MECHANISM OF COMPLEX FORMATION IN NON-AQUEOUS SOLVENTS

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ABSTRACT

The rate constants for the complex formation and dissociation of bivalent metal ions with unidentate ligands in different solvents ($CH_3 \cdot OH$, $CH_3 \cdot CN$, DMSO, DMF) have been summarized. The data are analysed in terms of the donor properties of the solvent. It is found that the rate constants for the rate-determining step for complex formation and the solvent exchange process are the same and that their activation parameters are in agreement. It is concluded therefore that the rate-determining step for complex formation is the release of a coordinated solvent molecule from the inner coordination sphere of the metal ion. The dissociation rate constants for a given complex in different solvents are found to correlate with the solvent donicity by Gutmann. The change in the activation enthalpy for the rate-determining step in different solvents is also discussed in terms of the donicity of the solvent. The exchange rate in methanol for different metal ions is found to show the same characteristic dependence on the metal ion as in water. The rate constants for the bis complexes are always observed to be faster than for the mono complexes.

INTRODUCTION

Most of the kinetic measurements that have been carried out over the years to elucidate the mechanism of complex formation between metal ions and ligands were done in aqueous solutions[1]. These investigations have led to a reasonably good understanding of the factors controlling the rate constants of the reactions. It was shown in many cases that the rate-determining step for complex formation between an octahedrally coordinated metal ion and a ligand was release of a water molecule from the inner coordination sphere of the metal ion. The reaction mechanism therefore can be formulated as a two-step process

$$M + L \underset{}{\overset{K_0}{\rightleftharpoons}} M(H_2O) L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M\text{---}L \tag{1}$$
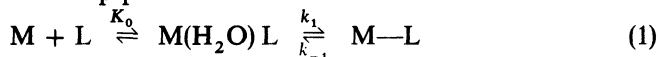
where K_0 is the outer sphere equilibrium constant and k_1 the rate constant for the controlling step. For many systems this rate constant k_1 was shown to be independent of the entering ligand and was usually close to the rate constant for the solvent exchange process

$$MS_5S^* + S \overset{k_S}{\rightarrow} MS_6 + S^* \tag{2}$$
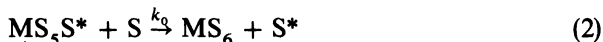
Even for many reactions with multidentate ligands the same rate-determining

step was found to control the over-all rate of the multistep process[2]. For a number of such complicated reactions it was possible to gain a detailed understanding of the individual processes taking place[3].

With a few multidentate ligands the sequence of the steps could be evaluated and in some cases even the rate constants for the specific steps have been determined[4]. Lately the research on the kinetics of complex formation in aqueous solutions has shifted to more and more complicated systems in which steric effects and the influence of coordinated groups on the over-all reactions are studied[5]. Other research groups became interested in reactions in non-aqueous solvents. Here the emphasis at the moment is still on simple systems that lend themselves to conclusions that are relevant for a general understanding of the role the solvent plays in kinetics.

GENERAL CONSIDERATIONS

While most of the kinetic studies in aqueous media could rely on available equilibrium constants[6] for the most favourable concentration range and on pH and redox indicators[7] to follow reactions, such information is mostly lacking in non-aqueous systems. Another complicating factor for the measurements is the water content of the solvents. Water, being a better donor than most of the solvent molecules, is in many systems preferentially coordinated and interferes with measurements even at very low concentrations. Extreme care must always be taken to dry the solvents, or at least it should be assured that the water content present in the solvent does not affect the measurements. This can be done by adding small amounts of water. On the other hand, there also are conditions that are most favourable for kintetic studies in non-aqueous systems. In aprotic solvents no hydrolysis and solvolysis reactions need to be considered. Another big advantage of many organic solvents by comparison with water for kinetic studies is their low melting point, which makes it possible to study reactions over a large temperature range. In a few systems the temperature varied by more than 100°C and rate constants could be shifted over eight orders of magnitude[8]. Reactions with some metal ions that are quite fast at room temperature can be made so slow that ordinary mixing techniques can be used to follow the rate. An example is given in *Figure 1*, which shows the relaxation times for Ni- and Co-trifluoracetate change from 10 µs to thousands of seconds, depending on the temperature.

At present the investigations in non-aqueous solvents usually have the following objectives:

1. Is mechanism 1 valid for all solvents or only for water?

2. Do the specific rate constants for different metal ions show the same graduation as in water?

3. Can exchange and dissociation rate constants be correlated and understood on the basis of the donor properties of the solvents?

The validity of mechanism 1 is usually checked by evaluating the rate constant k_1 for the reactions of several ligands with the same metal ion and by comparing k_1 whenever possible with the solvent exchange rate. Fortunately, this rate constant for the solvent exchange process 2 is known from n.m.r.
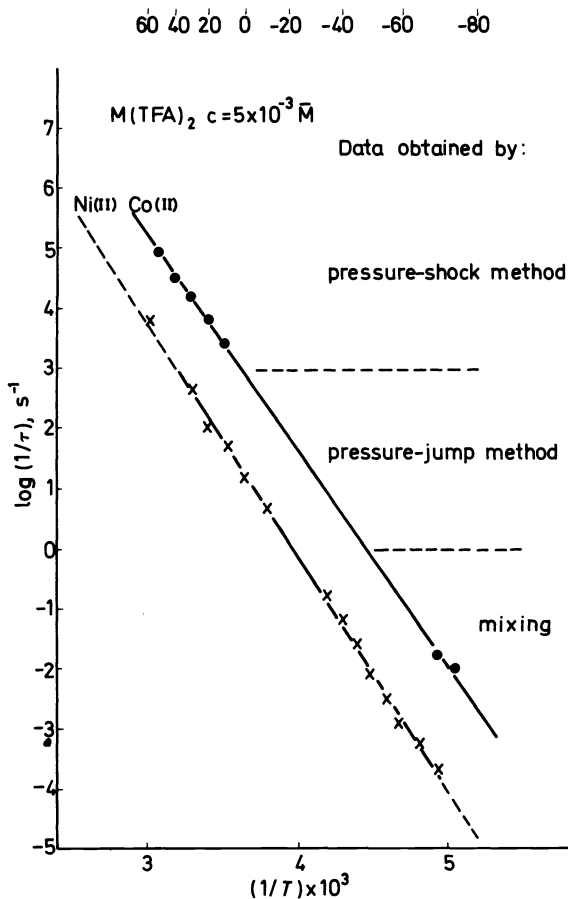
Figure 1. Temperature dependence of relaxation times in methanol for $Ni(CF_3COO)_2$ and $Co(CF_3COO)_2$.

measurements for many metal ions and solvents. A recent summary of the available data has been given by Langford and Stengle[9].

A selection of the literature values is given in *Table 1*. It is noteworthy that the values from different sources that are quoted for the same process vary somewhat, especially so in their activation parameters. The discrepancy in the k_0 values for 25°C is usually small enough (maybe a factor of 2) to make the comparison with the k_1 values relevant. Whenever k_0 values are not available, the validity of process 1 can be tested by comparing the rate constants k_1 for ligands with varying nucleophilicities. In order to avoid any complications that are due to steric or other effects, only rate constants for reactions with simple unidentate ligands should be used for this purpose.

The rate constants will generally be evaluated from relaxation or from stopped flow measurements. In relaxation experiments the reciprocal relaxation time τ is given by the equation (3)[10].

Table 1. Solvent exchange rates at 25°C and their activation parameters.

Solvent	Metal ion	k_0 (s^{-1})	ΔH^*(kcal/mol)	ΔS^*(e.u.)	Ref.
Methanol	Ni^{II}	1.0×10^3	15.8	8	13
	Co^{II}	1.8×10^4	13.8	7.2	13
	Fe^{II}	5×10^4	12	3	14
	Mn^{II}	9.5×10^5	7.4	-5.7	15
		3.7×10^5	6.2	-12	14
	Mg^{II}	4.7×10^3	16.7	14	16
DMSO	Ni^{II}	5.2×10^3	12.1	-1.3	17
		3.2×10^3	13.0	1.4	18
		1.1×10^4	12.3	1.2	19
DMF	Ni^{II}	3.8×10^3	15.0	8.0	20
		6.9×10^3	14.0	6.0	21
	Co^{II}	4×10^5	13.6	12.6	20
CH$_3 \cdot$CN	Ni^{II}	3.9×10^3	10.9	-8.8	22
		2.8×10^3	11.7	-3.6	23
		1.2×10^4	11.8	-0.2	24
		3×10^3	15.0	8.5	25
		2.1×10^3	16.4	12.0	26
NH$_3$	Ni^{II}	1.95×10^5	10.1	-0.5	27

$$1/\tau = k_{-1} + \frac{K_0 \times k_1(C_M + C_L)}{1 + K_0(C_M + C_L)} \tag{3}$$

In many cases it is possible to obtain the rate constant k_1 directly from the kinetic measurements without taking calculations or estimations of the size of the outer-sphere complex. At high concentrations a levelling off of $1/\tau$ is very often observed which directly indicates a two-step mechanism and facilitates the evaluation of k_1[11]. A typical plot for the levelling off of $1/\tau$ with increasing concentrations is shown in *Figure 2*. In many other systems the rate constant k_1 cannot be obtained directly for lack of solubility of the compound under investigation or for the reason that the K_0 values are not large enough for $K_0(C_M + C_{Cl})$ in the relaxation expression to become comparable with unity. In those circumstances only the product of K_0 and k_1 can be obtained from the data, and K_0 is usually calculated from the Fuoss expression[12]

$$K_0 = \frac{4\pi}{3} a^3 \times \exp\frac{z_1 z_2 e^2}{\varepsilon k T \alpha} \tag{4}$$

in order to obtain k_1.

RESULTS IN METHANOL

Most studies carried out so far to elucidate the mechanism of complex formation in non-aqueous solvents were carried out in the solvent methanol. Nickel ions have once again, as in water, proved the most popular of the labile ions for studies.

Table 2 contains a summary of the results that have been obtained recently by various authors using different techniques.

As indicated by the similarity of the k_1 values, all reactions proceed by the same rate-determining step. Furthermore, the value for k_1 is in good agreement with the rate constant k_0 for the solvent exchange reaction, which has been determined to be $1 \times 10^3 \, s^{-1}$ at 25°C. The activation enthalpy for this
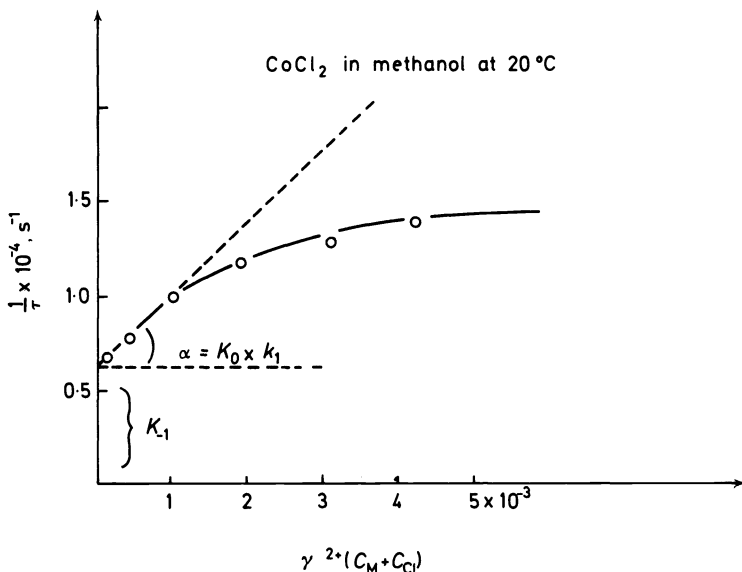

Figure 2. Evaluation of the rate constant k_1.

step is practically the same as the activation enthalpy for k_1. From all this evidence it can be concluded that the complex formation proceeds by an SN_1 mechanism, with the loss of a solvent molecule from the inner coordination sphere being the rate-determining step. It is noteworthy, however, that the $K_0 \times k_1$ values for substituted acetates differ somewhat, which seems to indicate that the basicity of the entering ligand has some influence on the rate-determining step[33]. These differences, according to the interpretation of the investigators, were due to a change in the K_0 value that was assumed to be due to a change in the negative charge density on the carboxylate group. However, it could also be possible that the effect is due to base catalysis. The equilibrium

$$Ni(CH_3OH)_6^{2+} + Ac^- \rightleftharpoons [Ni(CH_3OH)_5CH_3O]^+ + HAc \qquad (5)$$
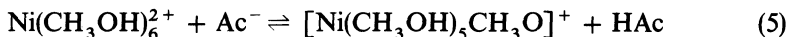
can be far enough on the right side for there to be a sufficiently high concentration of $[Ni(CH_3OH)_5CH_3O]^+$ present in solution for some of the over-all reactions to take place via the solvolysed species. Reaction scheme (6)

Table 2. Rate constants and activation parameters for the reactions between Ni^{II} and different ligands X in methanol at 20°C.
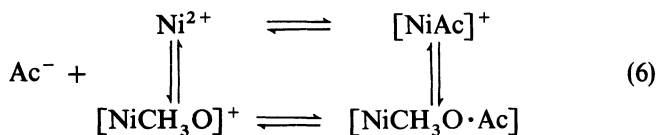
X	$K_0 \times k_1$ $(M^{-1} s^{-1})$	k_{-1} (s^{-1})	k_1 (s^{-1})	$\Delta H^{\ddagger}_{K_0 \times k_1}$ (kcal)	$\Delta S^{\ddagger}_{K_0 \times k_1}$ (e.u.)	$\Delta H^{\ddagger}_{k_{-1}}$ (kcal)	$\Delta S^{\ddagger}_{k_{-1}}$ (e.u.)	Ref.
Bipyr	51		510	17	7.4			28, 31
Phen	240		2400					32
Terpyr	46		460					28, 29, 30
SCN		1	750	16.8	5	19	6.6	35
Cl	1×10^5	100	800	19.5	30	15	+2	35
CF_3COO	0.9×10^5	30	600	20	33	18.5	6.5	33
CCl_3COO	0.7×10^5	80	400	19	34.5	18	12	33
$CHCl_2COO$	1.5×10^5	30	900	18.5	27	16.5	4.8	33
CH_2ClCOO	1.8×10^5	60	1000	19.5	32	17	7.8	33
$CH_3 \cdot COO$	2.5×10^5		2.2×10^3	17.5	25			33

Table 3. Rate constants and activation parameters for the reactions between bivalent metal ions M and chloride in the solvent methanol at 20°C.

M	$K_0 \times k_1$	k_{-1}	k_1	$\Delta H^{\ddagger}_{K_0 \times k_1}$	$\Delta S^{\ddagger}_{K_0 \times k_1}$	$\Delta H^{\ddagger}_{k_{-1}}$	$\Delta S^{\ddagger}_{k_{-1}}$	Ref.
Ni	1×10^5	100	600	20	33	15	+2	35
Co	3×10^6	7×10^3	1.75×10^4	16	26	13.2	4.2	11
Fe	8.5×10^6	1.0×10^4	5×10^4	13.6	20	12.8	3.7	11
Mn	6.8×10^7	2.7×10^4	4×10^5	10.7	14	11.4	0.8	11
Zn	4.4×10^9	7×10^5	26×10^7	7.5	11	4	-18	38

would then have to be considered for the formation of the Ni–Ac complex:

$$Ac^- + \quad \begin{array}{ccc} Ni^{2+} & \rightleftharpoons & [NiAc]^+ \\ \updownarrow & & \updownarrow \\ [NiCH_3O]^+ & \rightleftharpoons & [NiCH_3O\cdot Ac] \end{array} \qquad (6)$$

Unfortunately, the acidity constant of $Ni(CH_3OH)^{2+}$ in methanol, which would be needed for the calculation of the equilibrium constant, is not available. The acidity constant for bulk methanol is known to be very small. The basicity for the acetate ion has been determined[34]. It has to be emphasized, however, that the acidity of a coordinated CH_3OH molecule is certainly orders of magnitude larger than the acidity of a bulk solvent molecule. For water the change in acidity upon coordination is large. Such an explanation for the rate increase for Ac would also explain that the dissociation rate constant for the acetates is larger than for the substituted acetates.

In water it was observed that the dissociation rate constants decrease with increasing basicity of the leaving acetate. While in most of the systems in *Table 2* the rate constants k_1 had to be calculated from the over-all rate constant $K_0 \times k_1$ by calculating first a value for K_0 from the Fuoss equation, it was possible, for $NiCl_2$ and Ni-trifluoracetate $(Ni(TFA)_2)$, to obtain the k_1 values directly from the measurements[35]. In these two systems the equilibrium constants are rather small and consequently the relaxation times approach a constant value for high concentrations. This behaviour is indicative of the fact that the reaction proceeds by a two-step mechanism. With all its other favourable features $NiCl_2$ in CH_3OH can be used as a model system to demonstrate the two-step mechanism. Anhydrous $NiCl_2$ can easily be prepared by heating $Ni(H_2O)_4Cl_2$. The resulting anhydrous salt is very soluble in CH_3OH. Up to high concentrations only the mono complex is formed and solvolysis reactions do not have to be considered[36].
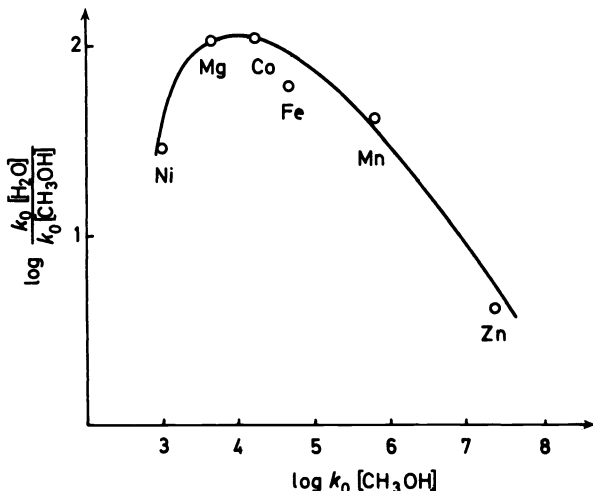

Figure 3. Comparison of solvent exchange rates in methanol and water for various bivalent metal ions. Plot of $\log[k_0(H_2O)/k_0(CH_3OH)]$ against $\log k_0(CH_3OH)$.

Recently other bivalent transition metal chlorides have also been studied[37]. The values for the rate constants and the activation parameters are given in *Table 3*. The k_1 values could be directly evaluated, and agreed fairly well with the n.m.r. values that have been obtained by different authors. It is interesting to note that the values for k_0 show the same characteristic graduation for different metal ions as the water exchange rates, with the sole difference that the values for CH_3OH are about 30–100 times slower at room temperature than in water. The ratio of the k_0 values for methanol against the k_0 values in CH_3OH and water are plotted in *Figure 3*.

The stability constants for the chloro complexes increase from Co^{2+} to Mn^{2+}, a tendency that is not clearly understood and normally not observed for other ligands. Very recently $ZnCl_2$ has been studied[38]. The rate and equilibrium constants and the activation energies are given in *Table 4*. Surprisingly, the stability constant for the bis complex is much larger than for the mono complex.

Table 4. Rate and equilibrium constants for $ZnCl_2$ at 20°C in the solvent methanol.

log K_1	log K_2	$K_{01} \times k_1$ (M.s^{-1})	k_{-1} (s^{-1})	$K_{02} \times k_2$ (M.s^{-1})	k_{-2} (s^{-1})
3.8	4.25	4.4×10^9	7×10^5	9.8×10^8	5.5×10^4

In the course of the interpretation of the two observed relaxation times, it became obvious that the slower of the two relaxation times was due to the bis complex and the faster to the mono complex. Normally it is the other way around, as will be discussed later.

The abnormal behaviour regarding the stability and rate constants is probably due to a symmetry change that takes place when the bis complex is formed. It is likely that the mono complex is octahedrally coordinated while the bis complex is tetrahedral. Using this assumption, the equilibrium constants evaluated from the rate constants agree with the values that are determined from potentiometric titrations. The high activation energy for the bis complex as compared with that of the mono complex must then be due to the transition from the octahedral to the tetrahedral symmetry, which requires the loss of two solvent molecules.

The formation of the tetrahedral bis complex proceeds probably over the octahedral bis complex, the stability constant of which should be smaller than that for the mono complex. Unfortunately, there is no rate constant for the methanol exchange on Zn^{2+} available from n.m.r. data, and it is not possible to compare the value k_1 with a known value for independent measurements. However, the fact that the activation parameters for k_1 fall on the line of the linear relation between $\Delta H^{\pm}$ and $\Delta S^{\pm}$ that has been reported previously for the methanol exchange[11] makes it very likely that the interpretation of the data is correct and that the value of k_1 is really the rate constant for the solvent exchange for the octahedrally coordinated Zn ion. The linear dependence between $\Delta H^{\pm}$ and $\Delta S^{\pm}$ for the methanol exchange is given in *Figure 4*. With the value of $\Delta H^{\pm}$ for k_1 of Zn of about 4–5 kcal the linear correlation has been established now over the wide range of about 15 kcal. This
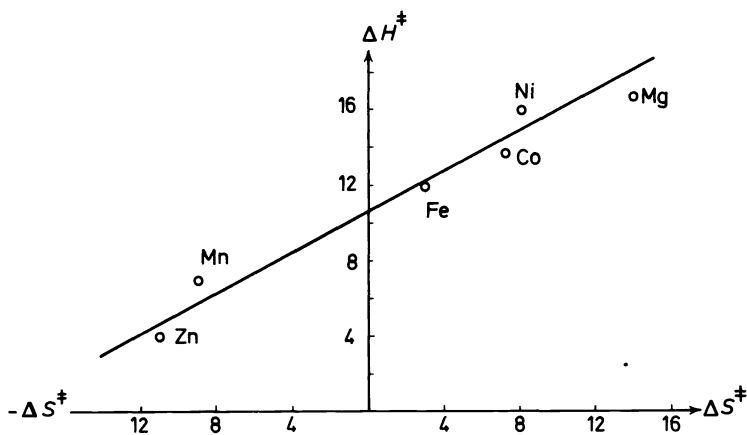
Figure 4. Activation enthalpy $\Delta H^{\ddagger}$ of the solvent exchange rate k_0 for various metal ions in methanol plotted against the activation entropy.

leaves absolutely no doubt that the observed correlation could be a fortuitous result. Even with very tolerant error limits of ± 2 kcal for the $\Delta H^{\ddagger}$ values, the correlation is clearly visible. Most of the measurements are certainly much more accurate. Some of the k_1 values could be directly evaluated from the relaxation times over a temperature range of at least 30–40° C and the $\Delta H^{\ddagger}$ values are clearly much better than 2–3 kcal. Several explanations have been proposed for the existence of the linear correlation. Based on the change of the sign for $\Delta S^{\ddagger}$, various authors have postulated that the correlation indicates a change in mechanism from SN_1 to SN_2 [39]. The entropy change for the dissociation of a diatomic molecule into atoms in the gas phase amounts typically to about 22 e.u.

In the extreme case the entropy difference between a purely SN_2 and an SN_1 reaction could account only for < 10 e.u., which is considerably less than the total entropy change on the linear correlation [40]. Therefore such an explanation could only account for part of the observed changes in $\Delta S^{\ddagger}$. Also, there is no further evidence to substantiate such an explanation. Zn^{2+} and Fe^{2+} have the same crystal radii and consequently the packing should be about the same. To answer this question unambiguously it would be desirable to have data on the pressure dependence of k_0, and it is hoped that such measurements can be done in the future. An SN_1 mechanism should have a positive volume of activation, while an SN_2 mechanism should have a negative volume of activation. Bennetto and Caldin, who first observed the linear relation, interpreted it on the basis of structure and viscosity properties of the solvent [41]. By their reasoning it seems to be difficult to comprehend it in the same solvent. Fischer, Hoffmann and Platz proposed therefore a new explanation, according to which the change in the degrees of freedom for rotation and vibration in the transition state is responsible for the $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ correlation [11]. At negative $\Delta S^{\ddagger}$ values the molecules in the inner sphere are more labile than in the solvent and consequently degrees of

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freedom are lost when a particle dissociates from the coordination sphere to the bulk solvent.

At larger $\Delta H^{\ast}$ values the interaction between the solvent molecules and metal ions increases, more and more degrees of freedom are frozen out and the inner solvation sphere becomes more crystal-like. During the dissociation process of one molecule, the remaining molecules take up the vacated room, which gives them more space again to build up rotations and vibrations that were frozen out in the six-coordinated ground state. Evidence for such an explanation has recently been provided by Kebarle and co-workers, who measured reaction enthalpies for the stepwise coordination of water molecules with alkali metal ions[42]. They observed an unusual high entropy loss when the sixth water molecule was coordinated. This clearly indicates that besides the degrees of freedom for translation that are lost with each coordination, some other degrees of freedom must also be lost. Furthermore, if the values for the last step are compared for different metal ions, a linear correlation between $\Delta H^{\ast}$ and $\Delta S^{\ast}$ becomes visible. In addition, evidence from n.m.r. measurements reveals that the rotation of coordinated solvent molecules is highly restricted in some complexes[43].

Recently the bivalent metal salts of the trifluoracetates have been investigated[37]. Fortunately, the stability constants are in the favourable range of 10^2–10^3, in which the rate constant k_1 can be directly evaluated from the relaxation times. The data are summarized in *Table 5*. For the metal ions Ni, Co, Fe, Mg, the agreement of the k_1 values with the k_0 values is satisfactory. The stability constants decrease in this order, which is the normal order to be expected. In *Figure 5* the inner-sphere stability constants
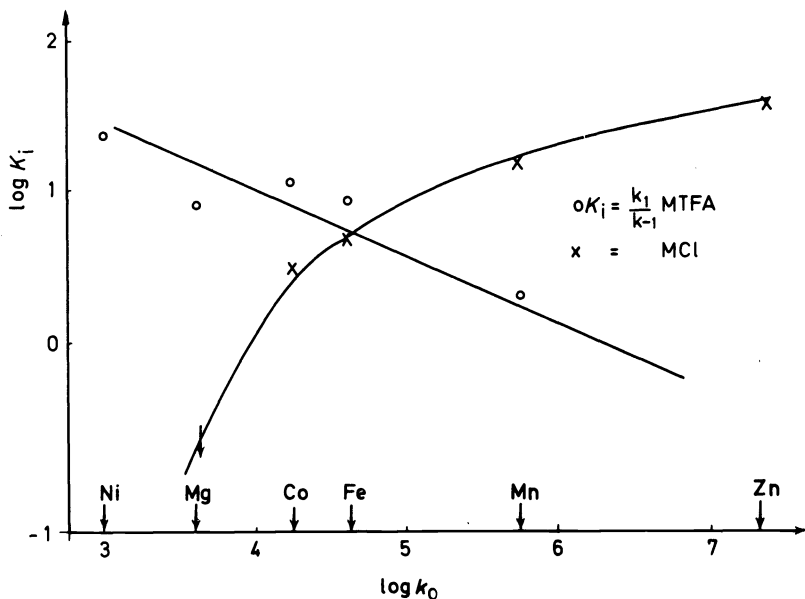

Figure 5. The inner-sphere constants for several Cl^- and CF_3COO^- complexes. Plot of log K_i against log k_0.

Table 5. Rate constants and activation parameters for the reactions between bivalent metal ions M and $CF_3 \cdot COO$ in the solvent methanol at 20°C (ref. 37).

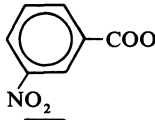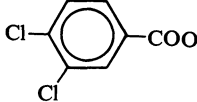| M	$K_0 \times k_1$	k_{-1}	k_1	$\Delta H^{\ddagger}_{K_0 \times k_1}$	$\Delta S^{\ddagger}_{K_0 \times k_1}$	$\Delta H^{\ddagger}_{k_{-1}}$	$\Delta S^{\ddagger}_{k_{-1}}$
Ni	0.9×10^5	30	600	19	34.5	18.5	12
Co	4.5×10^6	2.7×10^3	3.1×10^4	16.5	29	16	12
Fe	1.4×10^7	8.6×10^3	7.7×10^4	13.5	18	12.2	1.25
Mn	1.8×10^8	5×10^5	1×10^6	8.5	7	4	−18.6
Mg	7.6×10^5	5.4×10^2	4×10^3	20	36	13.4	0

$K_i = k_1/k_{-1}$ of the metal chlorides are compared with those for the trifluoracetates. The log K_i values are plotted against the log k_0 values to render the different behaviour visible.

For the trifluoracetate systems everything behaves as expected. The rate constants are predetermined by the solvent exchange rates and the over-all stability constants. The total reaction enthalpy for the complexes is considerably less endothermic than for the chlorides. The complex formation from the outer-sphere to the inner-sphere complex is slightly exothermic. As a consequence the k_1 values have only a slightly smaller temperature dependence than the $K_0 \times k_1$ values. This is probably due to the fact that the charge on the TFA is not localized as much as in the case of the chloride and consequently electrostriction plays a smaller role than with the chlorides.
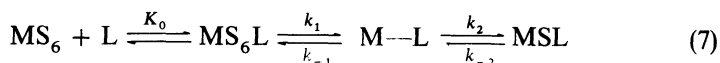
RESULTS IN DMSO

A few measurements on the mechanism of complex formation have also been undertaken in the solvent DMSO. In one of the first studies in this solvent, an unusually low rate constant was reported for the reaction between Ni and SCN, and it was speculated that the five-coordinated intermediate that results when a DMSO molecule dissociates from the octahedrally coordinated $Ni(DMSO)_6$ has an abnormal long lifetime[44]. However, later measurements on this system could not confirm the early results[45]. Instead, for the reactions with Cl and SCN quite normal rate constants were observed. A normal rate constant was also found for the reaction with pyridine[32]. For these three systems the interpretation of the data is simple and mechanism 1 is valid. In these systems the measured rate constants can be associated with a specific step. The situation is more complicated when rate

Table 6. Rate constants and activation parameters for the reaction between Ni^{II} with different ligands X in dimethylsulphoxide at 20°C.

X	$K_0 \times k_1$	k_{-1}	k_1	$\Delta H^{\ddagger}_{K_0 \times k_1}$	Ref.
Pyridine	2×10^3	70	10^4	4	32
Bipyr				12.6	32
Phen	350			8.3	32
Terpyr					
SCN	8×10^4	80	2×10^3		45
Cl	7×10^4	150	18×10^3		45
NO_2—C₆H₄—COO	1.9×10^4	16			46
C₆H₄(NO_2)—COO	1.3×10^4	16			46
Cl₂C₆H₃—COO	1.3×10^4	20			46

constants for multidentate ligands are interpreted and only rate constants for the over-all reaction are available, as was the case for the reactions with bipyr, phen, terpyr that have been measured by Bennetto and Caldin[31]. The rate constants obtained are given in *Table 6*. These rate constants are considerably lower than the rate constants for the unidentate ligands. This, however, does not necessarily mean that the formation of the first bond does not proceed at the same rate as in the first three examples because it is quite conceivable that the rate-determining step for the over-all reaction is the closing of the chelate ring. For the reaction scheme

$$MS_6 + L \underset{}{\overset{K_0}{\rightleftharpoons}} MS_6L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M\text{---}L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MSL \qquad (7)$$

the over-all rate constant for a bidentate ligand can be expressed by the equation $k_{12} = K_0 \times k_1 \times k_2/(k_{-1} + k_2)$ if the concentration of the open complex is negligible in comparison with the chelate. In the solvent DMSO, with its rather high donicity, many unidentate ligands form only rather weak complexes and consequently the rate constants for k_{-1} are rather high by comparison with k_1. Furthermore, the labilizing effect of the entering ligand is probably small, because its donicity is not much higher than that of the solvent molecule it has replaced. As a result of the two effects the rate constant k_{-1} can easily become larger than k_2, and k_2 can become rate-determining. In solvents with smaller donicity this is much less likely. While this seems to be a logical explanation for the rather small values of k_{12}, it is also possible that the rate constant k_1 is lower for the bidentates than for pyridine. All multidentates in *Table 6* are two-substituted pyridines and two-substituted pyridines are known for steric complications in replacement reactions, because the entering donor group is sterically shielded by the substituent in 2-position. For all these reasons these ligands should not be selected whenever conclusions are drawn for the first rate-determining step from the over-all reaction. In case this is done, at least comparison measurements should be made with pyridine and possibly a simple two-substituted pyridine like 2-methyl-pyridine. Some ambiguities in the interpretation of the data can then be avoided. *Table 6* contains also data that have been obtained recently by Dickert et al.[46]. The rate constants for the substituted benzoates, again, are lower than for the simple Cl and SCN unidentates. The ligands are assumed to coordinate as unidentates and the reason for the abnormal low rate constants is not clear. For the nitrobenzoates it seems conceivable that the charge on the electron-withdrawing nitro group becomes as large as that on the CO_2 group, and consequently the ligand does not orient into a favourable position in the outer sphere complex.

RESULTS IN DMF

A solvent very often used in both inorganic and organic chemistry is dimethylformamide (DMF). In many respects the solvent has similar properties to those of DMSO. It is especially useful when high solvating power for metal ions with an aprotic character of the solvent are required. Many bivalent metal ions are octahedrally coordinated in this solvent. Usually the oxygen

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is coordinated to the metal ion, as has been shown by different experiments, even in the case of Ni, which tends to favour nitrogen before oxygen[47]. Obviously, the amide nitrogen must have a rather low donicity. The solvent exchange of coordinated molecules with the bulk solvent has been measured for several metal ions (see *Table 1*). The agreement between measurements from different groups is fairly good. The rate constants do not vary by more than a factor of 2 and the activation energies are the same within 1 kcal. The existing data on this system therefore seem to be reliable. A few measurements have also been carried out on the kinetics of complex formation. Bennetto and Caldin reported values for the reaction between Ni and phen, and Dickert and Hoffmann have given in a brief communication the values of the rate constants for the reactions with SCN^{48}. In both cases the values were consistent with a mechanism in which the rate-determining step for the complex formation was the solvent exchange. In spite of the bulkiness of the solvent, no complication had been found. Further measurements carried out recently confirmed the original conclusions. Rate constants of systems that have been investigated are summarized in *Table 7*. Activation parameters for the rate constants are included. The stability constants of the studied systems vary almost over two orders of magnitude. The inner sphere constants range from about 1.2 for Ni-toluolsulphonate to about 150 for NiSCN. This difference is completely due to different dissociation rate constants. The formation rate constants are very similar. Together with very similar activation energies for the various systems, and the agreement of k_1 and k_0, this can be taken as proof that in DMF the solvent exchange is the rate-determining step for the complex formation.

The relatively small difference in the $K_0 \times k_1$ values, amounting to a factor of 2.5, are probably not large enough to deserve much emphasis. They can be caused by different outer sphere constants. For the calculation of the outer-sphere constant the same distance parameter for the Fuoss equation was used. A K_0 constant of 60 was assumed for all ions. It is quite conceivable that for the Cl ions, where the charge is localized on one rather small ion, a smaller distance should be used and consequently a larger K_0 value would result. A distance of 4.5 Å as compared with 5.5 Å would be enough to account for a difference of a factor of 2 in K_0. A smaller a and consequently a larger reaction enthalpy for the outer sphere complex would also explain the somewhat larger ΔH^+ value for the complex formation, because the closer the ions can move together in the outer-sphere complex, the more endothermic is the reaction enthalpy. The smaller ionic radius is probably also the reason for the more negative values for ΔS^+ of k_{-1}.

From electrostatic considerations the formation of the complex from the outer-sphere complex should always be accompanied by a positive reaction enthalpy and entropy.

This is indeed the case for $NiCl_2$ and $Ni(TFA)_2$, while the system $Ni(SCN)_2$ shows an exothermic reaction enthalpy and a positive reaction entropy. The system $Ni(TS)_2$, finally, has a slightly exothermic reaction enthalpy and a negligible reaction entropy. In this respect $Ni(TS)_2$ shows the behaviour that is typical for a complex with a neutral ligand, reflecting the fact that on this ligand the charge is not localized on one oxygen. It is noteworthy that the stability constants for $NiCl_2$ and $Ni(SCN)_2$ are rather similar at room

Table 7. Rate constants and activation parameters for the reaction between Ni^{II} with different ligands X in diphenylformamide at 20°C.

X	$K_0 \times k_1$	k_{-1}	k_1	$\Delta H^{\ddagger}_{K_0 \times k_1}$	$\Delta S^{\ddagger}_{K_0 \times k_1}$	$\Delta H^{\ddagger}_{k_{-1}}$	$\Delta S^{\ddagger}_{k_{-1}}$	Ref.
Bipyr	360							31
SCN	1.4×10^5	15	3×10^3	12.7	-3.3	15.7	-1.4	48
Cl	3.8×10^5	52	2.2×10^3	17.2	24	12.4	-8.4	48
$CF_3 \cdot COO$	1.8×10^5	280	6.3×10^3	19.2	33	12.7	-4	49
			3×10^3	18.2	29			
$CH_3-\!\langle\bigcirc\rangle\!-SO_3$	2.4×10^5	2800	4×10^3	18.1	28	16.5	13.7	49

temperature. At lower temperatures $Ni(SCN)_2$ is more stable and at higher temperatures $NiCl_2$ is more stable. The similarity of the stability constants and dissociation rate constants had been observed before in the solvent DMSO. The temperature dependence could not be measured in this system because of the rather high melting point of the solvent. It is likely that both systems would have shown the same tendencies in DMSO as in DMF. The similarity of the stability constants of the complexes of the two ligands in aprotic solvents is in sharp contrast to the behaviour in protic solvents such as water and methanol. In these solvents the SCN always forms a much stronger complex. The two ligands in the four solvents are compared in *Table 8*.

Table 8. Comparison of stability constants K_1 for $NiCl_2$ and $Ni(SCN)_2$ in protic and aprotic solvents at 20°C.

	DMF	DMSO	$CH_3 \cdot OH$	H_2O
$NiCl_2$	7×10^3	4.5×10^2	1.5×10^3	5
$Ni(SCN)_2$	9×10^3	1×10^3	1×10^5	70

The probable reason for the different behaviour has been given earlier. It was assumed that the release of a Cl ion from the coordinated state is facilitated by H bonds that can be formed from bulk solvent to the back of the coordinated Cl ion. Because of the hydrophobic nature of the sulphur group in the ligand, SCN hydrogen bonds can not be formed to the unco-ordinated site of the ligand. Consequently the ligand SCN does not dif-ferentiate so much between protic and aprotic ligands and the dissociation rate constants correlate with the donicity of the solvents.

RESULTS IN $CH_3 \cdot CN$

Until very recently, most of the kinetic measurements that were carried out in $CH_3 \cdot CN$ resulted in constants that were inconsistent with process 1 and it was therefore postulated that a different mechanism was operating. Employing the stopped-flow technique, Bennetto and Caldin reported constants for the reaction of Ni^{2+} with bipyridine that were much too high to be accounted for by a pure solvent exchange mechanism. Recently Coetzee and his colleague have published results for the reactions of nickel(II) with pyridine, bipyridine, terpyridine and phenanthroline[32]. For the reaction with pyridine they found a rate constant that can be considered 'normal' and consistent with process 1. The rate constants for the reactions with bipyridine and particularly with phenanthroline, on the other hand, were considerably higher than for pyridine. Furthermore, the activation enthalpy for the reaction with phenanthroline was considerably lower than the activation enthalpy for pyridine. A possible explanation for this abnormal behaviour could be an increased stabilization of the outer-sphere complex. An exo-thermic reaction enthalpy for the outer-sphere complex could lead to an

Table 9. Rate constants and activation parameters for the reaction between Ni^{II} and different ligands X in acetonitrile at 20°C (if not stated otherwise)

X	$K_0 \times k_1$ ($M.s^{-1}$)	k_{-1} (s^{-1})	k_1 (s^{-1})	$\Delta H^{\ddagger}_{K_0 \times k_1}$ (kcal)	$\Delta S^{\ddagger}_{K_0 \times k_1}$ (e.u.)	$\Delta H^{\ddagger}_{k_{-1}}$ (kcal)	$\Delta S^{\ddagger}_{k_{-1}}$ (e.u.)	Ref.
Pyridine (25°C)	8.3×10^2			14.7				32
Bipyr (25°C)	4.1×10^3			6.5				32
Phen (25°C)	5×10^4			4.7				32
Terpyr (25°C)	2.2×10^3			8.4				32
NO_3	1.9×10^5	7.5	2.6×10^3	17.5	24	13.5	−9.5	52
$CF_3 \cdot COO$	1.5×10^5	5	2.0×10^3	17	21	15	−3	52
$CH_3-\phi-SO_3$	1.3×10^5	26	1.8×10^3	17	22	18	+0.8	52
SCN	1×10^5	0.3						63

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increased rate constant and a lower activation energy for the over-all reaction.

It is noteworthy that nickel(II) halides and acetates which usually had proved ideal for relaxation studies in non-aqueous solvents proved to be too strongly coordinated in acetonitrile. Polarographic studies with these systems have been made, but accurate rate constants are lacking[51]. Salts of intermediate stability such as $Ni(NO_3)_2$, $Ni(TS)_2$ and $Ni(TFA)_2$, however, provided satisfactory relaxation effects and they have recently been studied[52]. The three systems showed concentration-dependent relaxation effects with large amplitudes over the concentration range $10^{-5}-10^{-3}$. For the above con-centration range two relaxation times were observed for each salt. At higher concentrations both $Ni(NO_3)_2$ and $Ni(TFA)_2$ exhibit one additional relaxa-tion time. Rate constants and activation parameters for reactions with Ni in CH_3CN are given in $Table\ 9$.

The rate constants $K_0 \times k_1$ for NO_3, TS and TFA are very similar in all three systems. This is a clear indication that all three complexes are formed by the same mechanism and are controlled by the same rate-determining step. It is very likely that this step is the loss of a solvent molecule from the inner sphere of the metal ion, because the rate constants k_1 and k_0 as reported by several authors agree fairly well. The reported ΔH^{+} values for k_0 vary considerably. These activation energies are usually determined from rather small temperature differences and in addition some theoretical curve fitting is required. The relaxation times of the complexes can easily be observed over a wider temperature range and the activation energies should be more accurate. Therefore the resulting data can be used to determine which of the reported ΔH^{+} values for k_0 are probably the most reliable.

According to the results on $Ni(NO_3)$, $Ni(TS)_2$ the values given by Richards $et\ al.$ are probably the most accurate ones[25]. The activation enthalpy for the dissociation rate constant k_{-1} is for $Ni(NO_3)_2$ smaller than for the rate cons-tant $K_0 \times k$, which means that the reaction enthalpy for the complex formation is endothermic by 8 kcal. The main reason for the rather high stability constants is therefore the increase of the reaction entropy that is associated with the complex formation.

It is interesting to note that the coordinated ligands NO_3^-, TS^- and TFA^- cause a considerable labilization of the remaining solvent molecules. The amount of labilization can be determined from the values of the formation rate constants for the bis complex that are given in $Table\ 10$. The values are larger than the corresponding values for the mono complexes, even though

$Table\ 10$. Rate constants for the bis complexes of Ni^{II} with different ligands X in the solvent $CH_3 \cdot CN$ at 20°C and their activation parameters.

X	$K_{02} \times k_2$	k_{-2}	$\Delta H^{+}_{K_{02} \times k_2}$	$\Delta S^{+}_{K_{02} \times k_2}$	$\Delta H^{+}_{k_{-2}}$	$\Delta S^{+}_{k_{-2}}$
NO_3	6.3×10^5	525	13.5	5	10	−14
CH_3—⟨O⟩—SO_3	1.4×10^6	1.2×10^3	12	8.5	12	−5.5
TFA	4.2×10^6	2×10^3				
SCN	1×10^6	50	12.5	11.2	15	0.2

the outer-sphere constants for the bis complex are ten times smaller than for the mono complex. This means that the solvent molecules have been labilized by a factor of 30–300, depending on the anion. A further labilization occurs with the coordination of the second ligand. This, again, can be concluded from the rate constant for the formation of the tris complex that is observed in the $Ni(NO_3)_2$ system. Since neutral ligands tend to labilize the coordination sphere if their reaction enthalpy is exothermic, the observed endothermic reaction enthalpy and high degree of labilization are quite surprising.

The labilization of the coordinated anions is also reflected in the rate constants k_1, k_2 and k_3 and their activation energies and entropies. The activation enthalpies become smaller and the entropies more negative with increasing substitution. For $Ni(NO_3)_2$ it was observed that the bis complex disproportionates according to the mechanism

$$Ni(NO_3)_2 \rightleftharpoons NiNO_3 + Ni(NO_3)_3 \qquad (8)$$
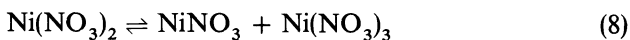
This reaction path is probably restricted to ligands similar to nitrate, which, because of their symmetrically placed donor groups, afford the possibility that non-coordinated donor atoms can react with a second metal ion or complex, forming in an intermediate state a bridged complex. Normally this newly formed bond opens faster than the one previously present and no net reaction occurs. But it is also possible that the first bond breaks, resulting in a nitrate transfer.

REMARKS ON SOLVENT MIXTURES

Binary solvent mixtures offer the possibility of changing properties of a solvent in a continuous manner from one solvent to another. The information that can be gained from such a transition can lead to a much better understanding of the characteristic properties of a solvent than would be possible from the studies of the pure solvent alone. If metal ions are dissolved in binary solvent mixtures, the solvation sphere of the metal ion usually has a composition different from that of the bulk solvent. If the solvent exchange is slow enough, the solvated metal ions with solvent spheres of varying composition can be isolated and analysed. Such studies have been carried out with Cr(III) and Co(III) in water–methanol mixtures by King and another[53]. For bivalent metal ions the solvent exchange and thus the change in composition is usually much faster than any attempt to separate different species, and an isolation from the bulk solvent is therefore impossible. However, in many cases the composition of the coordination sphere in solution has been analysed by different techniques mainly by n.m.r. methods[54, 61]. The The studies are undertaken in an attempt to understand the composition and the exchange rates of the coordinated species in the mixed-coordination sphere from the properties of the pure systems.

Qualitatively, the existing results can be summarized as follows. If a solvent of a higher donicity is added to a solution of a metal ion in a solvent with a lower donicity, the solvent with the larger donicity is preferentially coordinated. The coordination of the added solvent can be looked upon as normal complex formation and the stepwise replacement of the old solvent

sphere by the added solvent can be expressed in stability constants, as has been done in many examples, as in the system Co and Ni in methanol with added water, by Luz and Meiboom[55]. In these particular systems the mono complex has a stability constant of about 100 and the reaction enthalpy is exothermic. These values indicate that special care must be taken to dry the solutions if the properties of the pure methanol coordination sphere are to be studied. Water concentrations as low as 10^{-2} M cause considerable complex formation if the metal ion concentration is high enough. The coordination of the water has usually a strong labilizing effect on the solvent exchange rates of the remaining weaker solvent molecules. In the solvation sphere of mixed composition the solvent molecule with the larger solvation power seems to have the slowest dissociation rate constant. If more and more solvent molecules with the higher donicity are incorporated into the solvation sphere, both dissociation rate constants are increased. Very often, in the final state in which all the positions of the metal ion are occupied by the solvent of the higher donicity, the solvent exchange is faster than the solvent exchange when all positions are filled with the pure weaker solvent. Such a pattern has been observed for $H_2O–CH_3OH$[56], $CH_3OH–DMF$[57], $H_2O–NH_3$[58] and $CH_3\cdot OH–CH_3CN$[60] mixtures.

As a consequence, the medium rate constant $k_m = \frac{1}{6}[nk_{01} + (6 - n)k_{02}]$ can pass through a maximum. This rate constant k_m is normally measured when relaxation or stopped-flow measurements are carried out to obtain the rate-determining step for the complex formation.

If there is another ligand or anion present whose stability constant with the metal ion is measured while the solvent of higher donicity is added, the stability constant normally decreases continuously. These effects are due to the change in the inner coordination sphere of the metal ion. However, the added solvents can also dramatically influence existing equilibria without entering the inner coordination sphere. Such effects are particularly striking if a hydrogen-bond-forming solvent is added to a non-hydrogen-bond-forming solution in which an anion that is prone to hydrogen bonding is in equilibrium with a metal complex such as $NiCl_2$ or $CoCl_2$ in DMF. Only trace amounts of H_2O or CH_3OH are necessary to completely destroy the complex. For such systems the stability constant of the complex can pass through a minimum when the complex is dissolved in the better donor and the solvent of weaker donicity but of hydrogen-bond-forming capability is added[57]. This is the case with $NiCl_2$ in DMF and CH_3OH. The stability constant is drastically reduced when a little CH_3OH is added.

The chloride is thereby removed from the inner coordination sphere. When more and more CH_3OH is added and built into the first coordination sphere of the metal ion, the acidity of the Lewis acid NiS_5 is increased and the stability of NiCl is also increased again.

If a solvent is diluted with a non-coordinating solvent that does not directly interact with the coordinated ligand, the exchange rates are usually hardly affected. This has been shown with mixtures of DMSO or DMF with nitromethane[59] or propylenecarbonate.

GENERAL CONCLUSIONS

While the rate and the stability constants of the studied systems vary

widely, it is nevertheless possible to draw some conclusions that are valid for all systems.

1. It was already emphasized during the discussion of each solvent that substantial and convincing evidence exists that the rate of complex formation is controlled by the solvent exchange process of a solvated ion. The rate constants k_1 and k_0 and their corresponding activation parameter are in good agreement.

This result seems to be valid quite independently of the solvent and the bulkiness of the molecules that make up the solvent. The rate constant k_1 does not seem to depend on the structure of the solvent, as has previously been postulated on the basis of results that were obtained with bipyridine as a ligand. These results could not be confirmed with simple unidentate ligands.

The relative unimportance of the structure of the solvent for the rate-determining step can also be concluded from kinetic measurements over a wide temperature range in methanol.

Although the viscosity changes from 0.5 cP to 4 cP when the temperature is lowered from 30 to $-70°$ C, process 1 is not altered.

Furthermore, it was shown recently by Frankel[59] that the rate constant k_0 is not affected by the composition of the solvent as long as the inner coordination sphere of the metal ion is kept constant.

Both for DMF and DMSO it was found that the solvent exchange rates on Ni(II) and Co(II) did not change when the solvents were diluted with non-coordinating solvents such as $CH_3 \cdot NO_2$ and CH_2Cl_2. For protic solvents the situation could be different because the rate constant k_0 should depend on the strength and the number of hydrogen bonds between the inner and the outer coordination sphere, and consequently a change in the composition of the outer sphere would probably affect the exchange rates. But even in this case the changes are probably quite small. The rate constant k_1 in methanol seems to be fairly independent of the basicity of the entering ligand. On the the other hand, the reaction with ethylenediamine, for which the conjugate base mechanism was observed in water, has not yet been studied in methanol.

Clearly, most of the available evidence is consistent with the solvent exchange process being an SN_1 process.

2. Another simple result is that wherever it was possible to observe the mono complex and the bis complex it is found that the bis complex is less stable than the mono complex. The difference in the stability constants is mainly due to the difference in the outer-sphere stability constants; the inner sphere constants do not vary much. In this respect the complexes behave the same in non-aqueous solutions as in water. Whenever there are deviations from this normal behaviour, there is probably a special reason for it, such as a change in the symmetry or in the electronic state between the mono complex and the bis complex. But while the stability constants for the inner-sphere constants are of similar size, the characteristic rate constants are not. The bis complex was always found to form and dissociate considerably faster than the mono complex. This result might not be surprising, but it is still worth mentioning. Correspondingly, the activation energies for the bis complex are always lower than those for the mono complex.

The change in rate constant is caused by a change not only in the activation enthalpy but also in the entropy. The consequence, of course, is that the ratio of the dissociation rate constants of the two complexes is temperature dependent, and normally k_{-2}/k_{-1} becomes smaller with increasing temperatures. This behaviour is seen in *Figure 6*. If the trend that we observe at room temperature and below is extrapolated to higher temperatures, the rate constants
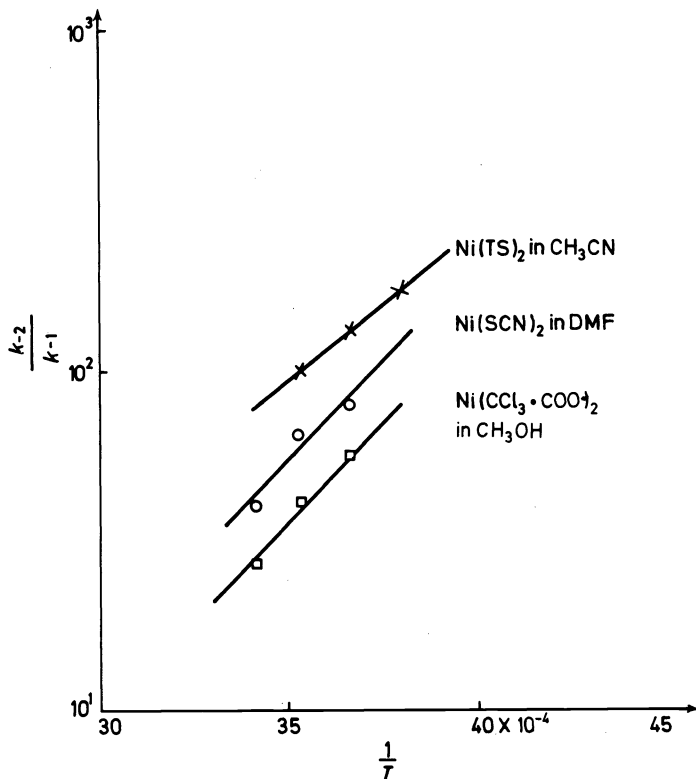

Figure 6. Dependence of the ratio of the dissociation rate constants for the bis and mono complexes on the temperature. Plot of log $(k_{-2})/(k_{-1})$ against $1/\tau$.

should cross. From this point it seems therefore quite fortuitous that the rate constants for the bis complex are faster than those for the monocomplex, and it is conceivable that solvents exist where the temperature at which the crossover occurs is at a lower level and that we observe the opposite trend. But even for this speculative case the activation energy for the mono complex should be higher than that for the bis complex. The behaviour resembles the one observed pattern for the activation parameter for the solvent exchange, where a decrease in activation enthalpy was partially compensated by a decrease in activation entropy. The reasons for this are probably the same as those already mentioned in the section on $CH_3 \cdot OH$.

3. As regards the variation of the inner-sphere stability constant $K_1^I =$

k_1/k_{-1} for a given complex in different solvents, it was recently pointed out that the stability constant increases with decreasing donicity of the solvent[52, 63]. Similar conclusions were put forward by Gutmann and Schmid[64]. Qualitatively, such behaviour is to be expected from simple arguments based on the solvating power of the solvent. Since the equilibrium

$$[MS_5 \cdot X]S \xrightleftharpoons[k_1]{k_{-1}} [MS_6]X \qquad (9)$$
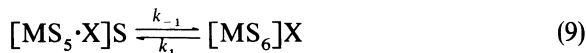
is the result of the competing reactions with the rate constants k_1 and k_{-1}, a quantitative interpretation of the result has to account for the change of these two rate constants with the variation of the solvent. The two rate constants will therefore be discussed separately.

4a. The dissociation process

$$MS_5 \cdot X \xrightarrow{k_{-1}} MS_5 + X \qquad (10)$$

can be regarded as a dissociation process of a compound composed of the Lewis acid MS_5 and the Lewis base X. The acidity of the Lewis acid A and the donicity of the Lewis base D determine the activation energy of the process. Both contributions can be investigated independently.

Influence of the acidity of MS_5 on k_{-1}. The acidity of MS_5 depends on the donicity of the solvent molecules. It is lowered by the increase of the donicity of the coordinated molecules. The influence can qualitatively be
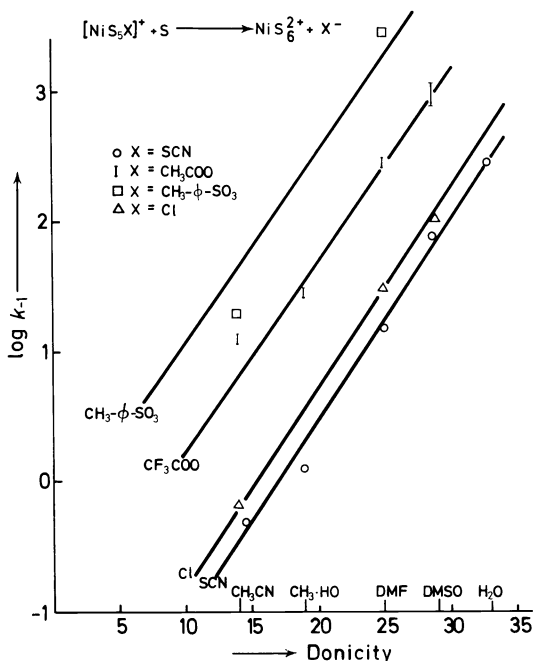

Figure 7. Dependence of the dissociation rate constant k_{-1} on the donicity of the solvent. Plot of log k_{-1} against donicity

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studied by measuring the dissociation rate constant for a given bond in different solvents. Recently it was assumed that the acidity decreases exponentially with the donicity[63]. With such an assumption it was possible to explain the trend in the activation enthalpies for the solvent exchange. However, judged from the dependence of the dissociation rate constants of a given complex in different solvents, it seems more likely that the acidity decreases linearly with donicity (DN). It was observed that for a given leaving group the log k_{-1} values increase about linearly over several orders of magnitude[63] with DN of the solvents[65]. These rate constants for several complexes are given in *Figure 7*.

Such linear relations can easily be explained by assuming that the activation energy for the dissociation process can be expressed as the product of the donicity of the leaving group DN_X and the acidity A of the remaining intermediate complex, which in turn decreases linearly with DN_S:

$$\Delta G^{\ddagger} = A \times DN_X = (A_0 - \alpha \cdot DN_S)DN_X \qquad (11)$$

with

$$k = \varphi \exp -\frac{\Delta G^{\ddagger}}{RT}$$

we obtain

$$\ln k = \ln \varphi - \frac{A_0 \cdot DN_X}{RT} + \frac{\alpha \cdot DN_S \cdot DN_X}{RT} \qquad (12)$$

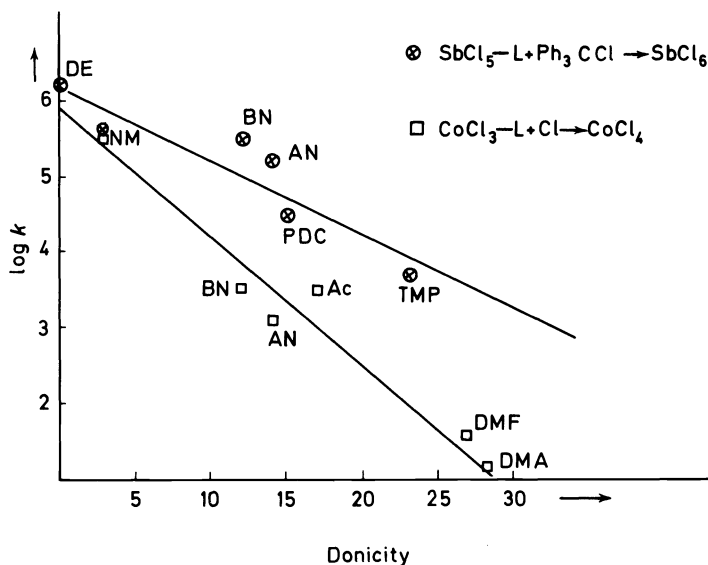As can be seen from equation (12), the log of the rate constant k_{-1} should

Figure 8. Dependence of the dissociation rate constant k_{-1} on the donicity of the leaving group.

linearly increase with the donicity of the solvent, with the slope of the plot depending on the donicity of the leaving group.

The influence of the leaving group on the activation energy of k_{-1} can be studied by keeping the Lewis acid MS_5 constant and varying the donicity of the leaving group. Such measurements have been done for various Lewis acids such as $SbCl_5$, $CoCl_3$ and $Ni(H_2O)_5$. Gutmann and Schmid, for instance, reported the rate constants for the reaction[64]

$$SbCl_5S + CPh_3Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SCl_6^+ + \overset{.}{P}h_3C^+ + S$$
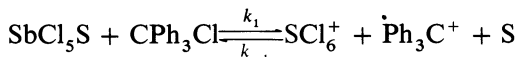
The log of the rate constant k_1 is plotted in *Figure 8* against the donicity of the leaving group S. As expected, log k_1 decreases linearly with the donicity of S. The rate-determining step for the rate constant k_1 is believed to be the breaking of the $SbCl_5$—S bond and probably independent of the entering ligand CPh_3Cl.

4b. Rate determining for the solvent exchange process is the dissociation of a solvent molecule from the inner coordination sphere of the metal ion. From the above considerations it is obvious that for the process

$$MS_6 \overset{k_1}{\longrightarrow} MS_5 + S$$
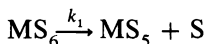
both acidity of MS_5 and donicity of the leaving group are varied when the solvent is varied. As shown, these effects on the rate constant tend to oppose each other. The increase in the acidity A is balanced by the decrease in the donicity of the leaving group if the donor properties of the solvent are
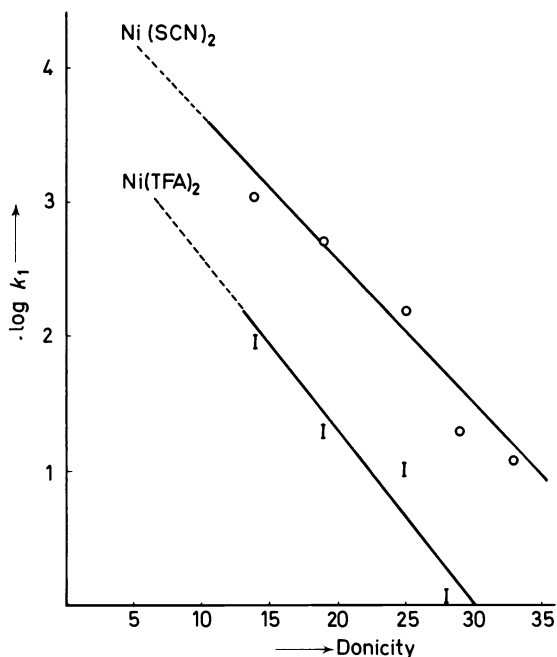

Figure 9. Dependence of the inner-sphere stability constant $K_i = (k_1)/(k_{-1})$ on the donicity of the solvent. Plot of log K_i against donicity.

lowered. Consequently, in many solvents the rate constants for complex formation and solvent exchange are very similar. As a result of this the log K values are linearly dependent on the donicity of the solvent. This is shown in *Figure 9*. This empirical relation lends itself to the extrapolation of equilibrium constants in non-aqueous solvents, using the values that have been determined in the solvent water. Therefore it should be possible to make use of the hundreds of stability constants that have been determined for various ligands and metal·ions to estimate values in non-aqueous solvents.

It should be remembered that while equation (12) can certainly be helpful for the estimation of rate constants, we should not be too surprised if the agreement with experiment leaves something to be desired. It has been shown that such simple correlations exist only for solvents in which hydrogen bonds play no role or if ligands are used which are not well suited for hydrogen bond formation, such as TSO_3, $CF_3 \cdot COO$ or even SCN. With simple ligands such as Cl no correlation can be observed.

5. Linear $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ relation for k_{-1}. For the methanol exchange for different ions it was shown that the exchange rates varied considerably less than would have been expected from their activation enthalpies alone. The changes in the activation enthalpies were always partially compensated by changes in the activation entropy. Such linear correlations have also been observed for organic reactions[66].

This behaviour seems typical not only for the solvent dissociation rate but also for the dissociations of ligands or anions from a solvated metal ion. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the dissociation of the trifluoracetate from a bivalent metal ion in CH_3OH are plotted in *Figure 10* against each other.

The activation enthalpies vary over the large range from 5 to 18 kcal and the entropies from -16 to $+12$ e.u. The rate constants change from $30\,s^{-1}$ for NiTFA to 5×10^5 for MnTFA. It is likely that similar plots will be found if more reactions are studied and more data become available. However, it has
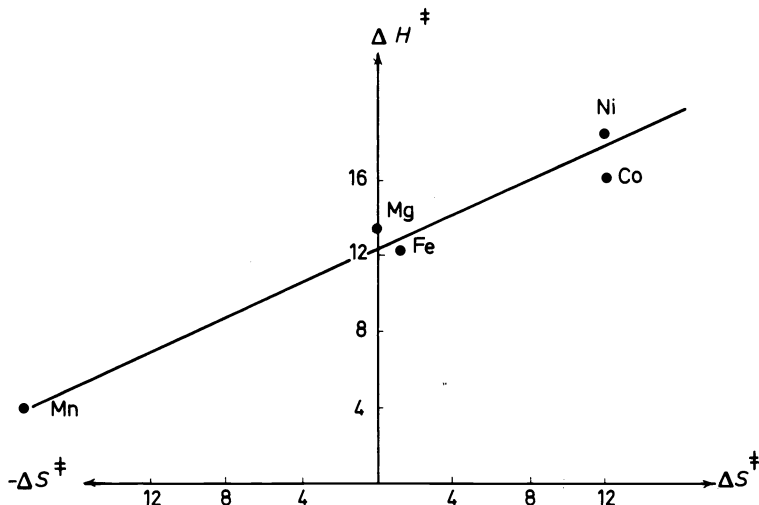

Figure 10. Plot of activation enthalpy against the activation entropy of the dissociation rate constant k_{-1} for $M(CF_3COO)$ complexes in methanol.

to be said that such correlations can be obtained fortuitously where in reality no interrelation exists between the studied systems.

If, for instance, different reactions are studied with equipment that is suitable for a limited time range only, all reactions that can be investigated will automatically have a narrow range of $\Delta G^{\neq}$ values. If these reactions happen to have different $\Delta H^{\neq}$ values, $\Delta H^{\neq} - \Delta S^{\neq}$ correlations must necessarily result for completely unrelated processes.

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