Kinetics of Hydroxylamine Reduction by Bivalent Chromium

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The results of kinetic study of hydroxylamine reduction by bivalent chromium are described. The reaction is one of the first order with respect to the bivalent chromium concentration as well as to hydroxylamine concentration. The rate constant does not depend on the concentration of hydrogen ions. In the presence of chloride ions the reaction rate increases what may be explained by the formation of Cr(II) complexes with chloride ions which react with hydroxylamine faster than Cr(II) hexa-aquo complexes. By using the Eyring equation the kinetic thermodynamic quantities have been determined: $\Delta H^{\neq} = 11.0$ kcal mole^{-1} and $\Delta S^{\neq} = -30.1$ cal deg^{-1} mole^{-1} at ionic strength 1.3. On the basis of kinetic data obtained by polarographic method the probable reaction mechanism is discussed.

A considerable attention has been paid to the kinetics of reduction of transition metal cations by bivalent chromium [1—3]. Less papers deal with the reactions of Cr(II) with neutral molecules. Recently *Schmidt, Swinehart,* and *Taube* [4] have described the oxidation of Cr(II) with hydroxylamine and some other N-oxides. Since the resulting Cr(III) complexes are stable with respect to substitution the authors [4] have used the spectrophotometric determination of resulting tervalent chromium concentration to follow the reaction. They have found that the reaction is one of the first order with respect to the Cr(II) concentration as well as to the concentration of oxidizing agent.

The kinetics of hydroxylamine and hydrazine reduction by bivalent chromium has also been investigated by *Wells* and *Salam* [5] who have found the rate constants to be of the values $k = 1.00$ l mole^{-1} s^{-1} for the hydroxylamine reduction and $k = 1.3$ l mole^{-1} s^{-1} for hydrazine reduction, respectively, these values being valid for ionic strength 1.0 at 25°C. On the other hand, according to the paper [4] the value of the bimolecular rate constant of the reaction between Cr(II) and hydroxylamine is $k = 1.4 \times 10^{-2}$ l mole^{-1} s^{-1} at 25°C for ionic strength 1.3. After 24 hours, they have observed no reaction between Cr(II) and hydrazine at 25°C. The authors of both papers [4, 5] agree that the rate constant does not depend on hydrogen ion concentration in the investigated region.

These discrepancies between the rate constants which exceed experimental errors have stimulated us to investigate the kinetics of the hydroxylamine reduction by bivalent chromium and for this purpose we have employed the polarographic method.

Experimental

The kinetics of the hydroxylamine reduction by bivalent chromium in the medium of perchloric acid was followed polarographically by recording the time dependence of the limiting diffusion current of bivalent chromium at the potential of -0.2 V against a normal calomel electrode. It was the polarograph LP 55A which was used in connection with the electron-tube recorder EZ-2. The Kalousek vessel equipped with a water thermostatic jacket was applied as a reaction vessel. The temperature control of reaction vessel was performed by means of a ultrathermostat U 10. A thorough removal of oxygen from solutions as well as the mixing of reaction mixture before recording were achieved by a stream of nitrogen bubbling up through the solution. The nitrogen from electric bulb industry was purified before using by bubbling through a solution of bivalent chromium.

Hydroxylamine was used in a considerable excess so that the rate constants of the reaction under investigation have been evaluated by using the kinetic equation of the first order reaction:

$$\log \frac{i_0}{i} = \frac{k_M}{2.3}\,t,$$

where i_0 and i being the heights of the limiting diffusion current corresponding to $t = 0$ or t, respectively, and k_M denoting the rate constant. This rate constant belongs to a pseudo-first order reaction and equals the product of the second order reaction rate constant k_B with hydroxylamine concentration. The accuracy of an individual rate constant determination was $\pm 5\%$.

The solutions were prepared of analytical grade chemicals and of distilled water. The solution containing bivalent chromium was prepared by dissolving electrolytically purified chromium in 4 M solution of perchloric acid after the initial removal of oxygen. Before this dissolution the metallic chromium was activated in 6 M hydrochloric acid. The concentration of bivalent chromium was determined spectrophotometrically and later it was determined polarographically because it was proved that the height of the limiting diffusion current of chromium(II) ions was proportional to their concentration. It was found that the anodic limiting diffusion current corresponding to the electro-oxidation of Cr(II) to Cr(III) did not change with time in the absence of hydroxylamine and that at the potential of -0.2 V against a normal calomel electrode the Cr(II) ions only gave rise to the limiting diffusion current in the system containing all reacting substances as well as products.

Results and Discussion

The order of the studied reaction with respect to the concentration of Cr(II) ions has been determined by differential method on the basis of time dependence of the anodic diffusion current as well as by integral method by plotting the relationship
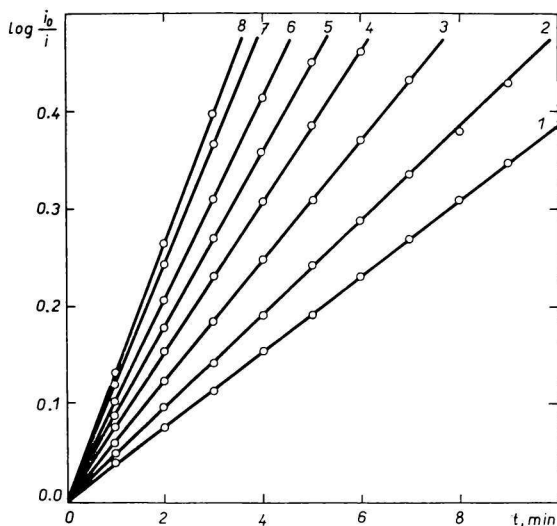
$$\log \frac{i_0}{i} = f(t).$$

Fig. 1. The proof of the first order reaction with respect to the Cr(II) concentration for the reduction of hydroxylamine by Cr(II).

5×10^{-3} M-Cr(II), 0.4 M-HClO$_4$.

Concentration of hydroxylamine: *1.* 0.08 M; *2.* 0.1 M; *3.* 0.125 M; *4.* 0.15 M; *5.* 0.175 M; *6.* 0.2 M; *7.* 0.225 M; *8.* 0.25 M.

Temperature 30°C.

The linear character of this relationship demonstrates that the reaction is one of the first order with respect to the concentration of Cr(II) ions (Fig. 1). The rate constant for the reaction of pseudo-first order k_M is proportional to the hydroxylamine concentration what means that the reaction is one of the first order with respect to hydroxylamine concentration too.

Thus the kinetic equation is given by

$$-\frac{\mathrm{d}\,[\mathrm{Cr(II)}]}{\mathrm{d}t} = k_B\,[\mathrm{Cr(II)}]\,[\text{hydroxylamine}]. \qquad (1)$$

The rate constant of this reaction does not depend on the concentration of hydrogen ions over the concentration range 0.4—3.6 M-HClO$_4$ at 25°C and at ionic strength 3.7. It suggests a low value of the hydrolysis constant for a Cr(H$_2$O)$_5$OH$^+$ complex formation [5].

The effect of ionic strength on the value of rate constant and activation parameters is presented in Table 1.

Moreover, the relationship between the rate constant and the concentration of chloride ions has been investigated for constant ionic strength. The rate constant increases with chloride ions concentration approximately up to the 1 M concentration of chloride ions according to the relationship

$$k_{\text{obs.}} = k_0 + k_{\text{Cl}} \cdot [\text{Cl}^-], \qquad (2)$$

where $k_0 = 1.52 \times 10^{-2}$ l mole^{-1} s^{-1} and $k_{\text{Cl}^-} = 3 \times 10^{-3}$ l^2 mole^{-2} s^{-1} at 25°C for ionic strength 3.7.

Effect of ionic strength on the kinetic parameters

Ionic strength	k (25°C) $[\text{l mole}^{-1} \text{s}^{-1}]$	$\Delta H^{\neq}$ $[\text{kcal mole}^{-1}]$	$\Delta S^{\neq}$ $[\text{cal deg}^{-1} \text{mole}^{-1}]$
1.3	1.33×10^{-2}	11.0 ± 0.4	-30.1 ± 1.5
3.7	1.60×10^{-2}	12.4 ± 0.5	-25.4 ± 1.5

Further increase in chloride ions concentration brings about a rise in reaction rate which is, however, less than it ought to be according the equation (2). But the reaction order does not change with it. The rate constant grows up to a definite limiting value k_1 (Table 2).

According to the paper [5] this relationship should be interpreted by the CrCl⁺ complex formation which reacts with hydroxylamine faster than the Cr(II) aquo--complex. The classification of coordination compounds according to *Taube* involves that the Cr(II) aquo-complexes belong into the group of complexes which are labil with respect to substitution. Thus the substitution for the molecule of water linked by coordination bond proceeds quickly and both aquo- and chloro-complex containing Cr(II) react with hydroxylamine. The limiting value of the rate constant k_1 corresponds to the reaction rate of Cr(II) chloro-complex with hydroxylamine. It follows that

$$\text{Cr}^{2+} + \text{hydroxylamine} \xrightarrow{k_0} k \quad \text{products,} \qquad (A)$$

$$\text{CrCl}^+ + \text{hydroxylamine} \xrightarrow{k_1} k_1 \quad \text{products,} \qquad (B)$$
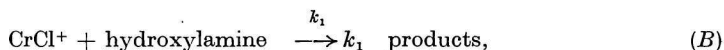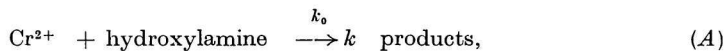
where $k_1 > k_0$.

Table 2

Effect of the chloride ions concentration on the rate constant

No.	$[\text{Cl}^-]$ $[\text{mole l}^{-1}]$	$k_{\text{obs.}} \cdot 10^2$ $[\text{l mole}^{-1} \text{s}^{-1}]$
1	0.1	1.59
2	0.3	1.69
3	0.5	1.72
4	0.9	1.80
5	1.3	1.93
6	1.7	2.02
7	2.1	2.12
8	2.5	2.17
9	2.9	2.22
10	3.1	2.24
11	3.3	2.26

5×10^{-3} M-Cr(II), 0.1 M-NH₂OH · HCl, 0.4 M-HClO₄, 25°C, ionic strength 3.7.

$CrCl^+$ is formed in a fast and in chemical sense reversible reaction

$$Cr^{2+} + Cl^- \overset{K}{\rightleftarrows} CrCl^+. \qquad (C)$$

The over-all concentration of bivalent chromium is

$$[Cr(II)] = [Cr^{2+}] + [CrCl^+]. \qquad (3)$$

By expressing $[CrCl^+]$ in terms of chemical equation (C) we get

$$[Cr(II)] = [Cr^{2+}] + K\,[Cr^{2+}]\,[Cl^-]. \qquad (4)$$

After rearranging (4)

$$[Cr^{2+}] = \frac{[Cr(II)]}{1 + K\,[Cl^-]}. \qquad (5)$$

According to the chemical equations (A) and (B) the reaction rate is

$$-\frac{d\,[Cr(II)]}{dt} = k_0\,[Cr^{2+}]\,[\text{hydroxylamine}] + k_1\,[CrCl^+]\,[\text{hydroxylamine}]. \qquad (6)$$

By substituting for $[Cr^{2+}]$ from equation (5) and for $[CrCl^+]$ from equation (C) we get

$$-\frac{d\,[Cr(II)]}{dt} = \frac{k_0\,[Cr(II)]\,[\text{hydroxylamine}] + k_1\,K\,[Cr(II)]\,[\text{hydroxylamine}]\,[Cl^-]}{1 + K\,[Cl^-]}. \qquad (7)$$

By comparing the equations (1) and (7) we get the final expression for the relationship between the observed rate constant and chloride ion concentration

$$k_{obs.} = \frac{k_0 + k_1\,K\,[Cl^-]}{1 + K\,[Cl^-]}, \qquad (8)$$

where $k_{obs.}$, k_0 and k_1 being the observed rate constant for a given chloride ion concentration, the rate constant in the absence of chloride ions, and the limiting value of rate constant, respectively.

A verification of the equation (8) is the relationship $k_{obs.}\,(1 + K\,[Cl^-]) = f\,[Cl^-]$, which must be linear (Fig. 2). The straight line is drawn for $K = 0.2$. By comparing the equations (2) and (8) we get for low concentrations of chloride ions

$$k_{Cl^-} = k_1\,K. \qquad (9)$$

The greatest value of rate constant is $k_{obs.} = 2.26 \times 10^{-2}\,1\,\text{mole}^{-1}\,\text{s}^{-1}$. Since $k_{Cl^-} = 3 \times 10^{-3}\,1^2\,\text{mole}^{-2}\,\text{s}^{-1}$, we get for the value of the equilibrium constant $K \leq 0.13\,1\,\text{mole}^{-1}$ for $k_1 \geq 2.26 \times 10^{-2}\,1\,\text{mole}^{-1}\,\text{s}^{-1}$.

The temperature-dependence of rate constant has been established for the 0.1 M and 3.3 M concentrations of chloride ions in a 0.4 M solution of perchloric acid with ionic strength 3.7 (Fig. 3). The thermodynamic quantities have been determined by means of the Eyring equation. It has been found that $\Delta H^{\neq} = 12.4 \pm 0.5$ kcal mole^{-1} and $\Delta S^{\neq} = -25.4 \pm 1.5$ cal deg^{-1} mole^{-1} for the 0.1 M concentration
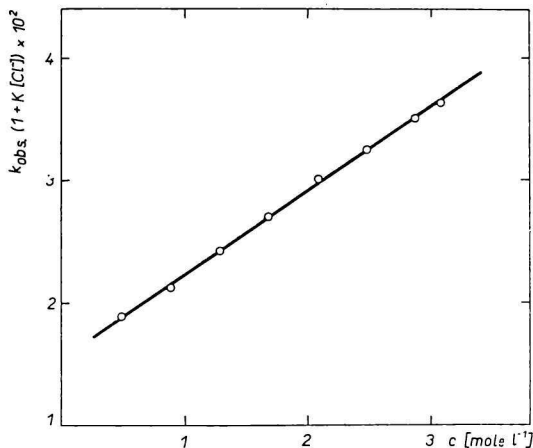
Fig. 2. Verification of the equation (*8*).
5×10^{-3} M-Cr(II), 0.1 M-NH$_2$OH $\cdot$ HCl, 0.4 M-HClO$_4$.
Ionic strength 3.7, temperature 25°C.

of chloride ions and $\Delta H^{\neq} = 12.4 \pm 0.4$ kcal mole^{-1} and $\Delta S^{\neq} = -24.4 \pm 1.3$ cal deg^{-1} mole^{-1} for the 3.3 M concentration of chloride ions. High negative values of activation entropy are probably due to the requirement of a specific orientation for both bivalent chromium and hydroxylamine which is under given reaction conditions protonated in the transition state. It is probable that the entropic term may be responsible for the increase in rate constant by the effect of chloride ions what may be due to the fall of the positive charge of Cr(II) complex from 2 to 1. In case the concentration of chloride ions is 3.3 M, the increase in rate constant
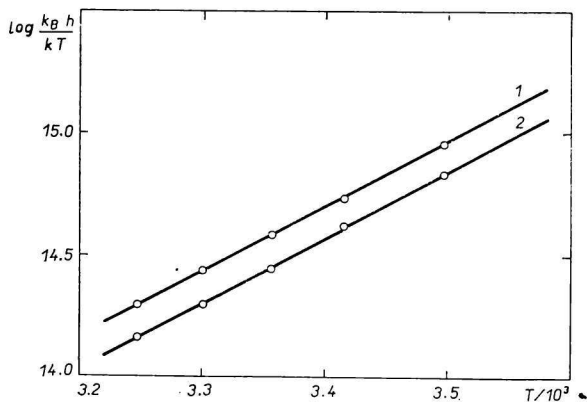

Fig. 3. Temperature dependence of the rate constant.
5×10^{-3} M-Cr(II), 0.1 M-NH$_2$OH $\cdot$ HCl, 0.4 M-HClO$_4$.
Concentration of chloride ions: *1.* 0.1 M; *2.* 3.3 M.
Ionic strength 3.7.

in comparison to the 0.1 M concentration of chloride ions amounts to $35 \pm 5\%$ for all temperatures at which the measurements have been made. That is conformable to the above-mentioned increase in activation entropy.

Schmidt and co-workers [4] have found the value of the rate constant for the reaction of Cr(II) with hydroxylamine to be $k = 1.4 \times 10^{-2}$ l mole^{-1} s^{-1} at ionic strength 1.3 and 25°C what agrees very well with our value of $k = 1.33 \times 10^{-2}$ l mole^{-1} s^{-1} found under the same conditions. A good agreement exists between the values of thermodynamic quantities too. According to [4] $\Delta H^{\neq} = 10.5 \pm 0.5$ kcal mole^{-1} and $\Delta S^{\neq} = -37 \pm 2$ cal deg^{-1} mole^{-1} at ionic strength 1.3.

In the paper [4] the effect of chloride ions on the reaction rate has been also investigated but only for a single, *i.e.* the 7×10^{-3} M concentration. It has been stated that at this concentration the chloride ions have no influence on the rate-determining step. It is evident from the equation (2) that this statement is not in contradiction with our results.
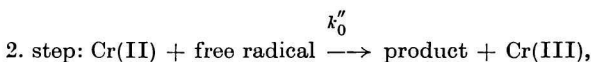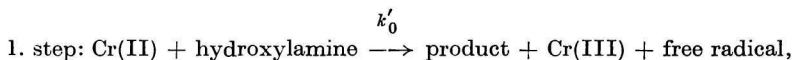
On the other hand, the values of rate constants presented in paper [5] are about 100-fold higher than the values we have measured under similar conditions. The value of the equilibrium constant $K = 1.5$ l mole^{-1} presented in paper [5] is also at least 10-fold greater than the value we have determined.

The stoichiometry of the reaction studied is according to [4, 5]:

$$2H^+ + 2Cr(H_2O)_6^{2+} + NH_3OH^+ = NH_4^+ + 2Cr(H_2O)_6^{3+} + H_2O.$$
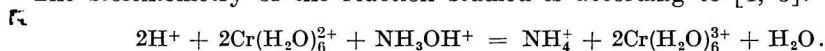
The resulting Cr(III) exists in the form of hexa-aquo complex in the presence of chloride ions too. This fact has been verified spectrophotometrically.

Our experimental results suggest that the probable mechanism in the absence of chloride ions is as follows

1. step: $\text{Cr(II) + hydroxylamine} \xrightarrow{k_0'} \text{product + Cr(III) + free radical,}$

2. step: $\text{Cr(II) + free radical} \xrightarrow{k_0''} \text{product + Cr(III),}$

where $k_0'' > k_0'$ what agrees with papers [4, 5].

The rate-determining step is

$$NH_3OH^+ + Cr(H_2O)_6^{2+} \longrightarrow \cdot NH_2 + Cr(H_2O)_6^{3+} + H_2O.$$
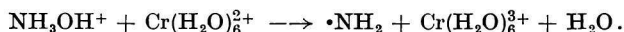
The free radical reacts with Cr(II) without being captured in the coordination sphere of resulting Cr(III).

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