410. *The Oxidation of Chromous Perchlorate Solutions by Molecular Oxygen.*

By Michael Ardon and Gabriel Stein.

Oxidation by molecular oxygen of chromous perchlorate solutions results in the primary formation of oxygen-bridged chromic complexes.

The kinetics of oxidation by molecular oxygen in aqueous solutions [1, 2] have been discussed with reference to the mechanism suggested by Weiss.[3] On the other hand investigations on the role of atom and group transfer in the mechanism of ionic oxidations in solutions [4] have renewed interest in the structure of stable complexes formed on oxidation of chromous salts. The present observations are relevant to both subjects.

When chromous perchlorate solutions prepared by Taube and Myers's method [4] are oxidised by, *e.g.*, hydrogen peroxide in 0·1N-perchloric acid, the blue solution of $Cr(H_2O)_6{}^{3+}$ is obtained, as described by them. The spectrum of such a solution is shown in curve *A*. This oxidised form is obtained also with other oxidising agents, *e.g.*, chromate. If however the solution of chromous perchlorate (2×10^{-2} to 1M) is oxidised in a very rapid reaction with molecular oxygen a green solution is obtained the spectrum of which is shown in curve *B*. The spectrum of the green solution changes on warming and approaches that shown in curve *A*.

The difference between the two solutions is likely to be due to the formation of oxygen-bridged chromic complexes. Lottermoser *et al.*[5] have reported the formation of a green solution when chromium(III) nitrate solutions were treated with only one equivalent of sodium hydroxide and then warmed at 50° for 160 hours. To their hydrolysis product they attribute structure (I). Their product is not readily converted into $Cr(H_2O)_6{}^{3+}$ even in N-acid. When we repeated their preparation we obtained the spectrum shown in curve *C*. The two products are thus similar. Both are precipitated by ammonia and on re-dissolution in cold N-perchloric acid give the green solutions again.

The solution obtained by oxidation with oxygen contains all the chromium in the tervalent form. Chloride ions were not formed in the process. Thus the product can only be a hydrolysis product containing chromium(III). This was supported by measurement of the conductance of solutions containing initially the same concentration of Cr^{2+} and finally the same concentration of Cr^{III}, prepared by means of hydrogen peroxide

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[1] George, *J.*, 1954, 4349.

[2] Cher and Davidson, *J. Amer. Chem. Soc.*, 1955, **77**, 793.

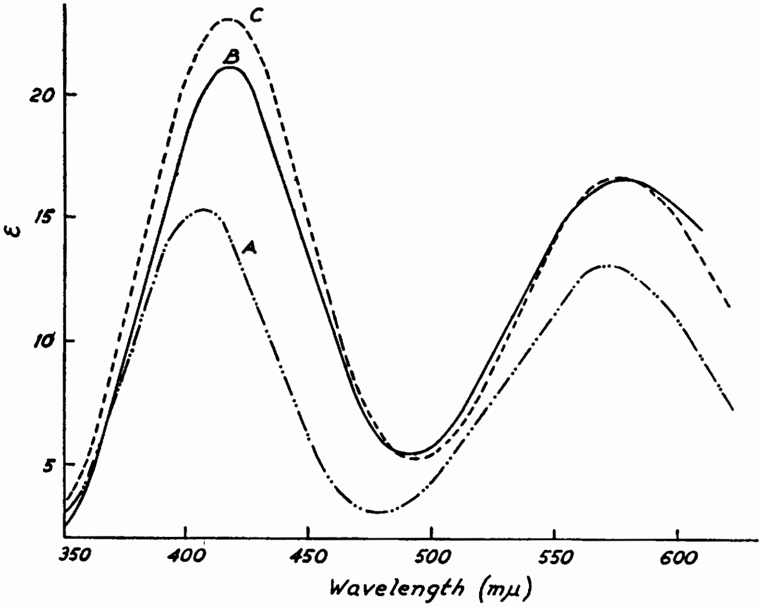
[3] Weiss, *Naturwiss.*, 1935, **23**, 64; *Experientia*, 1953, **9**, 61.

[4] Taube and Myers, *J. Amer. Chem. Soc.*, 1954, **76**, 2103.

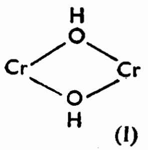
[5] Lottermoser, Schmied, and Peh Chuan Chi, FIAT Reports, Part III, p. 199.

and oxygen respectively. The green solutions produced by oxygen have a higher conductivity than the blue ones produced by peroxide. This is due to the higher concentration of H^+ ions remaining in solution after the process, $2Cr^{2+} + \frac{1}{2}O_2 \longrightarrow [Cr{-}O{-}Cr]^{4+}$, than after $2Cr^{2+} + H_2O_2 + 2H^+ \longrightarrow 2Cr^{3+} + 2H_2O$. The product is however not $Cr(OH)^{2+}$ or $Cr(OH)_2{}^+$ since these are in ready equilibrium with and are immediately convertible into $Cr(H_2O)_6{}^{3+}$ in 0·1N-perchloric acid. On the other hand, polynuclear complexes of the type $[Cr{-}O{-}Cr]^{4+}$ or (I) are known not to attain such equilibria rapidly and may exist for some time in strong acid solution.[6] The presumably binuclear product obtained by oxidation with oxygen from the chromous state is thus related to those obtained from chromic salts by prolonged hydrolysis.

Absorption spectra of chromic solutions.



A, Produced from chromous perchlorate solutions by H_2O_2.
B, Produced from chromous perchlorate solutions by O_2.
C, Produced from chromic perchlorate solutions by prolonged hydrolysis.



(I)

These considerations require that bridged complexes should not be formed in oxidation by hydrogen peroxide, *e.g.*, $Cr^{2+} + H_2O_2 \longrightarrow [CrOH]^{2+} + OH$ (in a mechanism similar to that postulated for the ferrous ion). The autoxidation of Cr^{2+} would however involve the formation of oxygen-bridged products and necessarily also the intermediate formation of labile peroxides, *e.g.*, $Cr^{2+} + O_2 \longrightarrow [Cr{-}O{-}O]^{2+}$. These could of course immediately react with the excess of Cr^{2+} present.

If however another suitable acceptor is present this may compete with Cr^{2+}. Indeed it has been observed [7] that autoxidation of chromous salts is capable of inducing oxidation of arsenious solutions to arsenate, otherwise not brought about by oxygen. The transient formation of a labile peroxide was also postulated by Piccard.[7] Our results explain also his finding that the formation of the labile peroxide is prevented by the presence of hydrogen peroxide in the solution.

The importance of metastable, oxygen-bridged, polynuclear forms for ceric ions was shown in another investigation.[8] For ferric ions a binuclear complex was also shown to play a role.[9]

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[6] Hall and Eyring, *J. Amer. Chem. Soc.*, 1950, **72**, 782.
[7] Piccard, *Ber.*, 1913, **46**, 2477.
[8] Ardon and Stein, *J.*, 1956, 104.
[9] Mulay and Selwood, *J. Amer. Chem. Soc.*, 1955, **77**, 2693.

EXPERIMENTAL

Chromic perchlorate solutions were prepared from " AnalaR " potassium dichromate by reduction with hydrogen peroxide in the presence of perchloric acid. From this solution chromous perchlorate was prepared by reduction with zinc amalgam,[4] in the absence of oxygen, the solution being flushed with purified nitrogen. Triple-distilled water was used throughout.

Optical density was measured with a Beckman B spectrophotometer, conductance with a Mullard conductance bridge and pH with a Beckman G meter.

The product of oxidation by oxygen showed a resistance of 270 Ω; under identical conditions the product of oxidation by peroxide showed a resistance of 312 Ω. The increase in conductivity of approx. 16% may be compared with our calculated approximate value of 18·8%, which is obtained if a structure $[Cr-O-Cr]^{4+}$ is assumed having an equivalent conductance of 53. Similarly, pH measurements gave differences which agreed approximately with the values calculated on the basis of the reactions above. Further support is given by measurements of conductivity in which the original chromous solutions (in the absence of oxygen) were compared with the two chromic solutions. Oxidation by peroxide decreased the conductivity whilst that by oxygen did not affect it appreciably. This would occur if the equivalent conductance of, *e.g.*, $[Cr-O-Cr]^{4+}$ is not appreciably different from that of Cr^{2+}. To ascertain whether Zn^{2+} ions which enter the solution in the reduction process affect the results, control experiments were carried out, in which the solution was reduced electrolytically at lead cathodes. The results were identical.

Qualitative experiments with chromous chloride and chromous sulphate solutions indicate that here too the product of oxidation by oxygen is an oxygen-bridged complex, since precipitation with ammonia and re-solution yields similar green solutions.

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