

The infra-red spectrum of the compound taken in nujol shows a carbonyl peak at 1980 cm.^{-1} . The crystals were found to be soluble in chloroform and nitrobenzene but were insoluble in water and alcohol. The substance is a non-electrolyte in nitrobenzene.

The tribromo compound $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Rh}(\text{CO})\text{Br}_3$ was prepared by treating the monobromo complex (0.24 gram) with the calculated quantity of bromine in chloroform at 0°C . The orange crystals (0.27 gram) could be isolated after evaporation under vacuum. Analysis of bromine and phosphorus gave a value of 26.41 and 6.73% respectively. Calculated values for the same in the tribromo complex require 26.78 and 6.92% respectively. The compound was soluble in chloroform and nitrobenzene and was a non-electrolyte in the latter.

The tribromo complex shows a carbonyl peak in the infra-red at 2110 cm.^{-1} . The occurrence of $\text{C}=\text{O}$ stretch in the infra-red at 1980 cm.^{-1} for the Rh(I) compound as compared to 2110 cm.^{-1} for the Rh(III) compound is similar to the observation made in the case of the corresponding chloro compounds.⁵ This suggests that the metal carbon bond in the Rh(I) complex is stronger than the one in the Rh(III) complex.

It is of interest to mention that earlier attempts to prepare such bromo complexes starting from $\text{L}_2\text{Rh}(\text{CO})\text{Cl}$ were not successful.⁶

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THE ELECTRON SPIN RESONANCE SPECTRUM OF GAMMA IRRADIATED SODIUM TETRATHIONATE

The authors have reported on the e.s.r. spectra of gamma irradiated thiosulphates.¹ It was

found to be of interest to record the electron resonance spectrum of sodium tetrathionate during a study of the effect of Co^{60} -gamma radiation on alkali tetrathionates.²

Sodium tetrathionate dihydrate, $\text{Na}_2\text{S}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$, was prepared by mixing c.p. grade sodium thiosulphate and iodine by the method given in Abegg's *Handbuch der Anorganischen Chemie*.³ The salt was purified by repeated precipitation from aqueous solution with 95% ethanol. The purity and composition of the final sample was carefully checked by (i) obtaining its infra-red spectrum,⁴ (ii) analyzing for tetrathionate content by the method of Goehring *et al.*,⁵ (iii) dehydration and (iv) conversion to sodium sulphate on heating to 600°C .

The irradiation source employed was a commercial unit "Gamma Cell 220 Co^{60} Irradiation Unit" manufactured by the Atomic Energy of Canada Ltd. The exposure dose was around 10^5 roentgens per hour. A Fricke dosimeter was used for measuring the dose absorbed by the samples.

A Varian Associates V-4500 E.P.R. Spectrometer was used for obtaining the e.s.r. spectrum of the irradiated samples. The unit is an X-band spectrometer with a nominal operating frequency of 9500 Mc./S. The experimental details are given elsewhere.¹ Electron spin concentrations were measured by graphical double integrations of the recorded spectra and comparison, through a substandard of gamma irradiated barium dichloroacetate, with solutions of D.P.P.H. in benzene.

The e.s.r. spectrum for the irradiated salt is shown in Fig. 1. The vertical line indicates the

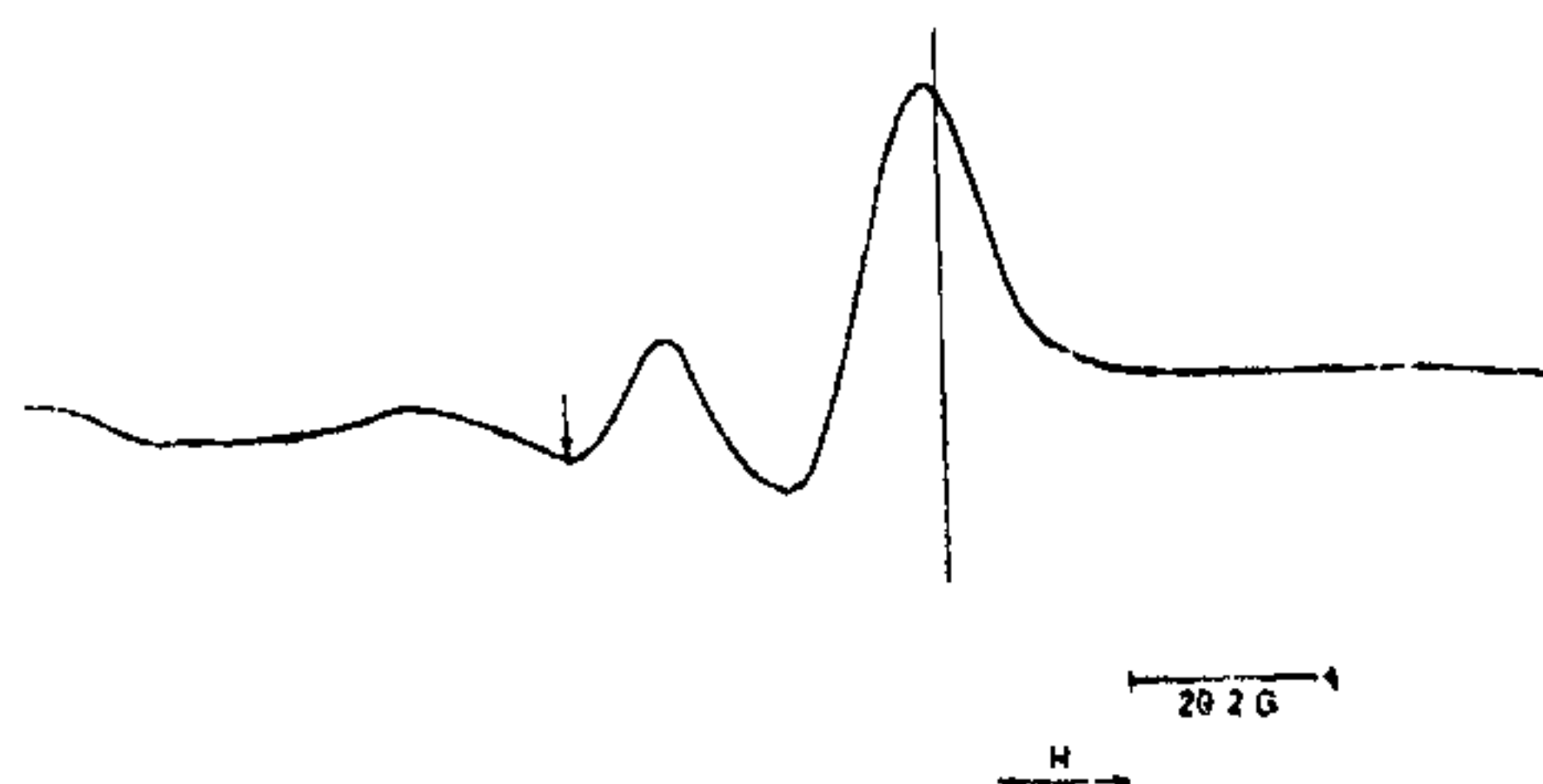


FIG. 1. Electron spin resonance spectrum of gamma-irradiated $\text{Na}_2\text{S}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ at room temperature. The vertical line indicates the position of the D.P.P.H. spectrum. The vertical arrow is at a g value of 2.024.

position of the D.P.P.H. spectrum. The magnetic field increases from left to right. The spectrum consists of a single absorption line with a low field structure and measures about 90 gauss. No hyperfine splitting was observed. The g value for the main cross-over point is 2.009. The

line width Δ_{ms} (the width between the points of maximum slope taken from the first derivative of the e.s.r. spectrum) is 13.1 gauss. The electron spin concentrations were found to increase at first with an increase in absorbed dose but became almost constant at higher doses. The maximum value observed was 6.8×10^{17} spins per gram of the irradiated salt for an absorbed dose of 5.7×10^{20} ev per gram.

The above results alone are not sufficient to make a positive identification of the radical (or radicals) responsible for the e.s.r. spectrum. By their observations on liquid sulphur and other sulphur compounds, Gardner and Fraenkel⁶ have made the tentative suggestion that polyatomic free radicals in which the odd electron is primarily associated with a sulphur atom would be expected to have a g value of about 2.02. However, if the odd electron is in a sulphur containing compound and is not primarily localized on a sulphur atom, the g value would be closer to the free spin value of 2.0023. The g value of 2.009 obtained for sodium tetrathionate has a considerable g shift from the free spin value. This could indicate that the unpaired electron is considerably involved with a sulphur atom in the free radical responsible for the spectrum. Further, the value is significantly higher than the g values reported for sodium dithionate⁷ and sodium dithionite,⁸ which could mean that the central line in the spectrum may not be due to SO_3 or SO_2^- radical ions.

The g factor calculated for the low field shoulder of the low field structure is 2.024. Spectroscopic splitting factors about 1% larger than the free electron spin g factor of 2.0023 have been reported in the e.s.r. spectra of sulphur dissolved in oleum⁹ and of chilled sulphur vapour.¹⁰ This is ascribed to spin orbit interactions and hence free radicals in which the odd electron is primarily involved with the sulphur atom could be responsible for this structure. Such a conclusion is supported by the observation that colloidal sulphur is produced when gamma irradiated tetrathionate is dissolved in water.²

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STUDIES ON THE USE OF 8-HYDROXY QUINOLINE AND SOME OF ITS DERIVATIVES AS REDOX INDICATORS

It has been observed that 8-hydroxy-quinoline and its derivatives, oxine-5-sulphonic acid and 7-iodo-oxine-5-sulphonic acid (ferron) undergo oxidation on adding cerium (IV) sulphate, to an almost colourless state through intermediate unstable red brown and red products respectively. If iron (II) is added to the solution of these oxidized substances while still the brown or red product is present, it is reduced back to the original oxine or its corresponding derivative, whereas if they are oxidized beyond the red stage, they cannot be reduced at all by adding iron (II). Thus the oxidation-reduction is reversible only up to the red stage. In this communication, the results of the studies on the use of these substances as redox indicators, based on the reversible nature of their oxidation, are recorded.

EXPERIMENTAL

Indicator Solutions.—0.005 M solutions of the oxine, oxine-5-sulphonic acid and ferron are prepared respectively by dissolving (1) 0.0725 gm. of oxine in 100 ml. 0.1 N sulphuric acid, (2) 0.1126 gm. of oxine-5-sulphonic acid in 100 ml. of warm distilled water and (3) 0.1756 gm. of ferron in 100 ml. of distilled water. 0.5 ml. of any of these indicator solutions is found adequate in titrations.

Cerium (IV) sulphate solution is prepared from a sample of (G.R., E. Merck) ceric ammonium sulphate by dissolving it in sulphuric acid and the solution is made up to the desired