# 2. *Unstable Intermediates. Part XII.* The Radical-ions* $SO_2^-$ *and* $NO_2^{2-}$.

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*X*-Irradiation of solid sodium or potassium dithionite results in the formation of a paramagnetic species having an ultraviolet absorption band in the 350 mμ region. This is tentatively identified as the radical-ion $SO_2^-$. Electron-spin resonance spectra of the irradiated solids are closely similar to that obtained from sodium dithionite moistened with water, having a *g*-value of 2·004 and a half-width of 11·5 gauss. A similar electron-spin resonance spectrum, obtained from the yellow solid formed by addition of excess of sodium nitrite to a solution of sodium in ammonia, is attributed to the ion $NO_2^{2-}$.

In seeking to extend our studies of ions structurally similar to chlorine dioxide (19 valency electrons),[1] we have attempted to prepare the ions $SO_2^-$ and $NO_2^{2-}$, and to measure their ultraviolet and electron-spin resonance spectra.

The ion $SO_2^-$ is thought to be formed when sodium dithionite is moistened with water.[2] We have exposed crystalline sodium and potassium dithionite to *X*-radiation in the hope that the sulphur–sulphur bond, known to be unusually long,[3] would break homolytically, and that the resulting $SO_2^-$ ions would remain trapped in the solid. Details of the electron

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* Part XI, preceding paper.

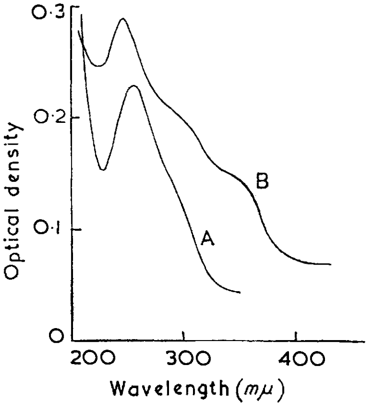
[1] McLachlan, Symons, and Townsend, *J.*, 1959, 952.

[2] Hodgson, Neaves, and Parker, *Nature*, 1956, **178**, 489.

[3] Dunitz, *J. Amer. Chem. Soc.*, 1956, **78**, 878.

resonance spectrum of the irradiated solid, which was indistinguishable from that obtained from moist dithionite, are given in the Table. The ultraviolet spectra of powdered sodium dithionite, before and after irradiation, are given in the Figure.

The ion $NO_2^{2-}$ is thought to be present in the yellow solid formed on addition of sodium nitrite to solutions of sodium in ammonia.[4,5] This solid is probably mainly the dimer, $Na_4N_2O_4$, but magnetic-susceptibility studies suggest that $NO_2^-$ is a minor constituent.[5]



*Spectra of solid sodium dithionite measured by diffuse reflectance methods at room temperature.*

(A) *Before irradiation.* (B) *After exposure to* 50 kv *X-rays.*

*Electron-spin resonance and optical spectra of various molecules and ions containing* 19 *valency electrons.*

| | $g$-Value | $\Delta_{MS}$ (gauss) * | $\lambda_{max.}$ (mμ) † | ε † |
|---|---|---|---|---|
| $O_3^-$ [1] ...................... | 2·012 ± 0·002 | 19 | 440 | 2000 |
| $NO_2^{2-}$ ...................... | 2·003 ± 0·002 | 9 | 400 | — |
| $ClO_2$ [e] ...................... | 2·02,[a] 2·01 [b] | — | *ca.* 350 | *ca.* 2000 |
| $SO_2^-$ [c] ...................... | 2·005 ± 0·002 | 11·5 | *ca.* 360 | — |
| $SO_2^-$ [d] ...................... | 2·005 ± 0·002 | 11·5 | — | — |

* $\Delta_{MS}$ = Width between points of maximum slope taken from the first derivative of the electron-spin resonance spectra.

† For the longest-wavelength bands in the visible and ultraviolet spectra.

[a] *gx* and *gy*. [b] *gz*. [c] *X*-Irradiated $Na_2S_2O_4$. [d] Paste of $Na_2S_2O_4$ in water. [e] Bennett, Ingram, and Schonland, *Proc. Phys. Soc.*, 1956, **69**, *A*, 556.

The electron-spin resonance spectrum of this solid was similar to that for irradiated dithionite, having a $g$-value of 2·003 ± 0·001 and a width between points of maximum slope of about 9 gauss at 77° K. We were unable to measure the ultraviolet spectrum, but can infer from the colour that there is a fairly intense band with a maximum at wavelengths shorter than 400 mμ.

## EXPERIMENTAL

*Materials.*—Purified anhydrous sodium dithionite was kindly supplied by Dr. C. A. Parker. Sodium nitroxylate was prepared by Zintl and Kohn's method.[4] Freshly fused and finely powdered sodium nitrite was added to a solution of purified sodium in liquid ammonia, which had been purified by distillation from metallic sodium. A bright yellow solid was formed immediately, and nitrite was added until the blue colour had been completely discharged. The solid was repeatedly washed with solvent before measurement to ensure that no metallic sodium was present. When traces of water were present during addition of nitrite, vigorous explosions occurred.

*Electron-spin Resonance.*—Spectra were measured at a wavelength of 3 cm., a modulation

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[4] Zintl and Kohn, *Ber.*, 1928, **61**, 189.

[5] Asmussen, *Acta Chem. Scand.*, 1958, **12**, 578.

field of 10 kc./sec. and a phase-sensitive detector being used. The samples, in 5 mm. quartz tubes, were placed in an $H_{102}$ rectangular cavity which was cooled to 77° K by immersion in liquid nitrogen. To obtain the *g*-values of the derivative spectra thus obtained, traces of diphenylpicrylhydrazyl were added. The very slight differences observed between the superimposed spectra were then estimated, and *g*-values calculated relative to $g = 2{\cdot}0032$ for diphenylpicrylhydrazyl.

*Spectrophotometry.*—Diffuse reflectance measurements were made directly on the powdered solids by use of a Unicam attachment fitted to an S.P. 500 spectrophotometer. To facilitate measurements in the ultraviolet region an S.Z.G. 500 photomultiplier was used as a detector, and lithium fluoride was used as a reference surface and diluent. Other precautions were used as outlined previously.[6]

X-*Irradiation.*—Polycrystalline specimens were contained in evacuated quartz tubes and irradiated for several hours with 50 kv *X*-rays at room temperature. It was established that the irradiated tubes made negligible contribution to the observed spectra.

## DISCUSSION

*Identification.*—That $NO_2^{2-}$ ions are formed under the conditions described is very probable. Our results add little to the work of others, but are consistent with this postulate. Similarly, no convincing proof for the formation of $SO_2^-$ ions has been obtained. However, the similarity between the electron-spin resonance results after *X*-irradiation and after treatment of dithionite with water, considered together with the remarkable stability of chlorine dioxide, which is isoelectronic with $SO_2^-$, add some weight to the postulate.

In the following, the magnetic and spectroscopic data are considered in terms of these identifications, and the effect of *X*-irradiation on dithionite is briefly discussed.

*Structure.*—The structure of molecules with 19 valency electrons has been discussed by Walsh,[7] and the specific case of chlorine dioxide by Bennett, Ingram, and Schonland.[8] These treatments differ in that outer *d*-orbitals on the central atom are not considered explicitly by Walsh, whereas Bennett *et al.* conclude that the $b_1$-orbital of chlorine dioxide, containing the unpaired electron, has about 70% 3*d*-character and 30% 3*p*-character, being almost entirely localised on chlorine.

Since the ions under consideration also have 19 electrons, they should be bent, probably with an apex angle between 110° and 120°. A simple alternative picture to that of Walsh would be that the molecule uses $sp^2$-hybrid orbitals on each atom to form orbitals for the $\sigma$-bonding and lone-pair electrons in the plane of the molecule. Three $\pi$-molecular orbitals can then be constructed from the remaining $p$–$\pi$ orbitals on the three atoms. Of the 19 electrons, 4 would be in the $\sigma$-bonding orbitals, 10 in the $\sigma$-lone-pair orbitals, and the remaining 5 in the set of three $\pi$-orbitals. The molecule is bent because of the lone-pair of electrons on the central atom. This structure is formally similar to that of the allyl radical, which has only three $\pi$ electrons. This analogy is useful because electron-spin resonance studies have shown that the outermost, unpaired electron is largely located on the end carbon atoms in the allyl radical. We can therefore say that the five $\pi$-electrons in chlorine dioxide and related ions will be distributed in such a way that the pair of lowest energy will be fairly evenly distributed on all three atoms, the next pair will be largely located on the end atoms, and the outermost unpaired electron will be located largely on the central atom. The results will be discussed in terms of these models.

*Electron-spin Resonance.*—The results can be compared with those obtained for $NO_2$,[9] $O_3^-$,[1] and $ClO_2$.[8] The hyperfine splitting from the nitrogen nucleus in $NO_2$ is quite large (107 gauss); and, had the splitting been at all comparable in $NO_2^{2-}$, a 1 : 1 : 1 triplet

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[6] Griffiths, Lott, and Symons, *Analyt. Chem.*, 1959, **31**, 1338.

[7] Walsh, *J.*, 1953, 2266.

[8] Bennett, Ingram, and Schonland, *Proc. Phys. Soc.*, 1956, **69**, *A*, 556.

[9] Bird, Baird and Williams, *J. Chem. Phys.*, 1958, **28**, 738.

should have been found rather than a single, relatively narrow line. This result is not readily understood in terms of the $\pi$-electron model given above, since the unpaired electron would be located largely on oxygen in $NO_2$, but largely on nitrogen in $NO_2^{2-}$. However, a consideration of Walsh's correlation diagram [7] suggests that, since the bond angle of $NO_2$ is about 140°, the $a_1'$ level stemming from $\pi_u$ of the linear molecular should lie above the $b_2'$ level. This orbital tends to pure $s$ on the central atom, and hence an unpaired electron in this level will have considerable $s$-character on nitrogen. This would explain the large isotropic hyperfine splitting observed. The lack of detectable splitting from $NO_2^{2-}$ can then be understood since on either model, the orbital involved is a pure $\pi$-level, having a node at the nitrogen nucleus.

The alternative, that fine structure is lost and the line narrowed by exchange phenomena in the solid, is unlikely, since, if most of the solid is $Na_4N_2O_4$,[5] the ions $NO_2^-$ would be suitably isolated from each other. It is nevertheless possible that the material was inhomogeneous, consisting of a mixture of $Na_2NO_2$ and $Na_4N_2O_4$, in which case exchange narrowing might well be important.

The $g$-values for $SO_2^-$ and $NO_2^{2-}$ are even closer to the free-spin value than that for $O_3^-$ and the spectra were not very sensitive to temperature changes. We conclude that spin–orbit coupling must be very weak, despite the occurrence of a fairly intense optical absorption for each ion in the near-ultraviolet region. In this respect, these ions differ from chlorine dioxide, probably because of strong, asymmetric electric fields from the neighbouring ions in the crystals.

*Optical Spectra.*—Little can be said about the spectra except that the long-wavelength transitions are probably similar to the fairly intense transition of chlorine dioxide which has been described by Mulliken [10] and Walsh [7] as

$$- - - - (a_2'')(b_2')^2(a_1')^2(b_1'')^2, {}^2A_2 \longleftarrow\cdots\cdots (a_2'')^2(b_2')^2(a_1')^2(b_1''), {}^2B_1$$

a transition which involves movement of negative charge from oxygen towards the central atom. Experimental details are given in the Table. On the simple $\pi$-electron model, this is a $\pi$–$\pi$-transition from oxygen to the central atom.

This allocation is internally consistent except that the transition for $SO_2^-$ would be expected to require somewhat greater energy than that for $ClO_2$. It is possible that the band at 300 mμ is due to the ${}^2A_2 \longleftarrow {}^2B_1$ transition of $SO_2^-$, superimposed upon the 300 mμ band of dithionite. In that case the shoulder at about 370 mμ remains unidentified. The other bands fit the pattern required by the postulate that there is charge transfer towards the central atom on excitation.

*Dimerisation.*—By measuring the electron-spin resonance spectra of solutions of chlorine dioxide at various temperatures we have found that dimerisation is unimportant even at the melting point of ethanol. In marked contrast, and despite the repulsion of like charges, $SO_2^-$ is present almost entirely as dimer in dilute aqueous solution at room temperature. Since $ClO_2$ and $SO_2^-$ are isoelectronic, this means that the major factor involved must be the decreased nuclear repulsion for $S_2O_4^{2-}$. However, although the dimer is favoured, the S–S bond is remarkably long.[3] Again, $O_3^-$ in liquid ammonia at $-80°$ is present entirely as monomer (no evidence for the formation of the dimer, $O_6^{2-}$ has yet been obtained), whereas the isoelectronic ion $NO_2^{2-}$ is thought to dimerise extensively at low temperature,[5] although our results show that this is by no means complete. Again the decreased nuclear repulsion is more important than the increased electrostatic repulsion between the ions.

X-*Irradiation of Dithionite.*—Exposure of crystals to high-energy radiation generally results in a relocation of electrons in the lattice. In alkali halide crystals the basic reaction is simply $Hal^- \longrightarrow Hal\cdot + e$, followed by the formation of $Hal_2^-$, $Hal_2$, or $Hal_3^-$.

The simplest fate of the electron is trapping at a halide vacancy, to give an $F$-centre.

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[10] Mulliken, *Rev. Mod. Phys.*, 1942, **14**, 204.

However, when such crystals contain impurity ions, it is common to find that these ions become involved in the decomposition, and that the *final* result of irradiation is quite different, even though equation (1) may still be a good representation of the fundamental process of absorption.[11] The net result is an apparent selectivity. Similar conclusions can be drawn regarding the effect of high-energy radiation on molecular crystals and crystals containing polyatomic ions. For example, *X*-irradiation of alkali-metal nitrates gives mainly nitrites and oxygen,[12] and in a recent study of the effect of *X*-rays on potassium chlorate it is postulated that the overall process amounts to $ClO_3^- \longrightarrow ClO + O_2^-$, ClO then bonding to an adjacent chlorate ion.[13] Probably chlorite and hypochlorite ions are also formed, and identification of the paramagnetic species is not certain, but there is no evidence for the formation of *F*-centres in these studies. Since, to a good approximation, the wavelength of the *F*-band in an ionic crystal can be estimated from the lattice parameter by use of Ivey's equation,[14] $\lambda_{\text{max.}}$ (Å) $= 703a^{1\cdot84}$, it is possible to state, on both magnetic and spectrophotometric evidence, that *F*-centres are not formed in such crystals. In general one can surmise that, for crystals containing simple cations and complex anions, after photo-ionisation has occurred, either the electron is recaptured by the electron-deficient radicals, to give " hot " ions which decompose, or that the expelled electron reacts with another anion to give break-down products.

Thus, for sodium dithionite, we can suppose that, if photo-ionisation occurs, the reaction teps may take the form

$$S_2O_4^{2-} \longrightarrow S_2O_4^- + e; \; S_2O_4^- \longrightarrow SO_2 + SO_2^-; \; S_2O_4^{2-} + e \longrightarrow SO_2^{2-} + SO_2^-,$$

rather than, or as well as, $S_2O_4^{2-} \longrightarrow 2SO_2^-$, in one step.

For ions such as nitrite, especially when in dilute " solution " in alkali halide crystals, photo-ionisation may lead to a net disproportionation:

$$2NO_2^- \longrightarrow NO_2 + NO_2^{2-}.$$

This would probably be a convenient method for preparing diluted and oriented $NO_2^{2-}$ ions.

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[11] Cf. Symons and Doyle, *Quart. Rev.*, 1960, **14**, 62.
[12] Cunningham and Heal, *Trans. Faraday Soc.*, 1958, **54**, 1355.
[13] Hasty, Ard, and Moulton, *Phys. Rev.*, 1959, **116**, 1459.
[14] Ivey, *Phys. Rev.*, 1947, **72**, 341.