Coordination Chemistry Reviews, 17 (1975) 253—279

KINETICS AND MECHANISM OF SUBSTITUTION REACTIONS IN COBALT(III) *trans*-DIOXIMES

A.V. ABLOV
Moldavian SSR Academy of Sciences, Institute of Chemistry, Kishinev, Moldavia (U.S.S.R.)
N.M. SAMUS
Kishinev State University, Kishinev, Moldavia (U.S.S.R.)
(Received 12 March 1975)

CONTENTS

A. INTRODUCTION

Substitution reactions in octahedral coordination compounds of transition metals have been the subject of numerous investigations in recent years. Most studies were carried out with cobalt(III) ammines [1—5]. However these compounds often undergo changes in spatial configuration during substitution reactions.

In contrast, the cobalt(III) dioximes first described by Tchugaev do not change their spatial configuration in the course of substitution [6]. As shown by X-ray investigations these dioximes have a *trans*-configuration [7—12]. The formal substitution process in dioximes is reduced to the replacement of either of the two axial ligands on the X—Co—Y coordination axis since the Co dimethylglyoxime $(DH)_2$ group remains unchanged through the reaction.

In 1961 Ablov and Sychev [13] investigated the aquation kinetics of the acids $H[Co(DH)_2X_2]$ (X = Cl, Br, I) in aqueous solution. Later [14] the aquation kinetics of aqueous solutions of $H[Co(DH)_2(NO_2)X]$ (X = Cl, Br) were studied. It was found that the aquation rate constants for nitrohalogen acids are somewhat lower than for dihalogen acids.

These facts are inconsistent with previous data concerning the stronger *trans*-influence of the nitro group in comparison with chloride and bromide ions [15—17].

Syrtsova [18—21] studying the aquation kinetics of halogen sulphite cobalt(III) dioximes has observed that halogen substitution by water on the SO_3—Co—X coordination axis decreases in the order I > Br > Cl as in the case of the cobalt(III) ammines.

In 1967 Halpern and Hague investigated the kinetics of water molecule substitution in iodoaquo and nitroaquo dioximes by different anions [22] in water—alcohol mixtures (the pH of the solutions was not varied by addition of either acids or bases). These authors observed that under these conditions the anation rates of both complexes are about the same.

We have previously studied the substitution reactions of acid ligands by amines on the coordination axis O_2N—Co—I [17] and shown that in water—alcohol mixtures on adding one mole of amine, at room temperature, the nitrogroup is first substituted by amine and then $[Co(Amine)(DH)_2I]$ is formed. The discrepancy between our data and those of Halpern is related, probably, to the different pH values. This variation plays an important role in the substitution of axial ligands by different reagents in cobalt(III) dioximes. In particular, it was shown spectrophotometrically [23] that at pH ~ 6 $[Co(DH)_2I(NO_2)]$ is converted gradually into $[Co(H_2O)(DH)_2I]$, but at pH ~ 3 the final aquation product is $[Co(H_2O)(DH)_2(NO_2)]$.

B. COBALT(III) *trans*-DIOXIMES AQUATION REACTIONS

While studying the substitution kinetics of halogen by water in halogen-aquo dioximes it was established that the aquation rates decrease in passing from the chloro- to the iodo compound [24], that is the reverse order when compared with cobalt(III) ammines. It was suggested that the unusual sequence of the halogen aquation rates in these compounds is connected with the presence of a water molecule in the inner coordination sphere.

The aquation kinetics of the dioximes $[Co(Amine)(DH)_2X]$, which are also nonelectrolytes were studied [25]. The investigation has revealed that the rate decreases in proceeding from the chloro- to the iodo complex for the compound with the same amine, i.e. the "abnormal" sequence is retained. It has been found that the aquation rate of $[Co(Amine)(DH)_2X]$ (Amine = NH_3, $C_6H_5NH_2$, Py) depends on the nature of the amine. The substitution proceeds quickly for a compound with a Py—Co—X coordination axis and more slowly for the NH_3—Co—X coordination axis (Table 1).

A careful examination of halogen substitution rate dependence on hydrogen ion concentration for $[Co(Amine)(DH)_2X]$ has shown (Table 2), that there is a region of pH for each complex, where the rate is practically constant. The rate begins to climb, sometimes considerably when the pH values increase beyond this region (See Table 2) [25].

The greatest substitution rate dependence on pH is observed for the iodobis(dimethylglyoximato)—ammine cobalt(III), compared with other dioximes studied (Table 2).

This circumstance probably produces the reversal of the rate sequence at pH > 4 observed for $[Co(NH_3)(DH)_2X]$.

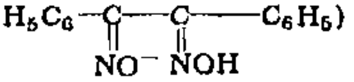
TABLE 1

The aquation rate constants for 1,6-[CoCl$(DH)_2$(Amine)] in ethanol (30%)—water (70%) mixture (pH = 4.0, $\mu = 0.1$, $C_{\text{complex}} = 5 \times 10^{-4}$ mole l^{-1} and $t = 50°C$)

Amine	NH_3	$C_6H_5NH_2$	Py
$k \times 10^6$ (sec^{-1})	18.2	28.8	152

The data certainly indicate that substitution reactions in cobalt(III) dioximes are dependent on the pH of the medium, change in which can affect the propagation rate, ligand substitution sequence, and even the mechanism itself. The deprotonated cobalt dioxime is accumulated in the solution at pH values close to neutral and its behaviour must differ from that observed for [CoX$(DH)_2$(Amine)]. Rate constants obtained under these conditions summarise the values characterising halogen substitution both in protonated and deprotonated dioximes. In order to examine the substitution reaction mechanism, the dependence of the aquation rate upon ionic strength (μ) and steric factors was investigated. Investigation of the dependence of reaction rate on ionic strength for [CoPy$(DH)_2$X] (X = Cl, Br) has shown that the logarithm of the rate constant is in a linear relationship to $\sqrt{\mu}$, the linear plot having a positive angular coefficient (Fig. 1). This is accounted for if one accepts that the reactions under investigation take a dissociative mechanism [26, 27].

Since the influence of steric factors upon rate sometimes permits one to obtain information about the mechanism of the process [28, 29] it was of interest to study the aquation kinetics for the compounds of the same composition with a more bulky dioxime. For this reason the aquation kinetics of [CoX$(DfH)_2$(Amine)] (X = Cl, Br, I; Amine = NH_3, $C_6H_5NH_2$, Py; DfH =



$H_5C_6-\underset{\displaystyle NO^-}{\underset{\|}{C}}-\underset{\displaystyle NOH}{\underset{\|}{C}}-C_6H_5$) were investigated [30].

When one proceeds from complex compounds with dimethylglyoxime to

TABLE 2

Dependence of the rate constants for substitution of halogen by water in [Co(Amine)$(DH)_2$X] on media pH ($t = 50°C$)

Complex	$k \times 10^6$ (sec^{-1}) for pH:			
	3.0	4.0	5.0	6.5
[CoPy$(DH)_2$Cl]	141	152	286	379
[Co$(C_6H_5NH_2)(DH)_2$Cl]	25.4	28.8	122	132
[Co$(NH_3)(DH)_2$Cl]	11.6	18.2	21.0	27.3
[Co$(NH_3)(DH)_2$I]		1.02		1380

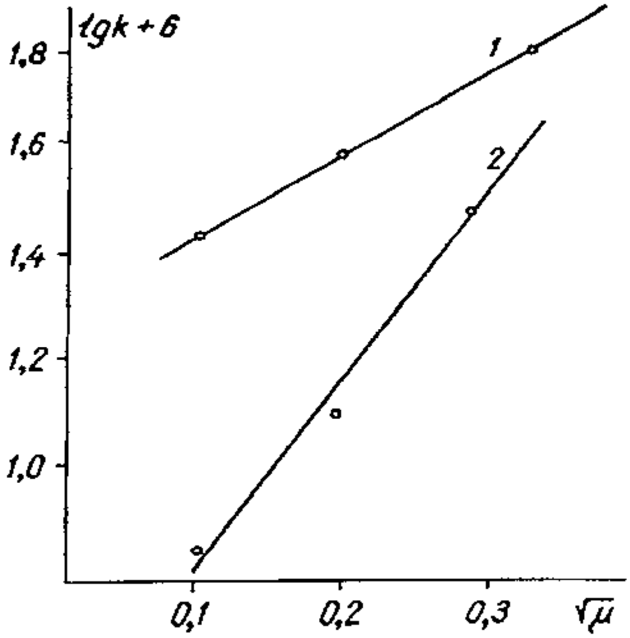


Fig. 1. Log k dependence on $\sqrt{\mu}$ (pH = 4; t = 60±0.1° C). Curve 1, [CoPy(DH)$_2$Br]; Curve 2, [CoPy(DH)$_2$I].

those with α-benzildioxime (DfH$_2$) the aquation rate enhances considerably with simultaneous decrease in activation energies. For example in ethanol (30%)—water (70%) mixture, t = 50° C, pH = 4.0 and μ = 0.1:

Complex	$k \times 10^6$ (sec^{-1})	E_a (kJ mole^{-1})
[CoBr(DH)$_2$Py]	18	99
[CoBr(DfH)$_2$Py]	305	74

The experimental data confirm the presence of dissociative elements in the mechanism, if the steric hindrance arising from the replacement of the methyl groups in the dioxime molecule by the phenyl radicals is taken into account. Keeping the axial groups constant and replacing the equatorial ligands causes not only an increase in the halogen aquation rates but also some other differences.

With the dimethylglyoxime ammine compounds there is reversion of the aquation rate sequence in passing to the neutral pH region, but in the case of α-benzildioxime compounds this phenomenon does not occur.

In some cases the reaction mechanism can be elucidated from the influence of the non-labile ligand inductive effect on the reaction rate [31, 32]. It was of interest therefore to study the aquation kinetics for dioximes containing in the inner sphere, aniline and its derivatives substituted in the benzene ring.

Investigation of the reaction kinetics for halogen substitution by water in $[CoX(DH)_2NH_2C_6H_4\text{-}Y]$ (Y = p-, m-, o-OCH_3; p-, m-CH_3; p-, o-OH; p-I; m-Br; p-Cl) [33] has shown that the rate constants depend upon the nature of the substituent and its position in the benzene ring relative to the amino group.

For dioximes containing p-anisidine, p-aminophenol, and m-toluidine, the rate of halogen substitution by water diminishes from the chloro to the iodo complex as is the case with $[Co(C_6H_5NH_2)(DH)_2X]$. The activation energies increase in the same sequence. Aquation rate constants depended upon the axial ligand in the following order:

$$C_6H_5NH_2 < m\text{-}H_3C{-}C_6H_4{-}NH_2 < p\text{-}H_3CO{-}C_6H_4{-}NH_2 < p\text{-}HO{-}C_6H_4{-}NH_2$$

Inversion of the halogen aquation rate sequence is observed for dioximes, containing inner sphere p-nitroaniline, p-iodoaniline, m-bromoaniline, i.e. the substitution rate of the bromide ion by water is larger than that of the chloride ion. The activation energy decreases in going from the chloro to the bromo complex.

Plotting the values of the aquation rate constant logarithms for 1,6-$[Co(Y\text{-}C_6H_4NH_2)(DH)_2Cl]$ against Hammett σ-constants for benzene ring substituents, Y [34, 35] yields two different straight lines (Fig. 2). Points for

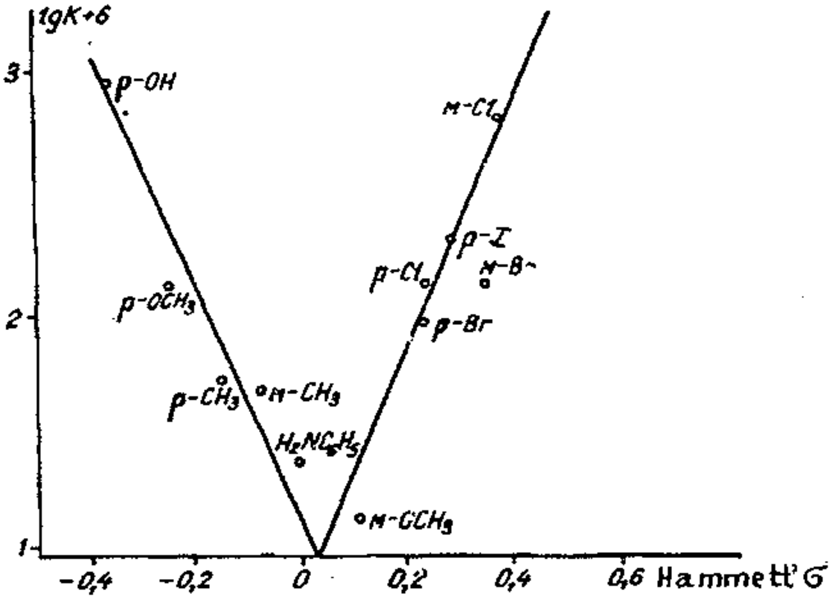


Fig. 2. Dependence of the logarithm of the halogen aquation rate constants on Hammett's σ constants.

TABLE 3

Kinetic characteristics of the aquation reaction of 1,6-[$Co(H_2NC_6H_4Y)(DH)_2X$] in ethanol (30%)—water (70%) mixture ($C_{complex}$ = 5 × 10^{-4} mole l^{-1}, μ = 0.1 and pH = 3.0)

Complex	$h \times 10^6$ (sec^{-1})						E (kJ $mole^{-1}$)	log Z (50°)	$\Delta S^{\neq}$ (50°)	log Z (60°)	$\Delta S^{\neq}$ (60°)
	30°	40°	45°	50°	60°	70°					
[$Co(H_2NC_6H_5)(DH)_2Cl$]		8.50		28.8	103	340	113			13.8	+10
[$Co(H_2NC_6H_5)(DH)_2Br$]		4.0		12.8	46	190	115			13.7	+ 8
[$Co(H_2NC_6H_5)(DH)_2I$]				4.02	14.9	50.6	118			13.6	+ 6
[$Co(m\text{-}H_2NC_6H_4CH_3)(DH)_2Cl$]		12.5		49.2	148		98	10.9	−37		
[$Co(m\text{-}H_2NC_6H_4CH_3)(DH)_2Br$]		7.0		22.9	73.3		102	11.8	−19		
[$Co(m\text{-}H_2NC_6H_4CH_3)(DH)_2I$]		3.0		10.2	35.3		106	12.1	−13		
[$Co(p\text{-}H_2NC_6H_4OCH_3)(DH)_2Cl$]	15.0	46.2		131	360		89	10.4	−46		
[$Co(p\text{-}H_2NC_6H_4OCH_3)(DH)_2Br$]		24.0		67.6	193		93	11.7	−21		
[$Co(p\text{-}H_2NC_6H_4OCH_3)(DH)_2I$]		4.50		16.1	48.3	166	111	13.2	+ 8		
[$Co(p\text{-}H_2NC_6H_4OH)(DH)_2Cl$]	129	345		920			78	9.6	−62		
[$Co(p\text{-}H_2NC_6H_4OH)(DH)_2Br$]		152	282	481			92	11.5	−34		
[$Co(p\text{-}H_2NC_6H_4OH)(DH)_2I$]	6.95	21		65.1	205		99	11.9	−17		
[$Co(p\text{-}H_2NC_6H_4NO_2)(DH)_2Cl$]		144	237	401			85	10.6	−51		
[$Co(p\text{-}H_2NC_6H_4NO_2)(DH)_2Br$]		338		853	1840		74	9.6	−70		
[$Co(p\text{-}H_2NC_6H_4I)(DH)_2Cl$]	34.0	84.0		209			88	9.5	−63		
[$Co(p\text{-}H_2NC_6H_4I)(DH)_2Br$]	58.5	184		510			77	9.1	−71		
[$Co(m\text{-}H_2NC_6H_4Br)(DH)_2Cl$]	12.8	42		142	412		103	12.8	− 9		
[$Co(m\text{-}H_2NC_6H_4Br)(DH)_2Br$]	46.1	138		460			96	12.2	−20		

the electron donor substituents lie on one of these lines ($\rho = -4.54$) while points for electron acceptor substituents lie on the other ($\rho = +5.26$).

It can be seen that the rates of acid hydrolysis for the dioximes investigated are increased both by good electron donors and by good acceptors. The occurrence of two branches is probably due to different mechanisms for the substitution of halogen by water. As can be seen from Table 3, activation energies for electron donor substituents decrease in the order $C_6H_5NH_2 >$ m-$H_3CC_6H_4NH_2 >$ p-$H_3COC_6H_4NH_2 >$ p-$HOC_6H_4NH_2$. The electron density on the nitrogen atom of the aminogroup in monosubstituted derivatives of aniline increases in the same order [36].

The data obtained for electron acceptor substituents confirm also the dependence of activation energies on the axial ligands. For example, E_a = 88 kJ mole^{-1} for $[Co(p\text{-}H_2NC_6H_4I)(DH)_2Cl]$ and E_a = 103 kJ mole^{-1} for $[Co(m\text{-}H_2NC_6H_4Br)(DH)_2Cl]$.

The change of electron density on the nitrogen atom of the amino group, caused by a substituent in the benzene ring, affects the basic properties of the aromatic amines. There is [35] a linear correlation between pK_a of monosubstituted aniline derivatives and Hammett σ-constants. This is shown in Fig. 3 for derivatives of interest to us. A plot of the logarithms of the aquation rate constants against amine pK_a for p-, m- and some o-derivatives yields two intersecting straight lines (Fig. 4). It is seen that for dioximes with electron donor substituents, Y, the rate constants increase simultaneously with increase of amine pK_a. For electron acceptor substituents in the benzene ring the aquation rate diminishes with increase of amine pK_a. The dioxime with axial coordinate Cl—Co—p-$NH_2C_6H_4NO_2$ falls outside this regularity. The

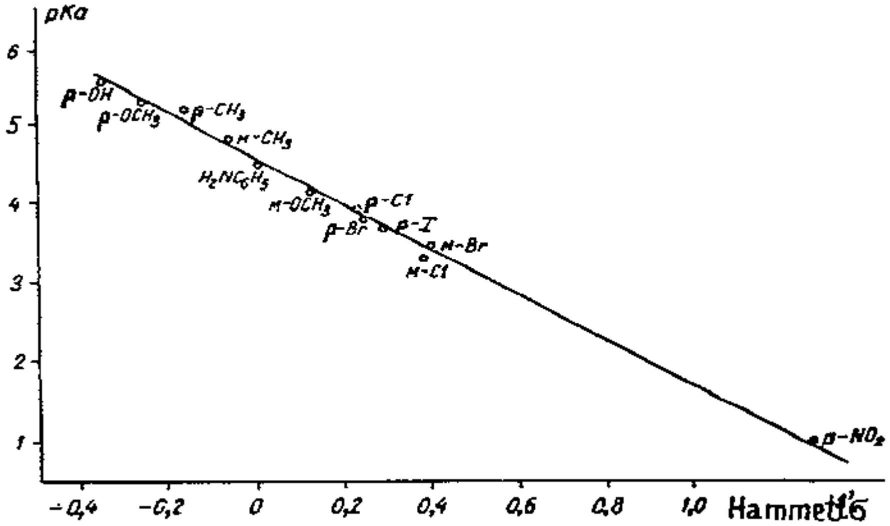


Fig. 3. The dependence of pK_a for monosubstituted benzene ring aniline derivatives on Hammett's σ constants.

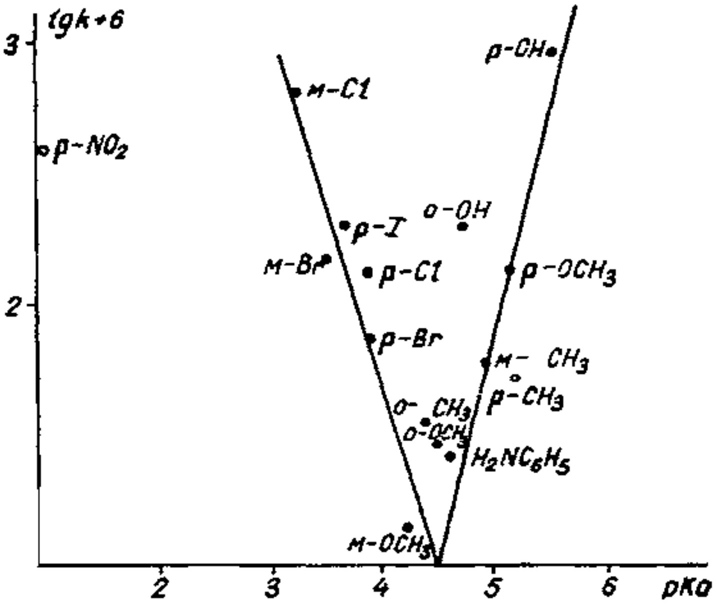


Fig. 4. The dependence of the logarithms of the halogen aquation rate constants on pK_a of monosubstituted benzene ring aniline derivatives.

experimental data infer that the inductive effect of the unsubstituted axial ligand affects the rate and, probably, the mechanism of the aquation reaction in our complex compounds.

The kinetic study of bromide ion substitution by water in α-benzildioximes, containing aniline derivatives, has shown (Table 4), that in the case of the aniline and *p*-anisidine complexes the aquation rate constants are larger than for analogous dimethylglyoxime compounds. In the case of the complex with axial Br—Co—*p*-$NH_2C_6H_4NO_2$ there is a fall in the rate constant.

Keeping in mind the probable increase of steric hindrance in α-benzildioximes in comparison with dimethylglyoximes, these experimental data can be accounted for if we assume that the aquation reactions of complexes with axial ligands $YC_6H_4NH_2$, where Y is an electron donor substituent, are dissociative in mechanism, while for $YC_6H_4NH_2$, where Y is an electron acceptor substituent, the aquation reaction mechanism includes an associative step. These assumptions were confirmed by investigation of the aquation rate dependence upon the ionic strength of the media.

It is seen (Fig. 5) that a straight-line dependence of log K upon $\sqrt{\mu}$ is observed for dioximes with $H_2NC_6H_5$ and *p*-$H_2NC_6H_4OCH_3$ as axial ligands but the rate constants for *p*-$H_2NC_6H_4I$ and *p*-$H_2NC_6H_4NO_2$ do not depend upon ionic strength.

In order to further investigate the effect of the axial ligand upon the aquation kinetics an aquation rate study of $[CoX(DH)_2L]$ was performed where

TABLE 4

The aquation rate constants for ethanol (30%)—water (70%) mixtures of dimethylglyoxime ($C_{\text{complex}} = 5 \times 10^{-4}$ mole l^{-1}) and α-benzildioxime ($C_{\text{complex}} = 5 \times 10^{-5}$ mole l^{-1}) complexes (t = 50° C, μ = 0.1, pH = 3.0)

Complex	$k \times 10^6$ (sec^{-1})	Complex	$k \times 10^6$ (sec^{-1})
$[Co(H_2NC_6H_5)(DfH)_2Br]$	39.1	$[Co(H_2NC_6H_5)(DH)_2Br]$	12.8
$[Co(p\text{-}H_2NC_6H_4OCH_3)\text{-}(DfH)_2Br]$	148	$[Co(p\text{-}H_2NC_6H_4OCH_3)\text{-}(DH)_2Br]$	67.6
$[Co(p\text{-}H_2NC_6H_4NO_2)(DfH)_2Br]$	51.2	$[Co(p\text{-}H_2NC_6H_4NO_2)(DH)_2Br]$	853

L = proton containing molecules such as thiourea (Thio) and thiosemicarbazide (Thios) [37,38]. From Table 5 it is seen that here too, the nature of the axial ligand affects the halogen aquation rates.

The considerably larger aquation rate constant for the thiosemicarbazide complex in comparison with thiourea indicates that the substitution rates are affected not only by the donor atom coordinated by the metal but other ligand atoms as well. The data obtained cannot be explained by simple ligand field theory considering the interaction only between the central metal ion and the neighbouring ligand atoms. The rate differences for complexes with L = thiourea and L = thiosemicarbazide may be related to the presence of the hydrazine group in the latter molecule.

This assumption is confirmed by the fact that the aquation rate constants for the Co^{III} dioximes containing semicarbazide (Scarb) are close to those obtained for thiosemicarbazide compounds (Table 5).

It must be noted that the aquation rates for complexes with thiourea, thio-

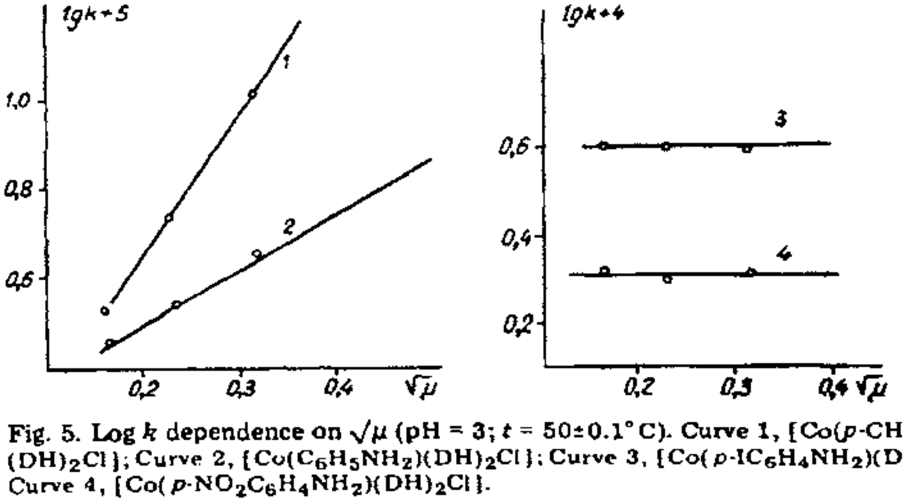


Fig. 5. Log k dependence on $\sqrt{\mu}$ (pH = 3; t = 50±0.1° C). Curve 1, $[Co(p\text{-}CH_3OC_6H_4NH_2)\text{-}(DH)_2Cl]$; Curve 2, $[Co(C_6H_5NH_2)(DH)_2Cl]$; Curve 3, $[Co(p\text{-}IC_6H_4NH_2)(DH)_2Cl]$; Curve 4, $[Co(p\text{-}NO_2C_6H_4NH_2)(DH)_2Cl]$.

TABLE 5
Aquation rate constants for [CoCl(DH)$_2$L]
(ethanol (20%)—water (80%) mixture, pH = 3.0, μ = 0.5 and t = 25° C)

Complex	$k \times 10^6$ (sec^{-1})
[CoCl(DH)$_2$(H$_2$O)]	26.7
[CoCl(DH)$_2$Thio]	86.1
[CoCl(DH)$_2$Thios]	4380
[CoCl(DH)$_2$Scarb]	3490

semicarbazide and semicarbazide also decrease from the chloro to the iodo dioxime. The effect of the axial ligand on the aquation rates leads to the conclusion that the rate-determining step includes the elements of dissociation. This is supported by the aquation rate dependence upon ionic strength (μ).

The results obtained indicate that in the case of the thiourea compounds the activated transition complex formation proceeds via a dissociative interchange mechanism. In thiosemicarbazide and semicarbazide complexes reaction occurs by a mechanism with more defined dissociative character. Just the same conclusion arises from the steric influence on the rate of halogen substitution by water in [CoX(dioximate)L] [39].

Study of the aquation kinetics of analogous complexes has shown that in

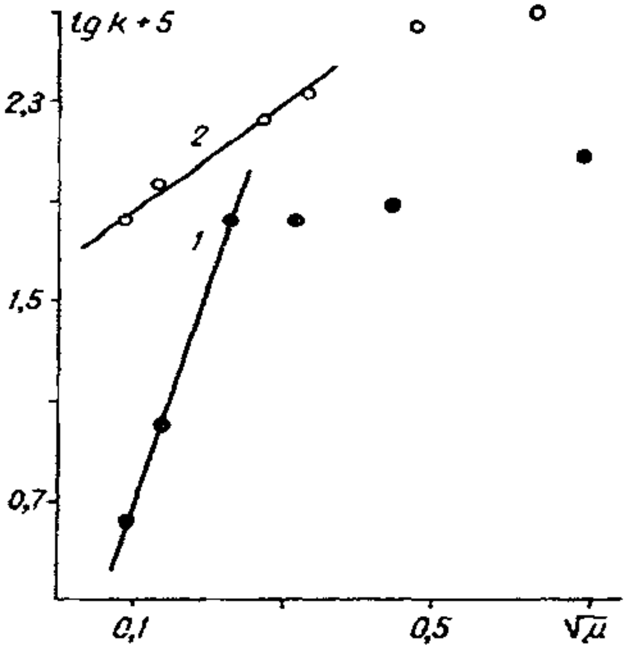


Fig. 6. Log k dependence on $\sqrt{\mu}$ for [Co(Scarb)(DfH)$_2$Br] (curve 1) and [Co(Scarb)(DH)$_2$-Cl].3H$_2$O (curve 2). (ethanol (20%)—water (80%) mixture, pH = 3; t = 25±0.1° C).

passing from dimethylglyoximes to α-benzildioximes an increase in aquation rate occurs. This fact confirms to some degree our assumption about the dissociative mechanism if one supposes that the latter complexes are sterically more hindered.

Experimental data (dependence of log K on $\sqrt{\mu}$) (Fig. 6) indicate that the replacement of methyl by phenyl groups in the dioxime molecules, constituting the equatorial plane of the complex, favours a reaction proceeding by the mechanism with more defined dissociative elements.

C. ACTIVATION PARAMETERS FOR AQUATION OF COBALT(III) *trans*-DIOXIMES

It was of interest to examine how the activation parameters ($\Delta S^{\neq}$ and $\Delta H^{\neq}$) influence the aquation rate constants for the dioximes investigated. It is known that the activation enthalpy ($\Delta H^{\neq}$) directly reflects the change in bond energy in passing from the ground state to the transition state of the complex formed via a dissociative mechanism; the activation entropy can serve as a qualitative characteristic of the relative "order" or "disorder" of the reaction intermediate.

In Table 6 the aquation rate constants for 1,6-[$CoL(DH)_2X$] (L = Thios, Scarb, Thio, H_2O) are represented together with the corresponding $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values.

As seen from Table 6 the $\Delta H^{\neq}$ values for complexes with the same leaving group increase from a thiosemicarbazide containing dioxime to the aquo compound in the sequence: Thios < Scarb < Thio < H_2O, i.e. the aquation rate constant grows with decrease of activation enthalpy. The ability of the axial ligand to diminish the activation enthalpy probably reflects the ligand's labilizing power. The activation entropy is negative in value for all these complexes except [$Co(H_2O)(DH)_2Cl$].

TABLE 6

Kinetic parameters for aquation of 1,6-[$CoL(DH)_2X$] (pH = 3, μ = 0.5 KNO_3 and HNO_3; ethanol (20%)—water (80%) mixture)

Coordinate	$k^{25°} \times 10^6$ (sec^{-1})	$\Delta H^{\neq}$ (kJ $mole^{-1}$)	$\Delta S^{\neq}$ (J $mole^{-1}$ deg^{-1})
Thios—Co—Cl	4380	68	−60
Thios—Co—Br	479	76	−52
Thios—Co—I	56.7	84	−45
Scarb—Co—Cl	3490	78	−31
Scarb—Co—Br	411	85	−24
Scarb—Co—I	48.5	95	− 8
Thio—Co—Cl	86.1	90	−20
Thio—Co—Br	15.9	91	−32
Thio—Co—I	1.9	99	−21
H_2O—Co—Cl	26.7	107	+33

In the case of a dissociative mechanism, the tetragonal pyramidal transition state is the most probable for cobalt(III) dioximes and in comparison with the initial octahedral state, the entropy changes will mainly be associated with the solvation of both leaving group and activated complex. The negative $\Delta S^{\neq}$ values are in accord with a more ordered transition state of the complex in comparison with the ground state.

Examination of the interrelationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for cobalt(III) dioximes, containing different axial ligands L, but the same leaving group (chloride ion), has shown (Fig. 7) that there is a straight-line dependence. The points corresponding to L = NO_2^-, Cl^- [14,24] also lie on the same plot. The ligands L can be arranged in the following order according to decreasing $\Delta H^{\neq}$: $H_2O > NO_2^- > Cl^- >$ Thio > Scarb > Thios.

The labilizing power of these axial ligands increases in the reverse order: Thios > Scarb > Thio > $Cl^- > NO_2^- > H_2O$. The axial ligand sequence obtained coincides with their trans-influence advanced previously on the basis of inner sphere substitution reaction studies in cobalt(III) dioximes [16,17, 40] (with the exception of the nitro group). The discrepancy in the relative positions of chloro and nitro groups in these two *trans*-influence sequence may be connected with the presence of protons in the compounds $H[Co(DH)_2Cl_2]$ and $H[Co(DH)_2(NO_2)_2]$ under investigation.

The interrelationship between the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$

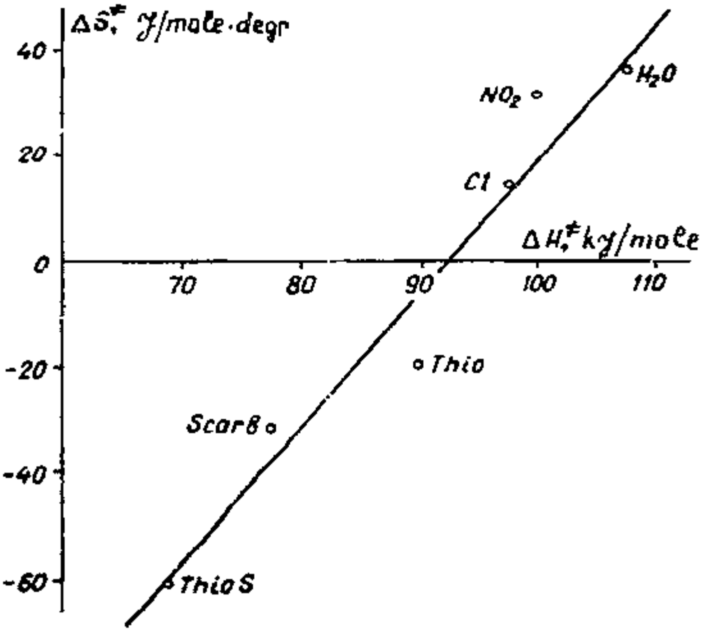


Fig. 7. The relation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for aquation reactions of $CoL(DH)_2Cl$. (L = Thios, Scarb, Thio, H_2O, Cl [14], NO_2 [15]).

TABLE 7

Kinetic parameters for aquation of 1,6-[$CoL(DfH)_2X$] (pH = 3, μ = 0.5; ethanol (30%)–water (70%) mixture)

Coordinate	$k^{25°} \times 10^6$ (sec^{-1})	$\Delta H^{\neq}$ (kJ $mole^{-1}$)	$\Delta S^{\neq}$ (J $mole^{-1}$ deg^{-1})
Scarb—Co—Cl	4540	93	+ 23
Scarb—Co—Br	1240	95	+ 20
Thio—Co—Cl	297	99	+ 19
Thio—Co—Br	79.0	104	+ 14
H_2O—Co—Cl	107	96	+ 7
H_2O—Co—Br	50.2	100	+ 1

(or E and log Z) is called the isokinetic relationship or compensating effect in the literature [35]. It was first studied for some organic reactions investigating slight changes in the structure of the reagent and solvent. In recent years the isokinetic relationship has been extended to complex compounds of the transition metals (Peshchevitskii and Kasakov for Pt^{II} [41,42] and Co^{III} [43] complexes).

Aquation rate constants and activation parameters for complex compounds with α-benzildioxime, analogous in composition with the dimethylglyoximes, mentioned above, are in Table 7. It is seen that the activation entropy in this case is positive and diminishes from the semicarbazide complex to aquodioxime in the order: Scarb > Thio > H_2O. The change in activation enthalpy is not large.

Positive activation entropy indicates a more "disordered" transition state than that present in the case of dimethylglyoximes; this contributes, probably, to an increase in aquation rate in passing from complexes with dimethylglyoxime to α-benzildioximes [compare Tables 6 and 7].

It may be thought that the difference in the entropy values is due to variation in the entropy of the equatorial ligand, being negative for dimethylglyoxime and positive for α-benzildioxime. However, it is seen from Table 8 that the activation entropy for the aquation of the amine-containing α-benzildioximes is negative, and for [$Co(Amine)(DH)_2X$] (Amine = $C_6H_5NH_2$, NH_3) is positive. It follows from these data (Tables 6—8) that the entropy value is affected not only by the equatorial ligand, but also by the axial ligands.

It must be pointed out that while [$Co(Amine)(DfH)_2X$] and [$CoL(DH)_2X$] (L = Thios, Scarb, Thio) have similar $\Delta H^{\neq}$ values, the aquation rate constants of these complexes are substantially different; for the former compounds the rate of the halogen release by water is considerably lower than might be predicted from the $\Delta H^{\neq}$ value. For example, at 25° C, [$Co(Thios)(DH)_2Cl$] $\Delta H^{\neq}$ = 68 kJ $mole^{-1}$, k = 4380 × 10^{-6} sec^{-1}, and for [$Co(NH_3)(DfH)_2Cl$], $\Delta H^{\neq}$ = 67 kJ $mole^{-1}$, k = 189 × 10^{-6} sec^{-1}. The lower value of the aquation

TABLE 8

Activation parameters for aquation of 1,6-[Co(Amine)(Dioxim)$_2$X]

[Co(Amine)(DH)$_2$X]	$k^{60°} \times 10^6$ (sec^{-1})	$\Delta H^{\neq}$ (kJ mole^{-1})	$\Delta S^{\neq}$ (J mole^{-1} deg^{-1})	[Co(Amine)(DfH)$_2$X]	$k^{50°} \times 10^6$ (sec^{-1})	$\Delta H^{\neq}$ (kJ mole^{-1})	$\Delta S^{\neq}$ (J mole^{-1} deg^{-1})
Py—Co—Cl	152	88	−44	Py—Co—Cl	fast	63	−97
Py—Co—Br	18.0	97	−38	Py—Co—Br	805	72	−81
Py—Co—I	8.24	112	+ 2	Py—Co—I	460	76	−72
$C_6H_5NH_2$—Co—Cl	28.8	111	+13	$C_6H_5NH_2$—Co—Cl	759	71	−87
$C_6H_5NH_2$—Co—Br	12.8	113	+ 9	$C_6H_5NH_2$—Co—Br	39.1	87	−64
$C_6H_5NH_2$—Co—I	3.02	116	+ 5	$C_6H_5NH_2$—Co—I	12.7	93	−50
H_3N—Co—Cl	18.2	112	+ 9	H_3N—Co—Cl	1305	67	−93
H_3N—Co—Br	4.45	116	+ 8	H_3N—Co—Br	186	78	−78
H_3N—Co—I	1.02	122	+19	H_3N—Co—I	130	82	−67

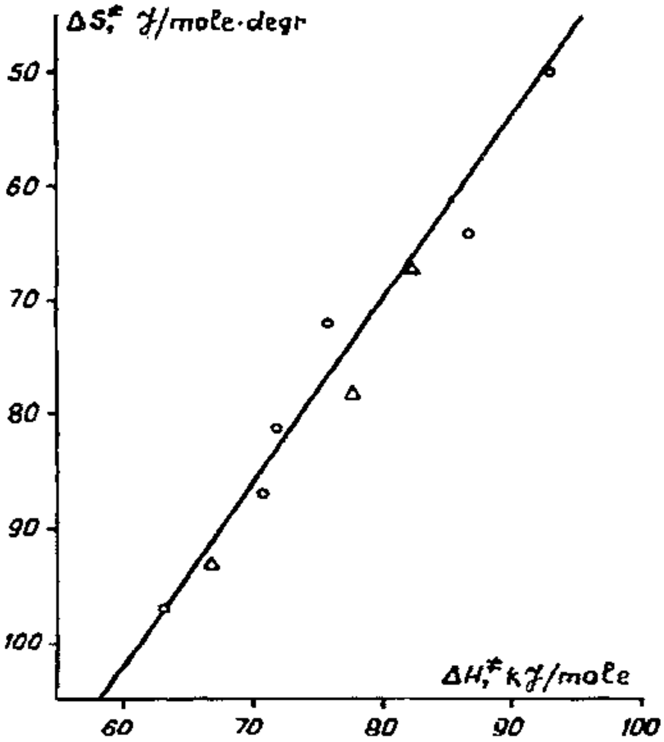


Fig. 8. The relation between activation entropy and activation enthalpy for aquation of $[Co(Amine)(DfH)_2X]$. (○), Amine = Py; (●), Amine = $C_6H_5NH_2$; (△), Amine = NH_3.

rate constant for the ammine containing dioxime is connected with a more negative activation entropy value (for $[Co(Thios)(DH)_2Cl]$ $\Delta S^{\neq} = -60$ J $mole^{-1}$ deg^{-1}, for $[Co(NH_3)(DfH)_2Cl]$ $\Delta S^{\neq} = -93$ J $mole^{-1}$ deg^{-1}).

There is an isokinetic relationship between the activation parameters for aquation of 1,6-$[Co(Amine)(DfH)_2X]$ independent of halogen (Fig. 8).

It is interesting to note that for all the dioximes investigated the sequence of the halogen aquation rates is: Cl > Br > I. Such a sequence can be accounted for in terms of Pearson's theory of soft (class b) and hard (class a) acids and bases [44]. The formation of M(a)—NCS and M(b)—SCN bonds is often used as a criterion of hard and soft acids [45,46]. Since the thiocyanate ion in these dioximes is linked with cobalt through the sulphur atom [7,8] the equatorial $Co(DH)_2$ group is probably a soft acid (class b) in character. According to Pearson, soft acids form their most stable complexes with soft bases; thus in dioximes the chloride ion must be released faster than bromide and iodide. This is the same order as was observed for $[Co(CN)_5X]^{3-}$ [3] and the reverse to that observed with $[Co(NH_3)_5X]^{2+}$ and $[Co(en)_2X_2]^+$ [1,2].

However, with the SO_3^{2-} ion present in the dioxime inner sphere the re-

TABLE 9

Rate constants for acid and base hydrolyses at 40° C ($\mu = 0.1$)

Complexes	$k_{H_2O} \times 10^6$ (sec^{-1})	$k_{OH}^{obs} \times 10^6$ (sec^{-1})	k_{OH}^{obs}/k_{H_2O}
$[CoPy(DH)_2Cl]$	63.3	1183	20
$[CoPy(DH)_2Br]$	5.14	1288	2×10^2
$[CoPy(DH)_2I]$	2.30	1648	7×10^2
$[Co(C_6H_5NH_2)(DH)_2Cl]$	8.51	fast	
$[Co(C_6H_5NH_2)(DH)_2Br]$	3.65	fast	
$[Co(C_6H_6NH_2)(DH)_2I]$	0.81	2362	3×10^3
$[Co(NH_3)(DH)_2Cl]$	5.23	920	2×10^1
$[Co(NH_3)(DH)_2Br]$	1.12	1656	15×10^2
$[Co(NH_3)(DH)_2I]$	0.30	4080	15×10^3

verse sequence of halogen aquation rates (I > Br > Cl) takes place [18]. This may be due to the "hardness" of the SO_3^{2-} group as a base, which is confirmed by the tendency of SO_3^{2-} to transform into HSO_3^-.

D. COBALT(III) *trans*-DIOXIMES -- BASE HYDROLYSIS

It was indicated above that with pH values in excess of ca. 7 the rate of halogen substitution in dioxime nonelectrolytes increases sharply. This increase in rate probably arises through the presence of both the acid and base hydrolysis. The base hydrolysis of cobalt(III) ammines has been investigated in detail [47—52] in contrast to the dioximes which have not been nearly so well studied [53—55].

We have studied the kinetics of base hydrolysis of $[Co(DH)_2X(Amine)]$ (Amine = Py, NH_3, $C_6H_5NH_2$; X = Cl, Br, I). In the case of pyridine containing complexes the reaction rate is independent of the hydroxide ion concentration, while for aniline and ammine complexes there is a reaction rate dependence on hydroxide ion concentration. The base hydrolysis reaction in the latter

TABLE 10

The kinetic characteristics for base hydrolysis of 1,6-$[CoX(DH)_2H_2O]$ ($C_{complex} = 5 \times 10^{-4}$ mole l^{-1}, $C_{KOH} = 5 \times 10^{-3}$ mole l^{-1}, $\mu = 0.15$ (K_2SO_4))

Complex	$k \times 10^3$ (l mole^{-1} sec^{-1})					E_a (kJ mole^{-1})
	0°	11°	15°	20°	25°	
$[CoCl(DH)_2H_2O]$	8.9	33.1	51.8	87.5		74.2
$[CoBr(DH)_2H_2O]$	12.7	47.3	78.0	177.0		87.4
$[CoI(DH)_2H_2O]$		4.68	10.4	25.3	60.8	111.9

cases is second-order, similar to that observed for other cobalt(III) complexes [1,2].

It follows from a comparison of the base hydrolysis rates that the nature of the amine affects the rate constants. Substitution reactions proceed quickly for the aniline complex, slower for the pyridine and still slower for the ammine compound.

Acid and hydrolysis rates are compared in Table 9.

A study of the base hydrolysis of acid aquodioxime, $Co(H_2O)(DH)_2X$, [56] has indicated that for complexes there is a dependence of the rate constant upon the alkali concentration, i.e. we have second order reactions. The rate constants are similar for chloro and bromo complexes but are substantially smaller for the iodo complex (Table 10).

From a comparison of the observed rate constants for the base hydrolysis of $[Co(H_2O)(DH)_2X]$ with those for aquation of these compounds it follows that the rate of base hydrolysis is about two orders of magnitude higher than the rate of acid hydrolysis (Table 11). The relative increase in rate constant for base hydrolysis is considerably smaller than that observed for cobalt(III) ammines [1,2].

It was of interest to elucidate the influence of the nature of the dioximate ion on the kinetics and mechanism of cobalt(III) dioxime base hydrolysis. The complexes $[Co(Dioxim)_2(H_2O)X]$ where Dioxim = methylglyoxime (MH_2), methylethylglyoxime (MEH_2), α-benzildioxime (DfH_2) and α-furildioxime ($DfurH_2$), were investigated.

The rate of base hydrolysis for 1,6-$[Co(H_2O)(MH)_2X]$ (X = Cl, Br, I) was studied with different concentrations of KOH and a second order rate law was observed (Table 12).

It can be seen that the substitutions of chloride and bromide proceed with similar rates, but iodide releases more slowly. The order is the same as that observed for halogen bis(dimethylglyoximate) aquocobalt(III).

The observed rate constants for base hydrolysis of monomethylglyoxime complexes (k_{OH}) are three orders of magnitude larger than the aquation rate constants (k_{H_2O}). This ratio, $k_{OH}/k_{H_2O} \sim 10^3$, is smaller than that obtained for cobalt(III) ammines, and an order of magnitude larger than for analogous complexes with dimethylglyoxime (Table 13). Hence the increase in rate of

TABLE 11

Rate constants for acid (pH = 3) and base hydrolysis ($C_{KOH} = 5 \times 10^{-3}$ mole l^{-1}) of 1,6-$[CoX(DH)_2(H_2O)]$ in water solution at 20°C.
$C_{complex} = 5 \times 10^{-4}$ mole l^{-1}, $\mu = 0.15$ (K_2SO_4)

Complex	$k \times 10^5$ (sec^{-1}) Aquation	$k_{obs} \times 10^5$ (sec^{-1}) Base hydrolysis
$[CoBr(DH)_2H_2O]$	1.46	106.2
$[CoI(DH)_2H_2O]$	0.05	15.2

TABLE 12

Kinetic characteristics for base hydrolysis of 1,6-[$Co(H_2O)(MH)_2X$]
($C_{KOH} = 5 \times 10^{-3}$ mole l^{-1}, $C_{complex} = 5 \times 10^{-4}$ mole l^{-1}, $\mu = 0.15$ (KNO_3)

Complex	$k \times 10^3$ (l $mole^{-1}$ sec^{-1})							E_a (kJ $mole^{-1}$)	log Z	$\Delta S^{\neq}$ (J $mole^{-1}$ deg^{-1})
	0°	5°	10°	15°	20°	25°	30°			
[$Co(H_2O)(MH)_2Cl$]		46.8	99.8	161	360			93	16.2	+57
[$Co(H_2O)(MH)_2Br$]		54.5	104	218	410			91	15.8	+50
[$Co(H_2O)(MH)_2I$]	10.3				153	233	503	94	15.2	+38

TABLE 13

Comparison of the rate constants of base hydrolysis (C_{KOH} = 5 × 10^{-3} mole l^{-1}) and aquation (pH = 3) for 1,6-[$Co(H_2O)(Dioxim)_2X$] (t = 20°C, μ = 0.15)

Complex	$k_{OH}^{obs} \times 10^6$ (sec^{-1})	$k_{H_2O} \times 10^6$ (sec^{-1})	k_{OH}/k_{H_2O}
[$Co(H_2O)(MH)_2Cl$]	2160	7.10	300
[$Co(H_2O)(MH)_2Br$]	2460	3.45	710
[$Co(H_2O)(MH)_2I$]	921		
[$Co(H_2O)(DH)_2Cl$]	525	22.6	25
[$Co(H_2O)(DH)_2Br$]	1060	14.6	70
[$Co(H_2O)(DH)_2I$]	152	0.5	300
[$Co(NH_3)_5Cl$]$^{2+}$			5 × 10^5 [a]

[a] See ref. 1.

halogen substitution in basic media in comparison with the rate of aquation takes place not only for complex compounds which form an amido-conjugate base in basic solution [57], but also for complexes which cannot form it.

Assuming the conjugate base mechanism the differences in base hydrolysis rates between monomethylglyoxime and the corresponding dimethylglyoxime complexes (Table 13) can be related to dissimilar acid properties of the coordinated water molecules in compounds with dimethylglyoxime and monomethylglyoxime on one hand, and to different acid properties of the coordinated dioximate ions themselves. However, investigation of the acid properties of [$Co(H_2O)(DH)_2X$] [58] and [$Co(H_2O)(MH)_2X$] (Table 14) shows that the nature of the dioxime does not greatly influence the proton departure from the coordinated water molecule.

The increase in base hydrolysis rate of halogen bis(methylglyoximate)aquocobalt(III) is probably due to the more defined acid properties of the coordinated monomethylglyoxime in comparison with dimethylglyoxime. Since the acid properties are affected by the inductive effect of the substituent in the molecule investigated [59] it may be hoped that the base hydrolysis rate

TABLE 14

pK_a values for [$Co(H_2O)(Dioxim)_2X$] [58]

Complex	pK_a	Complex	pK_a
[$Co(H_2O)(DH)_2Cl$]	6.30	[$Co(H_2O)(MH)_2Cl$]	6.35
[$Co(H_2O)(DH)_2Br$]	6.44	[$Co(H_2O)(MH)_2Br$]	6.65
[$Co(H_2O)(DH)_2I$]	7.40 [a]	[$Co(H_2O)(MH)_2I$]	7.40
[$Co(H_2O)(DH)_2NO_2$]	7.66	[$Co(H_2O)(MH)_2NO_2$]	7.24

[a] Our data.

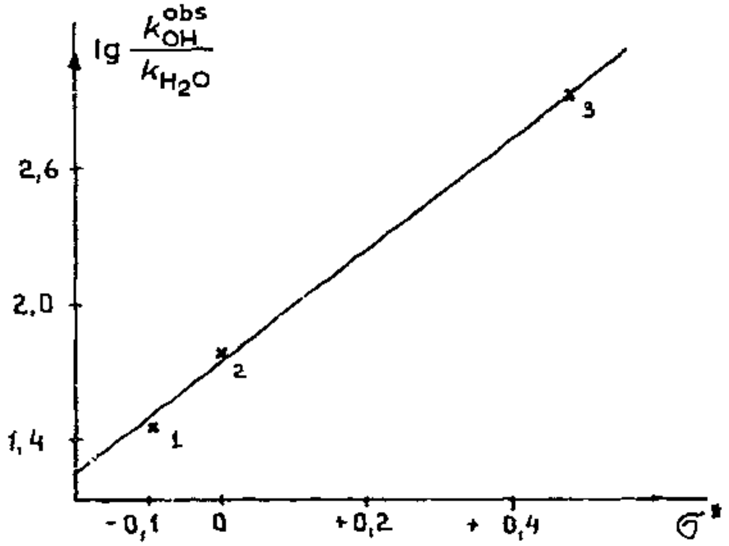
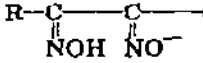
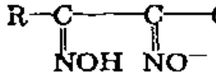


Fig. 9. The dependence of $\log(k_{OH}^{obs}/k_{H_2O})$ on Taft's σ^* for $[Co(H_2O)(Dioxim)_2Br]$ at 20±0.1°C. Dioxim =  $R-\underset{\overset{\|}{NOH}}{C}-\underset{\overset{\|}{NO^-}}{C}-CH_3$; point 1, R = C_2H_5; point 2, R = CH_3; point 3, R = H.

constants for $[Co(H_2O)(Dioxim)_2X]$, Dioxim =  $R-\underset{\overset{\|}{NOH}}{C}-\underset{\overset{\|}{NO^-}}{C}-CH_3$ (R = H, CH_3, C_2H_5) and Taft's σ^* will be related. Investigation has shown (Fig. 9) a straight line dependence between log k_{OH}^{obs}/k_{H_2O} and σ^*.

As indicated by the data obtained the base hydrolysis of dioximes $[Co(H_2O)(Dioxim)_2X]$ proceeds via a conjugate base mechanism and the ability of the coordinated dioxime to detach a proton plays a dominant role in conjugate base formation.

Conjugate bases of the cobalt(III) dioximes were isolated in crystalline form by Tchugaev [60], in contrast to cobalt(III) amine, for which the existence of the conjugate base is only hypothetical. An X-ray study of $[Co(D_2H)Py_2].2H_2O$ was undertaken and proved the presence of a deprotonated dioxime in the complex [61].

Study of the base hydrolysis of halogen bis(α-benzildioximate)aquocobalt-(III) has also shown in this case that the value of the rate constant is in accord with the inductive effect in the dioxime substituent series (Table 15): $C_2H_5 < CH_3 < H < C_6H_5$ [62].

From Table 15 the base hydrolysis rate constant for bromo bis(α-furildioximato)aquocobalt(III) is seen to be much larger than for the complex containing monomethylglyoxime, although furildioxime and methylglyoxime are similar in their acid properties (pK_a $(MH_2) = 9.74$; pK_a $(DfurH_2) = 9.80$).

TABLE 15

Observed rate constants for base hydrolysis of $[Co(H_2O)(Dioxim)_2X]$ in water solution at 0° C ($\mu = 0.15$ (KNO_3), $C_{KOH} = 5 \times 10^{-3}$ mole l^{-1}; $C_{complex} = 5 \times 10^{-4}$ mole l^{-1})

Complex	$k_{OH}^{obs} \times 10^5$ (sec^{-1})
$[Co(H_2O)(DH)_2Cl]$	5.34
$[Co(H_2O)(DH)_2Br]$	7.62
$[Co(H_2O)(MH)_2Cl]$	15.1
$[Co(H_2O)(MH)_2Br]$	16.6
$[Co(H_2O)(DfurH)_2Br]$	78.3
$[Co(H_2O)(DfH)_2Cl]$	161
$[Co(H_2O)(DfH)_2Br]$	110

Possibly the discrepancy between dioxime pK_a and base hydrolysis rate constant is related in this case to a steric factor. Probably, the values of the base hydrolysis rate constants for α-benzildioxime complexes larger than predicted from the inductive effect of C_6H_5, are also due to a steric effect.

The influence of a steric factor on the rate is in accord with the dissociative mechanism for the base hydrolysis reaction investigated. The straight line dependence of log k_{OH}^{obs} vs. $\sqrt{\mu}$ is in favour of this mechanism.

Thus the mechanism of base hydrolysis for non electrolyte dioximes involves conjugate base formation with subsequent release of halogen via dissociation of the conjugate base. It may be represented by the following scheme:

(a) For $[Co(Amine)(Dioxim)_2X]$

$$[Co(Amine)(Dioxim)_2X]^0 + OH^- \overset{K_2}{\rightleftharpoons} [Co(Amine)(Dioxim)(Dioxim\text{-}H)X]^-$$

The proton equilibrium is set up quickly. The following further reactions are possible:

$$[Co(Amine)(Dioxim)(Dioxim\text{-}H)X]^- \xrightarrow[slow]{k} [Co(Amine)(Dioxim)(Dioxim\text{-}H)]^0 + X^-$$

$$[Co(Amine)(Dioxim)(Dioxim\text{-}H)] + H_2O \xrightarrow[fast]{} [Co(Amine)(Dioxim)_2OH]$$

(b) for $[Co(H_2O)(Dioxim)_2X]$

$$[Co(H_2O)(Dioxim)_2X] + OH^- \overset{K_1}{\rightleftharpoons} [Co(Dioxim)_2(OH)X]^-$$

$$[Co(Dioxim)_2(OH)X]^- + OH^- \overset{K_2}{\rightleftharpoons} [Co(Dioxim)(Dioxim\text{-}H)(OH)X]^{2-}$$

$$[Co(Dioxim)(Dioxim\text{-}H)(OH)X]^{2-} \xrightarrow[slow]{k} [Co(Dioxim)(Dioxim\text{-}H)(OH)]^- + X^-$$

$$[Co(Dioxim)(Dioxim\text{-}H)(OH)]^- + H_2O \xrightarrow[fast]{} [Co(Dioxim)_2(OH)_2]^-$$

The base hydrolysis rate of $[Co(H_2O)(Dioxim)_2X]$ is a function of three variables K_1, K_2 and k, and of $[Co(Amine)(Dioxim)_2X]$, a function of two variables K_2 and k. K_1 and K_2 characterize the loss of a proton from the coordinated water and $Co(Dioxim)_2$ group, respectively, and k is the transition complex formation rate. The presence of the deprotonated dioxime accounts for the increase in the rate of base hydrolysis in comparison with the acid rate.

E. COBALT(III) *trans*-DIOXIME — ANATION REACTIONS

Investigation of the interaction between the *trans*-diaquo nitrate $[Co(H_2O)_2(DH)_2]NO_3$ and alkali metal salts MeX (X = Cl, Br, I, NCS) has shown that in the cases of X = I or NCS interaction takes place in two stages, forming firstly an acid aquo and then a diacid compound. If X = Cl or Br, only one compound, acid bis(dimethylglyoximate)aquo cobalt(III), is formed independently of the quantitative proportion of the reagents.

Substitution of coordinated water in a diaquo cation by an anion diminishes the acid properties of the dioxime, and provides a means to investigate the kinetics of the anation reaction by the pH-metric method.

The anation reactions under investigation can be subdivided into two types. Interaction between the diaquo cation and bromide or chloride ions is assigned to the first type of reaction, as a result of which bromo, or chloro aquo complexes, respectively, are formed. With small reagent concentration these reactions are reversible.

The kinetic characteristics for this type of reaction are summarised in Table 16.

The rate constants were calculated graphically from the linear dependence of $\log([H^+]_\infty - [H^+]_0)/([H^+]_\infty - [H^+]_t)$ on time where $[H^+]_0$ = hydrogen ion concentration in 10^{-3} mole l^{-1} solution of $K[Co(DH)_2X_2] \cdot nH_2O$ (X = I, NCS) or in 10^{-3} mole l^{-1} solution of $[CoX(DH)_2H_2O]$ (X = Cl, Br) in the presence of an appropriate excess of KX; $[H^+]_t$ = hydrogen ion concentration in the reaction mixture at time t.

It was found that the rate constants observed for anation by bromide and

TABLE 16

Kinetic characteristics for substitution of water by chloride or bromide ions in $[Co(DH)_2(H_2O)_2]^+$.
($C_{complex} = 10^{-3}$ mole l^{-1}, $C_{KX} = 5 \times 10^{-1}$ mole l^{-1}, $\mu = 0.5$)

Reaction	$k_{obs} \times 10^6$ (sec^{-1})				E_I (kJ mole^{-1})	log Z
	25°	30°	35°	40°		
$[Co(DH)_2(H_2O)_2]^+ + Cl^-$	196	444	852	1566	104	14.7
$[Co(DH)_2(H_2O)_2]^+ + Br^-$	460	806	1543	3063	90	12.6

chloride ions are dependent upon the concentration of the entering group.

The rate constants of reactions mentioned above can be characterised by the equation

$$k_{obs} = k_1 [y^-] + k_{-1}$$

where k_1 is the second order rate constant of anation (the slope of linear graph $k_{obs} = f([y^-])$; k_{-1} is the aquation rate constant (the intercept of $k_{obs} = f([y^-])$; $[y^-]$ is the reagent concentration (Fig. 10). The value of the aquation rate constant for the bromo aquo complex ($\sim 110 \times 10^{-6}$, sec^{-1} at 30° C) calculated from Fig. 10, is in satisfactory agreement with the corresponding value obtained earlier [24].

The interaction reactions of thiocyanate and iodide ions with bis(dimethylglyoximate) diaquo cobalt(III) cation is assigned to the second type of reaction. Diacid dioximes are their final products and they are practically irreversible.

In Fig. 11(a) the dependence of log $([H^+]_\infty - [H^+]_0)/([H^+]_\infty - [H^+]_t)$ on time for anation of the diaquo cation by thiocyanate ion is presented. It is seen that some points fall in one straight line, and some in another. This indicates different substitution rates for the first and second water molecules.

The observed rate constants, activation energies and log Z are summarised in Table 17.

The difference observed in anation rates (Table 19) can be related to the different nature of the entering group, the different labilising power of the axial ligand or to both factors. It should be noted that the rate increase on

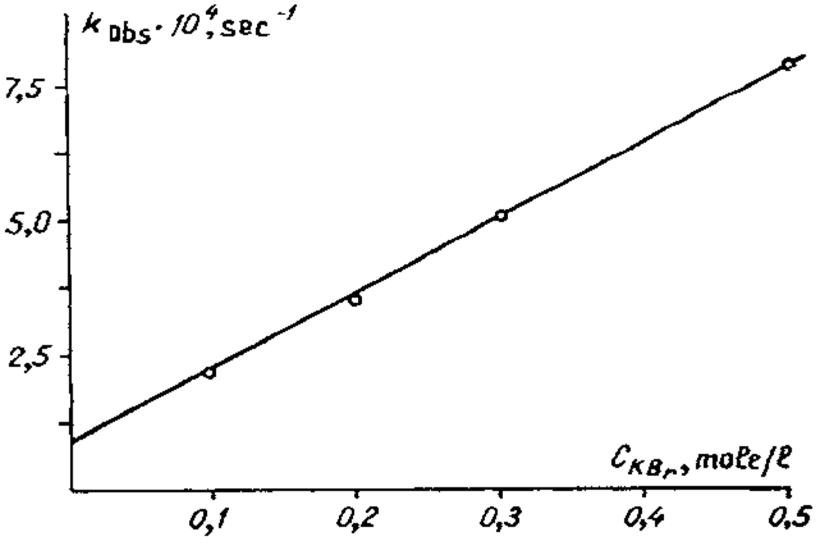


Fig. 10. The dependence of k_{obs} on reagent concentration for reaction $[Co(H_2O)_2(DH)_2]^+$ + Br^-. t = 30±0.1° C; μ = 0.5.

TABLE 17

The kinetics characteristics of substitution of the first and second water molecules in 1,6-$[Co(DH)_2(H_2O)_2]^+$ by thiocyanate ion
($C_{complex} = 10^{-3}$ mole l^{-1}, $C_{KNCS} = 10^{-1}$ mole l^{-1}, $\mu = 0.1$)

Reaction	$k^{I}_{obs} \times 10^6$ (sec^{-1})				E (kJ mole^{-1})	log Z
	30°	40°	45°	50°		
$[Co(DH)_2(H_2O)_2]^+$ + NCS	518	1462	2718	3616	87	11.7
	$k^{II}_{obs} \times 10^6$ (sec^{-1})					
	30°	40°	45°	50°		
$[Co(DH)_2(H_2O)(NCS)]$ + NCS^-	230	636	1359	1831	89	11.7

passing from the nitro to the iodo complex is in accord with results obtained earlier from investigations of the inner-sphere substitution reactions in acid media [16,17].

However, a limiting rate was not reached even with very large concentrations of the entering group.

Interaction between the diaquo cation and iodide ion may be characterised with the kinetic lines, presented in Fig. 11(b). Only the entrance of the second

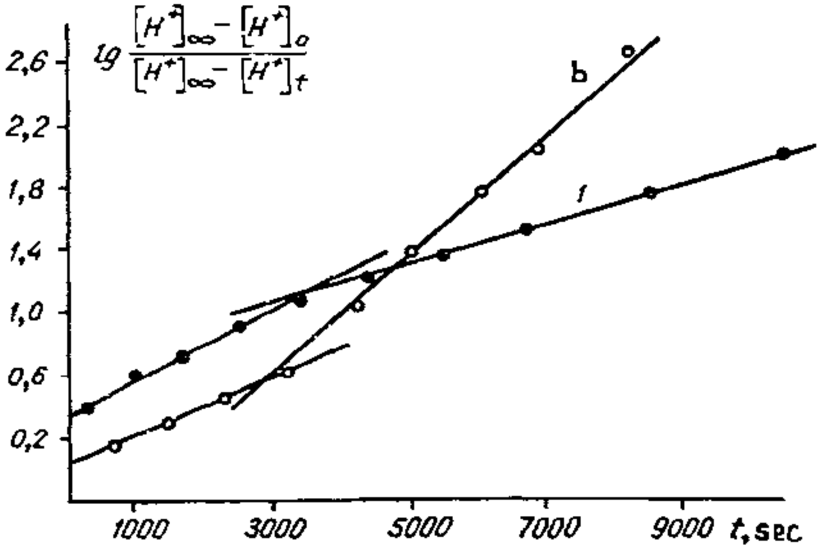


Fig. 11. The dependence of $\log([H^+]_\infty - [H^+]_0)/([H^+]_\infty - [H^+]_t)$ on time for reactions of diaquo cation with (a) NCS^-, $\mu = 0.1$; (b) I^-, $\mu = 0.5$; $t = 30 \pm 0.1$°C.

TABLE 18

The kinetic characteristics of substitution of the second water molecule by iodine ion in 1,6-$[Co(DH)_2(H_2O)_2]^+$
($C_{complex} = 10^{-3}$ mole l^{-1}, $C_{KJ} = 10^{-1}$ mole l^{-1}, $\mu = 0.5$)

Reaction	$k_{obs} \times 10^6$ (sec^{-1})				E (kJ mole^{-1})	log Z
	25°	30°	35°	40°		
$[Co(DH)_2(H_2O)_2]^+ + I^-$	507	967	1635	2725	85	11.6

iodide ion can be estimated quantitatively because it is faster than the substitution of the first water molecule (Table 18).

The second order rate constants for substitution of the second water molecule in the diaquo cation have been calculated from $k_{obs}/C_{reagent}$ and are summarized in Table 19 with Hague and Halpern's data [22] for anation of nitroaquo dioxime.

It is also noted that the observed rate constants k^1, k^{11} also in this case depend on the reagent concentration, but, in contrast to reactions with chloride and bromide ions, this dependence is less clear cut, for example

$C_{KNCS} = 10^{-1}$ mole l^{-1}, $C_{complex} = 10^{-3}$ mole l^{-1}
$k^1_{obs} = 3.45 \times 10^{-4}$ sec^{-1}, $k^{11}_{obs} = 2.37 \times 10^{-4}$ sec^{-1}
$C_{KNCS} = 5 \times 10^{-1}$ mole l^{-1}, $C_{complex} = 10^{-3}$ mole l^{-1}
$k^1_{obs} = 9.21 \times 10^{-4}$ sec^{-1} and $k^{11}_{obs} = 4.84 \times 10^{-4}$ sec^{-1}

Considering the second order rate constants for the substitution of the first water molecule in diaquo cation with different nucleophiles (Table 20) it can be concluded that the nature of the entering group does not practically influence the anation rate of the dioxime under investigation. Comparatively large values of the rate constant for I^- resulted from the substitution of the second water molecule, as seen above. From the non-dependence of the anation rate constants on the nature of the entering group it can reasonably

TABLE 19

Coordination axis	$k \times 10^4$ mole^{-1} sec^{-1} (30°C)		
	Entering group		
	I	NCS	NO_2
$I—Co—OH_2$	96		
$NCS—Co—OH_2$		23	
$O_2N—Co—OH_2$			3.5 [a]

[a] Hague and Halpern's data.

TABLE 20

Second order rate constants for substitution of the first water molecule in 1,6-$[Co(DH)_2(H_2O)_2]^+$ with different nucleophiles (30° C)

	Reagent					
	KCl	KBr	KI	KNCS	Py [a]	Thio [b]
$k \times 10^4$ ($l\ mole^{-1}\ sec^{-1}$)	8.88	16.1	44	18.4	20	27

[a] Extrapolated from [63].
[b] Rate constant at 45° C [64].

be suggested that substitution of the first water molecule is dissociative in mechanism in these cases [1,2].

It follows from all these experimental data that irrespective of the reaction type studied (aquation, base hydrolysis, anation) the most probable substitution reactions mechanism for *trans*-dioximes is dissociative.

REFERENCES

1 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, 2nd edn., Wiley, New York, 1967.
2 C.H. Langford and H.B. Gray, Ligand Substitution Processes, Benjamin, New York, 1965.
3 C.K. Poon, Inorg. Chim. Acta, 4 (1970) 123.
4 R.D. Archer, Coord. Chem. Rev., 4 (1969) 243.
5 C.H. Langford and T.R. Stengle, Annu. Rev. Phys. Chem., 19 (1968) 193.
6 A.V. Ablov, Dokl. Akad. Nauk SSSR, 97 (1954) 1019.
7 A.V. Ablov and I.D. Samus, Dokl. Akad. Nauk SSSR, 146 (1962) 1071.
8 I.D. Samus and N.V. Belov, Dokl. Akad. Nauk SSSR, 193 (1970) 333.
9 N.R. Kunchur and K.S. Viswanathan, Z. Anorg. Chem., 302 (1960) 289.
10 K.S. Viswanathan and N.R. Kunchur, Acta Crystallogr., 14 (1961) 675.
11 T.I. Malinovskii, Yu.A. Simonov and B.M. Shchedrin, Cristallografiya, 14 (1969) 995.
12 Yu.A. Simonov, A.A. Dvorkin, O.A. Bologa, A.V. Ablov and T.I. Malinovskii, Dokl. Akad. Nauk SSSR, 210 (1973) 615.
13 A.Ya. Sychev and A.V. Ablov, Zh. Neorg. Khim., 6 (1961) 2288.
14 A.V. Ablov and D.M. Palade, Dokl. Akad. Nauk SSSR, 144 (1962) 341.
15 A.V. Ablov and N.M. Samus, Zh. Neorg. Khim., 5 (1960) 852.
16 A.V. Ablov and N.M. Samus, Zh. Neorg. Khim., 3 (1958) 1818.
17 A.V. Ablov and N.M. Samus, Zh. Neorg. Khim., 4 (1959) 1753.
18 G.P. Syrtsova and L.N. Korletyanu, Izv. Sibirskogo Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 3 (1968) 48.
19 G.P. Syrtsova and Nguen Zui Liong, Zh. Neorg. Khim., 15 (1970) 1714.
20 Nguen Zui Liong and G.P. Syrtsova, Zh. Neorg. Khim., 16 (1971) 704.
21 G.P. Syrtsova and L.N. Korletyanu, Zh. Neorg. Khim., 13 (1968) 2161.
22 D. Hague and G. Halpern, Inorg. Chem., 6 (1966) 2059.
23 G.A. Konunova, Issledovaniya po khimii khelatnykh soedinenii, Shtiintsa, Kishinev, 1971, p. 69.
24 A.V. Ablov and A.Ya. Sychev, Zh. Neorg. Khim., 4 (1959) 2485.

25 N.M. Samus, A.V. Ablov and G.A. Konunova, Zh. Neorg. Khim., 18 (1973) 2651.
26 S. Glasstone, K. Laidler and H. Eyring, The Theory of Rate Processes, McGraw—Hill, New York, 1941, ch. 8.
27 V.D. Panasyuk, Izv. Sibirskogo Otd. Akad. Nauk SSSR, Ser. Khim., No. 7 (142), (1968) 54.
28 C.K. Ingold, Structure and Mechanism in Organic Chemistry, 2nd edn., Cornell University Press, 1969.
29 C.H. Langford and H.B. Gray, Ligand Substitution Processes, Benjamin, New York, 1965, p. 59.
30 N.M. Samus, A.V. Ablov and G.A. Konunova, Zh. Neorg. Khim., 19 (1974) 1559.
31 F. Basolo, J.G. Bergmann, R.E. Meeker and R.G. Pearson, J. Amer. Chem. Soc., 78 (1956) 2676.
32 G. Costa, G. Tauzher and A. Puxeddu, Inorg. Chim. Acta, 3 (1969) 41.
33 N.M. Samus, A.V. Ablov, G.A. Konunova and I.V. Khoroshun, Zh. Neorg. Khim., 19 (1974) 2788.
34 D.H. McDaniel and H.C. Brown, J. Org. Chem., 23 (1958) 420.
35 L.P. Hammett, Physical Organic Chemistry, 2nd edn., McGraw—Hill, 1970.
36 A. Albert and E.P. Serjeant, Ionisation Constants of Acids and Bases, Methuen, London, 1962.
37 N.M. Samus, O.N. Damaskina and A.V. Ablov, Zh. Neorg. Khim., 17 (1972) 1672.
38 N.M. Samus, O.N. Damaskina and A.V. Ablov, Zh. Neorg. Khim., 17 (1972) 2199.
39 N.M. Samus, O.N. Damaskina and A.V. Ablov, Zh. Neorg. Khim., 18 (1973) 436.
40 A.V. Ablov, N.M. Samus and M.P. Popov, Dokl. Akad. Nauk SSSR, 106 (1956) 665.
41 B.I. Peshchevitskii and V.P. Kazakov, Zh. Neorg. Khim., 8 (1963) 250.
42 B.I. Peshchevitskii and V.P. Kazakov, Izv. Sibirskogo Otd. Akad. Nauk SSSR, 2 (1963) 20.
43 B.I. Peshchevitskii and V.P. Kazakov, Zh. Neorg. Khim., 8 (1963) 2816.
44 R.G. Pearson, J. Amer. Chem. Soc., 85 (1968) 3533.
45 A. Wojcicki and M.F. Farona, Inorg. Chem., 3 (1964) 151.
46 C.K. Jørgensen, Inorg. Chem., 3 (1964) 1201.
47 H.C. Brown, C.K. Ingold and R.S. Nyholm, J. Chem. Soc., London, (1953) 2696.
48 S.C. Chan and M. Tobe, J. Chem. Soc., London, (1962) 4531.
49 F.J. Garric, Nature (London), 139 (1937) 507.
50 S.C. Chan, J. Chem. Soc., A, (1966) 1124.
51 R.D. Gillard, J. Chem. Soc., A, (1967) 917.
52 R.G. Pearson, R. Meeker and F. Basolo, J. Inorg. Nucl. Chem., 1 (1955) 342.
53 J.P. Birk, P.B. Chock and J. Halpern, J. Amer. Chem. Soc., 90 (1968) 6959.
54 S.C. Chan and P.Y. Leung, Aust. J. Chem., 22 (1969) 2569.
55 J. Zsako, Z. Finta and Cs. Varhelyi, J. Inorg. Nucl. Chem., 34 (1972) 2887.
56 N.M. Samus, T.S. Luk'yanets and A.V. Ablov, Zh. Neorg. Khim., 19 (1974) 2221.
57 D.P. Rillema, J.F. Endicott and J.R. Barber, J. Amer. Chem. Soc., 95 (1973) 6987.
58 D.M. Palade, T.N. Volokh, N.A. Breslavskaya and T.H. Golyshina, Zh. Neorg. Khim., 15 (1970) 2698.
59 R.W. Taft, in M.S. Newman (Ed.), Steric Effects in Organic Chemistry, Wiley, 1960, ch. 13.
60 L.A. Tchugaev, Ber., 39 (1906) 2692.
61 A.V. Ablov, A.A. Dvorkin, Yu.A. Simonov, O.A. Bologa and T.I. Malinovskii, Dokl. Akad. Nauk SSSR, 217 (1974) 89.
62 Yu.A. Zhdanov and V.I. Minkin, Korrelyatsionyi analiz v organicheskoi khimii, Rostov, 1966, pp. 313—315.
63 N.M. Samus and T.S. Luk'yanets, Zh. Neorg. Khim., 17 (1972) 745.
64 J. Ealey and J. Zimmerman, Inorg. Nucl. Chem. Lett., 8 (1972) 687.