. This establishes the presence of  $\text{O}_2\text{F}$  in the colored species. Whether  $\text{O}_2\text{F}$  is the sole paramagnetic species present in these systems or not, is more difficult to answer. As can be seen from trace B of Figure 1, the appearance of the observed signals can significantly vary. In some cases, the observed widths of the single line signals were as small as 7 G, i.e. much narrower than the fluorine hyperfine splitting of 13 G observed for the isotropic spectrum of  $\text{O}_2\text{F}$  [17]. Furthermore, the observed g values were generally less than 2.0. In no case was direct evidence found for the presence of either a chlorine or multiple fluorine atoms in the paramagnetic species. The narrow line widths and the low g values cannot be explained in terms of  $\text{O}_2\text{F}$  and indicate the presence of another paramagnetic species. In view of the overall information available, plausible candidates for such a species would be  $(\text{O}_2)_n^+$  or less likely  $(\text{O}_2)_n^+$ , where  $n \geq 2$ .

Another interesting observation was made when recording at ambient temperature the infrared spectra of the solid reaction products containing halogen fluoride  $\text{MF}_6^-$  salts in addition to some unreacted  $\text{O}_2^+\text{MF}_6^-$ . When these samples were pressed as dry powders in silver halide disks,

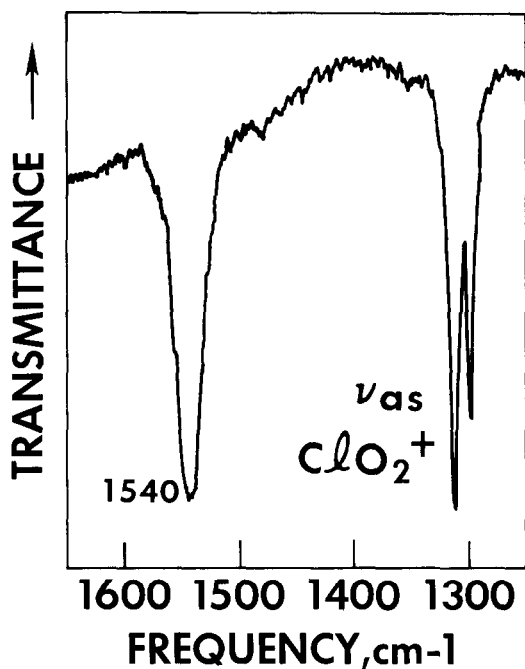


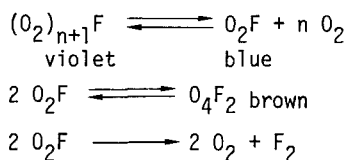
Fig. 2. The  $1540\text{ cm}^{-1}$  infrared absorption observed at  $25^\circ$  for the purple species formed when the solid from the  $\text{FCIO}_2 + \text{O}_2^+\text{SbF}_6^-$  reaction ( $\text{ClO}_2^+\text{SbF}_6^-$  and  $\text{O}_2^+\text{SbF}_6^-$ ) was pressed as a dry powder in an AgCl disk.

the disks initially showed a blue to violet color which usually disappeared within 0.5 to 1 hour. The infrared spectrum (see Figure 2) showed an intense band at  $1540\text{ cm}^{-1}$  which decayed with decreasing intensity of the color, while the rest of the spectrum remained unchanged. The frequency of this band is similar to those ( $1535$  and  $1527\text{ cm}^{-1}$ ) found by Gardiner and Turner [10] at  $-196^\circ$  for the violet and the blue species formed in the  $\text{O}_2\text{F}_2 + \text{ClF}$  reaction, and to those reported for  $\text{O}_4\text{F}_2$  ( $1516\text{ cm}^{-1}$ ) [18-21], solid oxygen ( $1550\text{ cm}^{-1}$ ) [22], and  $\text{O}_2\text{F}$  ( $1494\text{-}1500\text{ cm}^{-1}$ ) [19,20,23]. For pure  $\text{O}_2^+$  salts or halogen fluoride - Lewis acid adducts alone, no evidence for any band in this frequency region or for violet colors was found in pressed silver halide disks. Since matrix isolated and free gaseous species usually have very similar frequencies, the colored species in the silver halide disk is probably not  $\text{O}_2\text{F}$ , but a polyoxygen compound, such as  $(\text{O}_2)_n^+$  or possibly  $(\text{O}_2)_n^+$ .

Unfortunately, the region ( $550\text{-}600\text{ cm}^{-1}$ ) expected [19,20,23] for the O-F stretching mode in a species similar to  $\text{O}_2\text{F}$ , was obscured by intense bands due to  $\text{MF}_6^-$  and the cations formed in the displacement reaction. Attempts were unsuccessful to observe the  $1540\text{ cm}^{-1}$  band by placing a

stainless steel gas cell, containing 500 mm of  $O_2$  and 250 mm of  $F_2$ , in the infrared spectrometer and photolyzing the mixture through a sapphire window with a water filtered high pressure Hg arc. Attempts were equally unsuccessful to record at  $-120^\circ$  the Raman spectrum of the violet species, generated from  $O_2^+SbF_6^-$  and slightly wet HF at  $-78^\circ$ . Only the spectrum of  $O_2^+SbF_6^-$  was observable owing to the intense color of the sample and the relatively low concentration of the purple species.

An analysis of all the available data indicates that the violet and blue species observed in the reactions of oxygen fluorides or  $O_2^+$  salts, or in photolytic reactions involving oxygen and fluorine compounds, are identical. They are best explained by oxygen fluoride radicals and not by a variety of different unlikely compounds such as  $(ClF_3O_2)_n$ ,  $BrF_5O_2$ ,  $SF_6O_2$  [7-9],  $ClF_2OOF$  or  $ClF_2OOCIF_2$  [10,11]. The present esr study has shown that one of the key components in these systems is the  $O_2F$  radical. However, there is some evidence that  $O_2F$  and its diamagnetic dimer  $O_4F_2$  may not be the only species present. The existence of an oxygen pressure dependent equilibrium between the violet and the blue compound, the infrared frequency of the violet species which is closer to those in  $O_4F_2$  [18-21] or solid oxygen [22] than to that of  $O_2F$  [19,20,23], and the low g values and narrow line widths of some of the esr signals observed in this study might be interpreted in terms of the following equilibria involving a polyoxygen compound, such as  $(O_2)_nF$



Owing to the absence of resolved hyperfine splitting in the esr spectra, the existence of a polyoxygen fluoride radical could not conclusively be established. Esr experiments using  $^{17}O$  ( $I=5/2$ ) are desirable to verify the existence of such a polyoxygen compound. The postulate of a violet polyoxygen fluoride appears not unreasonable in view of the fact that  $NO$ , which is isoelectronic with  $O_2^+$ , readily interacts with  $NO^+$  to generate the violet  $N_2O_2^+$  cation [24].

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