Notes

Contribution from the Institut für physikalische
Chemie der Universität Erlangen-Nürnberg,
8520 Erlangen, Germany

The Mechanism of Formation of Binuclear Isopolybases

By Hartmut Wendt

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In connection with studies concerning the kinetics of the reactions that lead to isopolybases, there arises the question whether a reaction of the type

$$m\text{M}^{z+} + n\text{H}_2\text{O} \rightleftharpoons \text{M}_m(\text{OH})_n^{(z-n)+} + n\text{H}^+ \qquad (1)$$

may have something in common with the simple complex-forming reaction, type 2, of the same metal

$$\text{M}^{z+} + \text{X}^{y-} \rightleftharpoons \text{MX}^{(z-y)+} \qquad (2)$$

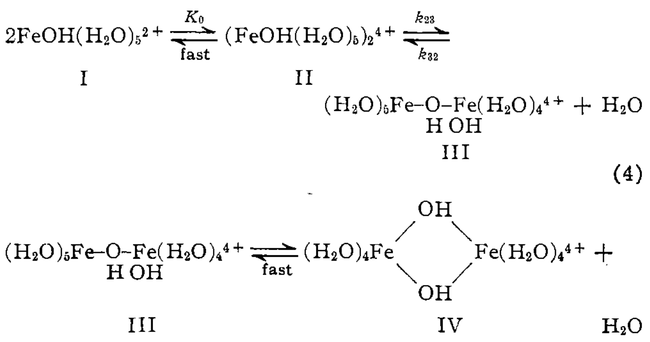
cation M^{z+}. As will be shown in two cases where sufficient kinetic data exist, namely, with the formation of the binuclear iron(III)–hydroxo complex $(\text{FeOH})_2^{4+}$ and with the formation of the binuclear vanadyl–hydroxo complex $(\text{OVOH})_2^{2+}$, a simple relation between the reaction of type 1 and reactions of type 2 exists: for both reactions the spontaneous exchange of water molecules in the inner hydration sphere of the monohydroxo complex of the participating metal cations obviously is the rate-determining step.

As has been shown previously[1] the formation of the binuclear iron(III) complex $(\text{FeOH})_2^{4+}$ proceeds *via* the bimolecular reaction of two iron(III)–monohydroxo ions

$$2\text{FeOH}^{2+} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} (\text{FeOH})_2^{4+} \qquad (3)$$

with the bimolecular rate constant $k_{12} = 450\ M^{-1}\ \text{sec}^{-1}$ (at $\mu = 0.6\ M$ and at 25°).

If the Eigen mechanism for the formation of complexes in solution is applied to reaction 3, then the following three-step reaction scheme for reaction 3 can be postulated

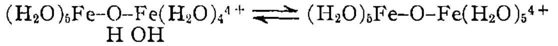


(4)

(a) The equilibrium I $\rightleftharpoons$ II (with nearly diffusion-controlled rates) is rapidly established between free iron(III)–monohydroxo cations and two iron(III)–monohydroxo cations with still intact inner hydration spheres touching each other in close contact. Equilibrium I $\rightleftharpoons$ II is characterized by the formation constant K_0 for the "contact complex."

(b) The rate-determining step II $\rightleftharpoons$ III is the loss of one water molecule from the inner hydration sphere of one of the two cations that form the "contact complex." It is to be postulated that the loss of this water molecule is immediately followed by the insertion of a hydroxyl ion that is bound to the neighboring iron–hydroxo cation, so that one OH bond between both cations of the "contact complex" is formed.

(c) Then follows the fast formation of the second OH bond by loss of another water molecule and insertion of a second hydroxyl ion (III $\rightleftharpoons$ IV). (This reaction might be a fast innermolecular protolytic reaction that leads to a μ-oxo complex instead of a diol complex as well



$$\underset{\text{H OH}}{(\text{H}_2\text{O})_5\text{Fe–O–Fe}(\text{H}_2\text{O})_4^{4+}} \rightleftharpoons (\text{H}_2\text{O})_5\text{Fe–O–Fe}(\text{H}_2\text{O})_5^{4+}$$

The question whether the dinuclear iron(III) complex is a diol or a μ-oxo complex is not yet settled.)

Then from eq 3 and 4, with the stability constant K_0 being small, the measured bimolecular rate constant k_{12} can be expressed

$$k_{12} = k_{23}K_0 \qquad (5)$$

k_{23} is the monomolecular rate constant for the transformation of the "contact complex" into the binuclear isopolybase. K_0 can be estimated according to Fuoss.[2]

If we insert in Fuoss' formula the macroscopic dielectric constant of water $\epsilon = 80$ and a distance between the centers of the cations in the "contact complex" of $d = 5$ Å we get $K_0(2+,2+)_{\mu=0} = 1.2 \times 10^{-3}\ M^{-1}$ (25°, $d = 5$ Å). The rate constant k_{12} can be extrapolated to zero ionic strength by use of the Bjerrum theory and the Davies formula:[3] $k_{12}(\mu = 0) = 25\ M^{-1}\ \text{sec}^{-1}$. Then we get from eq 5 $k_{23} = 2.2 \times 10^4\ \text{sec}^{-1}$.

From the kinetic investigation of the hydroxyl ion catalyzed path of the complex formation of the iron(III) cation the rate of water exchange in the inner hydration shell of the iron–monohydroxo ion can be estimated[4-6] as $k_{\text{H}_2\text{O exch}}(\text{FeOH}^{2+}) \approx 5 \times 10^3\ \text{sec}^{-1}$ (25°). Now as k_{23} and $k_{\text{H}_2\text{O exch}}$ are of the same order of magnitude, one may conclude that for the formation of the binuclear isopolybase the rate-determining step is the spontaneous water exchange in the inner hydration sphere of the monomer FeOH^{2+}. (The contact distance of 5 Å used to determine K_0 previously is somewhat arbitary and has no definite physical meaning.

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[1] H. Wendt, *Z. Elektrochem.*, **66**, 235 (1962).

[2] R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

[3] C. W. Davies, "Ion Association," Butterworth and Co. Ltd., London, 1962.

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[6] H. Wendt, Habilitationsarbeit, Erlangen, 1967; to be submitted for publication.

It has been chosen as this value together with $\epsilon = 80$ gives the best fit between calculated and experimentally determined stability constants for outer-sphere complexes[7] of Cr^{3+} and Co^{3+} [8] as well as for the complex OVH_2OSO_4.)

The same seems to hold for the hydrolysis reaction of the vanadyl cation. This reaction according to Rossotti and Rossotti[9] leads to the formation of a binuclear isopolybase

$$2VO^{2+} + 2H_2O \rightleftharpoons (VOOH)_2^{2+} + 2H^+ \qquad (6)$$

It is possible to study this reaction with the stopped-flow method.[10]

A rate law is found which formally allows for the bimolecular combination of two vanadyl–monohydroxo cations to the dimer

$$2VOOH^+ \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} (OVOH)_2^{2+} \qquad (7)$$

with $k_{12} = 2 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ (at $\mu = 0.3\ M$ and at 25°) and $k_{21} = 20\ \text{sec}^{-1}$. Then by extrapolation to zero ionic strength we get $k_{12}\ (\mu = 0) = 8 \times 10^3\ M^{-1}\ \text{sec}^{-1}$. Applying eq 5 and taking from the formula of Fuoss,[2] $K_0(+1,+1) = 8 \times 10^{-2}\ M^{-1}$ (25°, $d = 5$ Å). We finally get $k_{23} = 10^5\ \text{sec}^{-1}$.

Again from the hydroxyl ion catalyzed path of the complex-forming reactions of the vanadyl ion[8,11] the exchange rate of water in the inner hydration sphere of the vanadyl–monohydroxo cation can be estimated as $k_{H_2O\ \text{exch}}(OVOH^+) = 3 \times 10^4\ \text{sec}^{-1}$. Since in this case, too, the rate constant for the spontaneous water exchange and k_{23} are of the same order of magnitude, we may conclude that also with the formation of the binuclear complex $(OVOH)_2^{2+}$ the rate-determining step is the water exchange in the inner hydration sphere of the monomeric species $OVOH(H_2O)_4^+$.

It should be pointed out, however, that into the value of k_{23} enter all possible oversimplifications or mistakes of the Fuoss model. It is possible to apply the Fuoss model to all combinations of interacting species including equally or oppositely charged ions and ion dipoles since in this model only coulombic interaction and the volume of the complex-forming species are considered. However, there always arises the question of the appropriate "contact distance." The "contact distance" of two tightly solvated cations could well be somewhat greater than for solvated cation–anion complexes. Inserting 6 Å instead of 5 Å increases $K_0(2+,2+)$ and decreases $k_{23}(Fe^{3+})$ by a factor of 5 and $K_0(1+,1+)$ and $k_{23}(VO^{2+})$ by a factor of 2, respectively. This gives a better fit of k_{23} and $k_{H_2O\ \text{exch}}$ in both cases. However, although the values of K_0 used above may thus be very approximate, it is quite clear that k_{23} and $k_{H_2O\ \text{exch}}$ at any rate are of the same order of magnitude.

Obviously the formation also of other binuclear hydroxo complexes and certain inner-sphere redox reactions are expected to proceed *via* the same simple mechanism, which has long been known to operate in a general way with the complex-forming reactions of solvated cations and no special type of mechanism must be postulated for the olation reactions, which lead to binuclear isopolybases. So the suggestion of Eigen and Wilkins[12] can be confirmed although they used in their paper as a proof of their idea the direct comparison of bimolecular (k_{12} for the iron reaction) and monomolecular rate constants ($k_{H_2O\ \text{exch}}$ for $FeOH^{2+}$ which was obviously wrong) which can only be compared directly, when K_0 is approximately 1 M^{-1}.

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[7] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1960, p 380.

[8] H. Strehlow and H. Wendt, *Inorg. Chem.*, **2**, 6 (1963).

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CONTRIBUTION FROM THE REACTOR CHEMISTRY DIVISION,
OAK RIDGE NATIONAL LABORATORY,
OAK RIDGE, TENNESSEE 37830,
AND THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MAINE, ORONO, MAINE 04473

Association of Cd^{2+} and Br^- in the Solvent $KNO_3 + Ca(NO_3)_2 + H_2O$[1a]

BY JERRY BRAUNSTEIN[1b] AND HELEN BRAUNSTEIN[1c]

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The solution chemistry of electrolytes at concentrations intermediate between anhydrous fused salts and "ordinary" aqueous electrolytes has received little attention, in spite of its importance in the development of theories of electrolyte solutions.[2] The temperature dependence and water concentration dependence of equilibrium constants for the association

$$Cd^{2+} + Br^- \rightleftharpoons CdBr^+ \qquad (1)$$

in the solvent $\{\text{equimolar } (Li,K)NO_3\} + H_2O$ containing up to 50 mol % water have supported a quasilattice model of competing association and hydration equilibria.[3]

The present work is part of an extension of these studies to other solvent systems. Studies of transport properties[4,5] and volumetric properties[6] in $Ca(NO_3)_2 \cdot 4H_2O$ and in its mixtures with KNO_3 have suggested that these hydrate melts may be considered as analogs of molten salts, consisting of nitrate ions and hydrated cations. In this note we describe measurements of the

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[3] (a) J. Braunstein, *J. Phys. Chem.*, **71**, 3402 (1967); (b) P. C. Lammers and J. Braunstein, *ibid.*, **71**, 2636 (1967).

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