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On the Nature of the Radicals Formed in the Reaction of Metals with Sulphur Dioxide in Dimethyl Sulphoxide

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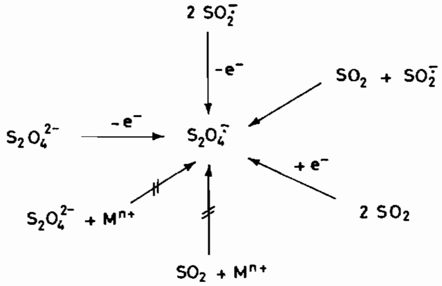
A number of metals may be dissolved in the mixed solvent dimethyl sulphoxide (DMSO)–SO_2, to form metal disulphates and/or dithionites [1–3]. In several cases, particularly in reactions with the more electropositive metals, the reaction is accompanied by the formation of a blue intermediate which has been tentatively assigned to some type of metal ion-pair, e.g. $[M^{x+}(SO_2^{\bar{\cdot}})_y]$. However, the absorption maximum,. lying within the range 550–590 nm according to the metal, is far beyond the energy region to be expected for a $SO_2^{\bar{\cdot}}$ to metal ion-pair charge transfer transition. Hence, this observation merits further study. We have therefore investigated the reaction of metallic zinc with sulphur dioxide in DMSO. Zinc forms one of the more stable blue intermediates which have been observed. Such intermediates are instantly destroyed on contact with oxygen.

Finely powdered zinc was dissolved in DMSO saturated with SO_2 at room temperature. Under anaerobic conditions a product was isolated, for which the elemental analysis corresponded to the formula 2.5 $ZnS_2O_4 \cdot Zn(DMSO)_6S_2O_7$. A product of such composition indicates that oxidation of sulphur(IV) to sulphur(VI) is incomplete. Dithionites have been previously observed as intermediates in the conversion of metals to disulphates. In the course of the reaction the formation of a species with an absorption maximum at 590 nm, which gives rise to the blue colour of the solution, was readily observed.

The same blue species was detected when sodium dithionite ($Na_2S_2O_4$) was dissolved in DMSO–SO_2. On the other hand, the solution remained colourless when no sulphur dioxide was present in the reaction system. As shown in Scheme 1, the blue product could also be generated by partial oxidation of dithionite using Fe(III) and Ce(IV) ions respectively as oxidants.

The ESR spectrum of $Na_2S_2O_4$ in DMSO exhibits a single line at g = 2.0062 ± 0.0005 with a linewidth of 0.3 mT. The line becomes sharper (ΔH = 0.1 mT) and is shifted toward a higher g value (g = 2.0070 ± 0.0003) when Ce(IV) is added. These findings are in agreement with previous observations on the $SO_2/SO_2^{\bar{\cdot}}$ couple in N, N-dimethyl formamide (DMF) [4–6]. Since the intensity of the ESR line at g = 2.0070 correlates with the optical density at 590 nm they obviously relate to the same species. From extensive electrochemical [7–9], spectroscopic [7, 10] and ESR studies [5, 6] it has been derived that the blue colour observed during the reduction of SO_2 in DMF may be attributed to the $S_2O_4^{\bar{\cdot}}$ radical. However, no evidence for the blue $S_2O_4^{\bar{\cdot}}$ radical was obtained from the electrochemical reduction of SO_2 in DMSO [11].



(M^{n+} = Li^+, Na^+, Zn^{2+} , Mg^{2+}, Fe^{2+})

Scheme 1.

This result reflects the greater tendency of the $SO_2^{\bar{\cdot}}$ radical to dimerize in DMSO (K = 10^5 M^{-1} at 328 K [11]) as compared with DMF (K = 24 M^{-1} at room temperature [7]). Hence, unlike the situation in DMSO, the formation of $S_2O_4^{\bar{\cdot}}$ by association of SO_2 and $SO_2^{\bar{\cdot}}$ (K = 8400 M^{-1} [8]) can compete with the dimerization of $SO_2^{\bar{\cdot}}$ in DMF even at low concentrations of sulphur dioxide. In our experiments, however, the SO_2 concentration was very high (>15 M), and considerable amounts of $SO_2^{\bar{\cdot}}$ radicals were scavenged by SO_2 to give $S_2O_4^{\bar{\cdot}}$. Direct oxidation of dithionite ions ($S_2O_4^{2-}$) provides another route to $S_2O_4^{\bar{\cdot}}$ radicals.

Some explanation is required for the observation that the position of the absorption maximum in the region 550–590 nm is dependent on the metal present. The absorption maximum in all cases is more likely, in terms of energy, to be associated with some kind of transition within $S_2O_4^{\bar{\cdot}}$, influenced by adjacent metal ions, rather than with a $S_2O_4^{\bar{\cdot}}$ to metal ion-pair charge transfer transition. However, such an explanation does not exclude the possibility that ion-pairs, either contact or solvent-separated, exist. It is more likely that solvent-separated ion-pairs

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would exist, since in such cases there would be a very considerable energy barrier to any charge transfer taking place from $S_2O_4^{\overline{\cdot}}$ to metal ion.

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