*Coordination Chemistry Reviews*, 28 (1979) 177—203

# KINETICS AND MECHANISM OF SUBSTITUTION REACTIONS OF COBALT(III) *trans*-DIOXIMINES IN NON-AQUEOUS MEDIA

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(Received 17 January 1979)

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## A. INTRODUCTION

According to Parker [1] solvents can be subdivided by their specific interaction with anions and cations into (1) dipolar aprotic and (2) protic. The tendency of protic solvents to form hydrogen bonds is the reason for their ability to solvate anions especially well. Dipolar aprotic solvents cannot be hydrogen donors, their interaction with anions arises from mutual polarisation of anions and solvent molecules. The existence of two different types of specific solvation probably can influence the kinetic parameters of substitution reactions, relative anion solvolysis rates and the mechanism of substitution.

Previously the influence of specific solvation of anions on the rates of nucleophilic substitution reactions was studied in detail for organic substances. The experimental data for such reactions have been summarised [2—4].

For coordination compounds there are few systematic studies of substitution reactions in non-aqueous media. To elucidate the effect of the nature of the solvent and specific ion solvation on the rate of substitution reactions one can study solvolysis kinetics of halogen-ion in cobalt(III) *trans*-dioximine nonelectrolytes in protic (monoatomic alcohols) and dipolar aprotic (dimethylformamide — DMF, dimethylsulfoxide — DMSO, acetonitrile) solvents, which like water are simultaneously solvents and nucleophiles. The aquation kinetics were previously studied in detail for this class of substances [5].

## B. KINETICS OF HALOGEN SUBSTITUTION IN Co(III) *trans*-DIOXIMINES BY PROTIC SOLVENTS

Previously substitution reaction kinetics of coordination compounds were studied in aqueous and water—organic solvents. Recently organic substances such as methanol, dimethylformamide, dimethylacetamide, dimethylsulfoxide, etc., have been used very frequently as solvents. However there is no unanimity in the estimation of the role of the solvent in the substitution processes. Some authors consider that organic molecules functioning as solvents do not form a bond with the central atom or if they form it, this bond is weak and solvato-complexes are unstable.

Brown et al. [6] studying, by different methods, the kinetics of chloride-ion substitution by other anions in *cis*-$[Co(en)_2Cl_2]^+$ in methanol arrived at the conclusion that the direct substitution of one anion by another takes place without methanol participation.

Holba [7] also suggested that the substitution of chloride ion in *cis*-dichlorobis(ethylenediamine)chromium(III) cation by thiocyanate ion in methanol occurs without participation of solvent.

There are however other studies in which it is demonstrated that methanol is involved in the formation of an intermediate complex.

Slaten and Garner [8] were the first to point out chloride-ion solvolysis from the inner sphere of *trans*-$[Cr(en)_2Cl_2]^+$ in anhydrous methanol.

Hunt and Taube [9] studying the influence of solvent on the water exchange in $[Co(NH_3)_5(H_2O)]^{3+}$ noted that the reaction rate in methanol mixed with some water did not depend significantly on the water concentration, i.e. the rates in water and anhydrous methanol were similar in value. The authors considered that water did not participate in activated complex formation and the process, probably, took place by formation of a Co—$(OHCH_3)$ bond via $S_N2$ mechanism with subsequent rapid substitution of methanol by water.

Asperger et al. [10,11] assumed that methanolysis was the rate-determining step in the substitution of chloride ion by thiocyanate in *trans*-$[Co(en)_2NO_2Cl]^+$.

The rates of the reaction investigated and that of chloride-ion exchange in methanol were similar; furthermore the exchange rate of $Cl^-$ in *trans*-$[Co(en)_2(NO_2)Cl]^+$ did not depend on chloride-ion concentration. It is interesting to point out that the substitution rate of $Cl^-$ by $NCS^-$ in $[Co(en)_2(NO_2)Cl]^+$ was greater than that of $[Co(en)_2Cl_2]^+$. In the case of an $S_N1$ mechanism the reverse phenomenon would be expected.

Tobe and co-workers [12] isolated 1,6-$[Co(en)_2(CH_3O)Cl]^+$ in crystalline form and showed that, in methanol solution, on adding acid, the above mentioned complex was transformed into 1,6-$[Co(en)_2(CH_3OH)Cl]^{2+}$. The latter was quite stable in solution and only in a large chloride-ion concentration converted into 1,6- and 1,2-$[Co(en)_2Cl_2]^+$. Considering the stability of this solvatocomplex, the authors excluded the possibility that it is an intermediate in chloride-ion exchange reactions of 1,2-$[Co(en)_2Cl_2]^+$.

Adamson [13] studied thiocyanate-ion substitution kinetics in $[Cr(NH_3)_2(NCS)_4]^-$ by protic solvents with different properties ($H_2O$, $CH_3OH$, $C_6H_5OH$). The data obtained could be accounted for if it is admitted that solvolysis reactions took place by a bimolecular mechanism including the formation of a hydrogen bridged bond between anion and solvent. In favour of this supposition is the extremely low value of the substitution rate of this complex anion in nitromethane, which cannot form a hydrogen bond.

The results mentioned above demonstrate that experimental data on substitution reactions in protic solvents R—OH are not numerous, their interpretation is quite contradictory, and there is no unanimity in estimation of the solvent's role in substitution reactions in octahedral complexes. Moreover it must be kept in mind that alcohols can enter into the inner sphere of complexes to form comparatively stable compounds.

In protic solvents the solvation interaction can be superimposed by strong hydrogen bonding, which is large for small anions. Concerning the cobalt(III) dioximines there are no systematic investigations of substitution reaction kinetics in non-aqueous media. One of us has shown preparatively [14], that methanol enters into the inner sphere of the complex forming methanol containing compounds. Their formation may be represented by the following scheme.

(a) $[Co(Amine)(DH)_2Hlg]^0 + CH_3OH \rightarrow [Co(Amine)(CH_3OH)(DH)_2]^+ + Hlg^-$

(b) $[Co(H_2O)(DH)_2Hlg]^0 + CH_3OH \xrightarrow{fast} [Co(CH_3OH)(DH)_2Hlg]^0 + H_2O$

$[Co(CH_3OH)(DH)_2Hlg] + CH_3OH \xrightarrow{slow} [Co(CH_3OH)_2(DH)_2]^+ + Hlg^-$

It was of interest to study the substitution reaction kinetics of the acid residue by methanol in the following series of dioximines: 1,6-$[CoHlg(DH)_2L]$ ($L = NH_3$, $C_6H_5NH_2$, Py, $H_2O$; Hlg = Cl, Br, I). Previously [15,16] the aquation kinetics of 1,6-$[CoHlg(DH)_2L]$ were studied and it was shown that substitution takes place by a mechanism with elements of dissociation.

One could expect that comparison of data obtained for methanolysis with those for aquation will permit us to elucidate how the substitution of water by alcohol influences the kinetics and mechanism of substitution reactions in cobalt dioximines.

As is seen in Table 1 halogen substitution rates by methanol depend upon the axial ligand. The halogen situated in *trans*-position to ammonia is substituted faster than the halogen in *trans*-position to pyridine. The comparison of rate constants obtained in methanol with those of aquation reveals (Table 2) that substitution reactions proceed more slowly in methanol than in water although activation energies are similar in both cases [16].

The amine (Table 2) influences in a different fashion the rates of halogen substitution by water and methanol. Axial ligands disposed in order of

TABLE 1 [a]

Kinetic data for substitution of halogen by methanol in 1,6-[CoHlg(DH)$_2$L] $C_{complex} = 10^{-3}$ mol l$^{-1}$

| Complex | $K \times 10^6$ (sec$^{-1}$) | | | | | $E$ (kJ mol$^{-1}$) | lg $Z$ | $\Delta S^{\neq}$ (J mol$^{-1}$ g$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | 40° | 45° | 50° | 55° | 60° | | | |
| [CoCl(DH)$_2$(NH$_3$)] | 24 | — | 80 | 160 | 290 | 108 | 13.4 | +2 |
| [CoBr(DH)$_2$(NH$_3$)] | 15 | — | 47 | 85 | 160 | 97 | 11.3 | −37 |
| [CoI(DH)$_2$(NH$_3$)] | 6.7 | — | 16 | 27 | 44 | 90 | 9.8 | −66 |
| [CoCl(DH)$_2$(C$_6$H$_5$NH$_2$)] | 16 | — | 49 | 92 | 160 | 110 | 13.0 | −5 |
| [CoBr(DH)$_2$(C$_6$H$_5$NH$_2$)] | 9.5 | — | 31 | 59 | 110 | 100 | 12.8 | −29 |
| [CoI(DH)$_2$(C$_6$H$_5$NH$_2$)] | 4.0 | — | 13 | 22 | 39 | 97 | 11.0 | −48 |
| [CoCl(DH)$_2$Py] | — | 6.4 | 12 | 22 | 38 | 100 | 11.5 | −31 |
| [CoBr(DH)$_2$Py] | — | 5.7 | 9.8 | 18 | 29 | 92 | 9.8 | −66 |
| [CoI(DH)$_2$Py] | — | — | 7.9 | 12 | 19 | 89 | 9.3 | −75 |
| [CoCl(DH)$_2$(H$_2$O)] | — | — | 28 | 55 | 91 | 101 | 14.7 | +28 |
| [CoBr(DH)$_2$(H$_2$O)] | — | — | 21 | 34 | 61 | 94 | 13.9 | +12 |
| [CoI(DH)$_2$(H$_2$O)] | — | — | 12 | 20 | 35 | 87 | 12.9 | −7 |

[a] N.M. Samus, T.S. Lukyanets and Ziong Kuang Fung, Zh. Neorg. Khim., 19 (1974) 2473.

TABLE 2

Comparison of rate constants for halogen substitution in 1,6-[CoHlg(DH)$_2$L] by methanol and water

$C_{\text{complex}} = 10^{-3}$ mol l$^{-1}$, 50°C

| Complex | $K \times 10^6$ (sec$^{-1}$) in water | $K \times 10^6$ (sec$^{-1}$) in methanol |
|---|---|---|
| [CoCl(DH)$_2$Py] | 310 | 12 |
| [CoBr(DH)$_2$Py] | 270 | 9.8 |
| [CoI(DH)$_2$Py] | 110 | 7.9 |
| [CoCl(DH)$_2$C$_6$H$_5$NH$_2$] | 250 | 49 |
| [CoBr(DH)$_2$C$_6$H$_5$NH$_2$] | 200 | 31 |
| [CoI(DH)$_2$C$_6$H$_5$NH$_2$] | 76 | 13 |
| [CoCl(DH)$_2$NH$_3$] | 550 | 80 |
| [CoBr(DH)$_2$NH$_3$] | 810 | 47 |
| [CoI(DH)$_2$NH$_3$] | 1200 | 16 |

diminishing halogen substitution rates by methanol are as follows: $NH_3 > C_6H_5NH_2 >$ Py. For aquation of the same complex the sequence is: $NH_3 >$ Py $> C_6H_5NH_2$.

The substitution rates of halogen by water and methanol depend upon the leaving group (Table 2). For complexes with L = Py or $C_6H_5NH_2$, the rates decrease from chloro- to iodo-compounds.

Ammonia-containing complexes behave in a different way in water and in methanol. While the rate sequence of halogen substitution by methanol is similar with that observed for pyridine- and aniline-containing complexes, in aqueous solution inversion of the rate substitution sequence takes place — the rate constants increase from chloro- to iodo-complex.

Hence regularities observed for aquation do not coincide completely with those obtained for halogen substitution reactions by methanol although water and methanol belong to the same category of solvent (protic).

Among other effects, the influence of the steric factor on the rate of substitution allows us to make certain deductions concerning the probable reaction mechanism. Previously [17—19] it was shown that substitution of the halogen in 1,6-[CoHlg(DfH)$_2$L] * by water occurs faster than for compounds of the same type containing dimethylglyoxime. This is possible in the case of aquation reactions occurring by a dissociative mechanism.

Investigation of halogen substitution kinetics in 1,6-[CoCl(DfH)$_2$L] by methanol (Table 3) shows that for complexes with α-benzildioxime the amine also influences the value of the rate constants, which decrease in the following sequence: Py $> NH_3 > C_6H_5NH_2$. It must be pointed out that the exchange of dimethylglyoxime by α-benzildioxime in case of pyridine-containing complexes leads to the rate constants increasing, while for compounds with axial coordinates $H_3N—Co—Cl$ and $C_6H_5—NH_2—Co—Cl$ a rate decrease takes place.

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* DfH-α-benzil dioximate ion.

TABLE 3

Effect of the dioxime on the substitution rate of halogen by methanol in 1,6-[CoHlg-(Dioxim)$_2$L] $C_{complex}$ = 5 × $10^{-4}$ mol $l^{-1}$, 50°C

| Complex | $K \times 10^6$ (sec$^{-1}$) | Complex | $K \times 10^6$ (sec$^{-1}$) |
|---|---|---|---|
| [CoCl(DH)$_2$Py] | 12 | [CoCl(DfH)$_2$Py] | 110 |
| [CoCl(DH)$_2$C$_6$H$_5$NH$_2$] | 49 | [CoCl(DfH)$_2$C$_6$H$_5$NH$_2$] | 34 |
| [CoCl(DH)$_2$NH$_3$] | 80 | [CoCl(DfH)$_2$NH$_3$] | 49 |

Such a different dependence on the steric factor for the halogen substitution rate in methanol in comparison with that in water is probably caused by a different degree of solvent participation in the formation of the intermediate.

A study of the behaviour of 1,6-[CoHlg(DH)$_2$L] in ethanol, and in n-propanol, has shown that the specific resistance of these solutions diminishes with time, and hence electrical conductivity increases. This fact indicates that methanol and some other alcohols can enter in the dioximine inner sphere.

It was of interest to investigate the effect of the alcohol on the halogen substitution rate. With this aim in mind the change of electrical conductivity with time of 1,6-[Co(C$_6$H$_5$NH$_2$)(DH)$_2$Cl] was studied in absolute ethanol and in n-propanol. The experimental data show that chloride-ion substitution rate decreases from methanol to n-propanol. For example, at 50°C in methanol $K = 49 \times 10^{-6}$ sec$^{-1}$ and in ethanol $K = 9.6 \times 10^{-6}$ sec$^{-1}$; at 60°C in n-propanol $K = 3.1 \times 10^{-6}$ sec$^{-1}$ and in methanol $K = 160 \times 10^{-6}$ sec$^{-1}$.

This decrease may be caused by the increase in size of the alcohol hydrocarbon radical or by decrease of the media dielectric permeability [20]. The latter plays an important role in the ion—dipolar interaction of the leaving group with solvent.

The dioximines discussed so far contain as axial ligands amines which differ in their basicity and steric bulk. It was of interest to study the substitution kinetics in methanol for complexes, where the number of the influencing factors is a minimum. The non-electrolyte dioximines 1,6-[CoCl(DH)$_2$-(H$_2$NC$_6$H$_4$X)] have been investigated further. In these complexes the axial ligands, the benzene ring substituted anilines, are practically unchanged in steric bulk near the central atom but differ in their basicity. Kinetic data for these complexes should throw light on the mechanism of the reactions investigated.

The rate constants for the substitution of the halogen by methanol in 1,6-[CoCl(DH)$_2$(H$_2$NC$_6$H$_4$X)] are presented in Table 4.

The rate of chloride-ion substitution by methanol in the complexes under investigation changes in the same order as the change in the inductive effect of the axial ligand (Table 4). If the logarithms of the rate constants for 1,6-[CoCl(DH)$_2$(H$_2$NC$_6$H$_4$X)] are plotted against Hammett's σ-constants for sub-

TABLE 4 [a]

Methanolysis rate constants for release of the chloride ion from 1,6-[$CoCl(DH)_2$-($H_2NC_6H_4X$)] 50°C, $C_{complex} = 1 \times 10^{-3}$ mol $l^{-1}$

| Complex | Hammett's $\sigma$ | $K \times 10^6$ ($sec^{-1}$) |
|---|---|---|
| [$CoCl(DH)_2$($p$-$H_2NC_6H_4OCH_3$)] | −0.268 | 105 |
| [$CoCl(DH)_2$($p$-$H_2NC_6H_4CH_3$)] | −0.170 | 62.0 |
| [$CoCl(DH)_2$($m$-$H_2NC_6H_4CH_3$)] | −0.069 | 35.0 |
| [$CoCl(DH)_2$($H_2NC_6H_5$)] | 0.000 | 25.0 |
| [$CoCl(DH)_2$($m$-$H_2NC_6H_4OCH_3$)] | +0.115 | 29.0 |
| [$CoCl(DH)_2$($p$-$H_2NC_6H_4Cl$)] | +0.227 | 40.0 |
| [$CoCl(DH)_2$($p$-$H_2NC_6H_4I$)] | +0.276 | 49.5 |
| [$CoCl(DH)_2$($m$-$H_2NC_6H_4Cl$)] | +0.373 | 51.0 |
| [$CoCl(DH)_2$($m$-$H_2NC_6H_4Br$)] | +0.391 | 56.0 |

[a] N.M. Samus and Ngyen Than Hong, unpublished data.

stituents in the aniline benzene ring, two different straight lines are obtained (Fig. 1).

One of the straight lines is formed by points characterising electron-donor substituents and another by electron-acceptor substituents.

An analogous dependence between log $K$ and Hammett's $\sigma$-constants has been pointed out previously in a study of the aquation reactions of the dioximines under investigation [21].

By analogy with aquation of 1,6-[$CoCl(DH)_2(H_2NC_6H_4X)$] it may be assumed that halogen substitution by methanol in these complexes proceeds by a different mechanism depending on the nature of the substituent in the aniline benzene ring. For dioximines with electron-donor substituents X sub-

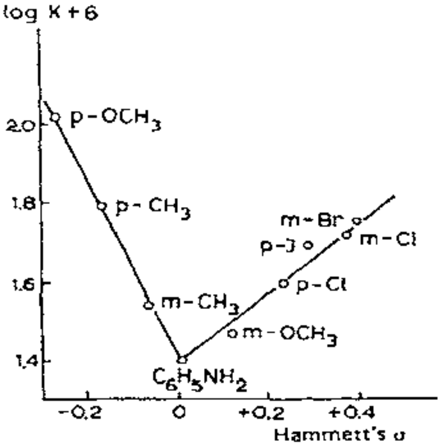

Fig. 1. Dependence of lg $K$ for methanolysis of [$CoCl(DH)_2(H_2NC_6H_4X)$] on Hammett's $\sigma$.

stitution reactions proceed via dissociative activation and for dioximines with electron-acceptor substituents X, associative elements in the mechanism prevail.

Further it was necessary to explore if the influence of the inductive effect on the substitution rate is typical of the whole class of dioximines or is a distinctive feature of the dioximines containing inner sphere aniline and its substituted derivatives.

For these reasons the kinetics of halogen substitution by methanol in dioximines 1,6-[CoHlg(DH)$_2$(XNH$_2$)] (X = $CH_3$, $C_2H_5$, n-$C_4H_9$) and 1,6-[CoHlg(DH)$_2${($CH_3$)$_2$NH}] (Hlg = Cl, Br, I), in which the axial ligands are alkyl derivatives of ammonia have been studied (Table 5). It is found that chloride ion is substituted faster than iodide ion. Such a sequence of substitution rates is analogous to that observed for aquation and methanolysis of 1,6-[CoHlg(DH)$_2$Amine)] (Amine = Py, $C_6H_5NH_2$, $NH_3$).

The rate constants of halogen substitution by methanol depend upon the axial ligand (Table 6).

From Table 6 it is seen that the rate of $Cl^-$ substitution increases from $NH_3$ to $CH_3NH_2$ and $C_2H_5NH_2$. Such a rate constant increase agrees with the Taft's induction constants for the amine substituents under investigation. A butyl group in accord with its induction effect must favour methanolysis in greater degree than, for example, an ethyl group. However, for a dioximine containing n-butylamine as axial ligand a decrease of the methanolysis rate constant is observed.

It may be that this fact is connected with the observation of the Nathan—Baker effect in the [CoHlg(DH)$_2$(XNH$_2$)] complexes. It is known that the

TABLE 5 [a]

Kinetic data for halogen solvolysis by methanol in 1,6-[CoHlg(DH)$_2$(XNH$_2$)]
$C_{\text{complex}} = 1 \times 10^{-3}$ mol l$^{-1}$

| Complex | $K \times 10^6$ (sec$^{-1}$) | | | | | $E$ (kJ mol$^{-1}$) | lg $Z$ |
|---|---|---|---|---|---|---|---|
| | 30° | 40° | 45° | 50° | 60° | | |
| [CoCl(DH)$_2$($CH_3NH_2$)] | 17.3 | 67.6 | 135 | 242 | 807 | 105 | 13 |
| [CoBr(DH)$_2$($CH_3NH_2$)] | 8.81 | 20.9 | 39.5 | 75.0 | 231 | 102 | 12 |
| [CoI(DH)$_2$($CH_3NH_2$)] | 2.30 | 7.68 | 13.8 | 23.0 | 71.4 | 95 | 11 |
| [CoCl(DH)$_2$($C_2H_5NH_2$)] | 69.7 | 184 | 313 | 598 | 1732 | 95 | 12 |
| [CoBr(DH)$_2$($C_2H_5NH_2$)] | 25.3 | 75.9 | 129 | 259 | 575 | 85 | 10 |
| [CoI(DH)$_2$($C_2H_5NH_2$)] | 10.1 | 25.8 | 46.1 | 75.4 | 188 | 83 | 9.9 |
| [CoCl(DH$_2$)(n-$C_4H_9NH_2$)] | 14.0 | 51.3 | 92.0 | 173 | 557 | 100 | 12 |
| [CoBr(DH)$_2$(n-$C_4H_9NH_2$)] | 7.0 | 21.9 | 39.9 | 66.0 | 199 | 95 | 11 |
| [CoI(DH)$_2$(n-$C_4H_9NH_2$)] | 3.91 | 9.14 | 10.9 | 20.4 | 63.4 | 92 | 10 |
| [CoCl(DH)$_2${($CH_3$)$_2$NH}] | 26.0 | 105 | 210 | 442 | 1768 | 120 | 16 |
| [CoBr(DH)$_2${($CH_3$)$_2$NH}] | 18.0 | 96.1 | 195 | 244 | 840 | 115 | 15 |
| [CoI(DH)$_2${($CH_3$)$_2$NH}] | 14.4 | 48.9 | 83.5 | 168 | 554 | 103 | 13 |

[a] N.M. Samus and Ngyen Than Hong, Zh. Neorg. Khim., 21 (1976) 1261.

TABLE 6

Rate constants for chloride-ion solvolysis by methanol in 1,6-[CoCl(DH)$_2$Amine] at 50°C

| Complex | Taft σ | $K \times 10^6$ (sec$^{-1}$) |
|---|---|---|
| [CoCl(DH)$_2$(NH$_3$)] | +0.49 | 80.0 |
| [CoCl(DH)$_2$(CH$_3$NH$_2$)] | 0.00 | 242 |
| [CoCl(DH)$_2$(C$_2$H$_5$NH$_2$)] | −0.10 | 598 |
| [CoCl(DH)$_2$(n-C$_4$H$_9$NH$_2$)] | −0.13 | 173 |
| [CoCl(DH)$_2$ {(CH$_3$)$_2$NH}] | — | 442 |

Nathan—Baker effect is observed in hydrolysis reactions of organic compounds in polar solvents [22], where strong solvation takes place.

The methanolysis rate increases from n-C$_4$H$_9$NH$_2$ to (CH$_3$)$_2$NH. This can be accounted for by an amine inductive effect increasing in consequence of the introduction of the second methyl group. It must be pointed out that the p$K_a$ values for dimethylamine and ethylamine are close to one another (p$K_a$ = 10.72 and 10.67 for (CH$_3$)$_2$NH and C$_2$H$_5$NH$_2$, respectively). Probably, the rate constant is also influenced by a steric factor, which becomes more apparent in case of dimethylamine.

To elucidate the effect of the protic solvent (alcohols) on the kinetics of halogen-ion solvolysis in 1,6-[CoHlg(DH)$_2$(XNH$_2$)] the rate of Cl$^-$ substitution in 1,6-[CoCl(DH)$_2$(XNH$_2$)] by ethanol and n-propanol (Table 7), was investiated.

The rate of chloride-ion substitution by alcohols (Table 7) decreases from methanol to n-propanol. Such a decrease in rate may be caused by alcohol radical increasing or by media dielectric permeability decreasing.

We should point out that the manifestation of the inductive effect and Nathan—Baker's effect decreases from methanol to n-propanol. While in

TABLE 7

Comparison of the rate constants of solvolysis of chloride ion in 1,6-[CoCl(DH)$_2$(XNH$_2$)] by methanol, ethanol and n-propanol
60°C, $C_{\text{complex}} = 1 \times 10^{-3}$ mol l$^{-1}$

| Coordinate | $K \times 10^6$ (sec$^{-1}$) | | |
|---|---|---|---|
| | ε = 32.6 methanol | ε = 24.3 ethanol | ε = 20.1 n-propanol |
| Cl—Co—NH$_3$ | 293 | 71.7 | 25.5 |
| Cl—Co—H$_2$NCH$_3$ | 807 | 171 | 25.6 |
| Cl—Co—C$_2$H$_5$NH$_2$ | 1732 | 384 | 69.0 |
| Cl—Co—n-C$_4$H$_9$NH$_2$ | 557 | 280 | 37.6 |
| Cl—Co—(CH$_3$)$_2$NH | 1768 | 499 | 81.0 |

methanol and ethanol substitution rates and Taft's constants are regularly interrelated, in propanol solution rate constants for $Cl^-$ substitution in 1,6-$[CoCl(DH)_2(NH_3)]$ and 1,6-$[CoCl(DH)_2(CH_3NH_2)]$ are close to one another. The rate of halogen substitution for the Cl—Co—n-$C_3H_7NH_2$ coordinate is somewhat lower than for dioximine, containing ethylamine.

The substitution rate is greatest for dimethylamine-containing dioximine. This fact allows us to assume that the rate increase is caused by a steric effect of the axial ligand. However steric hindrance increases from methylamine to butylamine as well. But this does not influence the solvolysis rate constants as much as dimethylamine. Probably, the introduction of a second methyl group in the tetrahedral structure of the amine nitrogen leads to greater space filling near the central atom than does increasing the hydrocarbon radical in the case of the primary amines. The different degree of space filling may be the cause of the different rate increase due to the replacement of methylamine by ethylamine and dimethylamine.

The methanolysis kinetics for Co(III)-coordination compounds with mono-*O*-methyl ether of diacetyldioxime — 1,6-$[CoHlg_2(DMe)$ * $(DHMe)]$ were also investigated. These compounds, as mentioned above, are non-electrolytes but contain an intramolecular hydrogen bond [23]. The data obtained should permit the elucidation of the influence of the equatorial and axial ligand on the rate constant, halogen substitution sequence and, probably, reaction mechanism.

It is seen from Table 8 that the substitution rates of the first chloride and bromide ions are approximately equal, while iodide-ion substitution takes place significantly faster.

This sequence of halogen substitution by methanol is the inverse of the order observed previously for methanolysis of the non-electrolyte dioximines: Cl > Br > I.

The experimental data show changing the complex structure significantly affects the sequence of the substitution of the acid residue by methanol.

Comparing the rate constant of halogen substitution in 1,6-$[CoHlg_2(DMe)$-$(DMeH)]$ by methanol with the aquation rate constants of these complexes we observe that the methanolysis rates are higher than the aquation rates. For example, at 50°C in methanol, the rate constants for 1,6-$[CoCl_2(DMe)(DHMe)]$ and 1,6-$[CoBr_2(DMe)(DMeH)]$ are, respectively, $59.8 \times 10^{-6}$ $sec^{-1}$ and $56.2 \times 10^{-6}$ $sec^{-1}$, whilst the aquation rate constants for these compounds are, respectively, $12.4 \times 10^{-6}$ $sec^{-1}$ and $5.07 \times 10^{-6}$ $sec^{-1}$. The increase of the methanolysis rate in comparison with aquation of the Co(III) dihalogeno-compounds, containing diacetyldioxime mono-*O*-methyl ether cannot be accounted for by a change in dielectric permeability of the solution.

The influence of the entering group, fulfilling both a nucleophile and solvent role, on the rate constants permits us to suggest the presence of associa-

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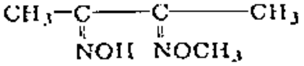
* DHMe = 

$$CH_3-\underset{\displaystyle NOH}{\overset{}{C}}\!\!=\!\!{}——\underset{\displaystyle NOCH_3}{C}——CH_3$$

TABLE 8 [a]

The substitution kinetics of halogen in 1,6-[CoHlg$_2$(DMe)(DHMe)] by methanol
$C_{complex} = 1 \times 10^{-3}$ mol l$^{-1}$

| Complex | $K \times 10^6$ (sec$^{-1}$) | | | | | $E$ (kJ mol$^{-1}$) | lg $Z$ |
|---|---|---|---|---|---|---|---|
| | 40° | 45° | 50° | 55° | 60° | | |
| [CoCl$_2$(DMe)(DHMe)] | 18.5 | 33.9 | 59.8 | — | 184 | 91 | 11 |
| [CoBr$_2$(DMe)(DHMe)] | 19.1 | 34.0 | 56.2 | — | 158 | 90 | 10 |
| [CoI$_2$(DMe)(DHMe)] | 89.1 | 149 | 230 | 403 | — | 82 | 9.8 |

[a] N.M. Samus, Ngyen Than Hong and O.A. Bologa, Zh. Neorg. Khim., 24 (1979) 98.

tion elements in the mechanism of this reaction.

Large negative absolute values of the activation entropies are in favour of this proposition (Table 8).

Summarising the data on the kinetics of Co(III) dioximine substitution reactions in protic solvents we concluded that the value of the rate constants, the acid residue substitution sequence, and reaction mechanism are influenced by the nature of the complex compound and also by the nature of the solvent, which is simultaneously the nucleophile.

## C. KINETICS OF HALOGEN SUBSTITUTION IN Co(III) *trans*-DIOXIMINES BY DIPOLAR APROTIC SOLVENTS

Some authors have isolated in crystalline form, complex compounds of chromium (III) and cobalt (III), containing in their inner coordination sphere, one or two molecules of dipolar aprotic solvents such as dimethylacetamide, dimethylformamide or dimethylsulfoxide [24,25]. Kinetic data for substitution reactions of Co(III) and Cr(III) coordination compounds in dipolar aprotic solvents are also in the literature [26—34].

The important role of the solvents in these substitution processes is recognised. The essential importance of ion association in aprotic solvents and the influence of solvation on the kinetics is also pointed out.

For cobalt(III) dioximines, as we know, there are no systematic investigations of the substitution reaction kinetics in non-aqueous media. The only exception is a Rumanian investigation of chloride and bromide ion substitution in H[Co(DH)$_2$Cl$_2$] and H[Co(DH)$_2$Br$_2$] in aqueous solution with addition of 10—20% dimethylformamide [35,36]. The authors suggested the possibility that dimethylformamide enters the inner sphere on the basis of a comparison of activation parameters, obtained in aqueous and mixed solvents.

Substitution reaction kinetics in Co(III) dioximines in non-aqueous solvents have been studied to elucidate the effect of solvent on the kinetics and mechanism, estimating solvation effects, and comparing kinetic data for protic and dipolar aprotic solvents.

Dimethylformamide (DMF), dimethylsulfoxide (DMSO), and acetonitrile

(ACN), which are simultaneously nucleophiles and solvents were investigated. Non-electrolyte dioximines are taken as the objects of investigation.

First it was shown that 1,6-[Co($C_6H_5NH_2$)$(DH)_2$Cl] in dimethylformamide is converted into [Co($C_6H_5NH_2$)(DMF)$(DH)_2$]$NO_3$ through action of $AgNO_3$ (in molar ratio 1 : 1) with heating. Dimethylformamide readily enters the inner sphere of *trans*-acidoaquodioximines. On adding dimethylformamide at room temperature to 1,6-[Co($H_2O$)$(DH)_2$Br] the latter is transformed into [Co(DMF)$(DH)_2$Br] · $\frac{1}{2}$ DMF.

The kinetics of solvolysis of halogen in 1,6-[CoHlg$(DH)_2$ Amine] (Hlg = Cl, Br, I; Amine = $NH_3$, $C_6H_5NH_2$, Py) in dimethylformamide was studied by measuring the variation of electric conductivity at 50—70°C.

Rate constants and other kinetic characteristics are summarised in Table 9. It is seen in Table 9 that for aniline and amine complexes dimethylformamide substitution is most fast for the iodide ion, followed by bromide, and then chloride ion. For pyridine complexes the sequence of halogen substitution is similar to that observed in protic solvents: Cl > Br > I, and the difference between the rate constants is very small.

The activation energy changes from chloro- to iodocomplex do not correspond to the change in rate constants — the activation energy grows with increasing rate constant and diminishes with decreasing rate constant. On the other hand there is accordance between lg $Z$ and variation in rate constant.

Probably, lg $Z$ influences the halogen substitution rate to a greater degree than does the activation energy.

In Table 10 kinetic parameters for halogen substitution by DMF in halogenoaquodioximines 1,6-[Co($H_2O$)$(DH)_2$Hlg] (Hlg = Cl, Br, I) are presented. It is seen that the rate of halogen substitution by dimethylformamide in these

TABLE 9 [a]

Kinetic characteristics for halogen solvolysis by dimethylformamide in 1,6-[CoHlg-$(DH)_2$Amine]
$C_{complex} = 1 \times 10^{-3}$ mol $l^{-1}$

| Complex | $K \times 10^6$ (sec$^{-1}$) | | | | $E$ (kJ mol$^{-1}$) | lg $Z$ | $\Delta S^{\neq}$ (J mol$^{-1}$ g$^{-1}$) |
|---|---|---|---|---|---|---|---|
| | 50° | 60° | 65° | 70° | | | |
| [Co($NH_3$)$(DH)_2$Cl] | 2.2 | 4.6 | 6.4 | 9.7 | 71 | 6.1 | −137 |
| [Co($NH_3$)$(DH)_2$Br] | 7.5 | 18 | 28 | 45 | 82 | 8.5 | −91 |
| [Co($NH_3$)$(DH)_2$I] | 12 | 37 | 62 | 100 | 99 | 11.5 | −34 |
| [Co($C_6H_5NH_2$)$(DH)_2$Cl] | 5.9 | 12 | 17 | 24 | 64 | 5.1 | −155 |
| [Co($C_6H_5NH_2$)$(DH)_2$Br] | 6.6 | 16 | 26 | 36 | 77 | 7.2 | −117 |
| [Co($C_6H_5NH_2$)$(DH)_2$I] | 7.0 | 19 | 33 | 55 | 93 | 9.8 | −67 |
| [CoPy$(DH)_2$Cl] | 2.3 | 6.6 | 11 | 19 | 102 | 10.7 | −50 |
| [CoPy$(DH)_2$Br] | 2.1 | 5.3 | 7.9 | 12 | 78 | 7.1 | −119 |
| [CoPy$(DH)_2$I] | — | 5.1 | 7.2 | 10 | 70 | 5.7 | −146 |

[a] N.M. Samus, T.S. Lukyanets and A.V. Ablov, Zh. Neorg. Khim., 19 (1974) 2477.

TABLE 10 [a]

Kinetic characteristics for halogen substitution in 1,6-$[Co(H_2O)(DH)_2Hlg]$ by dimethylformamide

$C_{complex} = 1 \times 10^{-3}$ mol $l^{-1}$

| Complex | $K \times 10^6$ ($sec^{-1}$) | | | | $E$ (kJ $mol^{-1}$) | lg $Z$ | $\Delta S^{\neq}$ (J $mol^{-1}$ $g^{-1}$) |
|---|---|---|---|---|---|---|---|
| | 50° | 60° | 65° | 70° | | | |
| $[Co(H_2O)(DH)_2Cl]$ | 6.3 | 14 | 20 | 31 | 75 | 7.3 | −113 |
| $[Co(H_2O)(DH)_2Br]$ | 7.1 | 18 | 28 | 45 | 86 | 9.2 | −78 |
| $[Co(H_2O)(DH)_2I]$ | 8.6 | 25 | 43 | 74 | 99 | 11.4 | −36 |

[a] N.M. Samus and T.S. Lukyanets, unpublished data.

cases also increases from chloro- to iodocomplex, while in protic solvents (water, methanol) the reverse sequence of halogen substitution is observed.

The interaction of dimethylformamide with halogenoaquocomplexes may be presented by the following scheme.

$$[Co(H_2O)(DH)_2Hlg] + DMF \xrightarrow{rapidly} [Co(DMF)(DH)_2Hlg] + H_2O$$

$$[Co(DMF)(DH)_2Hlg] + DMF \xrightarrow{k} [Co(DMF)_2(DH)_2]^+ + Hlg^-$$

The data in Table 11 confirm that the rate constants characterize only halogen substitution

Rate constants of halogen substitution in $[Co(H_2O)(DH)_2Hlg]$ and $[Co(DMF)(DH)_2Hlg]$ are equal within experimental error. This suggests that substitution of the water molecule in the halogenoaquocomplexes by dimethylformamide proceeds very rapidly and halogen substitution is the rate-determining reaction.

To elucidate the influence of a steric factor on the rate of halogen substitution the kinetics of substitution in 1,6-$[Co(Amine)(DfH)^*{}_2Hlg]$ were studied.

Rate constants for halogen substitution by dimethylformamide in $[CoCl(DH)_2Amine]$ and $[CoCl(DfH)_2Amine]$ are summarised in Table 12.

The rate constants (Table 12) for both groups of compounds are similar, while the aquation rate constants for analogous complexes of α-benzyldioxime are larger than for dimethylglyoximine compounds [47]. For example, at 30°C, pH = 3.0; $\mu = 0.1$ for $[Co(C_6H_5NH_2)(DH)_2Cl]$ $K_{aquation} = 8.01 \times 10^{-6}$ $sec^{-1}$, and for $[Co(C_6H_5NH_2)(DfH)_2Cl]$ $K_{aquation} = 127 \times 10^{-6}$ $sec^{-1}$.

Probably, in the case of solvolysis by dimethylformamide the influence of the steric factor on the rate cannot be a criterion for the reaction mechanism.

Table 13 summarizes the kinetic characteristics of the substitution reac-

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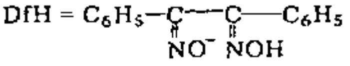
* DfH = 
$C_6H_5-\underset{NO^-}{\overset{\|}{C}}-\underset{NOH}{\overset{\|}{C}}-C_6H_5$

TABLE 11

The comparison of the rate constants of halogen substitution by dimethylformamide in 1,6-[Co($H_2O$)(DH)$_2$Hlg] and 1,6-[Co(DMF)(DH)$_2$Hlg]
50°C, $C_{\text{complex}} = 1 \times 10^{-3}$ mol l$^{-1}$

| Complex | $K \times 10^6$ (sec$^{-1}$) | Complex | $K \times 10^6$ (sec$^{-1}$) |
|---|---|---|---|
| [Co($H_2O$)(DH)$_2$Cl] | 6.3 | [Co(DMF)(DH)$_2$Cl] | 6.0 |
| [Co($H_2O$)(DH)$_2$Br] | 7.1 | [Co(DMF)(DH)$_2$Br] | 6.8 |

tions in dioximines 1,6-[CoL(Dioxim)$_2$Hlg] containing Thio *, Scarb * and Thios * as axial ligands L.

The sequence of halogen substitution by dimethylformamide in these complexes (Table 13) is also the reverse of that observed in water (Cl < Br < I).

Possibly inversion of the sequence of halogen substitution rates observed in a dipolar aprotic solvent — dimethylformamide — is connected with the phenomenon of specific solvation. It is known that in protic solvents anion solvation decreases in the order Cl > Br > I, while in dipolar aprotic solvents the iodide ion is solvated most strongly and bromide and chloride ions more weakly [37]. Table 13 demonstrates how the axial ligand (L) influences the rate constants. The substitution rates increase in the following sequence: Thio < Scarb < Thios. This sequence was also observed for aquation of the dioximines under investigation [38].

Comparison of solvolysis rates for dimethylglyoximine and $\alpha$-benzyldioximine complexes shows that substitution in the latter proceeds faster than in the former. For example, at 30°C, and $C_{\text{complex}} = 1 \times 10^{-3}$ mol l$^{-1}$, the rate constants for 1,6-[CoCl(DH)$_2$Scarb] · 3 $H_2O$ and 1,6-[CoCl(DfH)$_2$Scarb] are, respectively, $7.94 \times 10^{-6}$ and $3168 \times 10^{-6}$ sec$^{-1}$.

Taking into consideration the increase in steric hindrance in benzildioximine complexes the data above may be accounted for by assuming a dissociative mechanism for halogen substitution by the dipolar aprotic solvent, dimethylformamide.

However as we pointed out above for the amine-containing dioximines 1,6-[Co(Amine)(DH)$_2$Hlg] and 1,6-[Co(Amine)(DfH)$_2$Hlg], the change from dimethylglyoxime to $\alpha$-benzildioxime does not always lead to an increase in rate constant.

These facts suggest that even in the same solvent (DMF) the importance of the steric factor also depends on the nature of the complex.

Further it was of interest to determine if, in dimethylformamide solution,

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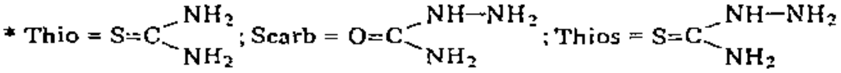

* Thio = $S{=}C\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}$; Scarb = $O{=}C\begin{smallmatrix}NH{-}NH_2\\NH_2\end{smallmatrix}$; Thios = $S{=}C\begin{smallmatrix}NH{-}NH_2\\NH_2\end{smallmatrix}$

TABLE 12

Influence of the dioxime on the rate of halogen substitution by dimethylformamide $50°C$, $C_{complex} = 1 \times 10^{-3}$ mol $l^{-1}$

| Complex | $K \times 10^6$ ($sec^{-1}$) | Complex | $K \times 10^6$ ($sec^{-1}$) |
|---|---|---|---|
| $[CoPy(DH)_2Cl]$ | 2.3 | $[CoPy(DfH)_2Cl]$ | 4.6 |
| $[Co(C_6H_5NH_2)(DH)_2Cl]$ | 5.9 | $[Co(C_6H_5NH_2)(DfH)_2Cl]$ | 6.6 |
| $[Co(NH_3)(DH)_2Cl]$ | 2.2 | $[Co(NH_3)(DfH)_2Cl]$ | 2.5 |

by analogy with methanol, manifestation of the inductive effect of the axial ligand takes place.

With this aim in mind halogen substitution kinetics by dimethylformamide were studied for dioximines containing ammonia and its alkyl derivatives in the inner sphere (Table 14).

As is seen in Table 14 the sequence of halogen substitution by DMF is the same as for the compounds mentioned above: $Cl < Br < I$.

The nature of the axial ligand influences differently the solvolysis rates in methanol and in dimethylformamide (Table 15). Whilst in methanol the rate constants depend upon the inductive effect, in dimethylformamide substitution of the hydrogen atom in ammonia by an alkyl radical ($-CH_3$, $-C_2H_5$) hardly influences the reaction rate.

These data demonstrate that steric and inductive factors do not manifest themselves in the solvolysis of amine-containing dioximines by dipolar aprotic solvents.

It should be pointed out that the rate constants of halogen substitution by dimethylformamide are considerably smaller than those obtained in methanol. This fact cannot be accounted for by media dielectric permeability alone because for methanol and dimethylformamide $\epsilon$ is nearly the same ($\epsilon^{25}_{CH_3OH}$ =

TABLE 13 [a]

Kinetic characteristics of halogen substitution by DMF in 1,6-$[CoL(DH)_2Hlg]$ at $60°C$

| Complex | $K \times 10^6$ ($sec^{-1}$) | $E$ (kJ $mol^{-1}$) |
|---|---|---|
| $[Co(Thio)(DH)_2Cl]$ | 1.99 | 61 |
| $[Co(Thio)(DH)_2Br]$ | 6.21 | 81 |
| $[Co(Thio)(DH)_2I]$ | 35.9 | 88 |
| $[Co(Scarb)(DH)_2Cl] \cdot 3\ H_2O$ | 83.1 | 56 |
| $[Co(Scarb)(DH)_2Br] \cdot 3\ H_2O$ | 776 | 74 |
| $[Co(Scarb)(DH)_2I] \cdot H_2O$ | 1630 | 84 |
| $[Co(Thios)(DH)_2Cl]$ | 259 | 64 |
| $[Co(Thios)(DH)_2Br]$ | 3513 | 86 |

[a] N.M. Samus and Ngyen Than Hong, Zh. Neorg. Khim., 21 (1976) 1802.

TABLE 14 [a]

Kinetic characteristics of halogen solvolysis by dimethylformamide in 1,6-[Co(XNH$_2$)(DH)$_2$Hlg]
$C_{complex} = 1 \times 10^{-3}$ mol l$^{-1}$

| Complex | $K \times 10^6$ (sec$^{-1}$) | | | | | $E$ (kJ mol$^{-1}$) | lg $Z$ | $\Delta S^{\neq}$ (J mol$^{-1}$ g$^{-1}$) | $\Delta H^{\neq}$ (kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| | 50° | 55° | 60° | 65° | 70° | | | | |
| [Co(CH$_3$NH$_2$)(DH)$_2$Cl] | | 1.65 | 3.17 | 5.70 | 10.3 | 108 | 12.0 | −8 | 105 |
| [Co(CH$_3$NH$_2$)(DH)$_2$Br] | | 4.42 | 7.52 | 13.8 | 22.8 | 95 | 9.8 | −56 | 92 |
| [Co(CH$_3$NH$_2$)(DH)$_2$I] | | 9.66 | 15.0 | 24.4 | 42.3 | 86 | 8.7 | −87 | 83 |
| [Co(C$_2$H$_5$NH$_2$)(DH)$_2$Cl] | | 2.47 | 4.78 | 8.65 | 13.3 | 102 | 11.0 | −30 | 99 |
| [Co(C$_2$H$_5$NH$_2$)(DH)$_2$Br] | | 6.90 | 13.5 | 19.3 | 36.1 | 94 | 10.0 | −58 | 91 |
| [Co(C$_2$H$_5$NH$_2$)(DH)$_2$I] | | 18.8 | 30.0 | 44.9 | 69.0 | 77 | 7.6 | −108 | 74 |
| [Co(n-C$_4$H$_9$NH$_2$)(DH)$_2$Cl] | | 5.68 | 10.0 | 18.1 | 29.9 | 91 | 9.3 | −67 | 88 |
| [Co(n-C$_4$H$_9$NH$_2$)(DH$_2$)Br] | 5.18 | 8.51 | 15.0 | 23.0 | | 88 | 9.0 | −75 | 85 |
| [Co(n-C$_4$H$_9$NH$_2$)(DH)$_2$I] | 9.20 | 12.0 | 23.0 | 35.0 | | 79 | 7.8 | −104 | 76 |
| [Co{(CH$_3$)$_2$NH}(DH)$_2$Cl] | 8.28 | 13.8 | 25.1 | 40.9 | | 95 | 10.0 | −60 | 92 |
| [Co{(CH$_3$)$_2$NH}(DH)$_2$Br] | 14.5 | 21.7 | 33.5 | 48.3 | | 72 | 6.8 | −123 | 69 |
| [Co{(CH$_3$)$_2$NH}(DH)$_2$I] | 19.4 | 28.2 | 42.2 | 59.8 | | 67 | 6.1 | −135 | 64 |

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[a] N.M. Samus, Ngyen Than Hong and I.A. Fridman, Zh. Neorg. Khim., 23 (1978) 994.

TABLE 15

Methanol and dimethylformamide solvolysis rate constants of chloride ion in 1,6-[CoCl(DH)$_2$(RNH$_2$)]
60°C, $C_{\text{complex}} = 1 \times 10^{-3}$ mol l$^{-1}$

| Complex | $K \times 10^6$ (sec$^{-1}$) in $CH_3OH$ | Complex | $K \times 10^6$ (sec$^{-1}$) in DMF |
|---|---|---|---|
| [Co(NH$_3$)(DH)$_2$Cl] | 293 | [Co(NH$_3$)(DH)$_2$Cl] | 4.61 |
| [Co(CH$_3$NH$_2$)(DH)$_2$Cl] | 807 | [Co(CH$_3$NH$_2$)(DH)$_2$Cl] | 3.17 |
| [Co(C$_2$H$_5$NH$_2$)(DH)$_2$Cl] | 1732 | [Co(C$_2$H$_5$NH$_2$)(DH)$_2$Cl] | 4.78 |
| [Co(n-C$_4$H$_9$NH$_2$)(DH)$_2$Cl] | 557 | [Co(n-C$_4$H$_9$NH$_2$)(DH)$_2$Cl] | 10.0 |
| [Co{(CH$_3$)$_2$NH}(DH)$_2$Cl] | 1768 | [Co{(CH$_3$)$_2$NH}(DH)$_2$Cl] | 25.1 |

32.6; $\epsilon^{25^\circ}_{\text{DMF}} = 36.7$). Decrease of the halogen substitution rate in DMF in comparison with halogen substitution in methanolic media cannot be caused by the nucleophilic properties of the reagents because DMF is a better nucleophile than methanol.

The rate decrease in dimethylformamide is probably connected with solvation properties of the solvent.

Kinetic investigation of halogen solvolysis by dimethylsulfoxide (DMSO) in the Co(III) dioximines, 1,6-[CoL(Dioxim)$_2$Hlg], has shown a sequence of halogen substitution rates analogous to dimethylformamide solvolysis (Table 16).

The axial ligand influences the halogen solvolysis rates both in dimethylsulfoxide as well as in dimethylformamide. For example, at 60°C rate constants for [Co(Thio)(DH)$_2$Cl], [Co(Scarb)(DH)$_2$Cl] · 3 H$_2$O and [Co(Thios)(DH)$_2$Cl] in DMSO are, respectively, $17.4 \times 10^{-6}$ sec$^{-1}$, $238 \times 10^{-6}$ sec$^{-1}$ and $458 \times 10^{-6}$ sec$^{-1}$. Hence the sequence of labilizing ability of axial ligands is the same as in dimethylformamide: Thios > Scarb > Thio.

Chloride-ion solvolysis by dimethylsulfoxide in these dioximines proceeds faster than Cl$^-$ substitution by dimethylformamide (Table 17). The rate sequ-

TABLE 16 [a]

Kinetic characteristics of halogen substitution by dimethylsulfoxide in 1,6-[Co(Thio)(DH)$_2$Hlg]
60°C, $C_{\text{complex}} = 1 \times 10^{-3}$ mol l$^{-1}$

| Complex | $K \times 10^6$ (sec$^{-1}$) | $E$ (kJ mol$^{-1}$) | lg $Z$ |
|---|---|---|---|
| [Co(Thio)(DH)$_2$Cl] | 17.4 | 63 | 5.1 |
| [Co(Thio)(DH)$_2$Br] | 78.2 | 68 | 6.6 |
| [Co(Thio)(DH)$_2$I] | 159 | 71 | 7.3 |

[a] N.M. Samus and Ngyen Than Hong, Zh. Neorg. Khim., 22 (1977) 1847.

TABLE 17

Rate constants for chloride-ion substitution by DMSO and DMF in 1,6-[$CoCl(DH)_2L$] at 60°C

| Complex | $K \times 10^6$ (sec$^{-1}$) | |
|---|---|---|
| | DMSO | DMF |
| [$CoCl(DH)_2$(Thios)] | 458 | 259 |
| [$CoCl(DH)_2$(Scarb)] · 3 $H_2O$ | 238 | 83.1 |
| [$CoCl(DH)_2$(Thio)] | 17.4 | 1.99 |

ence is the same as the order of increasing nucleophilic ability and dielectric permeability of these solvents. From comparison of the activation parameters (Table 18) it may be seen that entropies of activation for DMF and DMSO solutions are negative and large by absolute value. Taking into consideration the strong solvation of cations in dipolar aprotic solvents we propose that solvolysis proceeds via a dissociative mechanism both in DMF and DMSO.

The increase of the solvolysis rate constants of sterically hindered α-benzildioxime complexes in comparison with those of dimethylglyoxime also testifies in favour of dissociative activation. For example, rate constants for [$CoCl(DH)_2$(Thio)] and [$CoCl(DfH)_2$(Tbio)] at 60°C, ($C_{complex} = 1 \times 10^{-3}$ mol l$^{-1}$) are respectively $17.4 \times 10^{-6}$ sec$^{-1}$ and $41.1 \times 10^{-6}$ sec$^{-1}$.

Study of halogen solvolysis in 1,6-[$CoCl(DH)_2$Amine] (Amine = $NH_3$, $C_5H_5N$, $C_6H_5NH_2$) by dimethylsulfoxide has shown that rate constants are similar to one another (Table 19). Hence, the amine does not significantly influence the substitution rate.

Investigation of halogen substitution by dimethylsulfoxide in 1,6-[$CoHlg(DH)_2(XNH_2)$] has revealed that also in this case the nature of the axial ligand (aliphatic amine) does not influence the rate constants (Table 20).

It is seen from Table 20 that the rate of substitution increases from the

TABLE 18

Activation parameters for chloride-ion substitution by DMSO and DMF in 1,6-[$CoCl(DH)_2L$] at 60°C

| Complex | DMSO | | DMF | |
|---|---|---|---|---|
| | $\Delta H^{\neq}$ (kJ mol$^{-1}$) | $\Delta S^{\neq}$ (J mol$^{-1}$ g$^{-1}$) | $\Delta H^{\neq}$ (kJ mol$^{-1}$) | $\Delta S^{\neq}$ (J mol$^{-1}$ g$^{-1}$) |
| [$CoCl(DH)_2$(Thio)] | 60 | −156 | 58 | −179 |
| [$CoCl(DH)_2$(Scarb)] · 3 $H_2O$ | 63 | −130 | 53 | −167 |
| [$CoCl(DH)_2$(Thios)] | 71 | −106 | 61 | −130 |

TABLE 19 [a]

Kinetics of the $Cl^-$ solvolysis in 1,6-[$CoCl(DH)_2$Amine] by dimethylsulfoxide

| Complex | $K \times 10^6$ ($sec^{-1}$) | | | | $E$ (kJ $mol^{-1}$) | lg $Z$ |
|---|---|---|---|---|---|---|
| | 60°C | 65°C | 70°C | 75°C | | |
| $[CoCl(DH)_2NH_3]$ | 5.75 | 7.94 | 13.8 | 20.0 | 68 | 5.5 |
| $[CoCl(DH)_2(C_5H_5N)]$ | 5.43 | 9.35 | 16.6 | 27.3 | 95 | 9.7 |
| $[CoCl(DH)_2(C_6H_5NH_2)]$ | 6.45 | 10.9 | 19.1 | 30.4 | 95 | 9.8 |

[a] N.M. Samus and Ngyen Than Hong, unpublished data.

chloro- to iodocomplex, i.e. the sequence is the same as in dimethylformamide solution: Cl < Br < I.

Study of the chloride substitution kinetics of 1,6-$[CoCl(DH)_2(RNH_2)]$ in acetonitrile solution (Table 21) has shown that the rate constants are close one to another in value, independent of the axial ligand. We observe only a slight increase in the rate constants with the growth of the Taft $\sigma^*$ constants for the substituents X in the ammonia molecule. It can therefore be concluded that in dipolar aprotic solvents in contrast to protic solvents the inductive effect of the non-substituting axial ligand does not become apparent.

The kinetic characteristics of the first halogen-ion substitution in 1,6-$[CoHlg_2(DMe)(DHMe)]$ by dimethylformamide are presented in Table 22.

It is seen (Table 22) that the rate of bromide solvolysis is somewhat larger than that of chloride and in the case of the iodide-complex the substitution proceeds very fast. Comparing the rate constants of halogen substitution in these complexes in protic solvents (water, methanol) with those dipolar aprotic solvents (DMF) it may be seen that the solvolysis rates increase in the following sequence: $H_2O < CH_3OH <$ DMF (Table 23). The increase in rate constant from water to methanol and further to dimethylformamide shows

TABLE 20 [a]

Kinetic characteristics for halogen solvolysis in 1,6-$[CoHlg(DH)_2(X\text{-}NH_2)]$ by dimethylsulfoxide at 60°C

| Complex | $K \times 10^6$ ($sec^{-1}$) | $E$ (kJ $mol^{-1}$) | lg $Z$ |
|---|---|---|---|
| $[CoCl(DH)_2(CH_3NH_2)]$ | 7.35 | 61 | 4.5 |
| $[CoBr(DH)_2(CH_3NH_2)]$ | 12.1 | 76 | 7.0 |
| $[CoI(DH)_2(CH_3NH_2)]$ | 28.5 | 90 | 9.6 |
| $[CoCl(DH)(C_2H_5NH_2)]$ | 8.68 | 77 | 6.8 |
| $[CoBr(DH)_2(C_2H_5NH_2)]$ | 13.8 | 85 | 8.8 |
| $[CoI(DH)_2(C_2H_5NH_2)]$ | 35.1 | 95 | 10 |
| $[CoCl(DH)_2(n\text{-}C_4H_9NH_2)]$ | 10.9 | 77 | 6.9 |
| $[CoBr(DH)_2(n\text{-}C_4H_9NH_2)]$ | 15.0 | 95 | 10 |
| $[CoI(DH)_2(n\text{-}C_4H_9NH_2)]$ | 44.1 | 105 | 12 |

[a] N.M. Samus, Ngyen Than Hong and I.A. Fridman, Zh. Neorg. Khim., 23 (1978) 994.

TABLE 21

Rate constants for chloride-ion substitution in 1,6-$[CoCl(DH)_2(XNH_2)]$ by acetonitrile at 60°C

| Complex | $K \times 10^6$ ($sec^{-1}$) | Taft $\sigma^*$ |
|---|---|---|
| $[CoCl(DH)_2(NH_3)]$ | 5.50 | +0.49 |
| $[CoCl(DH)_2(CH_3NH_2)]$ | 8.20 | 0.00 |
| $[CoCl(DH)_2(C_2H_5NH_2)]$ | 10.1 | −0.10 |
| $[CoCl(DH)_2(n\text{-}C_4H_9NH_2)]$ | 13.0 | −0.13 |

TABLE 22 [a]

Kinetic characteristics for the first halogen substitution by DMF in 1,6-$[CoHlg_2(DMe)(DMeH)]$

$C_{complex} = 1 \times 10^{-3}$ mol $l^{-1}$

| Complex | $K \times 10^6$ ($sec^{-1}$) | | | | $E$ (kJ $mol^{-1}$) | lg $Z$ |
|---|---|---|---|---|---|---|
| | 25°C | 30°C | 35°C | 40°C | | |
| $[CoCl_2(DMe)(DMeH)]$ | 36.0 | 45.0 | 65.4 | 88.3 | 48 | 4.1 |
| $[CoBr_2(DMe)(DMeH)]$ | 46.0 | 58.4 | 78.2 | 123 | 60 | 6.1 |
| $[CoI_2(DMe)(DMeH)]$ | fast | | | | | |

[a] N.M. Samus, Ngyen Than Hong and O.A. Bologa, Zh. Neorg. Khim., 24 (1979) 98.

that the entering group plays an important role in substitution. This observation infers the elements of association in the mechanism of the reactions under investigation.

Investigation of the kinetics of halogen substitution in Co(III) dioximines by dipolar aprotic solvents has shown that the rate, substitution sequence and reaction mechanism depend upon the nature of dioximine and solvent, as is the case with protic solvents.

## D. COMPARISON OF THE KINETIC DATA OBTAINED IN PROTIC AND DIPOLAR APROTIC SOLVENTS

The experimental data on Co(III) dioximine substitution reactions in non-aqueous solvents have revealed that the solvent influences the substitution sequence of the coordinated anion by solvent. In the protic solvents the substitution rate of halogen by solvent in 1,6-$[CoHlg(DH)_2L]$ decreases from chloro- to bromo- and further to the iodo-complex. For the same complexes in dipolar aprotic solvents the halogen substitution sequence is reversed. The different sequence of halogen substitution by protic and dipolar aprotic solvents is probably connected with the specific solvation of the solvents.

The quantitative investigation of methanolysis of Co(III) coordination com-

TABLE 23

Activation parameters for halogen substitution in 1,6-$[\text{CoHlg}_2(\text{DMe})(\text{DMeH})]$ by $H_2O$, $CH_3OH$ and DMF

| Complex | $H_2O$ | | | $CH_3OH$ | | | DMF | | |
|---|---|---|---|---|---|---|---|---|---|
| | $K^{40^\circ} \times 10^6$ (sec$^{-1}$) | $\Delta H^{\neq}$ (kJ mol$^{-1}$) | $\Delta S^{\neq}$ (J mol$^{-1}$ g$^{-1}$) | $K^{40^\circ} \times 10^6$ (sec$^{-1}$) | $\Delta H^{\neq}$ (kJ mol$^{-1}$) | $\Delta S^{\neq}$ (J mol$^{-1}$ g$^{-1}$) | $K^{40^\circ} \times 10^6$ (sec$^{-1}$) | $\Delta H^{\neq}$ (kJ mol$^{-1}$) | $\Delta S^{\neq}$ (J mol$^{-1}$ g$^{-1}$) |
| $[\text{CoCl}_2(\text{DMe})(\text{DMeH})]$ | 3.54 | 106 | −7.9 | 18.5 | 89 | −51 | 88.3 | 45 | −175 |
| $[\text{CoBr}_2(\text{DMe})(\text{DMeH})]$ | 1.27 | 120 | −28 | 19.1 | 87 | −62 | 123 | 57 | −136 |

pounds, containing mono-*O*-methyl ether of the diacetyldioxime, 1,6-$[CoHlg_2(DMe)(DMeH)]$ (Hlg = Cl, Br, I) has shown that the sequence of halogen substitution by methanol (I > Br > Cl) is inverse to that observed for aquation and methanolysis of the amine-containing Co(III) dioximines (Cl > Br > I). This fact may be accounted for in terms of Pearson's theory of hard and soft acids and bases [39,40]. The metal atom in $[CoHlg(DH)_2L]$ has the character of the soft acid (class b), therefore according to [41] the bond strength Co—halogen increases with the growth of the softness of the base (halogen), i.e. it grows from the chloro- to iodocomplex, by analogy with $[Co(CN)_5X]^{3-}$ [42] and in contrast to $[Co(NH_3)_5X]^{2+}$ and $[Coen_2X_2]^+$ [43,44]. The Co(III) complexes with the ligand — mono-*O*-methyl ether of diacetyldioxime — in contrast to Co(III) dimethylglyoximines contain a single intramolecular hydrogen bond, as shown by X-ray investigation [45]. As a result the Co(III) atom in the former complexes is a harder acid than in the latter. Therefore the strength of the Co—Hlg bond decreases in the following sequence: Co—Cl > Co—Br > Co—I. Hence, the nature of the complex can also affect the sequence of halogen substitution.

Study of the halogen substitution in 1,6-$[CoHlg(DH)_2(RNH_2)]$ by different solvents has demonstrated that in methanol the rate constants depend both on the inductive effect and Nathan—Baker's effect of the non-substituted axial ligand. It is found that the manifestation of these effects diminishes from methanol to ethanol and further to n-propanol. In dipolar aprotic solvents the inductive effect of the substituent (R) in the aliphatic amine does not significantly influence the value of the rate constant.

The rate constants of halogen substitution by dipolar aprotic solvents (DMF, DMSO, acetonitrile) are two orders of magnitude smaller than those obtained in methanol (Table 24) although the dielectric permeability of DMF, DMSO and acetonitrile is larger than that of methanol [20]. Consequently, the dielectric constant of the medium cannot reflect all the changes the complex undergoes in the course of substitution.

The donor ability of the solvents probably does not play a paramount role in determining the substitution rate, because it is larger for DMF and DMSO

TABLE 24

Rate constants of halogen substitution in 1,6-$[CoHlg(DH)_2Amine]$ by different solvents

| Complex | $K \times 10^6$ (sec$^{-1}$) | | | |
|---|---|---|---|---|
| | $CH_3OH$ $\epsilon = 32.6$ | DMF $\epsilon = 36.7$ | Acetonitrile $\epsilon = 37.6$ | DMSO $\epsilon = 48.5$ |
| $[CoCl(DH)_2(NH_3)]$ | 290 | 4.60 | 5.50 | 5.75 |
| $[CoCl(DH)_2(CH_3NH_2)]$ | 807 | 3.17 | 8.20 | 7.35 |
| $[CoCl(DH)_2(C_2H_5NH_2)]$ | 1732 | 4.78 | 10.1 | 8.68 |
| $[CoCl(DH)_2(n\text{-}C_4H_9NH_2)]$ | 557 | 10.0 | 13.0 | 10.9 |
| $[CoCl(DH)_2\{(CH_3)_2NH\}]$ | 1768 | 25.1 | — | — |

than for methanol [46]. Decrease of the substitution rate of halogen by dipolar aprotic solvents is due to the effect of solvation.

Axial ligands such as Thios and Scarb are characterized by the most pronounced labilizing power independently of the nature of the solvents (protic or dipolar aprotic) in which the substitution processes were studied (Table 25). With respect to the other axial ligands their labilizing ability depends strongly upon the solvent. In protic solvents one sequence of rate constant variation is observed and in dipolar aprotic quite another.

This allows us to suggest that the values of the rate constants depend not only on the labilizing power of the axial ligands but also on some other factors, among which the effect of solvation plays the important role.

In Table 25, we see that rates of halogen substitution by DMSO in dioximines with Thio, Scarb, Thios as axial ligands are larger than in DMF, while for dioximines with $C_5H_5N$, $C_6H_5NH_2$, $NH_3$ as axial ligands the appropriate rate constants are similar in value. This is probably connected with interionic association, which retards the reaction, and is larger in DMF, than in DMSO. The interionic association influences the rate more strongly in dissociative reactions. On this assumption, we suggest that substitution reactions in dioximines, containing strong *trans*-influencing ligands such as Thio, Scarb, Thios, proceed in dipolar aprotic solvents as well as in water via a dissociative mechanism. The substitution reactions of the complexes with $C_5H_5N$, $NH_3$ and its alkyl derivatives, $C_6H_5NH_2$ and substituted benzene ring derivatives, as axial ligands, probably, proceed via a mechanism with associative elements. Analysis of the activation parameters of halogen substitution in 1,6-[$CoHlg(DH)_2L$] both in protic and dipolar aprotic solvents has shown that the activation entropy for the majority of the complexes under investigation are negative and in dipolar aprotic solvents large in value (Table 26).

In the case of a dissociative mechanism for cobalt(III) dioximines the tetragonal pyramid is the most probable geometry of the activated complex. During the transition from the original to the activated complex, the only changes are in the solvation of the complex and the leaving group.

Since bulky cations with small charge are strongly solvated by dipolar aprotic solvents the negative entropy values suggest a dissociative mechanism for the reactions under investigation.

The isokinetic relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is observed for these solvolysis reactions. This relationship, presented in Fig. 2, probably indicates a similar transition state in different solvents. The lack of dependence of the structure of the transition complex on the solvent also suggests that the solvolysis of halogen ions in Co(III) dioximines proceeds via a dissociative mechanism.

It is of interest to study the dependence of the solvolysis rate on dielectric permeability (Fig. 3). It is seen from Fig. 3 that two different straight line dependencies of lg $K$ on $(\epsilon - 1)(2\epsilon + 1)$ are observed, one for protic, and another for dipolar aprotic solvents. Suppose we take as a characteristic of a solvent its solvating ability. This can be described by an energy parameter

TABLE 25

The influence of axial ligand labilizing power on the halogen substitution rates in different solvents

| Complex | $H_2O$[a] |  | $CH_3OH$ | DMF | DMSO |
|---|---|---|---|---|---|
|  | $K^{25°} \times 10^6$ ($sec^{-1}$) | $K^{50°} \times 10^6$ ($sec^{-1}$) | $K^{50°} \times 10^6$ ($sec^{-1}$) | $K^{60°} \times 10^6$ ($sec^{-1}$) | $10^{60°} \times 10^6$ ($sec^{-1}$) |
| $[CoCl(DH)_2NH_3]$ |  | 550 | 80.0 | 4.60 | 5.76 |
| $[CoCl(DH)_2C_6H_5NH_2]$ |  | 250 | 49.0 | 12.0 | 5.43 |
| $[CoCl(DH)_2C_5H_5N]$ |  | 310 | 12.0 | 6.60 | 6.45 |
| $[CoCl(DH)_2Thio]$ | 86.1 |  |  | 1.99 | 17.4 |
| $[CoCl(DH)_2Scarb] \cdot 3H_2O$ | 3490 |  |  | 83.1 | 238 |
| $[CoCl(DH)_2(Thios)]$ | 4380 |  |  | 250 | 458 |

[a] Data of refs. 16, 38, 47.

TABLE 26

Activation parameters of halogen solvolysis by protic and dipolar aprotic solvents in 1,6-[CoHlg(DH)$_2$L]

| Coordinate | CH$_3$OH | | DMSO | | DMF | |
|---|---|---|---|---|---|---|
| | $\Delta H^{\neq}$ (kJ mol$^{-1}$) | $\Delta S^{\neq}$ (J mol$^{-1}$ g$^{-1}$) | $\Delta H^{\neq}$ (kJ mol$^{-1}$) | $\Delta S^{\neq}$ (J mol$^{-1}$ g$^{-1}$) | $\Delta H^{\neq}$ (kJ mol$^{-1}$) | $\Delta S^{\neq}$ (J mol$^{-1}$ g$^{-1}$) |
| Cl—Co—NH$_3$ | 105 | +2.0 | 65 | −136 | 68 | −137 |
| Cl—Co—CH$_3$NH$_2$ | 102 | −8.0 | 58 | −167 | 105 | −8 |
| Br—Co—CH$_3$NH$_2$ | 99 | −24 | 73 | −119 | 92 | −56 |
| I—Co—CH$_3$NH$_2$ | 92 | −47 | 87 | −67 | 83 | −87 |
| Cl—Co—C$_2$H$_5$NH$_2$ | 92 | −40 | 74 | −123 | 99 | −30 |
| Br—Co—C$_2$H$_5$NH$_2$ | 82 | −70 | 82 | −85 | 91 | −58 |
| I—Co—C$_2$H$_5$NH$_2$ | 80 | −77 | 92 | −62 | 74 | −108 |
| Cl—Co—n-C$_4$H$_9$NH$_2$ | 97 | −24 | 74 | −112 | 88 | −67 |
| Br—Co—n-C$_4$H$_9$NH$_2$ | 92 | −43 | 92 | −62 | 85 | −75 |
| I—Co—n-C$_4$H$_9$NH$_2$ | 89 | −62 | 102 | −24 | 76 | −104 |
| Cl—Co—(CH$_3$)$_2$NH | 117 | +41 | | | 92 | −60 |
| Br—Co—(CH$_3$)$_2$NH | 112 | +20 | | | 69 | −123 |
| I—Co—(CH$_3$)$_2$NH | 100 | −5 | | | 64 | −135 |
| Cl—Co—Thio | | | 60 | −156 | 58 | −179 |
| Br—Co—Thio | | | 65 | −127 | 78 | −110 |
| I—Co—Thio | | | 68 | −113 | 85 | −74 |
| Cl—Co—Scarb | | | 63 | −130 | 53 | −167 |
| Br—Co—Scarb | | | | | 71 | −91 |
| I—Co—Scarb | | | | | 81 | −61 |
| Cl—Co—Thios | | | 71 | −106 | 61 | −130 |
| Br—Co—Thios | | | | | 80 | |
| I—Co—Thios | | | | | 87 | −78 |
| Cl—Co—C$_6$H$_5$NH$_2$ | 108 | −5 | 92 | −67 | 61 | |
| Cl—Co—C$_5$H$_5$N | 97 | −31 | 92 | −68 | 99 | −50 |

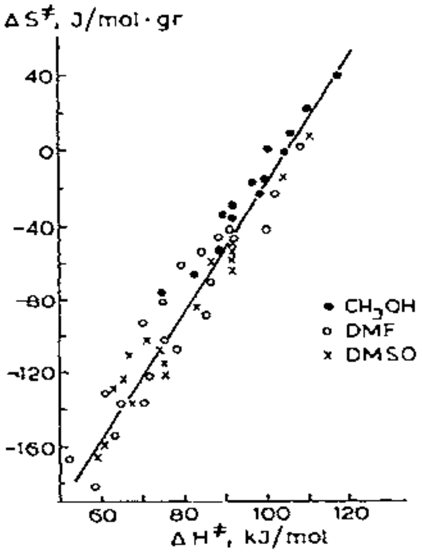
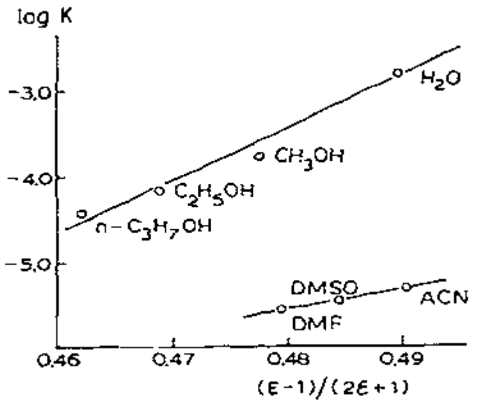


Fig. 2. Isokinetic relationship between $\Delta S^{\neq}$ and $\Delta H^{\neq}$ for solvolysis reactions of dioximes.



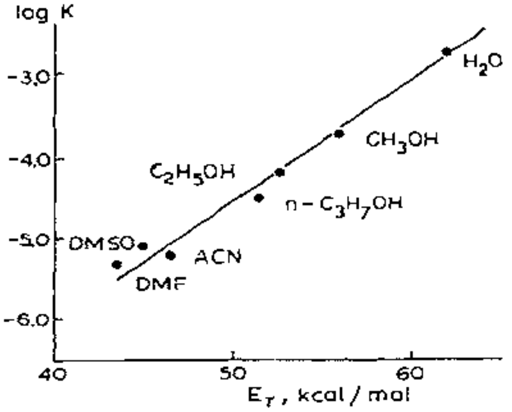


Fig. 3. Dependence of lg $K$ on $(\epsilon - 1)/(2\epsilon + 1)$ for solvolysis of $[CoCl(DH)_2(NH_3)]$ in protic and dipolar aprotic solvents.

Fig. 4. Correlation between lg $K$ and transition energy of the charge transfer band ($E_T$) for solvolysis of $[CoCl(DH)_2(NH_3)]$.

such as the energy $E_T$ of the charge transfer band associated with the $I^- \rightarrow \pi$-(N-heterocycle) internal charge transfer of 1-ethyl-4-methoxycarbonylpyridine iodide in various solvents [20]. We obtain then the single straight line dependence of lg $K$ against $E_T$ both for protic and dipolar aprotic solvents. In Fig. 4 this is presented for $[CoCl(DH)_2(NH_3)]$.

The experimental data show that the dielectric permeability of the solvent cannot characterize the specific intermolecular interactions between particles present in the solution. A better characteristic of such interactions is the energy of the charge transfer band $E_T$.

## E. CONCLUSION

The following principal conclusions can be drawn from the above experimental material.

(1) The rates of cobalt(III) dioximine substitution reactions depend upon the nature of the solvent as well as on the nature of the dioximines.

(2) The important factor, which influences both the kinetics and mechanism of the substitution reactions is the phenomenon of specific solvation.

(3) The medium dielectric permeability incompletely characterizes the interactions between different particles in the solution microvolume. The interactions discussed above are better described in terms of the energy of the charge transfer band.

(4) Substitution reactions in non-aqueous media involving Co(III) dioximines proceed via interchange mechanism. In some cases dissociative elements prevail in the mechanism, in others, associative.

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