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Review

Reactivity difference between protolytic forms of some macrocyclic chromium(III) complexes in ligand substitution and electron transfer processes

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Dedicated to the memory of Professor Fred Basolo

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ABSTRACT

The review provides insight into the mechanism of ligand substitution and electron transfer (from chromium(III) to iron(III)) by comparison of the reactivity of some tetraazamacrocyclic chromium(III) complexes in the conjugate acid–base forms. Use of two geometrical isomers made possible to estimate the influence of geometry and protolytic reactions in *trans* and *cis* position towards the leaving group on the rate enhancement. Studies on the reaction rates in different media demonstrated the role played by outer sphere interactions in a monodentate ligand substitution.

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1. Introduction

When in 1964 the library of Inorganic Chemistry Department of Nicolaus Copernicus University has purchased the monograph of F. Basolo and his colleague R.G. Pearson "Mechanisms of Inorganic Reactions" [1], in which crystal field theory was applied to other than spectroscopic areas of chemistry, a new era of inorganic chemistry courses for our students has begun. In this monograph, application of crystal field theory was put forward first in an attempt to explain the finer details of the reactivity differences between various metal ions [2]. Huge differences in reactivity of some metals complexes in the conjugate acid–base forms have been an area of considerable interest for many years and have inspired many chemists to attempt a molecular interpretation of the rate variation. This phenomenon of general importance is of particular significance for cobalt(III) complexes widely studied and described by Basolo and Pearson in their textbook. They suggested that the conjugate base intermediate is stabilized by π bonding from the deprotonated ligand to an empty *d* orbital [1]. If Basolo's investigations were concentrated first of all on amine complexes of cobalt(III), the interest on chromium(III) chemistry came later. On the turn of the 20th century development of chromium coordination chemistry have covered such areas as environmental problems [3,4], biochemistry and medicinal applications [5–26], catalysis [27–33], new materials including nanomaterials and heterometallic complexes [34–38]. In all these areas protolytic reactions play crucial role determining thermodynamic stability and reactivity of the applied species in solution.

A major goal of this review has been to provide further insight into the mechanism of ligand substitution and electron transfer by comparison of the reactivity of some tetraazamacrocyclic chromium(III) complexes in the conjugate acid–base forms. Outer sphere interactions between the reactant and counter ion of the supporting electrolyte play an important role in kinetics of these reactions determining the form of the rate law and molecular interpretation of the kinetic parameters. Use of two geometrical isomers made possible to estimate the influence of geometry and protolytic reactions in *trans* and *cis* position towards the leaving group on the rate enhancement. Studies on the reaction rates in different media demonstrated the role played by outer sphere interactions in a monodentate ligand substitution (*specific kinetic salt effect*).

2. Substrates, studied systems and reaction products

2.1. Substrates

Two geometrical isomers *cis* and *trans* of chromium(III) tetraazamacrocyclic complexes have been used as the reactants. Cyclic tetraamines are among the most intensively studied macrocyclic ligands forming stable and inert complexes with many transition metal ions. The hexamethyl derivatives of a very well known cyclam (1,4,8,11-tetraazacyclotetradecane), were obtained by Curtis [39] a half century ago. The cyc*a* or tet*a* and cyc*b* or tet*b* are commonly used abbreviations of *meso*- and *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane diastereoisomers, respectively (Scheme 1).

Tetraaza macrocycles usually coordinate with the N_4 donor set approximately coplanar giving *trans* pseudooctahedral arrangements. The more flexible macrocycles can also coordinate in folded arrangements giving *cis* pseudooctahedral isomers. The cyc*b* ligand, being a racemic mixture of two optical isomers with (R,R,R,R and S,S,S,S) *sec*-NH configuration, is such a one that readily folds giving *cis* isomers of hexacoordinated complexes with two equatorial and one axial methyl substituent on each six-membered chelate ring [40]. Thus, structure of *cis*-$[Cr(cycb)(OH)_2]ClO_4{\cdot}2H_2O$ resolved by Bang and Mønsted [41] can be treated as a prototype for a series of *cis*-[Cr(cyc*b*)XY] type complexes. Some important elements of this structure are presented in Fig. 1.

The complex cation has a distorted pseudooctahedral symmetry with the macrocycle folded to place N_3 and N_4 donor atoms *trans* to each other. The Cr–N_1(N_2), Cr–N_3(N_4), Cr–O bond lengths are as follows: 214.2, 214.0 and 191.8 pm; the N_3–Cr–N_4 and N_1–Cr–N_2 angles are equal to 165.30 and 94.85°, respectively. The significant difference between the N_3–Cr–O_2(N_4–Cr–O_1) and N_3–Cr–O_1(N_4–Cr–O_2) angles equal to 88.08 and 102.18°, respectively, show a pronounced tetrahedral distortion of the CrN_2O_2 – plane that may be accounted for by interactions of this plane with two methyl groups above and below it. The conformations of the five- and six-membered rings are *gauche* and *chair*, respectively [41]. The *cis* configuration has been found for a number of hexacoordinated metal (except of cobalt(III)) complexes with the cyc*b* ligand and is predicted to be the most stable one.

The cyc*a* ligand folds with difficulty and occupies the equatorial plane in pseudooctahedral complexes with *trans* position of two other monodentate ligands. This is due to unfavourable interaction between the axial methyl groups on six-membered chelate rings and the axial ligands in the coordination sphere [40]. Structure of the *trans*-$[Cr(cyca)(H_2O)_2](ClO_4)_3{\cdot}4H_2O$ resolved by Lemma et al. is shown in Fig. 2 [42].

The central ion is coplanar with the four nitrogen atoms. The N_1–Cr–N_3, N_2–Cr–N_4 and O_1-Cr-O_2 angles equal to 179.67, 179.50 and 179.83°, respectively and the lengths of chromium–nitrogen and chromium–oxygen bonds equal to 207.5(Cr–N_1), 204.2(Cr–N_2), 206.1(Cr–N_3), 205.1(Cr–N_4), 200.8(Cr–O_1) and 200.9(Cr–O_2) pm demonstrate quite high octahedral symmetry of the *trans*-$[Cr(cyca)(H_2O)_2]^{3+}$ isomer. The five- and the six-membered rings adopt the *gauche* ($\delta\lambda$) and the *chair* ($\rho\rho$) conformations, respectively. The *sec*-NH protons are in the lowest-energy *R,R,S,S* (*meso*) configuration.

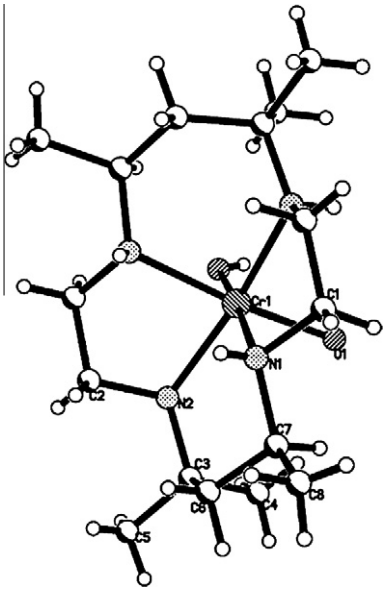


Fig. 1. X-ray structure of *cis*-$[Cr(cycb)(OH)_2]^+$ cation based on the data from [41].

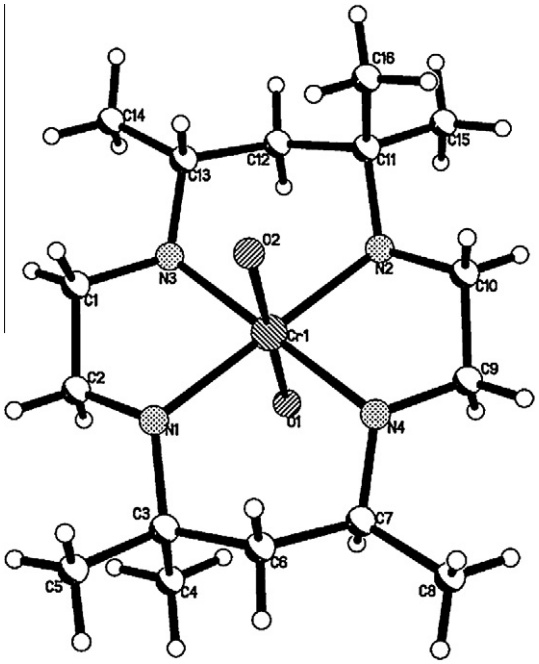
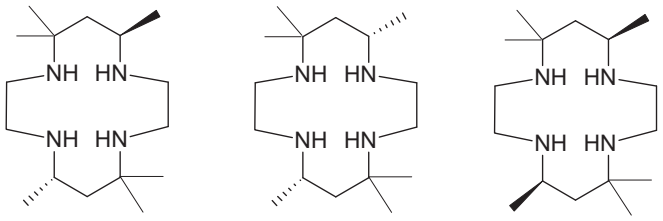


Fig. 2. X-ray structure of *trans*-$[Cr(cyca)(OH_2)_2]^{3+}$ cation based on the data from [42].



Scheme 1. The simplified structures of cyc*a* and cyc*b* ligands.

Tetraaza macrocyclic ligands coordinate to many metal ions giving *cis* or *trans* isomers; structures of complexes with the cyc*a* and cyc*b* ligands have been established for instance for Co(III), Co(II), Ru(III), Ru(II), Fe(II), Fe(III), Ir(III) [43–48]. Interconversion between the *cis* and *trans* isomers of complexes with the cyc*a* and cyc*b* ligands has been observed for some central ions, e.g. Rh(III), Ir(III), Co(III) [48–50] but not for chromium(III) species, though the slow *cis* to *trans* isomerization of chromium(III) – unsubstituted cyclam analogue takes place.

An interesting feature of the cyc*a* and cyc*b* ligands, like of other symmetrical 14-membered ones is a capability to stabilize metals at unusual oxidation states, e.g. chromium(IV) and chromium(V) [51–53].

Chromium(III) complexes with cyc*a* or cyc*b* ligand exhibit several unusual properties compared to other chromium(III) species. The both isomers are extremely resistant to the macrocycle dissociation (aquation) within the whole pH range even at high temperatures. They can be completely converted into dihydroxo conjugate bases without any stereochemical changes or any observable decomposition characteristic for many other chromium(III) species. The robustness, stereochemical rigidity of the [Cr(cyc*a*)] and [Cr(cyc*b*)] moieties and the higher lability of the fifth and sixth coordination positions than that of the coordinated macrocycle allow the synthesis and isolation of the complexes with several monodentate or bidentate ligands as well as studies on reactions at two unblocked coordination positions under very varied conditions under which aquation of other amine ligands takes place. Both *cis*-$[Cr(cyc\mathit{b})(H_2O)_2]^{3+}$ and *trans*-$[Cr(cyc\mathit{a})(H_2O)_2]^{3+}$ cations are medium strength Brønsted diprotic acids, significantly stronger than their *cis* or *trans* tetraamine analogues. This fact may be accounted for by lower hydration energy changes accompanying deprotonation of the complexes with more organic amine ligand [49]. Values of the acidity constants for some tetraamine chromium(III) complexes are given in Table 1.

Inspection of electronic absorption spectral data summarized in Table 2 [49,51,54] proves that the *d-d* transitions in the *cis*-$[Cr(cyc\mathit{b})(H_2O)_2]^{3+}$ ion and its mono and double deprotonated derivatives are characterized by much lower energy and much higher intensity than in other tetraamine chromium(III) complexes; the maximum of its long wavelength *d-d* band is shifted 30–45 nm towards the i.r. and value of the extinction coefficient is up to 5 times higher compared to its analogues with ammonia, ethane-1,2-diamine and even with unsubstituted cyclam. Both these effects may qualitatively be accounted for by tetrahedral distortion of the CrN_2O_2 plane described above.

Table 1
Values of the acidity constants for some tetraamine chromium(III) complexes.

Complex	pK_{a1}	pK_{a2}	Ref.
Cis-$[Cr(NH_3)_4(H_2O)_2]^{3+}$	4.96	7.53	[48]
Cis-$[Cr(en)_2(H_2O)_2]^{3+}$	4.75	7.35	[48]
Cis-$[Cr(trien)(H_2O)_2]^{3+}$	4.47	7.14	[48]
Cis-$[Cr(cyclam)(H_2O)_2]^{3+}$	4.21	7.25	[48]
Cis-$[Cr(cyc\mathit{b})(H_2O)_2]^{3+}$	3.33 (3.49)	7.02 (7.11)	[48]([55])
Trans-$[Cr(NH_3)_4(H_2O)_2]^{3+}$	4.38	7.78	[54]
Trans-$[Cr(en)_2(H_2O)_2]^{3+}$	4.12	7.71	[54]
Trans-$[Cr(cyc\mathit{a})(H_2O)_2]^{3+}$	2.4	6.9	[55]

2.2. Studied systems and reaction products

Differences in reactivity of chromium(III) complexes with the cyc*a* and cyc*b* ligands, collectively referred to as cyc, in their conjugate acid and conjugate base forms have been examined for the three ligand substitution types: (i) anation of the substrate by NCS^- in acidic media [56] or by $[Fe(CN)_6]^{4-}$ ions in slightly acidic, neutral or slightly basic solutions [57]; (ii) aquation of Cr–NCSHg species in acidic media [56] and (iii) base hydrolysis of Cr–X complexes, where X = Cl^-, N_3^-, NCS^-, ONO^-, in strongly alkaline solutions [57,58]. Additionally, electron transfer from chromium(III) to hexacyanoferrate(III) has been studied in basic solution [52,53,59–62]. The key role in the kinetics of these processes is played by protolytic preequilibria of two types:

$$Cr{-}OH_2 + H_2O \rightleftharpoons Cr{-}OH^- + H_3O^+ \quad (1)$$

$$Cr{-}NH + OH^- \rightleftharpoons Cr{-}N^- + H_2O \quad (2)$$

Reaction (1) affects the rate of the anation and mercury(II) induced aquation whereas reaction (2) is crucial in the redox and base hydrolysis processes.

2.2.1. Ligand substitution

Anation of the diaquacomplexes, *cis*-$[Cr(cyc\mathit{b})(H_2O)_2]^{3+}$ and *trans*-$[Cr(cyc\mathit{a})(H_2O)_2]^{3+}$, by thiocyanate [56] and hexacyanoferrate(II) [63] leading to one coordinated water molecule substitution has been studied within pH range 0–2 and 4.5–8.5, respectively. The reactions, practically irreversible under applied conditions, proceed according to Eqs. (3 and 4):

$$[Cr(cyc)(H_2O)_2]^{3+} + NCS^- \rightarrow [Cr(cyc)(H_2O)(NCS)]^{2+} + H_2O \quad (3)$$

$$[Cr(cyc)(X)(X)]^{n+} + [Fe(CN)_6]^{4-} \rightarrow [(X)(cyc)Cr^{III}NCFe^{II}(CN)_5]^{n+k-4} + X^{k-} \quad (4)$$

where X = H_2O or OH^-, n = 1, 2 or 3 and k = 0 or 1.

Kinetics of the reaction (3) have been measured at lower temperatures by an initial rate method under pseudo-zero order conditions up to conversion degree less than 5% and at higher temperatures – by conventional pseudo-first order method up to conversion degree 95%. Formation of the heterobimetallic complex, Eq. (4), has been examined under pseudo-first order conditions applying an excess of the iron(II) complex over the chromium(III) species up to 90–95% of the conversion degree.

Mercury(II)-assisted aquation of the monothiocyanatocomplex [56], Eq. (5):

$$[Cr(cyc)(H_2O)(NCSHg)]^{4+} + H_2O \rightarrow [Cr(cyc)(H_2O)_2]^{3+} + HgSCN^+ \quad (5)$$

has been followed in solution of 0.05–1.8 M $HClO_4$ up to 4 half lives.

Table 2
Characteristic spectral data for some tetraamine chromium(III) – type complexes.

Complex	λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$)	λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$)	λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$)	Ref.
Cis-$[Cr(NH_3)_4(H_2O)_2]^{3+}$	366(27)	495(36)		[50]
Cis-$[Cr(en)_2(H_2O)_2]^{3+}$	366(44)	485(68)		[50]
Cis-$[Cr(trien)(H_2O)_2]^{3+}$	372(36)	497(72)		[50]
Cis-$[Cr(cyclam)(H_2O)_2]^{3+}$	370(38)	483(26)		[50]
Cis-$[Cr(cyc\mathit{b})(H_2O)_2]^{3+}$	388(82)	529(169)		[48]
Cis-$[Cr(cyc\mathit{b})(H_2O)(OH)]^{2+}$	407(53)	572(130)		[48]
Cis-$[Cr(cyc\mathit{b})(OH)_2]^{+}$	380(73)	609(111)		[48]
Trans-$[Cr(NH_3)_4(H_2O)_2]^{3+}$	368(30)	476(21)		[50]
Trans-$[Cr(en)_2(H_2O)_2]^{3+}$	361(39)	442(29)	508(23)	[50]
Trans-$[Cr(cyclam)(H_2O)_2]^{3+}$	350(53)	405(39)	510(24)	[50]
Trans-$[Cr(cyc\mathit{a})(H_2O)_2]^{3+}$	418(42)	510(20)		[55]

Base hydrolysis [57,58], i.e. the monodentate X ligand release proceeding practically irreversibly according to Eq. (6):

$$[Cr(cyc)(OH)(X)]^{+} + OH^{-} \rightarrow [Cr(cyc)(OH)_2]^{+} + X^{-} \quad (6)$$

where X = NCS^-, N_3^-, Cl^- or ONO^- has been studied in 0.02–1.9 M NaOH till 3–4 half lives. Concentration of chromium(III) complex was at least two orders of magnitude lower than that of OH^- ions. Chromatographic separations of the reaction mixtures and spectroscopic identification of the separated complexes provided that the reactions (3)–(6) are accompanied by neither macrocyclic amine liberation nor isomerization; complete retention of configuration has been observed under the conditions applied. Thus, detailed studies on kinetics of these transformations make possible comparison of the *cis* and *trans* isomers reactivity and an evaluation of the labilizing effect of a hydroxide ligand at *cis* and *trans* positions to the substituted ligand.

2.2.2. Electron transfer

Electron transfer from chromium(III)–cyc complexes to hexacyanoferrate(III) has been studied under pseudo-first order conditions with respect to either the oxidant or the reductant in strongly alkaline solution (pH ⩾13) [52,53,60–62]. The reaction leads to long-lived chromium(V) species, detected by EPR method, finally transformed to chromate(VI), illustrated in Scheme 2 where X = OH^-, F^-, Y = OH^-, F^- or XY = $C_2O_4^{2-}$. Stoichiometry of the redox process has been established applying several analytical techniques. The Cr^{III}:Fe^{III} molar ratio assigned based on results of determination of: (i) hexacyanoferrate(II) produced during the reaction using potentiometric measurements with platinum indicator electrode and cerium(IV) or permanganate titration, and (ii) unreacted chromium(III) by chromatographic separation of the reaction mixture, has been found to be around 1:(7–9) depending on hydroxide concentration. It has been demonstrated by chromatographic separations of acidified reaction mixtures combined with electrospray ionization mass spectrometry that during the reaction course a multitude of chromium complexes with oxidized macrocyclic amine is produced. It has been postulated that an electron transfer from the chromium(III) t_{2g} orbitals to the hexacyanoferrate(III) t_{2g} one is followed by an intramolecular oxidation of the macrocyclic ligand. This results in reduction of chromium(V) back to chromium(III) coordinated to the organic ligand oxidized to loose hydrogen and/or to gain double bonded oxygen atoms. Then, the chromium(III) species produced in this way is oxidized to chromium(V) by hexacyanoferrate(III), Scheme 3, where cyc_{ox} and cyc'_{ox} denote oxidized forms of the macrocyclic ligand. Formation of multiple chromium(V) complexes has been further supported by the EPR spectroscopy showing in addition that ultimatively only one of them is stabilized. This most inert chromium(V) is coordinated to four equivalent or almost equivalent nitrogen atoms and one oxygen atom and its EPR characteristics is similar to that of perchloratooxochromium(V) porphyrins [59]. The last stage of the redox process, i.e. further oxidation of chromium(V) to chromate(VI) takes place only after macrocyclic ligand decomposition. Kinetics of the oxidation process have been followed by UV/Vis spectrophotometry. Special attention was focused on its first stage, i.e. Cr^{III} to Cr^{IV} conversion being the rate limiting step for the chromium(V) formation.

$$Cr^{III}(cyc)XY \longrightarrow Cr^{IV}(cyc)X \longrightarrow Cr^{V}(cyc)O \longrightarrow CrO_4^{2-}$$

Scheme 2.

$$Cr^{III}(cyc) \xrightarrow{-2e^-} Cr^{V}(cyc) \xrightarrow{-2H^+} Cr^{III}(cyc_{ox}) \xrightarrow{-2e^-,\,-2H^+} Cr^{V}(cyc'_{ox}) \ldots\ldots$$

Scheme 3.

3. The reactivity of some tetraazamacrocyclic chromium(III) complexes in their conjugate acid and conjugate base forms

3.1. Acidic media, enhanced reactivity due to coordinated water deprotonation

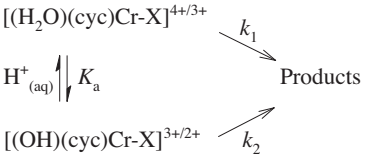
Kinetic effects accompanying deprotonation of the coordinated water molecule have been studied for the monodentate ligand liberation during aquation and anation processes shown by Eqs. (3)–(5). Difference in the reactivity of the aqua and hydroxo forms of the complexes can be evaluated based on the k_1 and k_2 parameters determined from the three parameters rate expression, given by Eq. (7), describing the dependence of the observed pseudo-first order rate constant (k_{obs}) on pH. Eq. (7) is derived assuming a fast protolytic equilibrium step followed by the parallel ligand substitution from the reactants in their conjugate acid (k_1) – base (k_2) forms (Scheme 4) [56], where X denotes H_2O or NCSHg ligand.

$$k_{obs} = \left(k_1 + \frac{k_2 K_a}{\left[H^+_{(aq)}\right]}\right) \Big/ \left(1 + \frac{K_a}{\left[H^+_{(aq)}\right]}\right) \quad (7)$$

Eq. (7) satisfies very well a decrease of value of the observed pseudo-first order rate constant (k_{obs}) with an increase of acid concentration; a representative example is given in Fig. 3.

The validity of the proposed reaction model has been verified by a very good agreement of values of the acidity constant (K_a) obtained from kinetic experiments with those determined independently by potentiometric titration. The k_2/k_1 quotient is a measure of the labilizing effect of hydroxide ion present in the inner coordination sphere of the reactant. Values of this quotient for the aquation (Eq. (5)) and anation (Eq. (3)) processes are summarized in Table 3.

The data in Table 3 show the strong accelerating effect of the water molecule deprotonation for the NCSHg ligand release similar



Scheme 4.

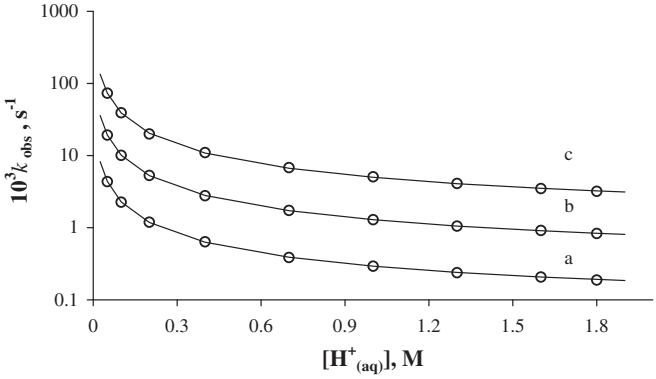


Fig. 3. Dependence of the k_{obs} on $[H^+_{(aq)}]$ for the aquation of *cis*-[Cr(cyc*b*)-(H_2O)(NCSHg)]$^{4+}$ ions at I = 2.0 M; (a) 310 K, (b) 319 K, (c) 329 K [56].

Table 3
Kinetic parameters for the aquation of $[Cr(cyc)(OH_2)(NCSHg)]^{4+}$-type complexes (Eq. (5)) and the anation of $[Cr(cyc)(OH_2)_2]^{3+}$-type complexes by NCS^- ion (Eq. (3)) in their aqua (k_1) and hydroxo (k_2) forms at 298 K, I = 2.0 M.

Complex	k_2/k_1	E_a (k_2), kJ mol^{-1}	E_a (k_1), kJ mol^{-1}	Ref.
Cis-$[Cr(cyc*b*)(OH_2)(NCSHg)]^{4+}$	1327	114	124	[56]
Trans-$[Cr(cyc*a*)(OH_2)(NCSHg)]^{4+}$	1000	89	113	[56]
Cis-$[Cr(cyc*b*)(OH_2)_2]^{3+}$ + Cl^-	$8.3 \times 10^{4*}$	-	125	[64]
Cis-$[Cr(cyc*b*)(OH_2)_2]^{3+}$ + NCS^-	1140	98	100	[57]
Trans-$[Cr(cyc*a*)(OH_2)_2]^{3+}$ + NCS^-	192	101	119	[57]

* I = 1.0 M.

for the both isomers – *ca.* three orders of magnitude – indicative that the labilization of the leaving group caused by OH^- is not directional. In the case of the Cl^- ligand liberation this effect is even larger – *ca.* five orders of magnitude for the *cis* isomer; unfortunately the analogous data for the *trans* one are not available due to the exceptional inertness of its aqua form. The rate enhancement found for the anation process is similar to that for the NCSHg ligand liberation, but is stronger for the *cis* than for the *trans* isomer. However, it is not a good proof for the labilization directionality of the OH^- ligand because the k_1 and k_2 rate constants for the anation are composite quantities, so they are not as good reactivity measures as for the aquation process. In terms of a simplified anation model, neglecting outer sphere interactions between the positive charged reactant and the counter ion of the supporting electrolyte, they are interpreted as the products of the encounter complex formation constant and the rate constant. The more complete model of the anation process including all outer sphere interactions leads to much more complex form of the rate expression giving difficult to separate set of parameters [65–67]. The rate constant increase due to the deprotonation of the coordinated water molecule is larger for the examined macrocyclic complexes than for many other chromium(III) species; the $[Cr(H_2O)_5(OH)]^{2+}$ ion, for example, exchanges its water molecule only 75 times faster than its conjugate acid, $[Cr(H_2O)_6]^{3+}$ [68]; however value of the rate constant for Cl^- ligand liberation from the *cis*-$[Cr(NH_3)_4(OH)Cl]^+$ ion is even 4.1×10^4 times higher than from its aqua analog [64]. The significant uncertainties in the activation parameters make mechanistic considerations hard or almost impossible, although it is noted that the rate enhancement is accompanied by the activation energy lowering for the both considered processes (Table 3).

Much more complicate dependence of the reaction rate on pH has been found for the anation of the macrocyclic chromium(III) species by hexacyanoferrate(II) leading to formation of heterobimetallic complexes, Eq. (4) [63]. The pseudo-first order rate constant (k_{obs}) versus pH profiles, illustrated in Figs. 4 and 5 can be accounted for in terms of the reaction model outlined in Scheme 5.

The observed variation of value of the k_{obs} with pH is a consequence of different reactivities of chromium(III) complexes in their diaqua, aquahydroxo and dihydroxo forms described by pseudo-second order rate constants k_{an1}, k_{an2} and k_{an3}, respectively. The rate law developed for this type of system, in which protolytic equilibria of the outer sphere complexes were omitted for the simplicity, is of the form:

$$k_{an} = \frac{k_{obs}}{[Fe^{II}]} = (k_{an1}[H^+_{(aq)}]^2 + k_{an2}K_{a1}[H^+_{(aq)}] + k_{an3}K_{a1}K_{a2})/([H^+_{(aq)}]^2 + K_{a1}[H^+_{(aq)}] + K_{a1}K_{a2}) \quad (8)$$

where K_{a1} and K_{a2} are the acid dissociation constants for the $[Cr(cyc)(H_2O)_2]^{3+}$ and $[Cr(cyc)(H_2O)(OH)]^{2+}$ ions, respectively. For *trans* isomer being a strong Brønsted acid, that practically does not exist as the $[Cr(cyc*a*)(H_2O)_2]^{3+}$ ion over the considered pH range, k_{an1} term is negligible and Eq. (8) reduces to Eq. (9):

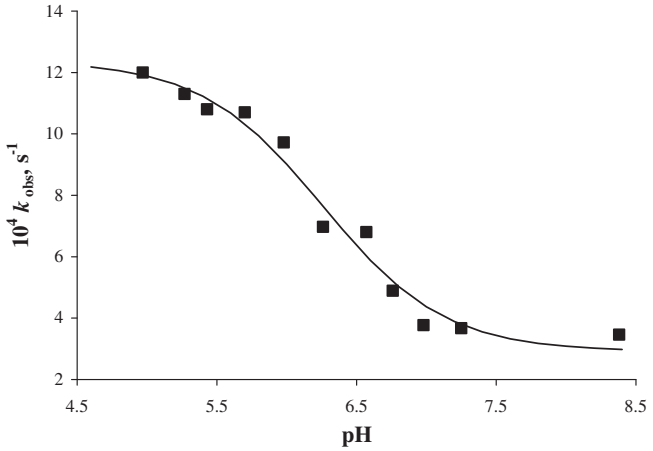


Fig. 4. Dependence of the k_{obs} on pH for the reaction between *trans*-$[Cr(cyc*a*)(H_2O)_2]^{3+}$ and $[Fe(CN)_6]^{4-}$ ions; $[Fe^{II}]$ = 0.10 M, I = 2.0 M, T = 308 K [63].

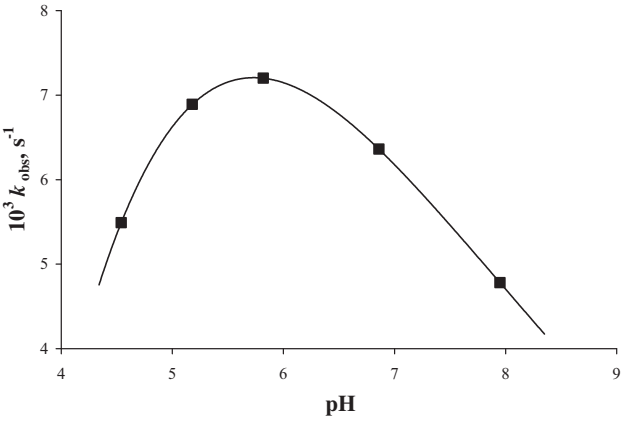


Fig. 5. Dependence of the k_{obs} on pH for the reaction between *cis*-$[Cr(cyc*b*)(H_2O)_2]^{3+}$ and $[Fe(CN)_6]^{4-}$ ions; $[Fe^{II}]$ = 0.12 M, I = 2.0 M, T = 298 K [63].

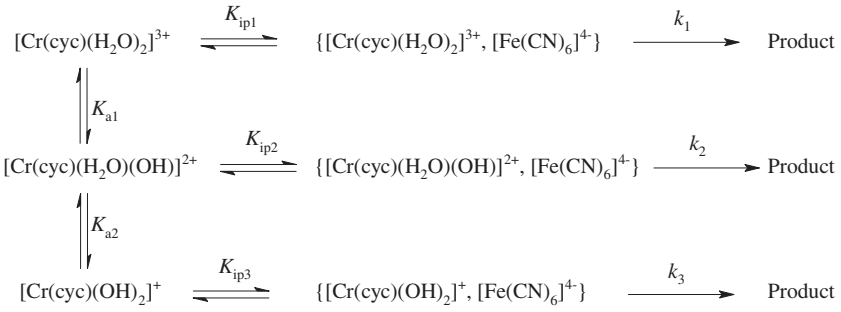
$$k_{an} = (k_{an2}[H^+_{(aq)}] + k_{an3}K_{a2})/([H^+_{(aq)}] + K_{a2}) \quad (9)$$

equivalent to the algebraic expression of the form:

$$k_{an} = \left(a + b\left[H^+_{(aq)}\right]\right)/\left(1 + c\left[H^+_{(aq)}\right]\right) \quad (10)$$

where $a/c = k_{an3}K_{a2}$, $b/c = k_{an2}$ and $1/c = K_{a2}$.

The chosen pH range was too narrow (at higher acidities of the solution the $[Fe(CN)_6]^{4-}$ anion exists in its protonated forms) to evaluate the reactivity difference of the diaqua and the aquahydroxo forms. Nevertheless, the collected data demonstrate that the OH^- ligand present in the inner coordination sphere labilizes the coordinated water molecule (Fig. 6). It is worth noting that substitution of the OH^- ligand is more difficult than of the H_2O one.



Scheme 5.

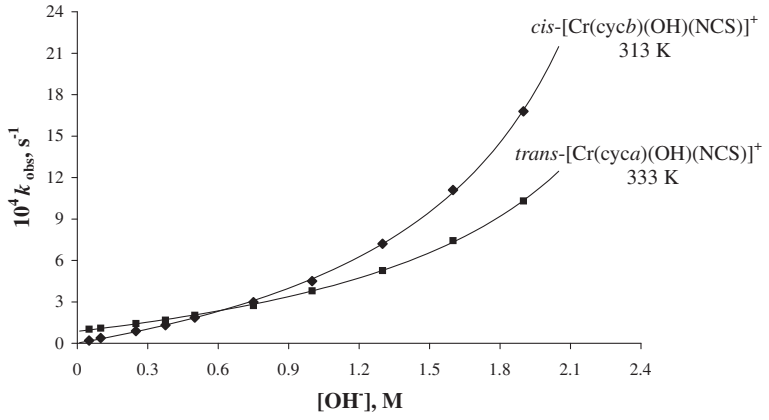


Fig. 6. Dependence of the observed rate constant on OH^- ion concentration for the base hydrolysis of the $[Cr(cyc)(OH)(NCS)]^+$ complexes [57].

Comparison of values of the rate constants shows that the reactivity of the *trans* aquahydroxo derivative (k_{an2}) is only one order of magnitude higher than that of its dihydroxo form (k_{an3}). This remarkably small effect arises from the lower value of the preassociation constant of the $[Fe(CN)_6]^{4-}$ and the $[Cr(cyc)(OH)_2]^+$ ions (K_{ip3}, Scheme 5) than of the $[Fe(CN)_6]^{4-}$ and the $[Cr(cyc)(H_2O)(OH)]^{2+}$ ions (K_{ip2}, Scheme 5) originating from the lower electric charge of the dihydroxo cation than of the aquahydroxo one. As a consequence, values of the rate constant of the rate limiting step, $k_2 = k_{an2}/K_{ip2}$ and $k_3 = k_{an3}/K_{ip3}$ for the aquahydroxo and dihydroxo chromium(III) derivatives, respectively, are expected to be close to each other.

Summing up, it has been found that kinetics of a monodentate ligand substitution from chromium(III) macrocyclic species in acidic media are strongly affected by pH. Kinetic parameters obtained from the established dependence of the observed rate constant on $[H^+_{(aq)}]$ allow one to compare reactivity difference between the aqua and the hydroxo chromium(III) complexes. In the case of the aquation process, the determined rate constants directly represent the reactivity of two protolytic forms of the complexes. In contrast, for the anation process the discussion is much less straightforward because it is based on the unseparated rate and preequilibrium constants.

3.2. Alkaline media, enhanced reactivity due to the macrocyclic amine ligand deprotonation

Exceptional inertness of the $[Cr(cyc)(F)_2]^+$, $[Cr(cyc)(C_2O_4)]^+$ and $[Cr(cyc)(OH)(X)]^+$ – type complexes, where $X = OH^-$, F^-, NCS^-, N_3^-, enables an evaluation of the reactivity difference between the reactants with the protonated and the deprotonated macrocyclic amine ligand in two groups of chemical processes, i.e. a monodentate ligand liberation and chromium(III) oxidation. Inspection of the variation of the observed rate constant values (obtained under pseudo-first order conditions) with pH over a wide OH^- concentration range (up to 2 M) has demonstrated the analogous nonlinear k_{obs} vs. $[OH^-]$ profile for the both groups of the studied processes [52,53,57,61,62], Figs. 6 and 7.

An increase of the reaction rate with an increase of pH demonstrates importance of the macrocyclic amine ligand deprotonation prior to a monodentate ligand release or an electron transfer. A higher order than linear dependence of the observed pseudo-first

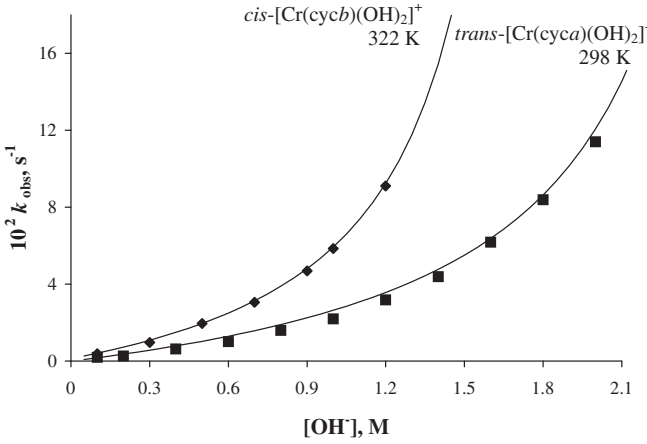
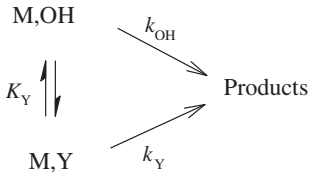


Fig. 7. Dependence of the observed rate constant on OH^- ion concentration for the oxidation of the $[Cr(cyc)(OH)_2]^+$ complexes by $[Fe(CN)_6]^{3-}$ ions [52,53].



Scheme 6.

order rate constant (k_{obs}) on the hydroxide concentration, particularly well marked at high [OH^-] could be rationalized in terms of the double deprotonation of the macrocyclic amine ligand or, alternatively, the competitive ion-pairing of the chromium(III) reactant with OH^-. The first mechanism leads to a parabolic k_{obs} vs. [OH^-] dependence. However, much better reproduction of the data is obtained using the hyperbolic function of the type:

$$k_{obs} = (a + b[OH^-])/(1 + c[OH^-]) \quad (11)$$

Eq. (11) is equivalent to the rate law given by Eq. (12), developed under isolation experimental conditions in terms of a model operating with a competitive ion-pair formation between the chromium(III) reactant (M) and the two anions – the OH^- and the counter ion of the supporting electrolyte (Y) followed by a single proton transfer within the hydroxide ion-pair {M,OH} to give a reactive conjugate base (CB). As a consequence, specific outer sphere interactions between the chromium(III) cation and a counter ion of the supporting electrolyte lead to the retardation of the reactive conjugate base formation. The reaction model is presented in Scheme 6, in which the conjugate base (CB) formed *via* the deprotonation of the macrocyclic amine ligand within the {M,OH} ion-pair is not *explicity* shown. The rate law derived from Scheme 6 is of the form:

$$k_{obs} = (k_Y c_Y + k_{OH} K_Y c_{OH})/(c_Y + K_Y c_{OH}) \quad (12)$$

where $c_Y + c_{OH} = I$, I being the ionic strength and k_Y is the pseudo-first order rate constant for reaction of the ion-pair formed by the conjugate acid and a counter ion of the supporting electrolyte. Comparison of Eqs. (11 and 12) gives the following relations among the parameters:

$$a = k_Y, b = (k_{OH} K_Y - k_Y)/I \text{ and } c = (K_Y - 1)/I \quad (13)$$

3.2.1. Ligand liberation

Some kinetic data for the base hydrolysis are collected in Table 4. The validity of the proposed reaction model has been proved by comparison of the k_{OH} values determined at the ionic strength equal to 1 and 2 M. The increase of the ionic strength doubles value of the k_{OH} (Table 4) whereas it does not affect the k_Y what is in accordance with Eq. (12). On the other hand, values of the k_Y show a statistically significant variation with the nature of the supporting electrolyte.

The k_{OH} is a composite parameter and can not be used as a direct measure of the conjugate base reactivity. It represents a cumulative reactivity of the conjugate base and the hydroxide ion-pair {M, OH}. Calculation of the k_{cb} component from the k_{OH} term requires an independent determination of the proton transfer equilibrium constant which is unobtainable for the studied systems. Nevertheless, the k_{OH} is two–three and one order of magnitude higher for *trans* and *cis* isomers respectively, than the k_Y demonstrating a much higher reactivity of the reactant in the form of the conjugate base. Values of the k_Y and k_{OH} given in Table 4 prove that: (i) the reactivity of the *cis* isomers is much higher than of their *trans* analogues; (ii) the rate of the monodentate ligand liberation increases (the k_Y and k_{OH} path) with the decreasing ligand field strength of the leaving group: $NCS^- < N_3^- \ll Cl^-$; (iii) specific kinetic salt effect reaches 30% for the *cis* and 95% for the *trans* isomers, respectively; (iv) value of the k_Y depends on the nature of the counter ion (Y).

3.2.2. Chromium(III) oxidation

Operation of the common rate law describing dependence of the k_{obs} on [OH^-] for the monodentate ligand liberation and chromium(III) oxidation processes (Eqs. (11 and 12)) illustrated in Fig. 7 implies the decisive role of the reductant deprotonation for the oxidation process and a higher reactivity of the reductant in the form of the conjugate base. Results of the nonlinear least square fitting of the k_{obs} – [OH^-] data to Eq. (11) are shown in Table 5. The best fit has been obtained for a equal to 0 indicating that the reaction path involving the reactants in their conjugate acid forms can be neglected. The k_Y reaction path (Eq. (13)) is observable only for oxidation of the *cis* dihydroxo complex but it is still statistically unimportant. Characteristic differences in the b and the c parameters variations with temperature are seen. Values of the b substantially increase together with the temperature whereas values of the c increase only 10–20% for the *trans* isomers and for the *cis* ones fluctuate irregularly round the value equal to −0.5. This is consistent with the mechanistic interpretation of these parameters (Eq. (13)). The c parameter is connected with the equilibrium constant for which minor changes with the temperature are expected but the temperature changes of the b are determined first of all by the substantial changes in the k_{OH} rate constant, Eq. (13).

Table 5
The results of the nonlinear least square fitting of the kinetic data, for the oxidation chromium(III) macrocycle complexes by $[Fe(CN)_6]^{3-}$ ions, to equation $k_{OH} = \frac{b[OH^-]}{1+c[OH^-]}$.

Reductor	T (K)	b, $M^{-2}s^{-1}$	c, M^{-1}	Ref.
Cis-[Cr(cyc*b*)$(OH)_2$]$^+$	312	1.52 ± 0.03	−0.49 ± 0.01	[69]
	322	2.75 ± 0.04	−0.53 ± 0.01	
	332	5.67 ± 0.36	−0.47 ± 0.05	
Trans-[Cr(cyc*a*)$(OH)_2$]$^+$	288	0.66 ± 0.01	−0.38 ± 0.03	[53]
	298	1.53 ± 0.05	−0.37 ± 0.05	
	308	3.42 ± 0.16	−0.36 ± 0.08	
	318	6.93 ± 0.18	−0.36 ± 0.05	
Trans-[Cr(cyc*a*)(F)(OH)]$^+$	288	0.51 ± 0.02	−0.40 ± 0.05	[60]
	298	1.05 ± 0.09	−0.39 ± 0.01	
	308	2.33 ± 0.09	−0.37 ± 0.08	
	318	5.14 ± 0.26	−0.34 ± 0.18	

Table 4
Comparison of the k_{OH} and k_Y rate constants for the base hydrolysis of the selected [Cr(cyc)(OH)(X)]$^+$-type species at T = 298 K [57].

Reactant			k_Y, s^{-1}			k_Y, s^{-1}
	I = 1.0 M	I = 2.0 M	I = 1.0 M			I = 2.0 M
	k_{OH}, s^{-1}	k_{OH}, s^{-1}	Y = ClO_4^-	Y = Cl^-	Y = Br^-	Y = ClO_4^-
Trans-[Cr(cyc*a*)(OH)(NCS)]$^+$	1.6×10^{-3}	3.4×10^{-3}	9.0×10^{-6}	1.6×10^{-5}	2.0×10^{-6}	1.3×10^{-5}
Trans-[Cr(cyc*a*)(OH)(N_3)]$^+$	1.3×10^{-2}	2.9×10^{-2}	4.7×10^{-5}	7.5×10^{-5}	5.6×10^{-5}	4.5×10^{-5}
Trans-[Cr(cyc*a*)(OH)(Cl)]$^+$	6.1×10^{-1}		5.7×10^{-3}	8.1×10^{-3}	7.6×10^{-3}	
Cis-[Cr(cyc*b*)(OH)(NCS)]$^+$	9.5×10^{-4}	1.7×10^{-3}	1.3×10^{-4}	1.7×10^{-4}	1.5×10^{-4}	1.5×10^{-4}
Cis-[Cr(cyc*b*)(OH)(N_3)]$^+$	2.8×10^{-3}	5.1×10^{-3}	3.3×10^{-4}	4.1×10^{-4}	3.3×10^{-4}	2.6×10^{-4}
Cis-[Cr(cyc*b*)(OH)(Cl)]$^+$	4.5×10^{1}		4.0	5.9	5.4	

Comparison of the reaction pattern and values of the kinetic parameters for the chromium(III) macrocyclic complexes (Table 5) with the data for analogous reaction of chromates(III) [52] and bis(bipyridine) complex [70], leads to the following conclusions: (i) chromium(V) species are efficiently stabilized to accumulate in solution only by the macrocyclic ligands; (ii) the deprotonation of all the examined chromium(III) complexes plays the crucial role in the electron transfer process resulting in a strong dependence of the reaction rate on the OH^- concentration; (iii) the *b* is a composite parameter that depends on the rate constant of the electron transfer from the reductant in the form of the conjugate base and value of the preequilibrium constant for the competitive Br^-/OH^- outer sphere complex formation between these anions and the chromium(III) complex, Eq. (13).

A quantitative evaluation of the reactivities of the complexes due to the macrocyclic amine ligand deprotonation is impossible because of the exceptionally slow rate of the oxidation process at $[OH^-] < 0.1$ M ($a \approx 0$). Moreover, if value of the *c* is close to -0.5 the separation of the parameters connected by Eq. (13) is unrealizable because then value of the K_Y is close to 0 and the quotient $2b/K_Y = k_{OH}$ is determined with a large error even if the *c* parameter is determined with a high accuracy.

For that reason the reactivities of the complexes can be compared based on the values of the *b* parameter at 298 K (Table 5) giving the following reactivity order: *cis*-$[Cr(cyc\mathit{b})(OH)_2]^+$ < *trans*-$[Cr(cyc\mathit{a})(F)(OH)]^+$ < *trans*-$[Cr(cyc\mathit{a})(OH)_2]^+$. It is remarkable that the *trans* isomer is oxidized faster than the *cis* one whereas the monodentate ligand substitution is faster in the *cis* than in the *trans* isomer. As it has been stated in the previous paper: "the chromium(V) species formed *via* oxidation of the *trans* isomer are less inert than the analogues chromium(V) complexes obtained from the *cis* isomer. It can be ascribed first of all to the discussed differences in the steric hindrances of the organic ligands" [53].

Differences in values of the *c* parameter (reflecting differences in the preequlibrium constant K_Y) are of important kinetic consequences; the lower value of the K_Y (the more negative value of the *c*) the stronger accelerating effect of the $[OH^-]$ on the rate of the electron transfer. As a consequence, the highest rate enhancement with the pH is observed for the oxidation of the *cis*-$[Cr(cyc\mathit{b})(OH)_2]^+$ (Table 5).

4. Concluding remarks

Protolytic equilibria strongly affect kinetics of reactions of examined chromium(III) tetraazamacrocyclic complexes. Modification of their reactivity *via* water or amine ligand deprotonation has been studied for two types of chemical processes: a monodentate ligand substitution and electron transfer from chromium(III) to iron(III). In the both cases a major difference in the reaction rate of the complex itself and its conjugate base has been observed. The labilizing effect caused by OH^- ion to the leaving group is practically non-directional for either the aquation or the anation processes. In accordance with the mechanism developed by Basolo and Pearson [1], conversion, in a rapid acid–base preequilibrium step, of the original aqua or ammine complex into its hydroxo or amido derivative, respectively, enables π bonding formation between the deprotonated ligand and the central atom. This enforces the π-antibonding character of the chromium(III) "t_{2g}" electrons (pseudo-O_h symmetry approximation) and increases the electron donor capability of the chromium(III) center.

The magnitude of the labilizing effect upon the deprotonation of the chromium(III) macrocyclic amine complexes can be estimated based on the parameters involved in a mathematical expression describing the observed pseudo-first order rate constant vs. H^+ or OH^- concentration profiles. These nonlinear dependences of the k_{obs} on the solution acidity or basicity give a better insight into the reaction mechanism although inclusion of all outer sphere interactions between the positive charged reactant and the counter ion of the supporting electrolyte makes a detailed interpretation of the obtained data difficult. Then, separation of the parameters of the experimental rate expression giving rate constants reflecting the reactivity of the complexes in their conjugate acid-base forms requires determination of the encounter complex formation constants in the separate nonkinetic experiments being very difficult to accomplish.

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