SHORT COMMUNICATIONS

On the ESR Study of Quinquevalent Chromium Complexes

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(Received August 24, 1962)

The author has been interested in the four characteristic ESR lines observed at room temperature of the chromium(VI) oxide (or potassium bichromate) - concentrated sulfuric acid system. As is shown in Fig. 1, a very remarkable feature of the absorption is that all the four lines are very narrow (ca. 1∼5 gauss), even narrower than the Cr^{3+} absorption lines which can be observed at room temperature. Observations of the same solution doped with Cr^{3+} show that the narrow lines in question are definitely different from that of Cr^{3+}. Also, careful purifications of concentrated sulfuric acid and potassium bichromate do not alter the signal intensity and the number of lines. It is suspected, therefore, that the paramagnetic species responsible for the narrow absorption lines be some chromium oxides of intermediate valence state, the best possiblity being chromium(V) oxide.

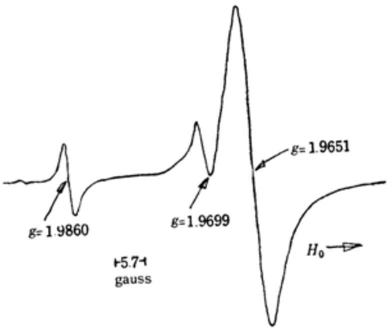

Fig. 1. ESR absorption of a CrO_3 - conc. H_2SO_4 solution. Observed *g*-value is accurate to ±0.0005.

The transition metal ions with one 3d electron (for example, Cr^{5+}, Ti^{3+}, etc.) usually show the electron spin resonance absorption which is so broad that the observation is sometimes prohibitively difficult, particularly at ambient temperatures. In fact, Ti^{3+} absorption was observed only at 4 to 8°K with remarkably anisotropic *g*-value and with very short relaxation time[1]. This is explained as due to the fact that the combined effect of the microcrystalline field and the spin orbit coupling is not so great as to lift the degeneracy of the ground spin orbitals very much and so, there is always an excited state fairly close to the lowest Kramer's doublet. A quinquevalent chromium compound was shown to behave in a similar fashion; its electron spin resonance was observed in CrO_4^{3-} at 20°K with very broad and temperature dependent absorption lines. Thus the assumption of quinquevalent chromium in chromium oxide-concentrated sulfuric acid system seems to be in conflict with the above consideration on the line width.

However, if the crystalline field perturbation would be greater and the deviation from the cubic symmetry extreme, then, there could be further decrease in the spin-lattice relaxation, and so the reduction in the ESR line width. In order to see if such is the case actually, a few complexes of quinquevalent chromium, such as K_2CrOCl_5, $HCrOCl_4X$ (where X is the base; pyridine, quinoline tetramethylamine) were prepared and their ESR absorption observed in solution and in polycrystalline form. If the structural unit of these compounds would be CrO^{3+}, the microcrystalline field symmetry would have a strong axial component and the line width could be smaller than in, for example, CrO_4^{3-}. A

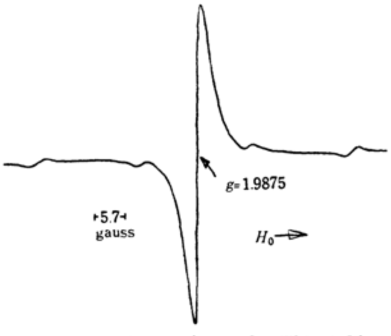

Fig. 2. ESR absorption of a $HCrOCl_4$-pyr. solution. The four satellites are the hyperfine components due to ^{53}Cr nucleus.

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[1] B. Bleaney and K. W. H. Stevens, *Rep. Prog. Phys.*, **16**, 108 (1953).

[2] A. Carrington, D. J. E. Ingram, D. Shonland and M. C. R. Symons, *J. Chem. Soc.*, **1956**, 4710.

typical solution spectrum shown in Fig. 2 indicates that this is the case at least in solution, and the peak to peak line width there, is only 2.7 ±0.2 gauss, a value much smaller than VO^{2+} which has an analogous structure. Though not conclusive, this result may lend a strong support to the assumption of chromium(V) existing in chromium(VI) oxide-concentrated sulfuric acid system. Several other ESR absorptions with even narrower line widths and with different *g*-values were also observed transiently during the course of the reaction of the chromium(VI) compounds with various acids (acetic, trifluroacetic, phosphoric, oxalic, lactic, citric, malonic acid and so on), and the paramagnetic species may be considered here again as some quinquevalent chromium oxyions.

Details of the result of these ESR observation will be published soon with the visible and infrared absorption data.

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