35. *Structure and Reactivity of the Oxyanions of Transition Metals. Part III.* The Hypochromate Ion.*

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In the absence of oxygen, aqueous solutions of potassium chromate containing potassium hydroxide in large concentration are slowly converted at high temperatures into green solutions which are shown by analysis to contain quinquevalent chromium. The optical absorption spectrum shows a broad peak at 625 mμ with a molar extinction coefficient of about 250, and another more intense band with a peak at 365 mμ. The reactivity and magnetic properties of these solutions are discussed.

IN Part I [1] it was shown that, provided protonation is avoided, both the manganate and the hypomanganate ion are extremely stable species. It therefore seemed surprising that the hypochromate ion, CrO_4^{3-}, is not normally found during the reduction of chromate solutions. This paper presents the results of attempts to prepare and study the hypochromate ion. Scholder [2] has already found that reactions such as :

$$Ba_3[Cr(OH)_6]_2 + Ba(OH)_2 \longrightarrow 2Ba_2CrO_4 + 6H_2O + H_2$$

and

$$2BaCrO_4 + BaCO_3 \longrightarrow Ba_3(CrO_4)_2 + CO_2 + \tfrac{1}{2}O_2$$

proceed in an atmosphere of nitrogen at about 1000°, the valency state of the chromium being determined by analysis and checked by magnetic susceptibility measurements, and the structure being determined by *X*-ray analysis.[3]

The ready reduction of permanganate to manganate by aqueous hydroxide is followed, provided the concentration of water is small, by the reduction of manganate to hypomanganate.[1] This simple procedure has three important features, namely, that protonation of the oxyanions is avoided, that the hydroxide ion, in the presence of small concentrations of water, is a powerful reducing agent, and that the other product of reaction, oxygen, can only be present in very small concentrations and hence neither interferes with analytical procedures nor reverses the reaction.

When solutions of potassium chromate in potassium hydroxide–water melts were heated in an atmosphere of nitrogen, oxygen was evolved and the colour changed from pale yellow to a clear, intense yellow-green. Analysis of these green solutions showed that the chromate had been reduced to a compound containing quinquevalent chromium, which, by comparison with other systems of this type, is almost certainly the hypochromate ion, CrO_4^{3-}. The analytical results are summarised in Table 1.

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* Part II, *J.*, 1956, 4710.

[1] Carrington and Symons, *J.*, 1956, 3373.

[2] Scholder, *Angew. Chem.*, 1954, **66**, 461.

[3] Klemm, *ibid.*, p. 468.

For ease of presentation of experimental procedures it will be assumed that the green solutions do in fact contain the hypochromate ion, which will be referred to as CrO_4^{3-}. When chromium is present in the tervalent form it will be referred to as Cr^{III}; under present conditions the ion obtained is probably $Cr(OH)_6^{3-}$.

EXPERIMENTAL

All reagents used were of " AnalaR " grade, and water was twice distilled from a concentrated alkaline solution of potassium permanganate.

Preparative Procedure.—A typical experiment was as follows: Potassium hydroxide (5 g.), water (1 g.), and potassium chromate (0·01—0·1 g.) were heated in a Pyrex-glass test-tube by means of a smoky flame for about 2 min. in an atmosphere of dry oxygen-free nitrogen. The resulting clear green solution solidified on cooling, to give an opaque emerald-green mass. When larger concentrations of potassium chromate were used the mass solidified before complete conversion into CrO_4^{3-} had occurred (Expt. No. 1, Table 1). If the concentration of chromium was of the order of 10^{-4}M the chromium was rapidly and irreversibly converted into a Cr^{III} compound, and it was impossible to arrest the reaction at the CrO_4^{3-} stage. However, when the reaction was carried out in a clear, fused-silica tube, reduction beyond the CrO_4^{3-} stage did not occur under any conditions. It is therefore considered that traces of iron dissolved from the Pyrex glass were instrumental in the reduction to Cr^{III}, rather than hydroxide ion. When potassium hydroxide was replaced by sodium hydroxide, a similar procedure to the above yielded no detectable CrO_4^{3-}. Marked differences between the two alkalis have already been observed in the reactions of the manganese oxy-ions.[1] Reduction to CrO_4^{3-} in experiments of the above type did not appear to be aided in any way by sodium azide or sodium sulphite as the presence of these substances in the melt did not shorten the time of heating required. Evidently the unhydrated hydroxyl ion in the fused alkali is itself as powerful a reducing agent as either of these substances.

Analytical Procedure.—The valency state of the chromium in the solidified mass resulting from this procedure was determined by estimating the oxidising power of such a mixture containing a known amount of chromium. If the whole of the CrO_4^{2-} originally present is converted into CrO_4^{3-}, the resulting solution should have two-thirds of its former oxidising power and titration figures will be two-thirds of those corresponding to the original amount of CrO_4^{2-}. Should disproportionation of the CrO_4^{3-} occur before titration this will evidently be without effect on results.

The mixture was analysed by one of the following procedures:

(*a*) The substance was dissolved in a known excess of acidified standard ferrous ammonium sulphate solution through which a stream of oxygen-free nitrogen continuously bubbled, and the remaining ferrous iron was back-titrated against standard dichromate. Typical results are given in Table 1 *A*.

TABLE 1. *Results of analyses on hypochromate solutions.*

A, Using ferrous ammonium sulphate. *B*, Using iodometric method.

A			*B*		Estimated valency	
Expt. no.	Approx. $[CrO_4^{2-}]$	Estimated valency	Expt. no.*	Time of heating	Uncorr.	Corr. for uptake of impurity from glass
1	1·4 × 10^{-1}M	5·47	4	½ min.	4·99	4·91
2	10^{-2}M	4·81	5	2 min.	5·05	4·97
3	1·4 × 10^{-2}M	5·08	6	5 min.	5·09	5·00

* In expts. 4, 5, and 6 the concentration of chromium was *ca.* 10^{-2}M.

(*b*) The substance was dissolved in an excess of potassium iodide solution in an atmosphere of nitrogen. The solution was acidified and the iodine liberated was titrated with a solution of sodium thiosulphate previously standardised against the original potassium chromate. Typical results are shown in column 6 of Table 1. Standardisation of the thiosulphate solution with potassium chromate previously heated in Pyrex glass in the presence of oxygen for 5 min. gave somewhat lower results (Table 1, column 7) because of uptake of iron and other impurities from the glass. Clearly, this correction should be applied for experiment 6 but not for experiment 4.

Absorption Spectra.—For spectrophotometric measurements it was essential to obtain clear transparent solutions of the substance. Solutions of CrO_4^{3-} which were fluid at room temperature proved unsatisfactory, as disproportionation to CrO_4^{2-} and Cr^{III} took place fairly rapidly. The compounds were accordingly studied in the form of clear alkali "glasses." Factors favouring "glass" formation were the addition of a small amount of sodium hydroxide to the potassium hydroxide before heating, and rapid cooling of the melt. Sodium borate was added in some cases as an aid to "glass" formation.

The absorption spectrum was measured between 300 and 1000 mμ, the instruments used being the Unicam SP 500 and SP 600. As "glasses" could not be prepared in the cells ordinarily used with these instruments the top of the test-tube containing the "glass" was cut off and the tube mounted in a specially designed carriage.

Variations in slit-width could easily lead to large errors, as the light falls on a curved surface. Accordingly a constant slit-width was used throughout. With the SP 500 this may be done simply by varying the sensitivity instead of the slit-width. However, the SP 600 has no sensitivity control and it was therefore necessary to adopt the following procedure. The slit-width was adjusted so that at no wavelength would a negative reading be obtained, and the reading on the optical-density scale was then taken for the required range of wavelengths without removal of the tube from the light path. This was done for the unknown and the control material, and the difference in reading gave directly the absorption of the solute. In this way the control readings could be obtained by using the original test tube, the CrO_4^{3-} glass having been replaced by potassium hydroxide solution. The effective cell length was estimated by measuring the spectrum of a 10^{-4}M-solution of potassium chromate in the tube. From the reading of optical density at the 373 mμ peak and the known value of $\varepsilon_{max.}$ at this peak the cell length was obtained. The concentration of chromium in the glass was thus found and values of extinction coefficients calculated. Owing to the experimental difficulties, values of $\varepsilon_{max.}$ obtained are somewhat inaccurate.

TABLE 2. *Details of the visible and ultraviolet absorption spectra of* CrO_4^{3-}, CrO_4^{2-}, *and* Cr^{III} *in alkaline solution.*

	1st band		2nd band	
Compound	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$	ε
CrO_4^{3-}	625 ± 5	250 ± 50	355 ± 5	500 ± 50
CrO_4^{2-}	373	4800	273	3688
Cr^{III}	595 ± 2	26·9 ± 0·2	430 ± 2	34·5 ± 0·2

Details of the two peaks observed are given in Table 2. Both bands, devoid of any fine structure, are extremely broad and thus the values recorded for the molar extinction coefficients at the peaks are not a true measure of the transition probabilities. This breadth could be a real characteristic of the CrO_4^{3-} ion or caused either by the distorting effect of the glassy medium or a general background opacity of the glass. However, measurements on a solution in aqueous potassium hydroxide, which was fluid at room temperature, although not precise because of continuous decomposition, showed conclusively that the first band is still very broad even in a clear, mobile solution, and thus it would seem that this breadth is probably a characteristic property of the CrO_4^{3-} ion.

At wavelengths shorter than 355 mμ the absorption of CrO_4^{3-} drops to a minimum at 340 and then rises rapidly to give an absorption greatly in excess of the value at 355 mμ. No further peak could be found before the absorption due to the alkali glass predominated.

Clear solutions of Cr^{III} were obtained by heating the appropriate amount of chrome alum with aqueous potassium hydroxide (8M). The optical absorption spectrum was measured, and the relevant details are recorded in Table 2, together with some details of the spectrum of CrO_4^{2-} in dilute alkaline solution.

Reactions of CrO_4^{3-}.—When a fused solution of CrO_4^{3-} was shaken with oxygen, oxidation rapidly occurred and the green colour changed to the pale yellow of CrO_4^{2-}. Analysis of a glass containing a known amount of chromium which had been so treated proved conclusively that the chromium was reconverted into CrO_4^{2-}.

When the concentration of alkali is reduced, the CrO_4^{3-} quickly disproportionates according to the equation $3Cr^{V} \longrightarrow 2Cr^{VI} + Cr^{III}$. Clear evidence of this was obtained when attempting to plot the spectrum of hypochromate in a solution which was fluid at room temperature. A hot solution of CrO_4^{3-} in potassium hydroxide was added to aqueous potassium hydroxide (8M) in an atmosphere of nitrogen, and the solution rapidly cooled in ice. The spectrum of the resulting green solution had a peak at 625 mμ, which quickly decreased in intensity, the reading at 625 mμ falling from 0·32 to 0·01 in 15 min. Meanwhile a new peak at 590 mμ appeared. After 1 hr. no further change was apparent, and the final spectrum was quantitatively identical with that obtained from an alkaline solution of CrO_4^{2-} and Cr^{III} in the molar ratio 2 : 1.

When solid sodium peroxide or an alkaline solution of hydrogen peroxide (Laporte's, unstabilised product) was added to fluid solutions of CrO_4^{3-} rapid oxidation to CrO_4^{2-} occurred, after which the peroxide was catalytically decomposed without further change.

The addition of sodium sulphite or sodium azide to the solutions had no effect, the spectrum being identical with that of CrO_4^{3-} even after prolonged refluxing with either reagent.

DISCUSSION

Whilst the analytical results can hardly be fortuitous, the green solutions postulated to contain hypochromate ion bear at least a superficial resemblance to solutions containing a mixture of chromate and chromic ions. Therefore, other evidence in accord with this postulate will now be discussed.

Magnetic Properties.—It has been found[4] that the strong paramagnetic resonance absorption of the green solutions observed at 20° K is no longer detectable at 90° K, whereas a similar glass containing Cr^{III} gives a broad, structureless absorption even at room temperature, as would be expected for an octahedral ion with three *d*-electrons. Since a tetrahedral oxyanion with one unpaired electron is expected on theoretical grounds to have a strongly temperature-dependent resonance absorption, and since other authentic examples, such as manganate, only show a detectable absorption at 20° K, it is concluded that the solutions studied contain the ion CrO_4^{3-} rather than a mixture of CrO_4^{2-} and $Cr(OH)_6^{3-}$. [The formulation $Cr(OH)_6^{3-}$ is used rather than the alternative $Cr(OH)_4^-$ since a d^3 ion of tetrahedral symmetry would be expected to have a strongly temperature-dependent resonance absorption.[4]]

Spectroscopic Evidence.—The results obtained from a study of the rapidly changing spectrum of a solution of the green compound in relatively dilute alkaline solutions not only show clearly that some new reactive species is present, but also that the original solution could not be simply a mixture of chromate and Cr^{III}. The final spectrum, which was identical with that of a synthetic mixture of chromate and Cr^{III} in the ratio 2 : 1, was quite different from that of the original green glass, not only in the position of the peaks, but particularly in the magnitudes of the absorptions.

It is remarkable that the first peak of the manganate absorption spectrum is only 2500 cm.$^{-1}$ away from that of the permanganate spectrum, whereas the energy difference between the first peaks of the isoelectronic chromate and hypochromate ions is 10,800 cm.$^{-1}$. However, analysis of the permanganate and chromate spectra made by Wolfberg and Helmholz[5] has been extended to include the manganate and the hypochromate ion,[6] and shows that, whilst the first transition for chromate should occur at shorter wavelengths than that of permanganate, the first transition for hypochromate should occur at somewhat longer wavelengths than that of manganate, as is found experimentally.

Reactivity.—On the assumption that the ion under investigation is hypochromate, the reactions studied may be represented by the equations :

$$(1)\quad 4CrO_4^{2-} + 4OH^- \rightleftharpoons 4CrO_4^{3-} + 2H_2O + O_2$$

$$(2)\quad 3CrO_4^{3-} + 4H_2O \rightleftharpoons 2CrO_4^{2-} + Cr(OH)_6^{3-} + 2OH^-$$

$$(3)\quad 2CrO_4^{2-} + HO_2^- + OH^- \longrightarrow 2CrO_4^{3-} + H_2O + O_2$$

$$(4)\quad 2CrO_4^{3-} + HO_2^- + H_2O \longrightarrow 2CrO_4^{2-} + 3OH^-$$

Reaction (1) proceeds in the forward direction only at high temperatures, with $[OH^-]$ large and $[H_2O]$ and $[O_2]$ small. The reverse reaction is rapid when oxygen is in excess.

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[4] Carrington, Ingram, Schonland, and Symons, *J.*, 1956, 4710.

[5] Wolfsberg and Helmholz, *J. Chem. Phys.*, 1952, **20**, 837.

[6] Carrington, Schonland, and Symons, unpublished results.

Reaction (2) occurs only when [H_2O] is relatively large. Probably a Cr^{IV} compound is formed in small concentration but all attempts to detect such an intermediate have failed. Reactions (3) and (4) together constitute a possible route for the catalytic decomposition of the hydroperoxide ion by chromate ion in alkaline solution. Since hypochromate is immediately oxidised to chromate, reaction (4) must be much faster than reaction (3).

From a consideration of the free energies of formation of the compounds other than hypochromate in the above reactions,[7] and reasonable values for the free energies of the reactions, a very approximate value of -179 kcal. mole^{-1} may be calculated for the free energy of formation of the hypochromate ion. That this value is reasonable may be seen by making a comparison with the values for the free energies of formation of the manganese oxy-anions recorded in Part I.[1] From the value $-44{\cdot}5$ cal./deg. for the entropy of the ion, calculated by use of the formula given by Connick and Powell,[8] the heat of formation of the ion is found to be approximately -237 kcal. mole^{-1}.

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[7] Latimer, " Oxidation Potentials," Prentice-Hall Inc., New York, 1952.

[8] Connick and Powell, *J. Chem. Phys.*, 1953, **21**, 2206.