A Peroxy-radical of Chlorine, Cl·O·O

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WE report the partial characterisation of a new paramagnetic oxide of chlorine, Cl·O·O. The electron spin resonance parameters of this radical have been measured, and will help to establish the nature of its electronic structure, and its relationship with the isoelectronic fluorine species, F·O·O.

A number of paramagnetic oxides of chlorine have been prepared and stabilised in the solid state by irradiation of chlorates and perchlorates. The nature of the products of X- or γ-irradiation is often temperature dependent, for example radiolysis of $KClO_4$ at 295° K produces both ClO_3 and ClO_2,[1,2] and at 77° K ClO_4.[3] At 190° K, a chlorine species is obtained which decays at room temperature to ClO_2.[4] Ultraviolet photolysis[4] of ClO_2 in $KClO_4$ at 295° K resulted in the loss of electron spin resonance absorption (other than that from the O_3^- ion). We now find that if, after photolysis, a crystal of $KClO_4$ is cooled to below about 100° K, signals from a new paramagnetic chlorine species appear. On standing at 295° K these disappear and, at the same time, the electron spin resonance absorption of ClO_2 reappears, the process being complete after about two days. This sequence is reversible so that the reaction scheme can be formulated;

$$KClO_4 \xrightarrow[195^\circ\text{K}]{\gamma\text{-irr.}} [A] + B \xrightarrow[295^\circ\text{K}]{\text{Anneal}} ClO_2 \underset{\text{Anneal } 295^\circ\text{K}}{\overset{\text{u.v. photolysis}}{\rightleftarrows}} A$$

Although the identification is not completely certain, strong features associated with A in a powered sample of $KClO_4$ can be seen in a freshly irradiated powder, together with features due to other radicals, represented by B.

Electron spin resonance powder spectra of A at 77° K, at both X- and Q-band frequencies, have been measured and show that the radical possesses considerable anisotropy. The parameters have been obtained by measuring the electron spin resonance spectra of A in a single crystal of $KClO_4$ at 77° K, in three orthogonal planes. The following principal values of the g- and A-tensors were obtained after diagonalisation;[5]

$$g_{11} = 1{\cdot}9983 \qquad A_{11} = 5{\cdot}3 \text{ gauss}$$
$$g_{22} = 2{\cdot}0017 \qquad A_{22} = 7{\cdot}2 \text{ gauss}$$
$$g_{33} = 2{\cdot}0130 \qquad A_{33} = 14{\cdot}9 \text{ gauss}$$

It has not been possible to determine a_{iso} independently, with the result that the signs of A_{11} *etc.* are not known.

The powder spectra of A (when signals arising from O_3^- have been subtracted) closely resemble those from a glass of ClO_2 in H_2SO_4 which has been subjected to ultraviolet photolysis at 77° K. In the H_2SO_4 matrix the radical was originally presumed to be ClO, although difficulty was experienced in attempts to accommodate the data fully.[2] One of us has since suggested[6] that the species in H_2SO_4 is Cl·O·O, the dioxygen monochloride or "chlorine peroxide" radical. We have been encouraged in supposing that the radical in both H_2SO_4 and $KClO_4$ (A) is Cl·O·O for the following reasons:

(i) The hyperfine interaction tensor of A is similar to that in F·O·O,[7] indicating that the spin density on Cl in A is comparable with that on F in F·O·O, *i.e.*, of the order of 10%.

(ii) The g-tensor resembles that in a number of other triatomic, nonlinear, 19-electron molecules,[9] such as ClO_2, O_3^-, and NO_2^{2-} in addition to F·O·O. Thus (i) and (ii) indicate that A and F·O·O have a similar structure.

(iii) Rochkind and Pimentel[8] have made the tentative proposal that Cl·O·O, produced by ultraviolet photolysis of ClO_2 in a rigid matrix, is responsible for a number of infrared absorption bands. We have detected a similar infrared spectrum after photolysis of ClO_2 in CCl_4 at 77° K.

We have also confirmed Norman and Porter's observation[10] that an intense absorption in the 260 mμ region appears after photolysis of ClO_2, which is characteristic of ClO. An additional shoulder was detected at about 380 mμ, and, by comparison with the optical spectra of O_3^- (440 mμ) and ClO_2 (340 mμ), this is tentatively attributed to Cl·O·O. ClO shows no detectable electron spin resonance absorption at 77° K, probably because of very rapid relaxation linked with the very strong dependence of the absorption on the "crystal field" of its environment.

We conclude that photolysis of ClO_2 in rigid media leads to (a) partial decomposition to ClO, and (b) partial isomerisation to Cl·O·O, possibly by a cage back-reaction, this latter reaction being readily reversed.

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