Journal of Fluorine Chemistry, 3 (1973/74) 226–229

Short Communication

Violet and blue compounds of chlorine, fluorine and oxygen

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(Received February 2, 1973)

In 1962, Streng[1,2] reported the preparation of highly coloured, deep violet addition compounds of dioxygen difluoride (O_2F_2) with ClF, BrF_3 and SF_4. These compounds, which were reported to be powerful oxidants, were prepared by mild cryogenic reactions. The reaction of O_2F_2 with ClF produced a compound which on analysis was shown to have the empirical formula O_2ClF_3. The preparation was carried out by first condensing O_2F_2 in a reaction tube cooled in a liquid oxygen bath; ClF was then added and the tube slowly warmed. In the temperature range 110–140°K, a reaction took place forming, together with other products, the violet compound. The most favourable reaction temperature was found to be 119°K, the melting point of ClF. The following reactions were thought to be taking place:

$$O_2F_2 + ClF \rightarrow O_2ClF_3$$
$$O_2ClF_3 \rightarrow O_2 + ClF_3$$
$$O_2F_2 \rightarrow O_2 + F_2$$

The violet compound can also be formed by the photolysis of ClF_3 under 2 atm of oxygen at Dry Ice temperatures[2,3], or by the reaction of O_2F_2 and Cl_2 or HCl at about 130°K.

Streng also noted that a greenish-blue compound, which exists over a very narrow temperature range, is formed if the violet compound is warmed up to about 140°K in the presence of ClF and ClF_3. A blue coloration was also noticed when the oxygen was pumped off from a solution of the violet compound in HF at 190–195°K.

In the work reported here, the violet compound was prepared by a 10 min photolysis of a mixture of ClF_3 and 2 atm of oxygen at 195°K using a medium-pressure mercury lamp. The deep violet solution which resulted was then cooled to 77°K and solidified, the oxygen being pumped off. The violet solid solution was warmed by placing it in a CO_2/acetone bath (195°K). As the violet compound warmed up and the ClF_3 melted, the violet compound turned blue and decomposed leaving yellow liquid ClF_3. This experiment was repeated but this time before the blue compound had reached its decomposition temperature 2 atm of oxygen were added when the blue compound immediately turned violet. On pumping off the oxygen again, the violet compound once more turned blue. In order to eliminate the possibility that the reversal from blue to violet was due to some warming effect of the incoming oxygen, the experiment was repeated using argon. This time the blue compound did not change back to violet, but simply decomposed as it warmed up.

A new preparation of the violet compound has also been devised. A 1:4 mixture of O_2:OF_2 was prepared in a low-temperature still which has been described elsewhere[5]. A small amount of ClF was condensed into the still where it solidified just above the level of the liquid O_2/OF_2 solution. The contents of the still were then photolysed for 10–15 min using a medium-pressure mercury lamp and a Pyrex glass filter to preclude the formation of ozone. The liquid O_2/OF_2 solution turned orange. The still was opened to the atmosphere and allowed to warm up. The oxygen boiled off and the remaining orange solution started to boil bringing it into contact with the ClF. A violet precipitate formed in the solution which remained for a while as a solid after all the OF_2 had boiled off and then decomposed.

It was found that the blue compound could easily be prepared by the reaction of excess ClF with O_2F_2 at 119°K. The visible spectrum was recorded and is shown in Figure 1. The visible spectrum of the violet compound in ClF_3 solution at 195°K is shown in Figure 2.

The most likely structure of the violet compound is F_2ClO_2F as opposed to the other possibility FOClFOF for, as Streng noted[1], decomposition of the violet compound produces O_2F_2 and ClF. The production of the blue compound by removal of oxygen from a solution of the violet compound in ClF_3 indicates that an equilibrium exists between the violet and blue compounds which is sensitive to oxygen pressure. In other words, removal of oxygen from the violet compound produces the blue compound plus oxygen in an attempt to restore chemical equilibrium, thus suggesting that the structure of the blue compound may be $F_2ClO_2ClF_2$, *i.e.*

$$2F_2ClO_2F \rightleftharpoons F_2ClO_2ClF_2 + O_2 + F_2$$

Assuming that the blue compound formed from the reaction between O_2F_2 and ClF is the same as that from the equilibrium experiments, then its production from O_2F_2 and excess ClF may be formulated as

$$O_2F_2 + 2ClF \rightarrow F_2ClO_2ClF_2$$

The preparation of the violet compound from the photolysis of an $O_2/OF_2/$ClF mixture would appear to support the F_2ClO_2F structure for the violet compound, as it has been shown that photolysis of an OF_2/O_2 mixture produces the O_2F radical[5]. Photolysis of an O_2/ClF_3 mixture as a method of preparation is related to the work of Mamantov[7] who has shown that the ClF_2 radical can be produced from the photolysis of ClF_3 and $ClF + F_2$. It is also possible to explain the violet ⇌ blue equilibrium in terms of O_2F and ClF_2 radical mechanisms.

The work discussed here is mainly observational but the systems described and briefly investigated do give some insight into the nature of these unusual compounds.

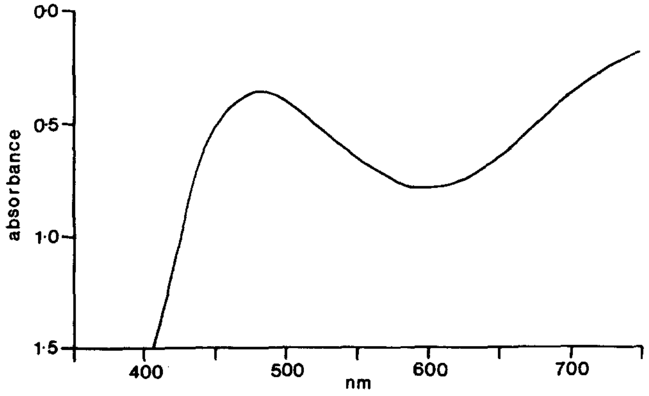

Fig. 1. Visible region spectrum of the blue compound in solid ClF at 77°K.

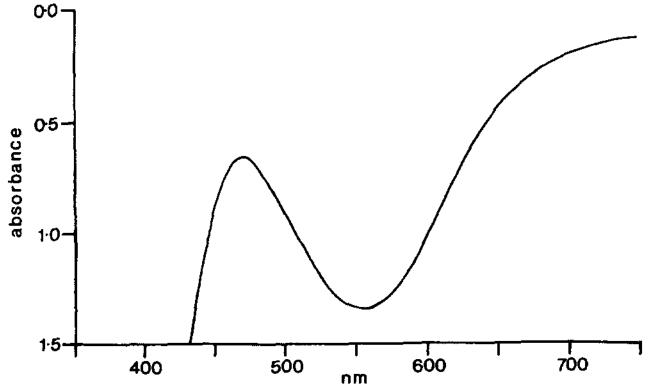

Fig. 2. Visible spectrum of the violet compound in ClF_3 solution at 195°K.

Experimental

Commercially available Cl_2, O_2, F_2 and OF_2 from cylinders were used throughout. Dioxygen difluoride, O_2F_2, was prepared by electric discharge of a 1:1 mixture of O_2:F_2 at 77°K and was purified by vacuum-line distillation[3]. Chlorine monofluoride, ClF, was prepared by passing Cl_2 and F_2 gases through a copper tube at 350° and condensing out the product[4] which was purified by vacuum-line distillation. Visible region spectra were recorded on a Perkin–Elmer 137 spectrometer, using a conventional cold infrared cell with CaF_2 windows for the blue compound and a specially designed cold liquid cell for the violet compound.

The author would like to thank Dr. J. J. Turner for helpful discussions.

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