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# KINETICS OF TYPICAL HYDROLYSIS REACTIONS OF MULTIVALENT CATIONS*

Hartmut Wendt
Institute for Chemical Technology, Darmstadt Technical
College, D-61 Darmstadt Hochschulstrasse, West Germany

This review summarizes kinetic investigations concerning the homogeneous hydrolysis reactions of multivalent metal cations in aqueous solution. – Three main types of reactions are discussed:

a) Protolysis of aquated cations to form mononuclear metal-hydroxo-complexes.
b) *The formation and fission of binuclear μ-hydroxo-bridged or μ-oxo-bridged metal hydroxo complexes.*
c) The formation and acid degradation reactions of higher polynuclear metal hydroxo complexes.

Whereas the *protolysis reaction of aquo-metal cations* is a simple and fundamental (acid-dissociation) reaction the formation of the binuclear complexes resembles in most cases closely the metal-anion-complex formation. The formation and degradation of the higher metal hydroxo complexes, however, mostly proceeds in two or more parallel reaction paths. – Both the *successive* addition of mononuclear metal-hydroxo-species to *metal hydroxo complexes of lower molecular weight* as well as the initial formation of discrete sub-complexes which finally combine to the stable complex are observed for the formation reaction.

## 1. Hydrolysis Equilibriums and Soluble Hydrolysis Products of Multivalent Metal Cations

### a. Hydrolysis Equilibriums

Since the studies of the Sillén school, hydrolysis reactions and equilibriums of multivalent metal cations in solution, some of which are very complicated, have been explained in principle [1]. First Bjerrum and later Sillén and coworkers as well as many other authors [2-4] were able to show that, in many cases, when the pH of aqueous metal nitrate and perchlorate solutions was increased, at first neither hydroxides, hydrated oxides, oxides, hydroxynitrates, or hydroxyperchlorates of the corresponding metals were precipitated, because hydrolysis of the metal ions resulted in formation of a large number of various types of soluble metal hydroxy complexes.

All metal ions hydrolyze in steps [1] and first form metal ion monohydroxy complexes by proton dissociation of a part of their molecules of hydration,

$$(1) \qquad Me(H_2O)_n^{z+} \rightleftharpoons MeOH(H_2O)_{n-1}^{(z-1)+} + H^+$$

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*Translated from the German by R. G. Mansfield, Office of Language Services, Oak Ridge National Laboratory, Oak Ridge, Tenn.

often followed by a continuous series of mononuclear hydroxy complexes (see Fig. 1, top series). In the case of most multivalent metal ions both the first and second hydrolysis steps are detectable, and the equilibrium constants for formation of the monohydroxy and dihydroxy complexes are known [1]. The cations of many metals can bind hydroxyl ions over and above the condition of equivalence ($m_{OH} = z^+$) and at a sufficiently high pH form monomeric anions (Fig. 1, first series on right). (That some transition metals of higher valence form very stable oxy complexes in aqueous solution, e.g., $VO_2^+$, $VO^{2+}$, $UO_2^{2+}$, is of only marginal interest in this connection; of principal importance here is the fact that such oxy-cation complexes behave similarly to normal cations---they become solvated and can in turn hydrolyze according to eq. 1).

A great many metal ions of higher valence associate during hydrolysis---especially when they are contained in higher concentrations in the solution---into complexes in which two or more metal ions are bound together by hydroxyl groups (μ-hydroxy bond) or by oxygen ($O^{2-}$) ions (μ-oxy bonds):

$$(2)\quad n\,\mathrm{MeOH}^{(z-1)+} + m\,\mathrm{H_2O} \rightleftharpoons \mathrm{Me}_n(\mathrm{OH})_{n+m}^{[(z-1)n-m]+} + m\,\mathrm{H}^+$$

The cationic polynuclear metalhydroxy (or oxy) complexes thus formed exhibit in most cases an increasing $OH^-$/metal ratio with increasing degree of aggregation and a positive total charge. They can therefore be regarded theoretically as connecting links between the monomeric metal-hydroxy-complexes and the metal hydroxide or hydrated oxide [$Me(OH)_z$] which represents the final product of hydrolysis. It may be pointed out that polynuclear metal hydroxy complexes are frequently thermodynamically unstable and would decompose into metal hydroxide and metal-aquo ion upon final establishment of equilibrium [5].

### b. Binding Conditions and Structures of Polynuclear Metal Hydroxy Complexes (Poly-MeOH Complexes)

The conditions which must be fulfilled by the metal ion in order to favor the formation of poly-MeOH complexes were first investigated by Mattock [6] and later mainly by Jezowska-Trzebiatowska [7]. According to them mainly metal ions which can make free d- or f- orbitals available for π-bonds form bi and higher nuclear metal-hydroxy (or oxy) complexes. In the poly-MeOH complexes strong electron coupling between these metal ions occurs through formation of molecular orbitals in which atomic orbitals of the oxygen of the bridge as well as those of the bridged metal cations participate. As a result, paramagnetic metal ions in one complex often lose their magnetic moments (by electron pairing in one of the common molecular orbitals); this occurs principally in binuclear complexes [6,7].

Spiro et al. [8-10] found indications of a direct metal-metal interaction between the cations bound in the complex in a tetranuclear and hexanuclear hydroxy complex of the Pb(II) cation [$Pb(OH)_4^{4+}$ and $Pb_6O(OH)_6^{4+}$, respectively], as well as in the hexanuclear complex of the bismuth cation $Bi_6(OH)_{12}^{6+}$.

Studies of a large number of metal ions have shown that some of them can form a continuous series of poly-MeOH complexes with increasing degree of aggregation:

$$(3)\quad \mathrm{Me}[\mathrm{Me}(\mathrm{OH})_{z-1}]_n^{(z+n)+} + \mathrm{Me}^{z+} + (z-1)\mathrm{H_2O} \rightleftharpoons \mathrm{Me}[\mathrm{Me}(\mathrm{OH})_{z-1}]_{n+1}^{(z+n+1)+} + (z-1)\mathrm{H}^+$$

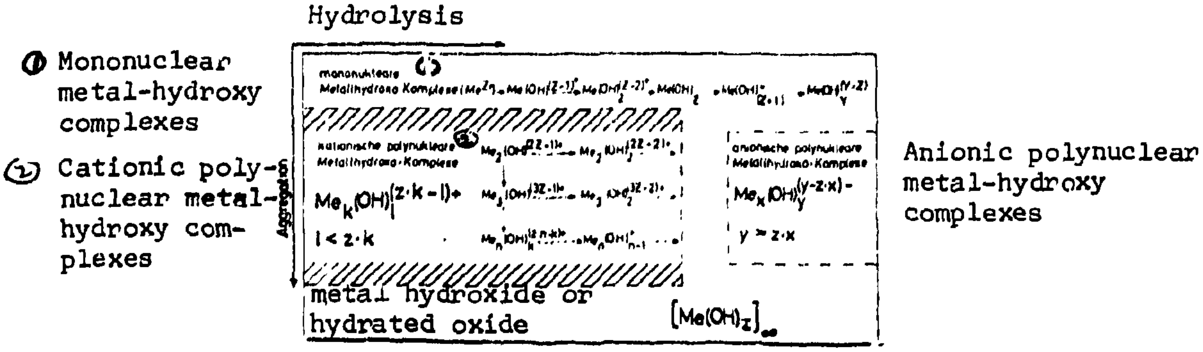

Hydrolysis
① Mononuclear metal-hydroxy complexes
② Cationic polynuclear metal-hydroxy complexes
Anionic polynuclear metal-hydroxy complexes
mononukleare Metallhydroxo Komplexe
kationische polynukleare Metallhydroxo-Komplexe
anionische polynukleare Metallhydroxo-Komplexe
Aggregation
$Me_k(OH)_l^{(z\cdot k-l)+}$
$l < z\cdot k$
$Me_x(OH)_y^{(y-z\cdot x)-}$
$y > z\cdot x$
metal hydroxide or hydrated oxide
$[Me(OH)_z]_\infty$

Fig. 1

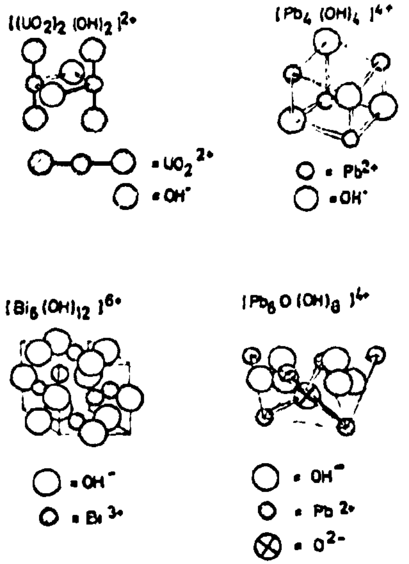
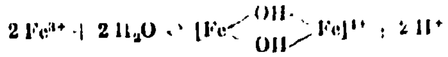

$[(UO_2)_2(OH)_2]^{2+}$
$= UO_2^{2+}$
$= OH^-$
$[Pb_4(OH)_4]^{4+}$
$= Pb^{2+}$
$= OH^-$
$[Bi_6(OH)_{12}]^{6+}$
$= OH^-$
$= Bi^{3+}$
$[Pb_6O(OH)_6]^{4+}$
$= OH^-$
$= Pb^{2+}$
$= O^{2-}$

Fig. 2

For this case Sillén has coined the concept "core and link" aggregation (which, freely translated, would be about the same thing as "continuous aggregation"). The greater number of cations do not react by continuous aggregation upon raising the pH but form mainly one or a few definite poly-MeOH complexes of relatively low degree of association [1, 11].

The formation of dimeric MeOH complexes as the first step of aggregation is especially pronounced in nearly all cations which form poly-MeOH complexes. A particularly impressive example of this is offered by the hydrolysis of the iron(III) cation, more than 50% of which in 0.1 M solution can be converted by cautious addition of base into the dimer (bis-μ-hydroxy bridged) without precipitation of ferric hydroxide:

(4) 

$$2\,Fe^{3+} + 2\,H_2O \rightleftharpoons [Fe(OH)_2Fe]^{4+} + 2\,H^+ \qquad (4)$$

Other cations form practically no dimers but instead form particularly stable trimeric, tetrameric, or hexameric hydroxy-complexes, e.g.

Trimer : $Be_3(OH)_3^{3+}$ [11], $Pb_3(OH)_4^{2+}$ [12]
Tetramer : $Pb_4(OH)_4^{4+}$ [12], $Ni_4(OH)_4^{4+}$ [13]
Hexamer : $Bi_6(OH)_{12}^{6+}$ [10,14], $Pb_6O(OH)_6^{4+}$ [9,12]

The structure of many polynuclear hydroxy complexes can be observed in some cases by solid state x-ray structural analysis [15] (provided the poly-MeOH complexes form definite salts), by x-ray diffraction on concentrated aqueous solutions of the poly-MeOH complexes [17], and by infrared or Raman spectroscopy of such solutions [8-10]. The structure of the poly-MeOH complexes is frequently of a high degree of symmetry, as shown in examples of the binuclear hydroxy complex of uranyl (U(IV)) cation, the tetranuclear complex of the Pb(II) ion, and the hexanuclear complex of the Bi(III) ion (Fig. 2). The lead complex exhibits tetrahedral and the bismuth complex cubic symmetry. Even a less symmetric complex, such as the hexanuclear Pb(II) complex, $Pb_6O(OH)_6{}^{4+}$, contains in its core a building block of high symmetry. The core consists of a very slightly distorted tetrahedral arrangement of four Pb(II) cations about a central $O^{2-}$ anion.

In conclusion it may be mentioned that in the hydrolysis of cations of higher valence, beyond the definite metal-hydroxy complexes of a low degree of association discussed above, relatively stable solutions of very highly aggregated complexes, which are better described as hydroxide sols, can be formed. Spiro [16], for example, was able to prove that, in the hydrolysis of FE(III) nitrate solutions with bicarbonate, a discrete, very stable, soluble highly polymerized species is formed in which, in addition to hydroxyl ions, nitrate ions are still incorporated and which has the composition $Fe(OH)_x(NO_3)_{3-x}$ (x = 2.3 to 2.5) and an average molecular weight of approximately $1.4 \times 10^5$ (accordingly, the particular species contains 900 to 1000 iron cations).

## 2. Kinetics of Hydrolysis of Multivalent Cations

### a. Difference in Kinetics of Various Types of Hydrolyses

In the case of the reactions illustrated in the first part, three fundamentally different types of reactions can be distinguished.

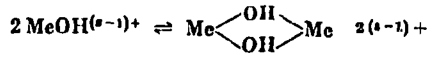
### i. Primary Hydrolysis

Primary hydrolysis corresponding to eq. 1, which results in formation of mononuclear monohydroxy complexes, may be interpreted as an acid dissociation reaction (eq. 1 from left to right) of water molecules of the inner hydration sphere of the cations or as proton-base recombinations ( in the reverse direction) and, as a simple association-dissociation reaction, belongs to the group of elementary reactions in solutions. It is, at the same time, the simplest and fastest of all hydrolysis reactions.

### ii. Formation of Binuclear Metal-Hydroxy Complexes

The formation of binuclear metal-hydroxy complexes for the case of association of two monomeric metal-hydroxy complexes to form a bis-(μ-hydroxy)-bridged complex may be shown as

(5)



$$2\,\mathrm{MeOH}^{(z-1)+} \rightleftharpoons \left[\mathrm{Me}\begin{matrix}\diagup\mathrm{OH}\diagdown\\ \diagdown\mathrm{OH}\diagup\end{matrix}\mathrm{Me}\right]^{2(z-1)+}$$

The aggregation of two metal-hydroxy complexes is very probably a complicated process which is composed of several individual steps. Theoretically, the addition of a metal-hydroxy cation to a second metal-hydroxy cation (eq. 5) is similar to the formation of a complex of the metal ions, and there is a question as to the extent to which the kinetic laws of formation of isopolybases are similar to those of formation of complexes of metal ions.

### iii. Formation of Polynuclear Metal-Hydroxy (or oxy) Complexes

If with increasing hydrolysis the more highly aggregated poly-MeOH complexes are formed (degree of association >2), e.g., a hexanuclear complex,

$$(6) \qquad 6\,\mathrm{Me}^{z+} + 12\,\mathrm{H_2O} \rightleftharpoons \mathrm{Me_6(OH)}_{12}^{6(z-2)+} + 12\,\mathrm{H}^+$$

then for the formation of such a complicated species it can be assumed that the overall reaction may be described as a series of several individual steps. In principle we have the following possibilities:

(a) The complex is built up in steps by the "core and link" principle by successive coupling of individual metal-hydroxide cations onto the still incomplete core of the complex:

$$\begin{array}{llll}
(7a) & \mathrm{MeOH}^{(z-1)} + \mathrm{MeOH}^{(z-1)+} + 2\mathrm{H_2O} & \rightleftharpoons \mathrm{Me_2(OH)}_4^{2(z-2)} + 2\mathrm{H}^+ & (I) \\
 & \mathrm{Me_2(OH)}_4^{2(z-2)+} + \mathrm{MeOH}^{(z-1)+} + \mathrm{H_2O} & \rightleftharpoons \mathrm{Me_3(OH)}_6^{3(z-2)} + \mathrm{H}^+ & (II) \\
 & & & \downarrow \\
 & \mathrm{Me_5(OH)}_{10}^{5(z-2)+} + \mathrm{MeOH}^{(z-1)} + \mathrm{H_2O} & \rightleftharpoons \mathrm{Me_6(OH)}_{12}^{6(z-2)} + \mathrm{H}^+ & (V)
\end{array}$$

It is conceivable that all individual steps of this kind take place at practically the same rate; however, a single step in the whole reaction chain could be rate-determining for the overall reaction.

(b) The complex is put together from definite MeOH complexes of lower degree of association:

$$\text{(7b)}\qquad \begin{aligned} 3\,Me^{z+} + 6\,H_2O &\rightleftharpoons Me_3(OH)_6^{3(z-2)+} + 6\,H^+ &\text{(I)}\\ 2\,Me_3(OH)_6^{3(z-2)+} &\rightleftharpoons Me_6(OH)_{12}^{6(z-2)+} &\text{(II)}\end{aligned}$$

The formation of the poly-MeOH complex (eq. 7bI), which has a lower degree of aggregation, could possibly be the rate-determining step of the overall reaction, or it could be the combination of these subunits (eq. 7bII).

## b. Experimental Methods for Investigating Metal Ion Hydrolysis Reactions in Aqueous Solutions

The primary hydrolysis step---the acid dissociation of aquated metal ions---usually proceeds so rapidly that in order to study it the fastest relaxation methods have to be used. Eigen and Kruse [18] and Eyring et al. [19], who have made an especially intensive study of this type of reaction, applied the field-change method [20].

The formation of binuclear or MeOH complexes of a higher degree of aggregation takes place more slowly and can be studied by means of slower relaxation methods such as the pressure-jump or the temperature-jump method [20]. However, in many cases the conventional flow tube procedure or the stopped-flow method [21, 22] proves superior to the relaxation methods. With the flow tube or the related conventional mixing reaction method, the irreversible dissociation of poly-MeOH complexes which occurs after acidification of prehydrolyzed metal salt solutions can be especially well observed. The reaction rate laws of this irreversible dissociation often prove to be appreciably simpler and more easily interpretable than the expressions for the reciprocal relaxation time for the quasi-reversible reactions of formation or decomposition of highly aggregated MeOH complexes [23]. In contrast to the irreversible decomposition reactions of the poly-MeOH complexes in acidified solutions which take place relatively slowly, the formation of these complexes or the precipitation of hydroxide which occurs upon mixing metal salt solutions with bases usually occurs with immeasurable rapidity. Nevertheless, the reaction rate laws as well as the rate constants of the formation reaction can be determined from the reaction rate laws of the irreversible dissociation of the poly-MeOH complexes.

## c. Mechanism and Reaction Rate Constants of Various Types of Hydrolysis Reactions

### 1. Acid Dissociation of Hydrated Metal Ions and Recombination Reactions of Protons and Metal-Hydroxy Complexes

The formation of mononuclear metal-monohydroxy cations,

$$\text{(8)}\qquad Me(H_2O)_n^{z+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MeOH(H_2O)_{n-1}^{(z-1)+} + H^+ \qquad (Ka_1)$$

and metal-dihydroxy cations,

$$(9)\ MeOH(H_2O)_{n-1}^{(z-1)+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Me(OH)_2(H_2O)_{n-2}^{(z-2)+} + H^+ \quad (Ka_2)$$

were first sutdied by Eigen and Druse and later very thoroughly by Eyring et al., [18, 19]. The measured rate constants for the acid dissociation ($k_1$, $k_2$) and for the recombination reaction ($k_{-1}$, $k_{-2}$) are shown in Table 1 for some divalent and trivalent cations.

The fact that the dissociation rate constants $k_1$ (or $k_2$) (with the exception of system 1) all lie within a narrow range---between $10^4$ and $3 \times 10^5$ $sec^{-1}$---does not mean that this is a situation typical of rate constants for all hydrated cations. Actually, the reason for this is that the recombination rate constants $k_{-1}$ (or $k_{-2}$) vary only within the narrow range between 0.1 and $1.5 \times 10^{10}$ $M^{-1}$ $sec^{-1}$ and, for reasons of the technique of measurement, cations were studied whose acidity constants for the first hydrolysis step ($K\alpha_1$) or (systems 9 and 10), whose acidity constants for the second hydrolysis step ($K\alpha_2$) lie within the narrow range between $10^{-6}$ and $10^{-5}$ M (exceptions: $Cu^{2+}$ and $Th^{4+}$). It may be expected that for appreciably more acid cations $k_1$ assumes greater, and for appreciably less acid cations, smaller values than $10^5$ $sec^{-1}$.

It is the recombination rate constants $k_{-1}$ and $k_{-2}$ in which the peculiarities of the cations involved (especially their charge) becomes evident. For all the cations listed in Table 1 the measured recombination rate constants are somewhat smaller than what corresponds to a diffusion-dependent recombination.

Table 1. Reaction Rate Constants for Acid Dissociation ($k_1$, $k_2$) and Proton Recombination ($k_{-1}$, $k_{-2}$) for, respectively, First and Second Hydrolysis Steps of Various Metal Cations

| No. | Cation | $k_1 \cdot 10^{-5}$ [$sec^{-1}$] | $k_{-1} \cdot 10^{-10}$ [$M^{-1} sec^{-1}$] | $Ka_1$ [M] | $k_2 \cdot 10^{5}$ [$sec^{-1}$] | $k_{-2} \cdot 10^{-10}$ [$M^{-1} sec^{-1}$] | $Ka_2$ [M] | ref. |
|---|---|---|---|---|---|---|---|---|
| 1 | $Cu(H_2O)_6^{2+}$ | 0,03* | 1 | $3 \cdot 10^{-7}$ | – | – | – | 24 |
| 2 | $UO_2(H_2O)_5^{2+}$ | 0,173 | 1,65 | $2 \cdot 10^{-6}$ | – | – | – | 19a |
| 3 | $(NH_3)_5CoH_2O^{3+}$ | 0,1* | 0,5 | $2 \cdot 10^{-6}$ | – | – | – | 18 |
| 4 | $Al(H_2O)_6^{3+}$ | 1,9 | 0,44 | $10^{-5}$ | – | – | – | 19b |
| 5 | $Cr(H_2O)_6^{3+}$ | 1,4 | 0,078 | $4 \cdot 10^{-5}$ | – | – | – | 19c |
| 6 | $In(H_2O)_6^{3+}$ | 1,0 | 0,9 | $10^{-5}$ | – | – | – | 19d |
| 7 | $Sc(H_2O)_6^{3+}$ | 1,7 | 1,0 | $2 \cdot 10^{-5}$ | – | – | – | 25 |
| 8 | $Th(H_2O)_6^{4+}$ | 0,9 | 0,07 | $10^{-4}$ | – | – | – | 26 |
| 9 | $GaOH(H_2O)_5^{2+}$ | – | – | – | 1,7 | 0,45 | $3 \cdot 10^{-5}$ | 19d,e |
| 10 | $FeOH(H_2O)_5^{2+}$ | – | – | – | 0,6 | 0,80 | $8 \cdot 10^{-6}$ | 19e |
| 11 | $BeOH(H_2O)_3^{+}$ | $2 \cdot 10^{-6}$+ | $10^{-4}$+ | $2 \cdot 10^{-6}$ | – | – | – | 22 |

*Calculated from $k_{-1}$ and $K_1 = c_{MeOH} \cdot c_H / c_M$ from the data in ref. 1; however, the value of $K_1$ for $Cu^{2+}$ is questionable [27].

+Schwarzenbach attributes the inordinately low values of the rate constants to slow re-solvation of the beryllium cation.

From the Eigen-Smoluchowski equation (20, page 1032) a rate constant of $k_{-1} \approx 2 \cdot 10^{10}$ $M^{-1}\,sec^{-1}$ [28], is calculated for the reaction $MeOH^{2+} + H^+ \xrightarrow{k_{-1}} Me^{3+}$ [28], a radius of recombination of 7.5 Å being assumed. On the other hand, in systems 3 to 7 the values for $k_{-1}$ lie between 0.5 and 1 x $10^{10}$ $M^{-1}$ $sec^{-1}$. The recombination rates $k_{-1}$ and $k_{-2}$ show on the whole the gradation derived by De Maeyer and Kustin [29] from the Eigen-Smoluchowski equation. According to De Maeyer and Kustin the rate constant becomes less for the (diffusion determined) reaction

$$H^+ + Me(OH)_n^{(z-n)+} \xrightarrow{k_{-1}} Me(OH)_{n-1}^{(z+1-n)+}$$

by a factor of 0.3 to 0.5 if the charge of the reaction partner $Me(OH)_n^{(z-n)+}$ is raised by one unit. Experiment shows that

$$k_{-1} \approx 10^{10}\,M^{-1}\,sec^{-1} \text{ for } (z-n) = 1$$

(for systems 1, 2 and $k_{-2}$ for no. 10)

$$k_{-1} \approx 0{,}5 \cdot 10^{10}\,M^{-1}\,sec^{-1} \text{ for } (z-n) = 2$$

(for systems 3 and 4)

$$k_{-1} \approx 0{,}1 \cdot 10^{10}\,M^{-1}\,sec^{-1} \text{ for } (z-n) = 3$$

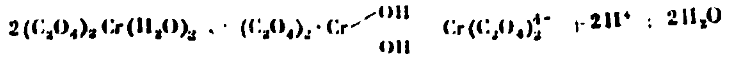
(for system 8)

The fact that the values for systems 6 and 7 are somewhat higher than the typical values for the charge +2 can be due to systematic inaccuracies in the experiments (in particular, in the equilibrium constant $K\alpha_1$). The low values for system 9 [$Ga(OH)^{2+}$] and especially for system 5 ($CrOH^{2+}$) are attributed by Eyring mainly to the different conditions of solvation of the individual cations.

The inordinately low value of the rate constants $k_1$ and $k_{-1}$, which Schwarzenbach [22] found for beryllium, according to him can be ascribed to a reorientation of the hydration shell.

## ii. Formation and Decomposition of Metal-Hydroxy Complexes

After the first qualitative investigations on the formation of the binuclear bis-(μ-hydroxy) Cr(III) complex in aqueous solutions [30-32], Grant and Hamm were the first to report on thorough quantitative kinetic studies of formation of the bis-μ-hydroxy-bis-oxalato-Cr(III) complex [33, 34]

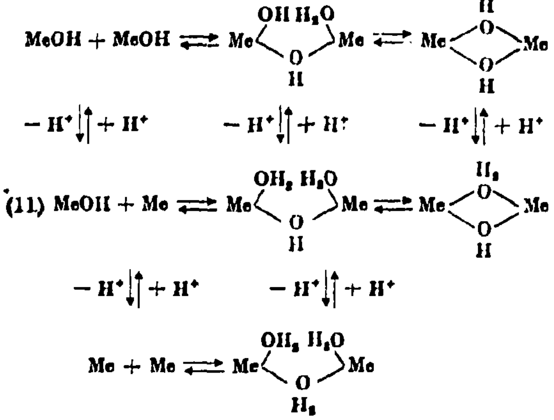
(10)


$$2(C_2O_4)_2Cr(H_2O)_2^- \rightleftharpoons (C_2O_4)_2Cr\begin{matrix}OH\\OH\end{matrix}Cr(C_2O_4)_2^{4-} + 2H^+ + 2H_2O$$

In spite of its negative charge and the oxalate ligands, this complex can serve as a suitable model for a binuclear bis-μ-hydroxy-bridged MeOH complex. Since Cr(III) ions are known to be kinetically inert, that is, they react only very slowly, reaction 10 could be investigated very thoroughly without the aid of modern rapid methods. Specifically, Grant and Hamm have already determined the general conformity to laws on the example of the dimerization reaction shown in eq 10, and these have proved valid for almost all dimerization reactions of hydrated or partially hydrated metal cations.

The rupture of the μ-hydroxy double bridge between the two Cr(III) ions takes place in steps and, at least in the second stage, is catalyzed by protons. Catalysis by protons, as recognized earlier by Grant and Hamm, may be explained by the assumption that the group of the μ-hydroxy bridges can be protonated and that the protonated group is split off appreciably more rapidly than is the intact μ-hydroxy bridge. The results of Grant and Hamm may be summarized by

(11)



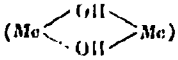
which is expanded by the results of later investigations [35]. The water of hydration, which is associated with the cations provided that it does not enter into the reaction, other possible ligands, and the charges of the species are not given in diagram 11 for reasons of conciseness. In diagram 11 the vertical double arrows denote rapid—that is, protolytic—reactions which are always in equilibrium, while horizontal double arrows indicate slow, rate-determining steps.

The splitting of binuclear MeOH complexes has been investigated on many examples in recent times. In contrast to the example of the dissociation of the tetraethylenediamino-μ-dihydroxydicobaltate-(III) [35], in the study of the dissociation of dimeric MeOH complexes the two-stage nature of the reaction could not be proved explicitly. In the case of the binuclear MeOH complexes investigated, apparently the rate-determining step of the dissociation (splitting off of either the first or second hydroxyl group) takes place very much more slowly than all the other steps, so that the more rapid individual steps cannot be resolved in time (see below). The theoretical reaction rate law for the irreversible dissociation of the binuclear complexes $Me_2(OH)_2^{(Z-1)+} = D$ in solutions with excess acid, which is confirmed for nearly all examples investigated, is written

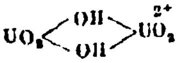
$$\text{(12)} \qquad \frac{dc_D}{dt} = -\left\{k_a + k_b \cdot c_{H^+}\right\} \cdot c_D.$$

In Table 2 are listed the rate constants $k_a$ and $k_b$ for the acid dissociation of various binuclear MeOH complexes. The data show that the rate constants for both the spontaneous decomposition of the dimeric complex ($k_a$) and the proton-catalyzed composition ($k_b$) have a strong dependence on the particular cation, and $k_a$ and $k_b$ vary independently of one another (see Nos. 3, 4, 5, 9, 12, and 13 in Table 2).

Sutin, et al., have expressed the opinion that the ratio of the rate constants $k_b/k_a$ is critically dependent on whether the bond to be split is a bis-μ-hydroxy


(Me<(OH)(OH)>Me)

or a mono-μ-oxy bridge (Me-O-Me) [39]. For μ-oxy bridges $k_2/k_1$ should equal about $10^5$ $M^{-1}$, and for bis-μ-hydroxy bridges, 1 to 100 $M^{-1}$. He asserts that the $k_2/k_1$ ratio can serve as a criterion as to whether a μ-oxy or a bis-μ-hydroxy bond is present. Accordingly, in the case of the uranyl dimer,


$UO_2<(OH)(OH)>UO_2^{2+}$

(Table 2, No. 12) we must conclude that it is a matter of a μ-mono-oxy bridged isopolybase.

However, studies of the crystalline structure show that the binuclear complex $(UO_2)_2(OH)_2^{2+}$ contains two μ-hydroxy bridges [15]. In the case of the binuclear complexes of Fe(III) (Nos. 2 to 5), the V(III) ion (No. 9), the vanadyl ion (No. 13), and the uranyl ion (No. 10), there is good evidence that we are dealing with bis-μ-hydroxy bridged complexes. For this series the $k_b/k_a$ ratios have been determined to be 8, 5, $10^4$, 12. Therefore the magnitude of $k_b/k_a$ can scarcely be considered as a specific index of the bonding conditions in binuclear μ-oxy or μ-hydroxy complexes. The quantity $k_b$ may be regarded as the product of the protonation equilibrium constant of the dimeric complex and the dissociation rate constant of the protonated dimer ($k_b = K_p \cdot K^{DH+}_{fiss}$). In the case of the dimeric uranyl complex it is possible to determine the constants of protonation (for the first and second protonation steps) and the rates of dissociation for the unprotonated ($k^D_{fiss}$), the singly protonated ($k^{DH+}_{fiss}$), and the doubly protonated ($k^{DH2++}_{fiss}$) dimers. The series

$$k^D_{fiss} = k_a \approx 5\ sec^{-1},\ k^{DH+}_{fiss} = 60\ sec^{-1},\ k^{DH_2++}_{fiss} = 900\ sec^{-1}$$

clearly shows that the dissociation of the dimer is facilitated by increasing protonation.

Thus the ratio $k_b/k_a$ depends on the basicity of the μ-oxy or μ-hydroxy bridge as well as on the change to an unstable state which the bridge undergoes upon protonation. Sutin's assertion holds true only in the case where the change to an unstable state of protonated μ-oxy or μ-hydroxy bridges is independent of the species of bridged cation and the difference in basicity between the μ-oxy, and μ-hydroxy bridges does not depend on the species of bridged cation. Neither appears true in general.

Sutin has discussed the question as to the significance of the rate constants $k_a$ and $k_b$ in the decomposition of bis-hydroxy bridged complexes:

Table 2. Reaction rate constants for dissociation of binuclear metal-hydroxy complexes (D) according to the reaction rate law $\frac{dc_D}{dt} = -\left\{k_a + k_b \cdot c_{H^+}\right\} \cdot c_D$

| No | Complex | $k_a$ [$sec^{-1}$] | $k_b$ [$M^{-1} sec^{-1}$] | Conditions $\mu$ [M] | $t$ [°C] | Method | Ref. |
|---|---|---|---|---|---|---|---|
| 1 | $Be_2(OH)_2^{2+}$ | | | | 25° | T-jp | 36 |
| 2 | $Fe_2(OH)_2^{4+}$ ** | 1 ± 0,5 | - | 0,6 | 25° | p-jp | 37 |
| 3 | $Fe_2(OH)_2^{4+}$ + | 0,4 | 3,1 ± 0,1 | 3,0 | 25° | st-fl | 38 |
| 4 | $Fe_2(OH)_2^{4+}$ | 0,42 | 3,33 | 3,0 | 25° | st-fl | 39 |
| 5 | $Fe_2(OH)_2^{4+}$ | 0,4 ± 0,1 | 3,1 ± 0,2 | 3,0 | 25° | st-fl | 40 |
| 6 | $Sc_2(OH)_2^{4+}$ ** | $10^3$ | - | 0,1 | 25° | T-jp | 25 |
| 7 | $Ga_2(OH)_2^{4+}$ ** | 72 | - | 0,5 | 25° | T-jp | 41 |
| 8 | $In_2(OH)_2^{4+}$ ** | 85 | - | 0,5 | 25° | T-jp | 42 |
| 9 | $V_2(OH)_2^{4+}$ | 0,35 | 1,75 | 1,0 | 25° | st-fl | 43 |
| 10 | $(UO_2)_2(OH)_2^{2+}$ *** | - | $10^5$ | 0,5 | 25° | T-jp | 45 |
| 11 | $(UO_2)_2(OH)_2^{2+}$ *** | - | - | 0,05-0,1 | 25° | T-jp | 46 |
| 12 | $(UO_2)_2(OH)_2^{2+}$ **** | ≤ 5 | $5 \cdot 10^4$ | 0,3 | 3° | st-fl | 47 |
| 13 | $(VO)_2(OH)_2^{2+}$ | 17 | 215 | 0,3 | 23° | st-fl | 40 |

* Reaction rate law incorrectly postulated by author for dissociation: $\frac{dc_D}{dt} = -k_a \cdot c_D$.

** Reaction rate law postulated by authors; $\frac{dc_D}{dt} = -k_a \cdot c_D$.

*** Reaction rate law for the dissociation $\frac{dc_D}{dt} = -k_c \cdot c_D \cdot c_H{}^2$, wrongly postulated by authors [48]

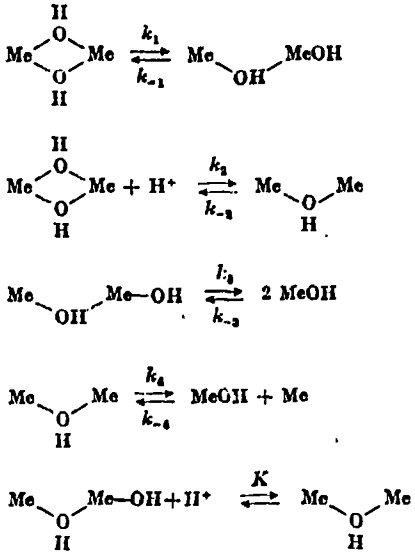
**** Reaction rate law verified by author for the dissociation:

$$(12a) \quad \frac{dc_D}{dt} = -\left\{k_a + k_b \cdot c_H + k_c \cdot c_H{}^2\right\} \cdot c_D.$$

\+ Authors observed anion catalysis for formation and decomposition of the binuclear hydroxy complex.

T-jp = temperature jump; st-fl = stopped flow; p-jp = pressure jump

Are $k_a$ and $k_b$ specific rates for the breeching of the first hydroxy bridge or the second one [39]? For elucidation of this question, in reaction diagram 13 the spontaneous and proton-catalyzed rupture of the first μ-hydroxy bridge is shown in the first two rows; the third and fourth rows contain the spontaneous or proton-catalyzed rupture of the second μ-hydroxy bridge. The fifth row shows the protolytic equilibrium for the protonated and unprotonated form of the "open," i.e., simply bridged dimer.



(13.1)
(13.2)
(13.3)
(13.4)
(13.5)

The system of these reactions yields, with the "stady-state" approximation, the following expression for the effective observed reaction rate constant $k_{obs}$ of the irreversible decomposition:

$$k_{obs} = \frac{k_1 + k_2 \cdot c_H}{1 + \dfrac{k_{-1} + k_{-2} \cdot K \cdot c_H}{k_3 + k_4 \cdot K \cdot c_H}}. \tag{14}$$

In the limiting case we find the following simplified expressions for $k_{obs}$:

(a) When $k_3 + k_4 \cdot K \cdot c_H \gg k_{-1} + k_{-3} \cdot K \cdot c_H$, we have

$$k_{obs} \approx k_1 + k_2 \cdot c_H, \text{ d.h. } k_1 = k_a;\ k_2 = k_b. \tag{14a}$$

Here the direct ($k_1$) and proton-catalyzed rupture ($k_2$) of the first hydroxy bridge in the intact complex is the rate-determining step for the irreversible decomposition of the isopolybase.

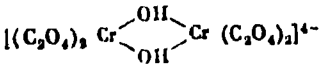
(b) When $k_3 + k_4 \cdot K \cdot c_H \ll k_{-1} + k_{-2} \cdot K \cdot c_H$; $k_{-2} \ll k_{-1}$ and $k_2 \cdot c_H \ll k_{-1}$, we have

$$k_{obs} \approx K_1 \cdot k_3 + K_1 \cdot K \cdot k_4 \cdot c_H \text{ with } K_1 = k_1/k_{-1}, \text{ i.e., } k'_a = K_1 \cdot k_3 \text{ and } k'_b = K_1 \cdot K \cdot k_4. \tag{14b}$$

Thus here the direct and proton-catalyzed rupture of the second hydroxy bridge is evidently the rate-determining step for decompostion of the complex.

Whether limiting case a or b exists has the following consequences for the formation of the binuclear complex. In case a, when there is rapidly completed formation of the simply bridged complex, the rate-determining step for the formation of the final complex must be the establishment of the second hydroxy bridge.

The previously cited studies of Grant and Hamm [33] on the formation of the complex



appear to confirm such a mechanism. If, in contridistinction to this the contacting of the first hydroxyl group is rate-determining for formation of the binuclear MeOH complex,

$$(15)\qquad \mathrm{HOMe} + \mathrm{HOMe} \xrightarrow{k_{-3}} \mathrm{HO{-}Me{-}\underset{H}{O}{-}Me}$$

then we have an interesting theoretical similarity between normal complex formation and the rate-determining primary step of formation of the dimeric OH-bridged complex.

$$(15a)\qquad \mathrm{HOMe} + \mathrm{X} \xrightarrow{k_{\mathrm{complex}}} \mathrm{HO{-}Me{-}X}$$

It can be shown that actually in the case of most of the dimeric MeOH complexes investigated up to the present time the formation of the first μ-hydroxy bridge is the rate-determining step for the cation combination.

Complex formation by metal ions in solution proceeds stepwise ("Eigen" mechanism). The rate constants for bimolecular formation of a complex may be represented by the product of the stability constant for the outer-sphere contact complex $K_0$ ($\mathrm{MeH_2OX}$) and the rate constant $k_{\mathrm{transf}}$ for the monomolecular transformation of the contact complex into the inner-sphere complex:

$$(16)\qquad \mathrm{Me} + \mathrm{X} \underset{}{\overset{K_o}{\rightleftarrows}} \mathrm{Me}\ldots\mathrm{X} \overset{k_{\mathrm{transf}}}{\rightleftarrows} \mathrm{MeX}$$

$$(16b)\quad k^{(\mathrm{Me})}_{\mathrm{complex}} = K_o^{(\mathrm{Me}\ldots\mathrm{X})} \cdot k_{\mathrm{transf}} \approx K_o^{(\mathrm{Me}\ldots\mathrm{X})} \cdot k^{(\mathrm{Me})}_{\mathrm{H_2O\text{-}exch.}}$$

For most complexes this rate of transformation, $k_{\mathrm{transf}}$, is very nearly equal to the water-exchange rate of the cation. The application of the Eigen mechanism to the formation of a metal-hydroxy complex then yields

$$(16c)\qquad k^{(\mathrm{MeOH})}_{\mathrm{complex}} = K_o^{(\mathrm{MeOH}\ldots\mathrm{X})} \cdot k^{(\mathrm{complex})}_{\mathrm{transf}} \approx K_o^{(\mathrm{MeOH}\ldots\mathrm{X})} \cdot k^{(\mathrm{MeOH})}_{\mathrm{H_2O\text{-}exch}}$$

In principle, in the formation of dimeric MeOH complexes the reactor sequence

$$(17a)\quad \mathrm{MeOH} + \mathrm{MeOH} \underset{\text{fast equilibrium}}{\overset{K_o^{(\mathrm{MeOH}\ldots\mathrm{MeOH})}}{\rightleftarrows}} (\mathrm{MeOH}\ldots\mathrm{MeOH})_{\mathrm{contact}}$$

$$(\mathrm{MeOH}\ldots\mathrm{MeOH})_{\mathrm{contact}} \overset{k_{\mathrm{transf}}}{\rightleftarrows} \mathrm{Me{-}\underset{H}{O}{-}Me{-}OH}$$

may likewise be assumed. In the establishment of the first hydroxy bridge, the slowest step is reaction of formation; eq. 16c applies similarly for the specific rate $k_{-3}$ (eq. 13.3)

$$(17) \qquad k_{-3} = K_0(\text{MeOH} \dots \text{MeOH}) \cdot k_{\text{transf}}^{(\text{MeOH}-\text{MeOH})}$$

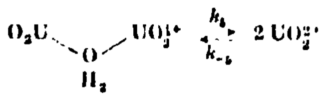
In case the identity

$$(18) \qquad k_{\text{transf}}^{(\text{MeOH}-\text{MeOH})} \approx k_{\text{transf}}^{(\text{Komplex})} \approx k_{\text{H}_2\text{O-exch}}^{(\text{MeOH})}$$

proves true, it must be concluded that for the formation of a complex of the metal-hydroxy cation and of the first μ-hydroxy bridge between two metal-hydroxy cations there is the same underlying rate-determining elementary step, namely, the exchange of water of the metal-hydroxy cation.

For examining this agreement, the bimolecular rate constants obtained from various studies, (a) for the union of two metal-hydroxy complexes $k_{-3}$, eq. 13.3; (b) for the union of a metal-hydroxy complex and a solvated metal cation $k_{-4}$, eq. 13.4; and (c) the rate constant (for the uranyl cation) for the union of two metal cations, $k_{-5}$,

(13.6)



$$\text{O}_2\text{U}\cdots\underset{\text{H}_2}{\text{O}}-\text{UO}_2^{4+} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} 2\,\text{UO}_2^{2+}$$

to form a simple bridged complex are compiled in Table 3. In addition to the ionic strengths, the equilibrium constants of the contact complexes $K_0$(MeOH. . . MeOH), $K_0$ (MeOH . . . Me), and $K_0$ (MeOH . . . Me) are shown. (The constants were calculated by the Fuoss formula for the ionic strength $\mu = 0M$ and extrapolated by means of the Davies formula [49] in each case to the particular ionic strength). The desired constants for the rate of transformation are calculated by eq. 17 from the bimolecular rate constants of formation, and then the values of $K_0$ are calculated.

Finally, Table 3 contains the cation-specific water-exchange or contact-complex transformation rates which are either directly measured (NMR) or calculated from the rates of formation of the complex. The water-exchange rates on metal-monohydroxy ions are not in all cases higher than on simple metal ions. However, as a rule it holds true that $k_{\text{H}_2\text{O}_{\text{exch}}}^{(\text{MeOH})} \gg k_{\text{H}_2\text{O}_{\text{exch}}}^{(\text{Me})}$.

The data assembled in Table 3 can be interpreted as follows [40, 47]:

1. In the union of two metal-monohydroxy complexes to form the dimeric MeOH complex (Table 3, Nos. 1, 2, 3) the contact complexes are transformed into the bridged complex (eq. 17a) at about the same rate as that at which the conversion of the contact complex is converted into the inner-sphere complex in the formation of a complex between metal-hydroxy cations and any complexing ligands. This rate coincides with the water exchange rate of the MeOH cation.

   Of almost the same magnitude is the rate of transformation in the combining of a metal-hydroxy cation with a metal-anion complex (Table 3, Nos. 1', 1", 1'").

Table 3

| No. | Reactants | $k_{-1}$ $[M^{-1}sec^{-1}]$ | $k_{-2}$ $[M^{-1}sec^{-1}]$ | $k_{-3}$ $[M^{-1}sec^{-1}]$ | $\mu$ $[M]$ | $t$ °C | $K_0$ $[M^{-1}]$ | $k_{transf}^{(MeOH-MeOH)}$ $[sec^{-1}]$ | $k_{transf}^{(MeOH-Me)}$ $[sec^{-1}]$ | $k_{transf}^{(Me-Me)}$ $[sec^{-1}]$ | $k_{H_2O\,exch}^{(MeOH)}$ $[sec^{-1}]$ | $k_{H_2O\,exch}^{(Me)}$ $[sec^{-1}]$ | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $FeOH^{2+} + FeOH^{2+}$ | 35 ± 3 | – | – | 0 | 25 | $5\cdot10^{-3}$ | $7\cdot10^{3}$ | – | – | $\sim10^{4}$ | – | [illegible] |
| 1a | $FeOH^{2+} + Fe^{3+}$ | – | $2{,}5\cdot10^{-2}$ | – | 0 | 25 | $5\cdot10^{-4}$ | – | 50 | – | – | 10 | [illegible] |
| 1' | $FeOH^{2+} + FeCl^{2+}$ | 9 | – | – | 0 | 25 | $5\cdot10^{-3}$ | $1{,}8\cdot10^{6}$ | – | – | $\sim10^{4}$ | – | [illegible] |
| 1" | $FeOH^{2+} + FeSCN^{2+}$ | 7 | – | – | 0 | 25 | $5\cdot10^{-3}$ | $1{,}4\cdot10^{6}$ | – | – | $\sim10^{4}$ | – | [illegible] |
| 1''' | $FeOH^{2+} + FeSO_4^{+}$ | 30 | – | – | 0 | 25 | $1{,}5\cdot10^{-2}$ | $2\cdot10^{3}$ | – | – | $\sim10^{4}$ | – | [illegible] |
| 2 | $VOOH^{+} + VOOH^{+}$ | $10^{4}$ | – | – | 0 | 25 | $2\cdot10^{-1}$ | $5\cdot10^{6}$ | – | – | $\sim3\cdot10^{4}$ | – | [illegible] |
| 2a | $VOOH^{+} + VO^{2+}$ | – | 1 | – | 0 | 25 | $1{,}5\cdot10^{-2}$ | – | 66 | – | – | 300 | [illegible] |
| 3 | $UO_2OH^{+} + UO_2OH^{+}$ | $2\cdot10^{4}$ | – | – | 0,5 | 3 | 0,365 | $\leq 10^{6}$ | – | – | $\leq 10^{6}$ | – | [illegible] |
| 3a | $UO_2OH^{+} + UO_2^{2+}$ | – | $3\cdot10^{4}$ | – | 0,5 | 3 | 0,165 | – | $2\cdot10^{5}$ | – | – | $10^{6}$ | [illegible] |
| 3b | $UO_2^{2+} + UO_2^{2+}$ | – | – | 10 | 0,5 | 3 | 0,057 | – | – | ≈ 200 | – | $10^{6}$ | [illegible] |
| 4a | $VOH^{2+} + V^{3+}$ | – | 0,13** | – | 1 | 25 | 0,01 | – | 13 | – | – | $8\cdot10^{*}$ | [illegible] |
| 5 | $ScOH^{2+} + ScOH^{2+}$ | $3\cdot10^{8}$ | – | – | 0,1 | 25 | $2\cdot10^{-2}$ | $1{,}5\cdot10^{6}$ | – | – | $10^{6}$(?) + | $10^{6}$ | [illegible] |
| 6 | $GaOH^{2+} + GaOH^{2+}$ | $3{,}2\cdot10^{3}$ | – | – | 0 | 25 | $5\cdot10^{-3}$ | $6\cdot10^{4}$ | – | – | $2\cdot10^{3}$ + |  | [illegible] |
| 7 | $InOH^{2+} + InOH^{2+}$ | $3{,}6\cdot10^{4}$ | – | – | 0 | 25 | $5\cdot10^{-3}$ | $7\cdot10^{-4}$ | – | – | $3\cdot10^{5}$ | – | [illegible] |
| 8 | $CuOH^{+} + CuOH^{+}$ | $10^{8}$*** | – | – | – | – | – | – | – | – | – | – | – |

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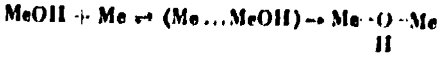
*Estimated from the formation of $VN_3^{2+}$ and $VSCN^{2+}$ complexes, which are not catalyzed by hydroxyl ions [51, 52].

**Calculated from decomposition kinetics [44] and equilibrium constant for $V_2(OH)_2^{4+}$ formation [53].

+Water exchange rate for $Sc^{3+}$ is $10^6$ $sec^{-1}$, determined as in ref. 54 from formation rate of the $Sc^{3+}$-murexide complex (G. Geier, Ber. Bunsenges 69: 617, 1965), while the $GaOH^{2+}$ and $ScOH^{2+}$ rates, $2\times10^3$ $sec^{-1}$ and $3\times10^5$ $sec^{-1}$, respectively, were estimated from the complex-formation rate of $MeOH^{2+}$ $+SO_4^{2-}$ (J. Miceli and J. Stuehr, J. Am. Chem. Soc. 90: 6967, 1968).

***Estimated by Schwarzenbach [42].

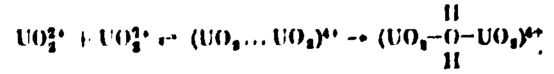
2. In the union of a metal-hydroxy cation with an unhydrolyzed metal cation (Table 3, Nos. 1a, 2a, 3a, 4a), the rate of transformation for the contact complex

(13.4a) 

$$MeOH + Me \rightleftarrows (Me \ldots MeOH) \rightarrow Me-\underset{H}{O}-Me$$

is appreciably lower than the water-exchange rate of the metal-hydroxy cation; its magnitude, however, is approximately the same as that of the water-exchange rate of the unhydrolyzed cations.

3. The union of two unhydrolyzed cations to form a water-bridged binuclear complex, which is conceivable only for the uranyl cation (Table 3, No. 3b)

(13.5a) 

$$UO_2^{2+} + UO_2^{2+} \rightleftarrows (UO_2 \ldots UO_2)^{4+} \rightarrow (UO_2-\overset{H}{\underset{H}{O}}-UO_2)^{4+}.$$

proceeds with a transformation rate which is some two orders of magnitude lower than the water-exchange rate of the unhydrolyzed uranyl ion. This situation which actually indicates a far-reaching analogy between formation of a complex and formation of binuclear MeOH complexes, requires illustration.

In the formation of a metal ion complex, the transformation rate constant for the process

Outer-sphere complex inner-sphere complex

in most cases agrees very well with the water-exchange rate of the complex-forming cation. In the exchange of solvated molecules therefore it is theoretically a reaction which follows an $SN_1$ mechanism. As Strehlow [54] was able to show, in the formation of a complex as well as in the exchange of water the ligand and the newly entering water molecule, respectively, with the temporarily increased coordination number of the cation must penetrate into the inner hydration sphere of the cation. The solvation shell, in absorbing the new water molecule---or the complex former---and losing an old water molecule is finally reoriented, and the individual process of complex formation or exchange of water in concluded. It is found that the activation energy to be applied for this process (and hence the rate of transformation also) is determined essentially by the properties of the particular metal ion and not by the properties of the entering ligand.

That the same conformity to natural laws prevails in the formation of binuclear MeOH complexes (at any rate in the cases treated up to the present time) as in the formation of complexes and exchange of water is understandable if it is considered that in formation of a bridge essentially a hydroxyl ion (on which a metal ion sits as an appendage) as a ligand must penetrate into the inner solvation sphere of the reaction partner.

In Fig. 3 the physical interrelationships deduced from examples 1 to 4a of Table 3 are again shown diagrammatically. Figure 3 (third row) clearly shows why it is that in the union of a metal ion with a metal-monohydroxy cation the relatively low rate of exchange of water (more accurately, rate of penetration into the hydration shell) of the metal ion is the rate-determining step for the establishment of the bridge and not the much higher rate of water exchange of the metal-monohydroxy cation.

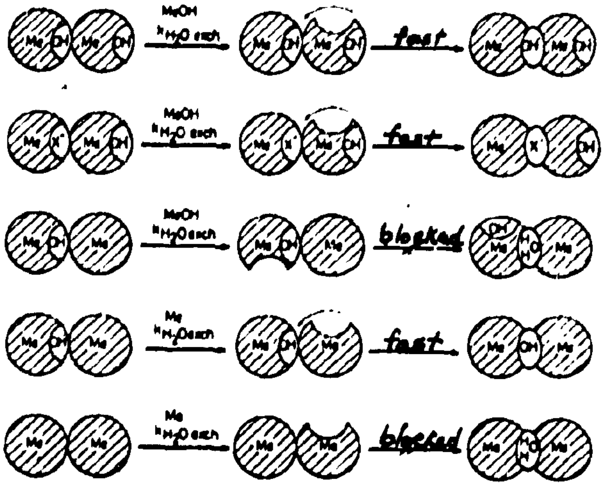


Fig. 3

For electrostatic reasons the hydroxyl ion always indicates a neighboring metal cation in the contact complex. An exchange of water (more accurately, a deformation of the hydration shell which precedes further reaction) on the metal-monohydroxy cation thus always takes place at sites which are not available for establishment of a bridge, i.e., not at the critical surface of contact of the two cations. In this situation nothing is changed by the fact that the hydroxyl group in the contact complex can jump back and forth rapidly between the two cations by means of proton exchange. The "proton vacancy" (namely the hydroxyl group) preferentially stays at the place of contact between the two cations, and therefore this hydroxyl ion must penetrate into the hydration shell of the unhydrolyzed cation for initiating the formation of the bridge, and with this it may be expected that the exchange of water (or the rate of transformation) of the metal ion (and not the transformation rate or exchange of water of the metal-hydroxy ion, which in most cases is appreciably higher) determines the rate of the reaction (13.4a). For the same reason, in the union of a metal-hydroxy cation and a metal anion complex (Fig. 3, second row) the exchange of water of the metal-hydroxy cation proves to be rate-determining (Table 3, Nos. 1', 1", 1"'). Here the bridge is closed by the anion $x^-$ which is bound in the complex and which penetrates into the hydration shell of the metal-hydroxy cation.

According to the model illustrated in Fig. 3, it is likewise understandable why the combining of two unhydrolyxed cations is greatly hindered and takes place more slowly, by some orders of magnitude, than what corresponds to the exchange of water on the metal ion. Hence the reaction is "forbidden" because the water of hydration of the "attacking" metal ion entering into the hydration shell cannot close the bridge; the possible coordination positions of the oxygen of this molecule are blocked by protons.

Examples 5, 6, and 7 of Table 3, however, do not confirm the picture outlined here. The rate constants given by the authors in every case yield rates of transformation which are higher by a factor of 30 to 150 than the water-exchange rates. It is possible that the kinetic data determined for $In^{3+}$, $Ga^{3+}$, and $Sc^{3+}$ are too high owing to the method used---the three metal ions were studied by a relaxation method. Margerum has made a careful comparison of the kinetic data for the dissociation of the binuclear complex $Fe_2(OH)_2^{4+}$, one set of which was determined by a relaxation method [37] and the other by the stopped-flow method. He showed that in many cases the accuracy of a relaxation method with measurements in quasi-equilibrium is insufficient to determine the complete reaction rate law. He proved [38] that the relaxation spectrometric determination of the rate constants for the formation of the binuclear complex must be in error and gives results which are too high. (On the other hand, the determination of the rate constants for the uncatalyzed decomposition of the complex even from relaxation experiments is relatively reliable.)

Therefore for the time being the question must remain unresolved as to whether the transformation rates which are too high for $Sc^{3+}$, $Ga^{3+}$, and $In^{3+}$ are real, i.e., typical of the third group and subgroup, or whether the kinetic data presented must be examined for systematic or other reasons. With the exception of these three cases, however, all the reactions listed in Table 3 fit easily into the complex-forming kinetics scheme of the metal ions, so that the formation of dimeric metal-hydroxy complexes seems to be no unique reaction.

## iii. Formation and Dissociation of Polynuclear Metal-Hydroxy Complexes

The kinetics of the irreversible dissociation of multinuclear MeOH complexes in acidified solutions have been studied in only three prior cases. Margerum, et al. investigated the dissociation of the tetranuclear nickel complex, $Ni_4(OH)_4^{4+}$, while Frei and Wendt were concerned with the acid decomposition of the hexanuclear bismuthyl [23] complex, $Bi_6(OH)_{12}^{6+}$ and the tetranuclear lead [56] complex, $Pb_4(OH)_4^{4+}$. Attempts to elucidate the kinetics of formation and dissociation of the bismuth complex by methods of relaxation kinetics, owing to the complicated nature of the reaction rate laws, have met with little success [23].

On the other hand, the study of the irreversible dissociation of this species of complex in acidified solutions gave unequivocal results, which in turn permit drawing conclusions concerning the kinetics of formation. While in the case of the nickel and bismuth complexes the dissociation of the species mentioned, $Ni_4(OH)_4^{4+}$ and $Bi_6(OH)_{12}^{6+}$, is observed, directly upon admixture of excess acid with a prehydrolyzed Pb(II) perchlorate solution an "open" type, $Pb_4(OH)_6$, is formed from the "closed" $Pb_4(OH)_4$ complex probably by the incorporation of two protons in a very rapid reaction (Fig. 4). The relatively slow dissociation of this "open" form can be studied [56].

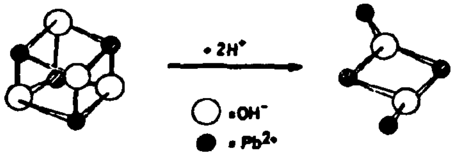


Fig. 4

All polynuclear complexes decompose monomolecularly, and this decomposition can also be catalyzed by protons. However, in the dissociation of the lead and bismuth complexes, still further terms in the reaction rate law of the dissociation must be considered, where the order of the reaction of the MeOH complex is $n_{\text{poly MeOH}} = 1/2$. The generalized reaction rate law for the irreversible dissociation of the three complexes investigated is illustrated by

$$(19)\quad \frac{dc_{\text{Poly}\cdot\text{MeOH}}}{dt} = -\left\{(k_6 + k_7 \cdot c_H) \cdot c_{\text{Poly}\cdot\text{MeOH}} + (k_8 + k_9 \cdot c_H) \cdot c^{1/2}_{\text{Poly}\cdot\text{MeOH}}\right\}$$

The reaction rate constants for the dissociation of the nickel, lead, and bismuth hydroxy complexes, and the conditions under which the experiments were made are shown in Table 4.

Table 4. Kinetic Data for Acid Decomposition of Polynuclear MeOH Complexes (see eq. 19)

| Species | $k_6$ [$sec^{-1}$] | $k_7$ [$M^{-1}sec^{-1}$] | $k_8$ [$M^{1/2}sec^{-1}$] | $k_9$ [$M^{-1/2}sec^{-1}$] | $\mu$ [M] | $t$ [°C] | Ref |
|---|---|---|---|---|---|---|---|
| $Ni_4(OH)_4^{4+}$ | 5 ± 3* | $(7 \pm 0{,}5) \cdot 10^3$ | 0 | 0 | 1,5 | 25 | 55 |
| $Pb_4(OH)_4^{4+}$ | 8 ± 5 | $(4 \pm 1) \cdot 10^3$ | 0,4 ± 0,1 | 200 ± 30 | 1,0 | 3 | 34 |
| $Bi_6(OH)_{12}^{6+}$ | 0,15 | 0,25 | 0 | 0,034 | 3 | 20 | 23 |

*Later evaluation of Margerum's results by eq. 19 [55].

The first two terms in eq. 19 correspond to the direct and proton-catalyzed dissociation of the particular species of complex. This may be interpreted in such a way that in the rate-determining step a MeOH bond in the intact polynuclear complex is broken either directly ($k_6$) or after addition of a proton ($k_7$), and then in a rapid subsequent reaction the complex dissociates completely. (Margerum, et al. who, for the nickel complex $Ni_4(OH)_4^{4+}$, considered $k_6$ as definitely nil, interpret the process of decomposition described in the second, proton-dependent term in eq. 19 ($k_7$) somewhat differently by assuming two steps of comparable rate as the rate-determining reactions for the dissociation: (a) rapid opening and closing of an MeOH bond and (b) addition of a proton onto the open bond. They assume that, as soon as the proton has been added, which competes with the closing of the bond the complex dissociated completely. With this hypothesis they explain a decrease in the rate constant $k_7$ with increase in the proton concentration. At sufficiently high proton concentrations any opening of the OH bond is followed immediately by protonation. Other papers [47, 35], however, indicate that the same observation may also be explained by a simple rapid protolytic equilibrium.)

The third and fourth term in eq. 19 can be explained only if the poly-MeOH complex can dissociate into subunits of half the molecular weight in a fast dissociation equilibrium and the irreversible decomposition of these subunits opens a parrallel reaction path. This is illustrated for the lead and bismuth complexes, respectively, by

$$(20a)\quad Bi_6(OH)_{12}^{6+} \rightleftharpoons 2Bi_3(OH)_6^{3+};\ K_D^{Bi} = \frac{c_{Bi_6(OH)_{12}^{6+}}}{c^2_{Bi_3(OH)_6^{3+}}}$$

$$(20b)\quad Bi_3(OH)_6^{3+} + H^+ \rightleftharpoons Bi_3(OH)_6^{4+};\ K_p^{Bi} = \frac{c_{Bi_3(OH)_6^{4+}}}{c_{H^+} \cdot c_{Bi_3(OH)_6^{3+}}}$$

$$(21a)\quad Pb_4(OH)_4^{4+} \rightleftharpoons 2Pb_2OH^{3+};\ K_D^{Pb} = \frac{c_{Pb_4(OH)_4^{4+}}}{c^2_{Pb_2OH^{3+}}}$$

$$(21b)\quad Pb_2OH^{3+} + H^+ \rightleftharpoons Pb_2OH_2^{4+};\ K_p^{Pb} = \frac{c_{Pb_2OH_2^{4+}}}{c_{H^+} \cdot c_{Pb_2OH^{3+}}}$$

Both the dissociation equilibrium ($K_D$) and the protonation equilibrium ($K_p$) (eqs. 20b and 21b) are fast, i.e., always established equilibrium.

The third and fourth term in eq. 19 take into account the portion of the poly-MeOH complex which disappears through the spontaneous and the proton-catalyzed decomposition of the half-complex subunit. For the case of irreversible dissociation of the lead complex $Pb(OH)_2^{6+}$ this is again illustrated by

$$(22)\quad \frac{dc_{Pb_4(OH)_4^{4+}}}{dt} = (k_6 + k_7 \cdot c_{H^+}) \cdot c_{Pb_4(OH)_4^{4+}} + \frac{1}{2} k_8^{\bullet} \cdot c_{Pb_2OH^{3+}} + \frac{1}{2} k_9^{\bullet} \cdot c_{Pb_2OH_2^{4+}}$$

$$(22a)\quad c_{Pb_2OH^{3+}} = (K_D^{Pb})^{-1/2} \cdot c^{1/2}_{Pb_4(OH)_4^{4+}}$$

$$(22b)\quad c_{Pb_2OH_2^{4+}} = (K_p^{Pb}) \cdot c_{H^+} \cdot (K_D^{Pb})^{-1/2} \cdot c_{Pb_4(OH)_4^{4+}}$$

In order to show the connection between the phenomenological rate constants $k_8$ and $k_9$ corresponding to formula 19 and the true rate constants $\dot{k}_8$ and $\dot{k}_9$ in the case where

$$c_{Pb_2OH_2^{4+}};\ c_{Pb_2OH^{3+}} \ll c_{Pb_4(OH_4^{4+})}$$

we can write

$$c_{Pb_4(OH)_4^{4+}} = c_{Pb_4(OH)_4^{4+}}\ (\text{total}),$$

and from a comparison of eqs. 19 and 22 we obtain

$$(23a)\quad k_8 = \frac{1}{2} k_8^{\bullet} (K_D^{Pb})^{-1/2}$$

$$(23b)\quad k_9 = \frac{1}{2} k_9^{\bullet} (K_D^{Pb})^{-1/2} \cdot (K_p^{Pb})$$

Of the rate constants given in Table 4 only the values for $k_6$ are directly comparable with each other.

All three poly-MeOH complexes prove to be relatively inert, i.e., they decompose slowly; this is true especially for the hexanuclear complex of bismuth ($k_6 \approx 0.1$ sec$^{-1}$).

The equilibrium constants $k_7$ are the products of the protonation equilibrium constants of the poly-MeOH complexes and the decomposition rate of the protonated poly-MeOH complexes. The particularly low value of $k_7$ for the bismuth complex leads to the conclusion that this can be protonated only with great difficulty (especially for reasons of the Coulomb repulsion) and/or the protonated form decomposes only slowly.

Accordingly, from the very low value of $k_9$ for the bismuthyl complex, it can be reasoned that the constant $K_8^{Bi}$ is probably very large, i.e., only very few trimers $[Bi_3(OH)_6^{3+}]$ exist in equilibrium along with the hexamers; these are difficult to protonate; and/or the protonated species $Bi_3(OH)_5^{4+}$ decomposes only slowly. The reaction rate law for the formation of the poly-MeOH complexes of Table 4 can be derived from the reaction rate law for decomposition and the equilibrium constant for the formation of the complexes. For example, for the tetranuclear nickel complex we write

$$\text{(24a)} \quad \frac{dc_{Ni_4(OH)_4^{4+}}}{dt} \text{(formation)} \quad k_{-6}\cdot c^4_{Ni^{2+}}\cdot c^{-4}_{H^+} + k_{-7}\cdot c^4_{Ni^{2+}}\cdot c^{-3}_{H^+}$$

The first and second term may be explained by the kinetic "core and link" mechanism: In a fast pre-equilibrim a trimer is rapidly formed from the monomers $Ni^{2+}$ and $NiOH^+$, and the addition of the last monomer unit is rate-determining for the formation of the tetramer,

$$\text{(24b)} \quad 3Ni^{2+} + 3H_2O \rightleftharpoons Ni_3(OH)_3^{3+} + 3H^+ \xrightarrow{+NiOH^+} Ni_4(OH)_4^{4+}$$

Likewise, a mechanism which provides for a rapid equilibrium between monomers and an "open" tetramer and assumes as the rate-determining step the formation of the "closed" complex is theoretically in agreement with the reaction rate law (eq. 24a).

The kinetics of formation for the lead complex, in conformity with eq. 22, yield a reaction rate law with four terms,

$$\text{(24c)} \quad \left(\frac{dc_{Pb_4(OH)_4^{4+}}}{dt}\right) \text{(formation)} = k_{-6}c^4_{Pb}\cdot c^{-4}_{H^+} + k_{-7}c^4_{Pb}\cdot c^{-3}_{H^+} + k_{-8}\cdot c^2_{Pb}\cdot c^{-1}_{H^+} + k_{-9}\cdot c^2_{Pb}$$

The third and fourth term therefore describe the combining of a $Pb^{2+}$ and a $PbOH^+$ ion ($k_{-8}$) or two $Pb^{2+}$ cations $k_{-9}$ to form the dimer $Pb\text{-}OH\text{-}Pb^{3+}$ or $Pb\text{-}OH_2\text{-}Pb^{4+}$ (see also the formation of the dimeric $Me_2(OH)_2$ complexes, eqs. 13.4a and 13.5b). Accordingly, in the reaction rate law for the formation of the bismuthyl complex a term appears which describes the formation of the trimeric subunit $Bi_3(OH)_5^{4+}$, which, according to eqs. 20a and 20b exists in fast equilibrium with the hexamer.

In conclusion it can be stated that for the formation of complicated, more highly aggregated metal-hydroxy complexes the kinetic "core and link" principle can be verified as well as the second reaction path observed, namely the formation of subunits which unite rapidly to the complete and stable complex.

## Outlook

The polynuclear metal-hydroxy complexes occupy a position in relation to thermodynamic theory between the monomeric metal-hydroxy complexes and the metal hydroxides or hydrated oxides. The process of precipitation or redissolution of metal hydroxides, which is very important industrially, frequently takes place through the metastable step of polynuclear metal-hydroxy complexes. It may be hoped that a deeper knowledge of the kinetics of formation and dissociation of more highly aggregated metal-hydroxy complexes will facilitate the approach to the kinetics of precipitation and redissolution of metal hydroxides.

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