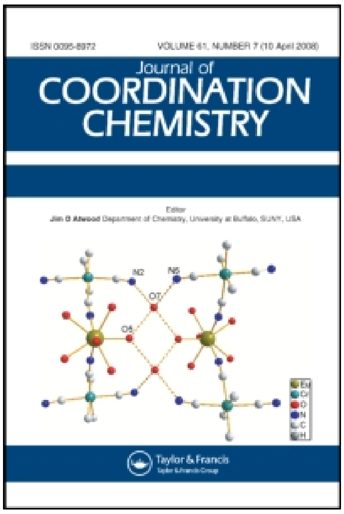


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

The Effect of Pressure on the Kinetics of the Formation Reactions of the Oxalato—Chromium—(III)—Complex Ions in Aqueous Solutions

Christa Schenk[a]; Hartwig Kelm[a]
[a] Institut für physikalische Chemie der Universität Frankfurt, Robert Mayerstr., West Germany

To cite this Article Schenk, Christa and Kelm, Hartwig(1972) 'The Effect of Pressure on the Kinetics of the Formation Reactions of the Oxalato—Chromium—(III)—Complex Ions in Aqueous Solutions', Journal of Coordination Chemistry, 2: 1, 71 — 73

To link to this Article: DOI: 10.1080/00958977208072952

URL: http://dx.doi.org/10.1080/00958977208072952

J. Coord. Chem., 1972, Vol. 2, pp. 71–73

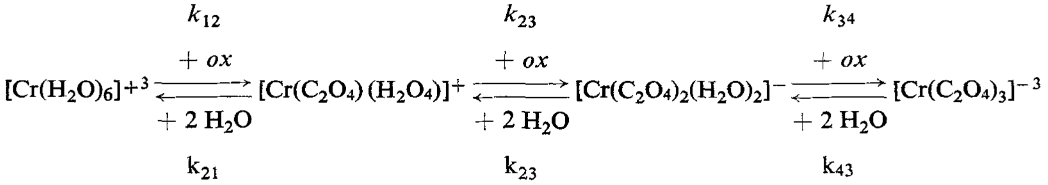
The Effect of Pressure on the Kinetics of the Formation Reactions of the Oxalato—Chromium—(III)—Complex Ions in Aqueous Solutions

CHRISTA SCHENK and HARTWIG KELM

Institut für physikalische Chemie der Universität Frankfurt
6000 *Frankfurt am Main, Robert Mayerstr.* 11, *West Germany*

(*Received January* 7, 1972; *in final form March* 6, 1972)

The formation reactions of the complex ions $[Cr(C_2O_4)_n(H_2O)_{6-2n}]^{3-2n}$ (with $n = 1,2,3$) and their hydrolyses can be represented by the following scheme of consecutive reactions:[1,2,3,4]



$$[Cr(H_2O)_6]^{+3} \underset{\substack{+\,2\,H_2O \\ k_{21}}}{\overset{\substack{k_{12} \\ +\,ox}}{\rightleftharpoons}} [Cr(C_2O_4)(H_2O_4)]^{+} \underset{\substack{+\,2\,H_2O \\ k_{23}}}{\overset{\substack{k_{23} \\ +\,ox}}{\rightleftharpoons}} [Cr(C_2O_4)_2(H_2O)_2]^{-} \underset{\substack{+\,2\,H_2O \\ k_{43}}}{\overset{\substack{k_{34} \\ +\,ox}}{\rightleftharpoons}} [Cr(C_2O_4)_3]^{-3}$$

The symbol *ox* indicates free oxalate in its deprotonated, singly protonated and doubly protonated form, respectively, depending on the pH-value of the solution. All reactions are highly sensitive to medium effects such as pH-value, ionic strength, and temperature. A comparison of the rate data for the formation reactions is therefore only justified when all data have been obtained at identical medium conditions. During the evaluation of the results it is necessary to take in account the possible consecutive reactions, since all rate constants k_{ij} for the system of formation steps are of the same order of magnitude. If one compares the rate constants of the formation reactions obtained in such a manner[5] with those of the aquo ligand exchange reactions of the corresponding complex ions, one arrives at the conclusion that the ligand water dissociation cannot be rate determining.[6,7] Because of the much faster formation reactions, when compared with the ligand water exchange processes, a bimolecular mechanism with a seven-coordinated transition state must be taken into consideration.

The volume of activation, which can be obtained from the pressure dependence of the rate constants, offers an additional useful criterion in the discussion of the reaction mechanisms because its sign as well as its magnitude can be estimated from models.

In order to determine the volume of activation for the formation reactions of the oxalato–chromium(III) complexes, these reactions were investigated at pH = 2.7, 25°C, and an ionic strength of $\mu = 1$ with respect to their pressure dependences. The same spectrophotometric method was employed as in the case of the study under normal pressure[5] except that a specially designed cuvette made of NIMONIC steel equipped with sapphire windows was used, which permitted the application of pressures up to 2000 atm. The cuvette was part of a high pressure apparatus consisting, in the main part, of a pressure generator, a manometer and a separation column. Within the steel column the oil branch of the high pressure system on the generator side was separated from the aqueous branch on the sample side by means of a flexible teflon tube. The rate constants obtained under pseudo first order conditions have been converted into second order constants and are listed in Table I.

According to the relation $(d \ln k/dP)_T = -\,\Delta V^{\neq}_{exp.}/)RT)$ following volumes of activation for the formation reactions were determined:

$\Delta V^{\neq}_{12,\text{exp.}} = -(2.2 \pm 1)$ ml mol^{-1}; $\Delta V^{\neq}_{23,\text{exp.}} = -(8.2 \pm 0.5)$ ml mol^{-1}; $\Delta V^{\neq}_{34,\text{exp.}} = -(10.0 \pm 0.5)$ ml mol^{-1}.

TABLE I

Pressure dependence of the second order rate constants of the formation reactions of the complex ions

$[Cr(C_2O_4)_n(H_2O)_{6-2n}]^{3-2n}$ (n = 1,2,3,)

Pressure (atm)	10^3k_{12}[a] (min^{-1}M^{-1})	10^3k_{23} (min^{-1}M^{-1})	10^3k_{34} (min^{-1}M^{-1})
1	2.50	30.4	14.8
100	2.52	34.5	15.7
250	2.52	35.9	17.3
500	2.59	39.0	17.5
750	2.64	39.1	21.0
1000	2.78	40.9	21.3
1500	2.87	40.8	21.9
2000		41.9	23.7

[a] Each of the listed constants represents a mean value of at least three individual runs.

As a first approximation one assumes that the experimentally determined volume of activation, $\Delta V^{\neq}_{\text{exp.}}$ of a reaction consists of two contributions. The first, $\Delta V_1^{\neq}$, represents the change in volume of the reacting molecules when they form the transition state and the second, $\Delta V_2^{\neq}$, corresponds to the change in solvation during this process. Experience has shown that the intrinsic part, $\Delta V_1^{\neq}$, is positive and small when a bond cleavage takes place in the rate determining step. However, it is negative and somewhat larger in absolute value when an additional bond is formed in the transition state. The second contribution, $\Delta V_2^{\neq}$, can be estimated for reactions in which the polarity of the reacting species is drastically changed or where ions are involved. In such cases it can be approximated by the electrostriction effect, i.e. by the pressure dependence of the dielectric constant of the solvent. For complex ions as used in the present study with radii of about 2.8 to 3.0 Å the electrostatic contribution to the volume of solvation can be calculated from Born's equation,[9] which reduces in the present cases to $\Delta V^{\neq}_{\text{el.}} \approx 2z^2$ (ml mol^{-1}) with z being the ionic charge.

On the basis of these well established general effects on the volume of activation one can estimate its expected value for a reaction assuming a certain model mechanism. Considering the formation reactions of the oxalato–chromium(III) complex ions, the rate determining step of the substitution process could be either a unimolecular dissociation of an aquo ligand or the bimolecular entrance of the free oxalate into the first coordination sphere. The formation of the transition state in the first mechanism requires the stretching of a chromium–oxygen(water) bond, the charge remaining constant. This should result in a positive or near zero contribution for $\Delta V_1^{\neq}$ and no substantial contribution in $\Delta V_2^{\neq}$. Furthermore, since the principal step is the same for all three formation reactions, no major differences with respect to the series of overall activation volumes should occur. The bimolecular mechanism on the other hand requires an essentially constant contribution from $\Delta V_1^{\neq}$ for all formation reactions, which is superimposed by a $\Delta V_2^{\neq}$ contribution that changes in sign and magnitude depending on the charges of the reacting ions.

Under the condition selected for the present study, i.e. pH = 2.7, the complex ions are all present in the aquo form and the free ligand as bioxalate, which means that the charges of the reactants amount to $z_1 = (3 - 2n)$ and $z_2 = -1$, that of the transition state $z_{\neq} = (2 - 2n)$ (n = 0,1,2). For the first two formation reactions of the scheme a reduction of the charges occurs during the formation of the transition state; the third involves an increase in negative charge. One should therefore expect positive but different values of $\Delta V_2^{\neq}$ for the first and second reaction and a negative value for the formation of the trioxalato complex.[10] In total the expected values for the overall activation volumes, when a bimolecular mechanism is followed, should become smaller or more negative as one proceed to the formation reactions of the higher oxalato complexes. The value of $\Delta V^{\neq}_{34}$ should clearly carry a negative sign.

A comparison of the expected values with those obtained experimentally points toward a bimolecular mechanism for the formation reactions of the oxalato-chromium(III) complex ions. Such a mechanism might be acting for all substitution reactions of the system, because the water exchange reaction of the hexaaquo-chromium(III) cation also shows a negative volume of activation, as has been recently reported.[11]

The financial support of the Deutsche Forschungsgemeinschaft and the Science Committee of the North Atlantic Treaty Organisation is greatly appreciated.

REFERENCES

1. D. Banerjea and M. S. Mohan, *Z. anorg. allg. Chem.* **347**, 107 (1966).

2. D. Banerjea and D. Chaudhuri, *J. inorg nucl. Chem.* **32,** 1617 (1970).
3. H. Kelm and G. M. Harris, *Inorg. Chem.* **6,** 706 (1967).
4. K. V. Krishnamurty and G. M. Harris, *J. physic. Chem.* **64,** 346 (1960).
5. C. Schenk, H. Stieger and H. Kelm, *Z. anorg. allg.Chem.* (in press).
6. J. P. Hunt and H. Taube, *J. chem. Physics* **18,** 757 (1950). R. A. Plane and H. Taube, *J. chem. Physics* **20,** 33 (1952).
7. H. Stieger, G. M. Harris and H. Kelm, *Ber. Bunsenges. physik. chem.* **74,** 262 (1970).
8. M. G. Evans and M. Polanyi, *Trans. Faraday Soc.* **31,** 875 (1935).
9. M. Born, *Z. Physik* **2,** 45 (1920).
10. The difference in solvation between cations and anions as experimentally established is not shown by the simple theory.
11. D. R. Stranks and T. W. Swaddle, *J. Am. Chem. Soc.* **93,** 2783 (1971).