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Oxidation of Chromium(II) Amines by Water

AN interest in reactive reducing agents has led us to investigate aqueous solutions of chromium(II) containing excess of polyamines. We have observed that, in the absence of oxygen, these deep blue solutions ($pH > 9$) evolve hydrogen in accordance with the reaction:

Although the reaction is quite slow when the amine is ethylenediamine or diethylenetriamine¹, with purified triethylenetetramine or *tris*(β -aminoethyl)amine² the reaction is sufficiently rapid to be studied conveniently. It is apparently autocatalytic with excess of the linear tetramine, and first-order in chromium(II) when the branched amine is present.

Hydrogen evolution from rapidly stirred solutions of chromium(II) perchlorate (0.02 – $0.05 M$) in $0.3 M$ *tris*(β -aminoethyl)amine ($\mu = 1.2$) was followed manometrically; it exhibited a strong dependence on pH . At 25° , the first-order rate constant was a maximum near pH 11 ($4 \times 10^{-4} \text{ sec.}^{-1}$) and lower by a factor of 10 at pH 9.5. No reaction was observable near pH 13. When all exchangeable hydrogen in reactants and solvent was replaced by deuterium, the rate constant was slightly decreased (1.0×10^{-4} to $1.3 \times 10^{-4} \text{ sec.}^{-1}$ at a glass electrode pH of 10.3). In isotopically normal media saturated with deuterium gas, the reaction did not yield measurable amounts of HD .

The other product of oxidation of chromium(II) by *tris*(β -aminoethyl)amine solutions, a violet chromium(III) complex, was subjected to chromatographic analysis on a column of 'Dowex 50×8 ' cation exchanger. Although it was slowly displaced as a single band by $0.01 M$ barium hydroxide, the complex could not be eluted by $0.01 N$ sodium hydroxide or, on the acid side, by N perchloric acid or $0.02 M$ lanthanum perchlorate in $0.01 N$ perchloric acid. This behaviour suggested that the oxidized chromium was bound as a binuclear complex carrying a charge of +4 or more in acidic solution³, until it was determined that *cis*-diaquobisethylenediamine cobalt(III) ion behaved similarly. The complex itself was isolated as the chloride by evaporation of the barium hydroxide eluate after precipitation of barium as the carbonate and subsequent acidification. This product had the same visible absorption spectrum as the reaction mixtures at complete reaction, maxima at 537 and 402 $m\mu$, and gave chromium and nitrogen

analyses indicating a ratio of chromium to *tris*(β -aminoethyl)amine of 1. The analytical results were not sufficiently precise to allow determination of a complete formula.

Although the observations detailed above do not suggest or rule out a mechanism for hydrogen evolution from aqueous chromium(II)-polyamine solutions, they are reported here since such evolution from homogeneous solution is uncommon.

A related observation, that chromium(II) added to a solution of *tris*(β -aminoethylamine) containing excess acrylamide is instantly oxidized to a complex different from that described, is still being investigated.

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Polarographic Behaviour of Chromium-Dipyridyl Complexes

It has been shown previously that dipyridyl (dipy) complexes of cobalt and nickel are reduced at the dropping-mercury electrode with the formation of uni- and zero-valent complexes, respectively^{1,2}. Further work led to the conclusion that iron(II)-dipyridyl complex is not reduced at the dropping mercury electrode and that the complex $Mn(dipy)_2^{2+}$ is reduced with the formation of manganese(I) complex (unpublished results).

The complex $Cr(dipy)_3^{3+}$, prepared by Hein and Herzog's method³, is reduced at the dropping-mercury electrode in three waves, the ratio of which is 1 : 1 : 1. The comparison with the wave-height of the complex $Cr(NH_3)_6^{3+}$ has shown that each of the waves of $Cr(dipy)_3^{3+}$ corresponds to the acceptance of one electron for each particle of the complex. In aqueous $0.5 M$ sodium chloride solution, the slope of the first wave is identical with that of a reversible one-electron wave. The second wave, on the other hand, has a discontinuous character and the third one is drawn out (Fig. 1). In a solution of lithium chloride in 50 per cent ethanol, the first and second waves have the shape of a reversible one-electron wave, but the third one shows a sharp beginning. Furthermore, a very small adsorption wave is observed in ethanolic solutions almost at the same potential as that at which the discontinuous wave in aqueous solution appears (Fig. 1). The half-wave potentials (measured against the saturated calomel electrode) are summarized in Table 1.

Table 1. HALF-WAVE POTENTIALS OF THE WAVES OF $Cr(dipy)_3^{3+}$ (V., $20^\circ C$.)

Solution	First wave	Second wave	Third wave
0.5 M Sodium chloride, water	-0.36	-0.73*	-1.38
0.5 M Lithium chloride, 50 per cent ethanol	-0.36	-0.71†, -0.895	-1.35*

* Discontinuous wave.

† Adsorption wave.