

determining step have in fact been observed^{1,5} for a number of the above metals in acid solutions. For these metals of intermediate hydrogen overpotential, therefore, equation (4) determines the rate, whereas for the metals mercury, lead and thallium, it appears that the proton discharge is the rate-determining reaction (cf. ref. 1), and at platinum the desorption by recombination of adsorbed hydrogen atoms determines the rate.

The relation of i_0 to the structure of the metallic substrate arises as follows. It has been recently established⁷ that decrease of d -character is associated with increased heat of adsorption of hydrogen. The exchange current density would therefore be expected to decrease with decreasing d -character, as is experimentally verified⁵. The relationship to ϕ arises similarly, as ϕ increases with the amount of d -character⁵, owing to the lower energy of electrons when more are paired as the d -band becomes more filled.

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¹ Bockris, J. O'M., "Modern Aspects of Electrochemistry", chapter 4 (Butterworths, London, 1954).

² Horinti, J., and Polanyi, M., *Acta Physicochimica, U.S.S.R.*, **2**, 505 (1935).

³ Conway, B. E., Ph.D. thesis, London, 270 (1949).

⁴ Bosworth, R. C. L., *J. Proc. Roy. Soc. N.S.W.*, **74**, 538 (1941).

⁵ Conway, B. E., and Bockris, J. O'M., *J. Chem. Phys.* (in course of publication).

⁶ Ruštschi, P., and Delahay, P., *J. Chem. Phys.*, **23**, 195 (1955).

⁷ Beeck, O., *Discuss. Farad. Soc.*, **8**, 118 (1950).

Detection of Free Radicals in Sodium Dithionite by Paramagnetic Resonance

It has been shown¹ that the photochemical oxidation of a bound oxalate ion leads to the formation of a free radical (assumed to be $C_2O_4^{\cdot-}$ or $CO_3^{\cdot-}$). In view of the formal analogy between the oxalate ion, $C_2O_4^{2-}$, and the dithionite ion, $S_2O_4^{2-}$, and the possibility of their undergoing oxidation by similar mechanisms², we have investigated the possibility of producing the corresponding free radical from the dithionite ion. The paramagnetic resonance apparatus was similar to that previously described¹. All measurements of paramagnetic resonance absorption were made at liquid-oxygen temperature with the samples sealed in thin-walled evacuated glass tubes.

Samples of anhydrous sodium dithionite showed a weak paramagnetic resonance absorption having a g -value of 2.01 ± 0.01 and width of 12 ± 3 gauss, suggesting that it was due to a free radical. This weak absorption could still be detected after pumping under high vacuum at a temperature of $60-70^\circ C$. Treatment of the crystals *in vacuo* with a small quantity of degassed water caused an increase in the free radical content which grew during 1 hr. at room temperature. When sufficient water was added to dissolve the crystals completely at room temperature, and the solution was again frozen at liquid-oxygen temperature, no free-radical absorption could be detected. Part of the water was then evaporated into the side-arm until crystals separated. On freezing in liquid oxygen, a free-radical signal was again observed. On admittance of air the free radicals did not disappear until the mixture had stood for some time. The free-radical content of the anhydrous dithionite was also found to increase when wetted with ethyl alcohol.

The free radicals observed in the wetted anhydrous crystals were found to be quite stable in the absence of air and were observed after storage for several days at room temperature. The free-radical content was estimated to be approximately 6×10^{17} per gm., corresponding to the dissociation of about 0.01 per cent of the dithionite ions. This may not, however, represent the total quantity of free radicals present, owing to possible broadening of the absorption band in solution. It is not yet clear, therefore, whether the radicals are present only in the crystals or whether they are also present in the aqueous solution. It is possible that the radicals are stabilized by adsorption on the crystal surfaces³. Certainly no signal has so far been detected in those tests in which the crystals had completely dissolved.

The two most probable formulæ which have been suggested for the dithionite ion are $[O_3S.SO_2]^{2-}$ and $[OS.O.SO_2]^{2-}$. The second (mixed anhydride) formula is supported by chemical evidence⁴. Bassett and Durrant⁴ postulate the existence of two forms of the free acid, one corresponding to each of these ionic structures. The first form has a similar structure to that of the oxalate ion. From the results of an X-ray analysis of crystals of anhydrous sodium dithionite, Dunitz⁵ concludes that the dithionite ion can be regarded as a pair of SO_2^- units linked by a weak S—S bond, and he suggests that the SO_2^- radical occurs at least as a transitory species. The existence of SO_2^- radicals in aqueous solutions of dithionite has already been suggested⁶ to account for the polarographic behaviour of sodium dithionite in neutral or alkaline medium. The SO_2^- radical would be expected to act as a reducing agent, analogous to the oxalate radical, owing to the reaction $SO_2^- \rightarrow SO_2 + e$, as suggested by Dunitz⁵.

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¹ Ingram, D. J. E., Hodgson, W. G., Parker, C. A., and Rees, W. T. *Nature*, **176**, 1227 (1955).

² Parker, C. A., *Analyst* (in the press).

³ Bijl, D., Kainer, H., and Rose-Innes, A. C., *Nature*, **174**, 830 (1954).

⁴ Sidgwick, N. V., "The Chemical Elements and Their Compounds", 907 (Clarendon Press, Oxford, 1950). Bassett, H., and Durrant, R. G., *J. Chem. Soc.*, 1401 (1927).

⁵ Dunitz, J. D., *J. Amer. Chem. Soc.*, **78**, 878 (1956).

⁶ Furness, W., *Analyst* (in the press). Čermák, V., *Chem. Zvesti*, **8**, 714 (1954).

Moult Adaptation in Relation to Long-Distance Migration

Marshall and Serventy¹ have recently directed attention to moult adaptation in the short-tailed petrel, *Puffinus tenuirostris*, of Tasmanian waters. In this species post-nuptial head and body moult takes place in the breeding quarters while moult of tail- and wing-feathers is postponed until the bird has arrived at its northern non-breeding quarters. From this the authors decide that "from the data there emerges clear evidence of the evolution of a moult adaptation related to the migratory requirements of species that undergo a long post-