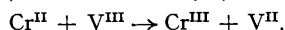


## The Chromium(II) Reduction of Vanadium(III) in Aqueous Perchloric Acid Solutions

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THE recent paper by Espenson<sup>1</sup> on the reaction of chromium(II) with vanadium(III),



at ionic strength  $\mu = 0.5\text{M}$ , has coincided with a similar but less complete study of this reaction in these laboratories at  $\mu = 2.0\text{M}$ . In the mechanism proposed by Espenson it is surprising that a path involving hydrolysed species, (*i.e.* the reaction of  $\text{Cr}^{2+}$  with  $\text{VOH}^{2+}$ ), is not effective. A closer look at his results at  $25^\circ$  has shown that there is in fact ample evidence for such a path.

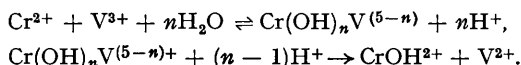
The reaction is first order in both reactants

$$d[\text{Cr}^{\text{III}}]/dt = k_{\text{obs}}[\text{Cr}^{\text{II}}][\text{V}^{\text{III}}],$$

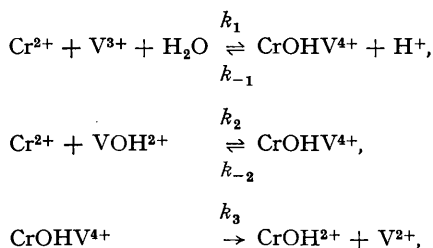
and from the hydrogen-ion dependence of  $k_{\text{obs}}$  details concerning the mechanism of the reaction can be inferred. Espenson believed the hydrogen-ion dependence to be of the form

$$k_{\text{obs}} = q/(r + [\text{H}^+]),$$

and in agreement with this proposed the mechanism



In these equations  $n$  is almost certainly 1 or 2 and the binuclear intermediate either  $\text{CrOHV}^{4+}$  or  $\text{Cr}(\text{OH})_2\text{V}^{3+}$ , where the latter can be written in the simpler form  $\text{CrOV}^{3+}$ . For convenience a value of  $n = 1$  has been assumed. With the inclusion of the further reaction between  $\text{Cr}^{2+}$  and  $\text{VOH}^{2+}$  the mechanism becomes



and assuming stationary-state kinetics for the binuclear intermediate  $\text{CrOHV}^{4+}$  it can be shown that

$$k_{\text{obs}} = \frac{k_1 k_3 + k_2 k_3 K_{\text{H}} [\text{H}^+]^{-1}}{k_{-2} + k_3 + k_{-1} [\text{H}^+]}$$

where  $K_{\text{H}}$  is the hydrolysis constant for  $\text{V}^{3+}$ . An identical expression is obtained here if the binuclear intermediate  $\text{CrOV}^{3+}$  and not  $\text{CrOHV}^{4+}$  is formed, *i.e.* with a value  $n = 2$  *etc.* The above expression may be written in the form

$$k_{\text{obs}}(c + [\text{H}^+]) = a + b[\text{H}^+]^{-1},$$

and assuming different values for  $c$  the left-hand side of the equation can be plotted against  $[\text{H}^+]^{-1}$ , (Figure 1). This equation corresponds to that used by Espenson if  $a = q$ ,  $b = 0$  and  $c = r$ . Thus a plot of the data at  $25^\circ$  with  $c = 0.108$  should give a straight line parallel to the  $[\text{H}^+]^{-1}$  axis. With two exceptions however it can be seen that the points lie on a smooth curve. A

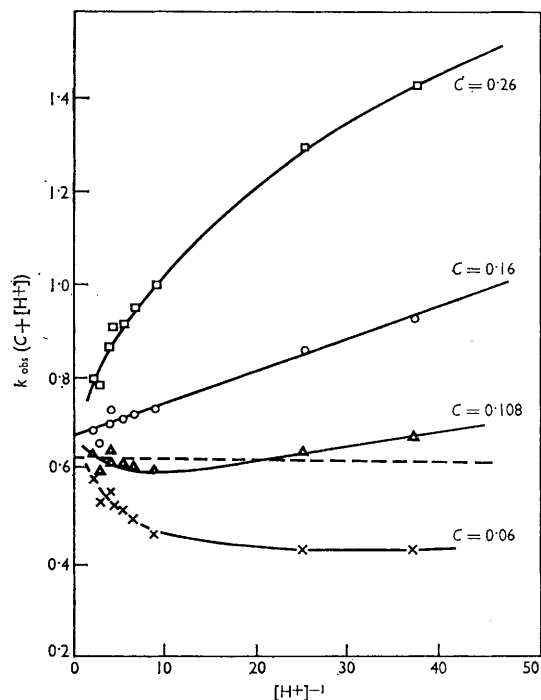


FIGURE 1.

The line  $c = 0.160 \text{ l.}^{-1} \text{ mole}$  is a better fit of experimental data than the horizontal (broken line) for  $c = 0.108 \text{ l.}^{-1} \text{ mole}$ .

<sup>1</sup> J. H. Espenson, *Inorg. Chem.*, 1965, 4, 1025.

linear plot is in fact obtained with  $c = 0.160$  l.<sup>-1</sup> mole, when  $a = 0.67$  sec.<sup>-1</sup> and  $b = 0.0073$  l.<sup>-1</sup> mole sec.<sup>-1</sup> (the latter using the literature value of  $K_H = 0.002$  l.<sup>-1</sup> mole).<sup>2</sup> It is concluded that the equation  $k_{\text{obs}} = q/(r + [H^+])$  does not provide an adequate fit of the experimental data, and that the further reaction of Cr<sup>2+</sup> with VOH<sup>2+</sup> is required to explain satisfactorily the variation of  $k_{\text{obs}}$  with  $[H^+]$ . Individual rate constants cannot be obtained from this treatment. From the ratio of  $b$  to  $a$ , a value of  $k_2/k_1 = 5.4$  is obtained, which is considerably less than values generally observed for such reactions.

Formation of a binuclear intermediate is particularly favourable in this instance because both the product ions have  $t_{2g}^3$  electronic configurations. The substitution-inert properties of hexaquo-chromium(III) are well known, but (2+)-ions are generally more labile. Thus while vanadium(II) is the most inert of the first-transition-series

(2+)-ions, characteristic rates of substitution<sup>3</sup> are believed to be of the order 10<sup>4</sup> sec.<sup>-1</sup>. The mechanism found here is of significance since it raises again the question as to whether reactions between hexaquo-ions are in fact by an outer-sphere electron-tunnelling mechanism. If in the above inner-sphere mechanism  $k_1$ ,  $k_2$ , and  $k_3$  are much bigger than  $k_{-1}$  and  $k_{-2}$  (which could well be the case with other reactants), then the expression for  $k_{\text{obs}}$  reduces to the more usual form

$$k_{\text{obs}} = k_1 + k_2 K_H [H^+]^{-1}.$$

As is to be expected rate constants at 25° and  $\mu = 2.0M$  are somewhat bigger than corresponding values at  $\mu = 0.5M$ . Thus at hydrogen-ion concentrations 0.395, 0.48, 1.08, and 1.82 experimental values of  $k_{\text{obs}}$  are 1.91, 1.63, 0.82, and 0.54 l. mole<sup>-1</sup> sec.<sup>-1</sup> respectively.

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<sup>2</sup> S. C. Furman and C. S. Garner, *J. Amer. Chem. Soc.*, 1950, **72**, 1785.

<sup>3</sup> M. Eigen, "Seventh Conference on Co-ordination Chemistry," Butterworths, London, 1963, p. 105.