

KINETICS OF THE RAPID INTERACTION OF CHROMIUM(III)
WITH IODATE AND SULFITE

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Received November 11, 1974

Relaxation techniques have been used to study the kinetics of the rapid interaction of Cr(III) with iodate and sulfite. Rate data and H⁺-catalysis indicate that complex formation occurs via an oxygen exchange mechanism which does not involve Cr(III)-O bond breaking.

Техника релаксации была использована для изучения кинетики быстрого взаимодействия Cr(III) с иодатом и сульфитом. Данные скорости и H⁺-катализ указывают на то, что комплексообразование протекает согласно механизму кислородного обмена, который, однако, не включает в себя разрыв связи Cr(III)-O.

Owing to ligand field effects, complexes of Cr(III) are very inert towards substitution at the metal center /1-3/. Certain oxyanions nevertheless form complexes with Cr(III) rather rapidly, e. g. molybdate /4/, chromate /5/, iodate /6, 7/, nitrite /8, 9/ and sulfite /10/. For some systems equilibrium constants have been reported /7, 10/, but quantitative kinetic data are not available except for the reaction of Cr(NH₃)₅H₂O³⁺ with nitrite /9/.

Therefore, a systematic study of the kinetics of these fast complex formation processes of Cr(III) has been undertaken /11/; some preliminary results have already

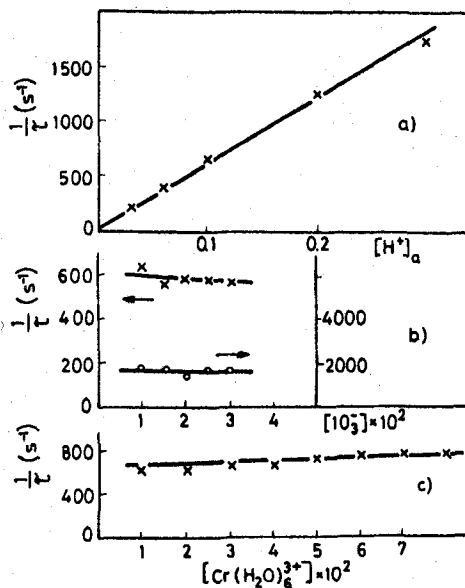


Fig. 1. Dependence of the reciprocal relaxation time on the reactant concentrations (mol dm^{-3}) in the system $\text{Cr}(\text{H}_2\text{O})_6^{3+} - \text{IO}_3^-$ (20.5°C ; $I = 0.5$, $\lambda = 435 \text{ nm}$). a) $[\text{Cr}(\text{H}_2\text{O})_6^{3+}] = 0.02$, $[\text{IO}_3^-] = 0.02$. b) $[\text{Cr}(\text{H}_2\text{O})_6^{3+}] = 0.02$, x: $[\text{H}^+]_a = 0.1$, left-hand scale, o: $[\text{H}^+]_a = 0.3$ right-hand scale, c) $[\text{IO}_3^-] = 0.02$, $[\text{H}^+]_a = 0.1$

been reported /12/. The highest rates have been found in the reactions with iodate and sulfite. These systems are discussed here in detail.

The kinetics of complex formation between $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and iodate was measured by means of the temperature-jump relaxation technique at reactant concentrations $[\text{Cr}^{3+}] = 0.01 - 0.08 \text{ mol dm}^{-3}$, $[\text{IO}_3^-] = 0.01 - 0.03 \text{ mol dm}^{-3}$ and $[\text{H}^+] = 0.01 - 0.03 \text{ mol dm}^{-3}$ and $[\text{H}^+] = 0.03 - 0.3 \text{ mol dm}^{-3}$. These concentration ranges are determined mainly by technical and solubility conditions. A summary of the results is shown in Fig. 1. A characteristic feature of the kinetics of this system is that under the given conditions the value of the reciprocal relaxation time

is almost independent of the concentration of Cr^{3+} and IO_3^- (Fig. 1b and 1c) but increases linearly with $[\text{H}^+]$ (Fig. 1a), with no measurable intercept. A quantitative interpretation of the kinetic data is difficult, however, owing to the fact that a di-iodato-complex is the predominant species in solution /7/. Its stability is given by $\beta_2 = [\text{Cr}(\text{IO}_3)_2^+]/[\text{Cr}^{3+}][\text{IO}_3^-]^2 \approx 132 \text{ mol}^{-2} \text{ dm}^6$, whereas the stability of the 1 : 1 complex is very low (one of the methods applied gave $\beta_1 = [\text{CrIO}_3^{2+}]/[\text{IO}_3^-] \approx 3 \text{ mol}^{-1} \text{ dm}^3$, but this value is of "doubtful validity" according to the authors /7/).

Assuming that the 1 : 1 complex is present in a steady state concentration (only one relaxation effect was observed), an expression for $1/\tau$ has been calculated. Since IO_3^- as well as HIO_3 have to be taken into account as reactants, this expression is of a somewhat complicated form. A comparison with the experimental data (Fig. 1) leads to the conclusion that the predominant term in $1/\tau$ is due to the dissociation of a monoprotonated di-iodato-Cr(III)-complex. Data for the kinetics of formation and dissociation of the 1 : 1 complex cannot be evaluated.

Therefore, the reaction of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ with iodate was also investigated. Of course, this metal ion can form only a mono-iodato-complex. Its equilibrium constant was determined spectrophotometrically. Since complex formation is rather weak, the Benesi-Hildebrand approximation /13/ may be applied which leads to a relationship given by eq. (1), where M_0 and L_0 denote the total metal and total ligand concentration, A the absorbancy at a given value of L_0 , and A_0 initial absorbancy ($L_0 = 0$).

$$\frac{L_0}{A - A_0} = \frac{1}{K(A_\infty - A_0)} + \frac{M_0 + L_0}{A_\infty - A_0} \quad (1)$$

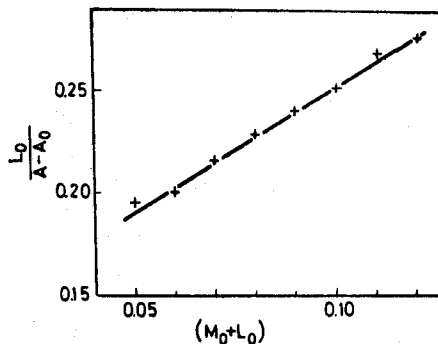


Fig. 2. Spectrophotometric determination of the stability constant of the mono-iodatopentaammine-Cr(III)-complex; $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}]_0 = M_0 = 0.04 \text{ mol dm}^{-3}$; $[\text{IO}_3^-]_0 = L_0 = 0.01 - 0.08 \text{ mol dm}^{-3}$; 25°C ; $I = 1.0 \text{ mol dm}^{-3}$; $\text{pH} = 1.5$; $\lambda = 535 \text{ nm}$, optical path length 1 cm

A_∞ is the limiting value at very high concentrations of the ligand. Figure 2 shows a plot of $L_0 / (A - A_0)$ vs. $(M_0 + L_0)$. From the slope and intercept one obtains

$$K = [\text{Cr}(\text{NH}_3)_5\text{IO}_3^{2+}] / [\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}] [\text{IO}_3^-] = 9.7 \pm 1.5 \text{ mol}^{-1} \text{ dm}^3$$

(ionic strength $I = 1.0 \text{ mol dm}^{-3}$, 25°C). This value was used to calculate the equilibrium concentration of the reactants in the kinetic studies.

The results of the temperature-jump measurements are summarized in Fig. 3. Qualitatively this system shows the same type of behaviour as described above for the reaction of iodate with $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. The reciprocal relaxation time is almost independent of the concentrations of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ and IO_3^- and increases linearly with $[\text{H}^+]$, with an intercept close to zero, i. e. $1/\tau \approx \underline{a} [\text{H}^+]$. Using an experimentally determined value of 0.75 for the apparent activity coefficient of H^+ in $1.0 \text{ mol dm}^{-3} \text{ NaClO}_4$, one obtains $\underline{a} = 1.6 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ sec}^{-1}$.

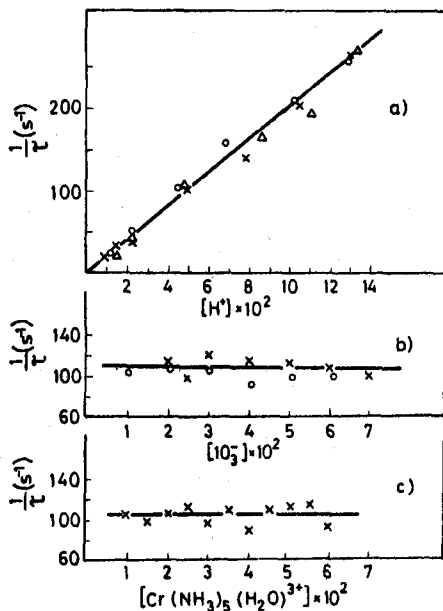
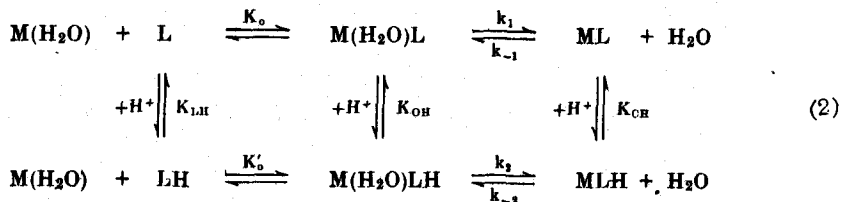


Fig. 3. Dependence of the reciprocal relaxation time on the reactant concentrations (mol dm^{-3}) in the system $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+} - \text{IO}_3^-$ (26°C ; $I = 1.0 \text{ mol dm}^{-3}$; $\lambda = 546 \text{ nm}$). a) Δ : $[\text{M}] = 0.02$, $[\text{L}] = 0.02$, x : $[\text{M}] = 0.04$, $[\text{L}] = 0.04$, o : $[\text{M}] = 0.02$, $[\text{L}] = 0.04$; b) x : $[\text{M}] = 0.02$, $[\text{H}^+]_a = 0.05$, o : $[\text{M}] = 0.04$, $[\text{H}^+]_a = 0.05$; c) $[\text{L}] = 0.04$, $[\text{H}^+]_a = 0.05$

The kinetics of this system is discussed in terms of reaction scheme (2), which includes the outer-sphere complexes $\text{M}(\text{H}_2\text{O})\text{L}$ and $\text{M}(\text{H}_2\text{O})\text{LH}$ and where M stands for the pentaamminemetal species and $\text{L} = \text{IO}_3^-$. With $[\text{H}^+] \gg 0.01 \text{ mol dm}^{-3}$, hydrolyzed species can be neglected. The outer-sphere processes (K_o and K_o') represent rapidly equilibrating reaction steps as compared to the inner-sphere processes (k_1, k_{-1}, k_2, k_{-2}). The same applies to the protolytic equilibria (dissociation constants K_{LH} , K_{OH} and K_{CH}). Thus only one relaxation time constant due to

complex formation is to be expected, in agreement with



the observations (in addition, a very fast $< 1 \mu$ /sec absorbancy change was observed also in the absence of iodate/with NO_3^- or ClO_4^- as anions/, which is apparently due to the temperature dependence of the molar absorbance of the Cr(III) species). Since $K_{\text{LH}} = [\text{H}^+][\text{IO}_3^-]/[\text{HIO}_3] = 0.47 \text{ mol dm}^{-3} / 18$, the concentrations of $\text{M(H}_2\text{O)LH}$ and MLH are small compared to those of $\text{M(H}_2\text{O)L}$ and ML are small compared to those of $\text{M(H}_2\text{O)L}$ and ML , respectively, and can be considered as steady states. The expression for $1/\tau$ calculated under these conditions for reaction scheme (2) is

$$\frac{1}{\tau} = \left(k_1 + k_2 \frac{[\text{H}^+]}{K_{\text{OH}}} \right) A + k_{-1} + k_{-2} \frac{[\text{H}^+]}{K_{\text{CH}}} \quad (3)$$

where

$$A \approx \frac{K_o([\text{M}] + [\text{L}])}{1 + K_o([\text{M}] + [\text{L}])}$$

Comparison with the experimental data indicates that the first two terms of eq. (3) do not contribute measurably to $1/\tau$, i. e. $1/\tau \approx k_{-2} [\text{H}^+]/K_{\text{CH}}$. The reaction thus proceeds exclusively via the protonated species, pathway 2.

The value of the outer-sphere stability constant K_o for reactants of the charge type +3, -1 is often around 1 at an ionic strength of $1.0 \text{ mol dm}^{-3} / 14$. With $K_o \approx 1$ and $K = K_o(1 + K_1) \approx 9.7 \text{ dm}^3 \text{ mol}^{-1}$, an inner-sphere constant $K_1 =$

$= k_1/k_{-1} = (k_1 + k_2([\text{H}^+]/K_{\text{OH}}))/(K_{-1} + k_{-2}([\text{H}^+]/K_{\text{CH}})) \approx 8.7$ would be expected. Then, however, the forward terms of eq. (3) would not be negligibly small and the value of $1/\tau$ should increase by 30–40% over the concentration ranges covered in Figs. 3b and 3c, contrary to the observations. It must therefore be concluded that K_{O} is unusually large for the system $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+} - \text{IO}_3^-$. If, for instance, $K_{\text{O}} = 7$ and therefore $K_1 \approx 0.4$, then the variation of $1/\tau$ would be 8% only, which is within the experimental uncertainty.

The equilibrium relationships of scheme /2/ lead to

$$k_2 = k_{-2} \frac{K_{\text{OH}}}{K_{\text{CH}}} \quad K_1 = \frac{k_{-2} K_{\text{LH}}}{K_{\text{CH}} K'_{\text{O}}} \quad K_{\text{O}} K_1 = \frac{k_{-2} K_{\text{LH}}}{K_{\text{CH}} K'_{\text{O}}} (K - K_{\text{O}})$$

with $k_{-2}/K_{\text{CH}} = 1.6 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ sec}^{-1}$, $K_{\text{LH}} = 0.47 \text{ mol dm}^{-3}$ and $K'_{\text{O}} \approx \approx 0.3 \text{ mol}^{-1} \text{ dm}^3$ (outer-sphere association with a neutral ligand), a value of $K_{\text{O}} = 7$ yields $k_2 \approx 7 \times 10^3 \text{ sec}^{-1}$. The value of k_2 would be lower if K_{O} were even larger than 7.

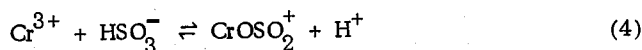
The forward rate of complex formation

$$R = k_2 [\text{M}(\text{H}_2\text{O})\text{LH}] = k_2 [\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+} \cdot \text{HIO}_3]$$

with k_2 most likely close to $7 \times 10^3 \text{ sec}^{-1}$, is entirely analogous to the first-order $[\text{H}^+]$ -term which has been found for the rate of oxygen exchange between iodate and water /15/, $R' = 3.2 \times 10^4 [\text{H}^+] [\text{IO}_3^-] = 3.2 \times 10^4 \cdot K_{\text{LH}} [\text{H}_2\text{O} \cdot \text{HIO}_3]$, with $3.2 \times 10^4 \cdot K_{\text{LH}} = 1.5 \times 10^4 \text{ sec}^{-1}$.

The rate of complex formation of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ with sulfite is even higher than that with iodate. In temperature-jump studies of this system a very fast absorbancy

change is observed, the amplitude of which depends on the concentration of Cr(III) and sulfite ($[\text{Cr(III)}] = 0.05 \text{ mol dm}^{-3}$ [sulfite] = 0.1 mol dm^{-3} , $[\text{H}^+] = 0.016 \text{ mol dm}^{-3}$). However, the time course of the absorbancy change could not be resolved by this technique, i. e. the equilibration of the reaction

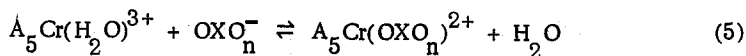


is complete within $1 \mu \text{ sec}$.

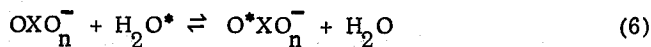
Measurements of the ultrasonic absorption of this system revealed an absorption maximum at about 5 MHz at the above reactant concentrations. This result is consistent with a relaxation time of about $4 \times 10^{-8} \text{ sec}$ for reaction /4/, but it does not represent proof of it since the rapid hydration-dehydration reaction of SO_2 in aqueous solution (in the absence of Cr(III)) leads to an absorption maximum in the same frequency range /16/. The rapid hydration-dehydration reaction of SO_2 is the pathway for oxygen exchange between sulfite and water.

The results of this study confirm the conclusions which have been outlined before /11/:

(i) The rates of the unusually fast complex formation reactions of Cr(III) with oxyanions

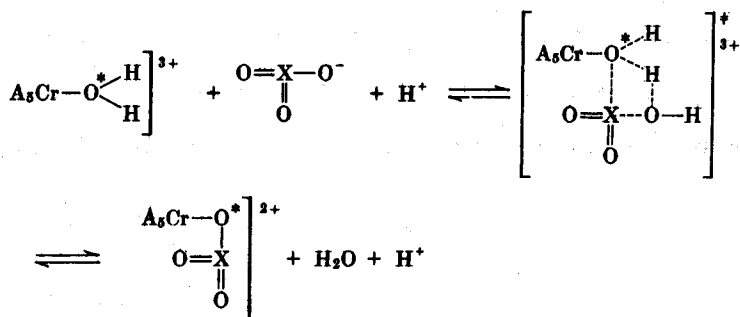


are closely related to those of the oxygen exchange between the corresponding oxyanions and water,



(ii) In contrast to "normal" substitution reactions of Cr(III) /2, 3/, but in line with the oxygen exchange reactions /eq. 6/, the fast complexation with oxyanions /eq. 5/ is accelerated by H^+ -ions.

The kinetic data reported in this study thus provide very strong evidence for the assumption that complex formation of Cr(III) with iodate and with sulfite proceeds via substitution at the center atom of the oxyanion, for instance:



A mechanism without Cr-O bond cleavage has been assumed earlier for these /6, 10/ and similar reactions /8,9/.

EXPERIMENTAL

The $[\text{Cr}(\text{H}_2\text{O})_6]\text{ClO}_4$ and $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]\text{NO}_3$ complexes have been prepared according to literature procedures /17/. All other reagents used were of p. a. quality (E. Merck, Darmstadt). The ionic strength and the pH of the solutions were adjusted with NaClO_4 and HClO_4 , respectively. A Radiometer PHM 51 digital pH-meter was used for measuring pH-values, these were converted to H^+ -concentrations by means of experimentally determined apparent activity coefficients.

All spectra were taken on a Beckman Acta III recording spectrophotometer. Kinetic measurements by sound absorption and temperature-jump relaxation ($\Delta T = 6.0^\circ\text{C}$ within $\sim 1\ \mu\text{sec}$) techniques were performed with the equipment built at the MPI of Biophysical Chemistry.

ACKNOWLEDGEMENT

Gy. B. would like to thank the Max-Planck-Gesellschaft for the award of a fellowship. The authors are indebted to Prof. M. T. Beck for helpful discussions and comments, and to Dr. F. Eggers for help with the sound absorption measurements.

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