998. *Oxides and Oxyions of the Non-metals. Part VII.*[1]
SO_2^- *and* ClO_2.

By P. W. ATKINS, A. HORSFIELD, and M. C. R. SYMONS.

Four weak hyperfine components in the electron spin resonance spectrum of aqueous solutions of sodium dithionite are assigned to SO_2^- radicals containing [33]S in natural abundance, and the isotropic hyperfine coupling constant of 14·2 gauss is shown to be in accord with this assignment. These hyperfine components, in contrast with those for similar solutions of the isoelectronic chlorine dioxide, are very narrow. The effect of changing environment on the spin resonance spectrum of chlorine dioxide has been investigated in an attempt to discover reasons for this difference.

THE structure of sodium dithionite[2] is marked by an unusually long sulphur–sulphur bond, which led Dunitz to suggest that SO_2^- radicals might readily be formed from dithionite.[2] Hodgson *et al.*[3] and others[4,5] detected a free radical in low concentration in moist dithionite[3,4] and in deaerated aqueous solutions.[5] This was identified as SO_2^- on the basis of chemical expectation.

A radical formed on γ-irradiation of solid sodium dithionite was similarly identified, although only a single structureless line was obtained.[4]

Recent extensive studies of the spin resonance spectra of oxy-radicals of this general type[6] have revealed well defined patterns in hyperfine and g-tensors which fit satisfactorily

[1] Part VI, Atkins, Symons, and Wardale, preceding Paper.
[2] Dunitz, *Acta Cryst.*, 1956, **9**, 579.
[3] Hodgson, Neaves, and Parker, *Nature*, 1956, **178**, 489.
[4] Clark, Horsfield, and Symons, *J.*, 1961, 7.
[5] Rinker, Gordon, Mason, and Corcoran, *J. Phys. Chem.*, 1959, **63**, 302.
[6] Symons, " Free Radicals in Inorganic Chemistry," No. 36, Adv. in Chem., A.C.S., 1962.

View Online

[1964]   *Oxides and Oxyions of the Non-metals. Part VII.*   5221

with theoretical predictions,[7,8] and which enable reasonably accurate conclusions to be drawn regarding these parameters for unknown radicals.   Pertinent results are summarised in the Table.

Bennett and Ingram [9] found that the spin resonance spectrum from dilute solutions of chlorine dioxide in ethyl alcohol consisted of a single broad line at room temperature, which separated into four components at $-80°$.   Solutions in sulphuric acid give a spectrum of four, broad, overlapping lines at room temperature, but rigid solutions at $77°K$ have relatively narrow hyperfine components from which the anisotropic hyperfine and g-tensors could be derived.[10]

Our aim was to identify more certainly the radical formed in aqueous solutions of dithionite, and to probe reasons for the very large but variable line-width of the hyperfine components in the spin-resonance spectra of chlorine dioxide in different media.

EXPERIMENTAL AND RESULTS

Materials.—Chlorine dioxide.   Chlorine dioxide was obtained by heating a mixture of oxalic acid, potassium chlorate, and water to $60°$.   Chlorine, carbon dioxide, and water were removed from the resulting gas by passage through concentrated aqueous sodium hydroxide and over phosphoric oxide.   Solutions in sulphuric acid were obtained by adding potassium chlorate which disproportionates in this medium to give perchloric acid and the dioxide.

γ-Irradiation.—Samples were exposed to a 1900-c ^{60}Co source at room temperature.   The dose rate was 0.3 mrad/hr.

Electron Spin Resonance.—Measurements were made at X-band frequencies with a spectrometer described previously [11] and with a Varian 4502-03 spectrometer with a variable temperature attachment.

Optical Spectra.—Ultraviolet spectra were obtained with a Unicam S.P. 700 spectrophotometer.   Diffuse reflectance spectra were obtained with a Unicam S.P. 500 spectrophotometer with diffuse reflectance attachment;   precautions previously described [12] were observed.

Dithionite.—The four hyperfine components due to radicals containing ^{33}S are clearly resolved in Fig. 1, although the signal to noise ratio is poor.   The hyperfine lines have about the same width between points of maximum slope as that of the central line and by suitable adjustment of the amplifier gain it was found that the intensity ratio of the ^{33}S lines was close to 1.85×10^{-3}, which is expected for ^{33}S in natural abundance.

Electron spin resonance and molecular parameters for 19-electron oxides, XO_2.

	Hyperfine tensor (gauss)				g-Tensor				Orbital population on X		
Species	A_x	A_y	A_z	A_{iso}	g_x	g_y	g_z	g_{av}	a_p^2	a_s^2	Ref.
$NO_2{}^{2-}$	16·6	−9·3	−7·3	14·3	2·0038	2·0099	2·0070	2·0070	0·64	0·03	a, b
$O_3{}^-$	—	—	—	—	2·0025	2·0174	2·0013	2·0104	—	—	c
$SO_2{}^-$	—	—	—	14·5	2·0024	2·0102	2·0057	2·0061	—	0·01	
ClO_2	57·6	−30·8	−26·8	15·4	2·0036	2·0183	2·0088	2·0102	0·69	0·01	c, d
$SeO_2{}^-$	109·3	−59·1	−50·2	141·4	1·9976	2·0305	2·0094	2·0125	0·39	0·03	e

The z-axis is the C_2 axis with the x-axis perpendicular to the molecular plane.

a Jaccard, *Phys. Rev.*, 1961, **124**, 60.   b Atkins and Symons, *J.*, 1962, 4794.   c Atkins, Brivati, Keen, Symons, and Trevalion, *J.*, 1962, 4785.   d Cole, *Proc. Natl. Acad. Sci. U.S.*, 1960, **46**, 506.   e Atkins, Symons, and Wardale, preceding Paper.

The hyperfine splitting, averaged over four spectra, was 14.2 gauss, and g_{av} 2.0057.   In view of the poor signal to noise ratio, it was not possible to carry out saturation studies of the ^{33}S spectrum, but there was practically no change in the width between points of maximum slope of 0.7 gauss for the central line on changing the power over a wide range.

7 Mulliken, *Rev. Mod. Phys.*, 1942, **14**, 204.
8 Walsh, *J.*, 1952, 2266.
9 Bennett, Ingram, and Schonland, *Phil. Mag.*, 1955, **46**, 443.
10 Atkins, Brivati, Keen, Symons, and Trevalion, *J.*, 1962, 4785.
11 Brivati, Keen, and Symons, *J.*, 1962, 237.
12 Griffiths, Lott, and Symons, *Analyt. Chem.*, 1959, **31**, 1338.

The spectrum obtained from $K_2S_2O_5$ after exposure to γ-radiation (Fig. 2) is tentatitively attributed to SO_2^- radicals since the three g-factors derived therefrom accord so well with expectation (Table). Studies of irradiated single crystals confirmed that only one major radical was present, and in particular, that SO_3^- radicals were not formed under these conditions. We stress, however, that frozen aqueous solutions containing SO_2^-, and also irradiated $Na_2S_2O_4$, give only single broad lines. Whilst this broad spectrum could well embrace the g-factors assigned to SO_2^- it is equally possible that the variation is somewhat smaller than indicated, and that the radical in $K_2S_2O_5$ is $OS(SO_3)^-$, which would be expected to have magnetic properties somewhat similar to those of SO_2^-.

Chlorine Dioxide.—(i) *Electron spin resonance* (a) *In hydrogen-bonding solvents.* At room temperature a solution of chlorine dioxide in water gave a quartet spectrum in which the ^{37}Cl hyperfine spectrum could not be distinguished from that due to the ^{35}Cl nuclei. The resonance was not saturated. Although the resolution was very slightly improved when sodium or calcium chloride were added, no effect was observed on removing oxygen from the solution or on adding chlorite ions. When glycerol was added the resolution was increased significantly
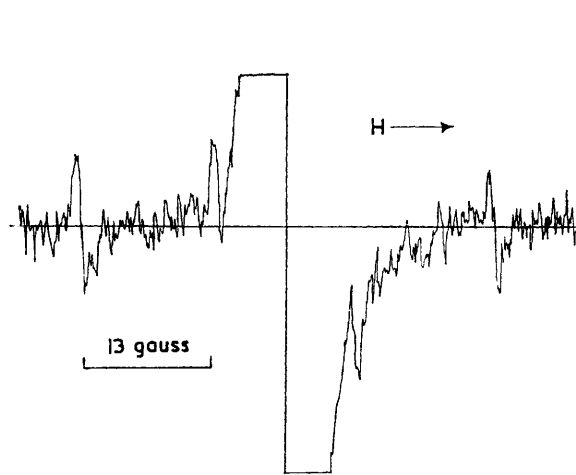

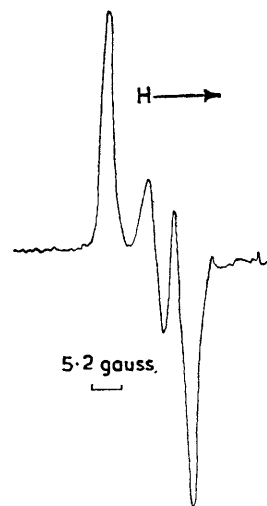Fig. 1. Electron spin resonance spectrum from an aqueous solution of sodium dithionite.

Fig. 2. Electron spin resonance spectrum from γ-irradiated potassium metabisulphite powder.

until in pure glycerol there was a suggestion of ^{37}Cl splitting distinct from the ^{35}Cl splitting. In sulphuric and phosphoric acids there was also a quartet, the resolution being slightly better in the latter solvent. In sulphuric acid it has been estimated [13] that the relaxation parameters $T_2^{-1} \sim 10$ and $T_1^{-1} \sim 10^{-3}$ gauss. The resolution in 98% D_2O was no better than in ordinary water.

(b) *In " non-interacting " solvents.* In carbon tetrachloride at room temperature a broad line was observed with the suggestion of an inflexion in the centre (confirmed by a double derivative spectrum). As the solution was cooled, the resolution increased even after solidification, being greatest at about $-35°$. Below this temperature an anisotropically broadened spectrum was obtained. This is shown in Fig. 3. The resolution was independent of the concentration. When methanol was added to the solution in carbon tetrachloride, resolution increased (Fig. 4). The resolution was unaltered when paraffin wax was added to the carbon tetrachloride solution. Except in those cases when asymmetry was marked, the quartet spectra could be fitted to spectra computed on the basis of overlapping Gaussian derivative curves (Fig. 5). No spectrum was observed in the gas phase.

(ii) *Ultraviolet spectra.* The ultraviolet spectrum of chlorine dioxide in various solvents is

[13] Mackor and Van Reijen, personal communication.

View Online

[1964]   *Oxides and Oxyions of the Non-metals.   Part VII.*   5223

illustrated in Fig. 6.   Considerable vibrational structure was observed in carbon tetrachloride. The resolution was reduced on the addition of methanol.   In water the spectrum was much less well resolved although it was perhaps slightly improved when glycerol was added.
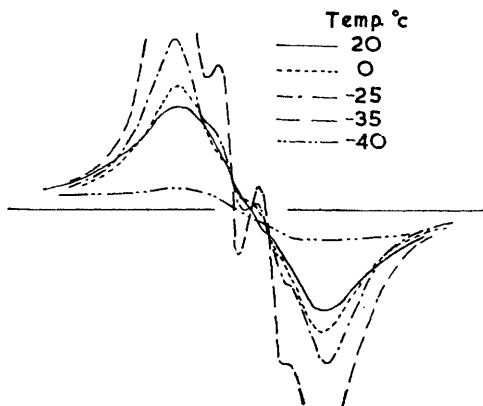

Fig. 3.   Temperature variation of the electron spin resonance spectrum from chlorine dioxide in carbon tetrachloride.
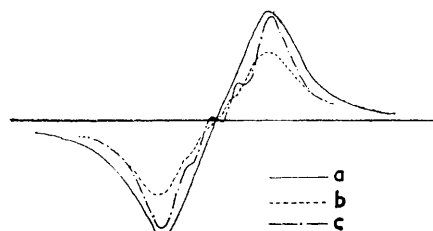

Fig. 4.   The effect of adding methanol on the electron spin resonance spectrum of chlorine dioxide in carbon tetrachloride at room temperature.

(a) Pure carbon tetrachloride;   (b) 5% methanol;   (c) 50% methanol.
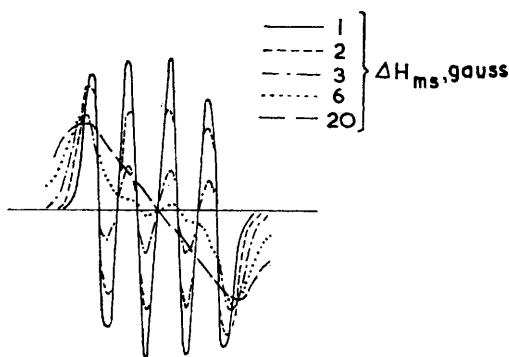

Fig. 5.   Calculated Gaussian derivative curves for chlorine dioxide.
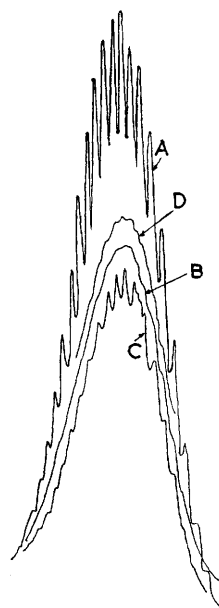

Fig. 6.   Ultraviolet spectrum of chlorine dioxide in various solvents.

A, Carbon tetrachloride; B, water; C, carbon tetrachloride with 50% methanol; D, water with 50% glycerol.

DISCUSSION

Identification of SO_2^-.—In addition to chemical expectation, the following arguments support the postulate that dithionite ions dissociate reversibly in aqueous solution,

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^-$$

5224 *Oxides and Oxyions of the Non-metals. Part VII.*

View Online

(i) The isotropic hyperfine coupling to ^{33}S of 14·2 gauss shows that the electron is in a π orbital associated with only one sulphur atom and comparison with the result for chlorine dioxide shows that there has been a slight increase in the apparent s-character (Table). With the usual reservations, this can be taken as an indication that there is a slight increase in the spin density on the central atom on going from ClO_2 to SO_2^-. It is stressed, however, that since the unpaired electron is in a π level, the s-character on ^{33}S is not directly a measure of spin-density.

(ii) The principle values of the g-tensor for the radical thought to be SO_2^- in γ-irradiated $K_2S_2O_5$ are close to those for ClO_2 (Table) and in good agreement with expectation for SO_2^-.

Relaxation Mechanisms.—The considerable difference between the line widths of chlorine dioxide and SO_2^- is unexpected and requires explanation. The anisotropies in the g-tensors of SO_2^- and chlorine dioxide are similar ($\Delta g = 0·0078$ and $0·0147$, respectively) and the anisotropic hyperfine coupling tensor of the chlorine compound $A^{Cl} = (57·6, -30·8, -26·8)$ gauss, can be compared with the tensor which may be estimated for the sulphur compound by considering the magnitude of the nuclear moments as $A^S = (33, -17, -15)$ gauss. The anisotropies of A^{Cl} and A^S are 88 and 50 gauss, respectively. The quadrupole moments, Q, in units of $e \times 10^{-24}$ cm.^{2}, of ^{35}Cl, ^{37}Cl, and ^{33}S are $-6·4 \times 10^{-2}$, $-6·21 \times 10^{-2}$, and $7·97 \times 10^{-2}$, respectively. None of these quantities appear to differ sufficiently to account for the large line width difference between the spectra of the two compounds in water. Superimposed upon these difficulties is the anomalous viscosity dependence of the line widths. Chloride dioxide has a much greater line width in non-interacting than in hydrogen-bonding media; the interaction is reflected in its effect upon the vibrational structure of the optical spectrum. Also the line width decreases with increasing microscopic viscosity of the medium, as the effect of adding methanol shows.

The experimental results show that the relaxation is not primarily dependent upon concentration and that exchange is not important. Dodgen and Taube [14] have estimated the rate constant of the exchange reaction of ClO_2 with ClO_2^- in dilute solution as about 10^4 l. mole^{-1} min.$^{-1}$. This tends to support this view. Also, oxygen appears to have no deleterious effect on the resolution and in this instance the importance of relaxation by interaction with the fluctuating field of the neighbouring protons in water is eliminated by the negative effect of deuteration.

In carbon tetrachloride solution, we suggest that the interaction with the solvent is sufficiently weak for the chlorine dioxide to behave essentially as a short-lived gas. The magnetic moment associated with each sufficiently long-lived rotational state would alter and modulate the local field at the electron and the spectrum of the complete ensemble of molecules would be broadened. This view is supported by the optical spectrum of chlorine dioxide in carbon tetrachloride, which closely resembles that of the free gas, linked to the fact that no gas phase electron spin resonance was observed. A higher viscosity leads to a shorter lifetime of rotational states and a rapid modulation of the rotational fields; hence the lines narrow as the viscosity increases. It is difficult to believe that this is the mechanism involved in the relaxation in the hydrogen-bonding solvents, nor is it likely that any other spin–rotation relaxation mechanism could be invoked to explain it.

Mackor and Van Reijen [13] have suggested to us that the line broadening may be due to a rapid relaxation of the nuclear spins. The T_2 of the electron would then be determined by the T_1 of the chlorine nucleus. This mechanism need not invoke any other driving force than the anisotropies we have discussed. It will predominate when the anisotropy of the hyperfine interaction is sufficiently great with respect to the isotropic hyperfine interaction and the anisotropy of the Zeeman effect. Anomalous viscosity dependence of the line width according to this mechanism will only be expected at rather low tumbling

[14] Dodgen and Taube, *J. Amer. Chem. Soc.*, 1949, **71**, 2501.

rates, *i.e.*, at rather high viscosities. The large discrepancy between the T_1 and T_2 observed for the sulphuric acid solution is then accounted for. The SO_2^- results still seem difficult to accommodate without a more precise calculation of the mechanisms involved.

A similar mechanism may be involved in the case of nitrogen dioxide for in no solvent has anything but a broad structureless line been observed at room temperature.[15] It is quite likely, however, that dimerisation is the predominant mechanism in this instance.

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, LEICESTER. [*Received, December 23rd, 1963.*]

[15] Atkins, Keen, and Symons, *J.*, 1962, 2873.