Inorganica Chimica Acta, 53 (1981) L65–L68
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Ligand Substitution in Copper(II) Chelate Complexes: Mass-Law Retardation for the Solvent Path

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Received August 4, 1980

Introduction

In kinetic studies on ligand substitution the occurrence of mass-law retardation is taken as strong evidence for a dissociative type of mechanism [1]. As an example, a reduction in rate observed for reaction (1) upon addition of the leaving group A suggests strongly that the dissociation of MA according to (2) is rate controlling; A and B compete for the intermediate M.

$$MA + B \rightleftarrows MB + A \qquad (1)$$

$$MA \xrightarrow{\text{slow}} M + A \qquad (2)$$

Our recent studies [2] on the kinetics of ligand substitution in bis(N-alkylsalicylaldiminato)copper(II) complexes, MA_2, MB_2 ≙ $Cu(SA{=}N{-}R)_2$ have shown that the rate of reaction (3)

$$MA_2 + 2\,HB \rightleftarrows MB_2 + 2HA \qquad (3)$$

in methanol follows the simple rate law (4):

$$v = k_{obs}[MA_2] \qquad (4)$$

The experimental rate constant k_{obs} is independent of the ligand concentration but strongly solvent dependent. Therefore, (4) clearly describes a solvent path for ligand substitution and $k_{obs} = k_s$ [2b]. It is obvious that the conversion of MA_2 into MB_2 has to take place stepwise with the mixed ligand complex MAB as intermediate:

$$MA_2 + HB \rightleftharpoons MAB + Ha, K_1 \qquad (5)$$

$$MAB + HB \rightleftharpoons MB_2 + HA, K_2 \qquad (6)$$

Despite of that it was observed for MA_2 ≙ $Cu(Sa{=}N{-}tBu)_2$ ≙ bis(N-t-butylsalicylaldiminato)copper(II) and HB ≙ HSA=N–Et ≙ N-ethylsalicylaldimine under pseudo-first-order conditions ($[HSA{=}N{-}Et] \gg [Cu(SA{=}N{-}tBu)_2]$) in methanol that the conversion of MA_2 into MB_2 can be described completely and very accurately by just one exponential function [2b]. Hence, any slow consecutive reaction is ruled out and the conclusion is that the first step, $MA_2 \rightarrow MAB$, is slow compared to the second one, $MAB \rightarrow MB_2$.

The present study was undertaken to provide kinetic evidence for the nature of the rate controlling step in reaction (3), which was studied in the presence of additional amounts of the leaving ligand HA. This search for kinetic mass-law effects was carried out in methanol for the following 3 reactions:

I: $Cu(SA{=}N{-}tBu)_2 \rightarrow$
$Cu(SA{=}N{-}tBu)(SA{=}N{-}Et) \rightarrow Cu(SA{=}N{-}Et)_2$

II: $Cu(SA{=}N{-}tBu)_2 \rightarrow$
$Cu(SA{=}N{-}tBu)(SA{=}N{-}iPr) \rightarrow Cu(SA{=}N{-}iPr)_2$

III: $Cu(SA{=}N{-}iPr)_2 \rightarrow$
$Cu(SA{=}N{-}iPr)(SA{=}N{-}Et) \rightarrow Cu(SA{=}N{-}Et)_2$

Experimental

The solvent methanol (reagent grade, Merck, Darmstadt) was dried dynamically over 3 Å molecular sieves and had a final water content of 1.04×10^{-2} *M* (Karl-Fischer-titration).

The preparation of the various complexes and ligands for reactions I–III has been described previously [2b, 3] as well as the procedure for carrying out the kinetic measurements with a modified DURRUM D110 stopped-flow spectrophotometer [2b]. The reactions were monitored at 600 nm (reaction II and III) and at 540 nm (reaction I), where there is no absorption by the ligands. The studies were made under pseudo-first-order conditions ($[MA_2]_o \ll [HA]_o, [HB]_o$).

The least square fitting of k_{obs} to function (7) was done with a computer program [4]. Estimated values of k′, k″ and k‴ were obtained from experimental values of k_{obs} at very small and at very large values of x, respectively.

TABLE I. Rate Constants and Equilibrium Constants for Reactions I–III at 25 °C.

	Reaction Studied	k′ (s^{-1})	k″ (s^{-1})	k‴	k_{obs}[a] = k_s (s^{-1})	k″/k‴ (s^{-1})	$\log K_1$[b]	$\log K_2$[b]	log(k″/k′)
(I)	$Cu(SA{=}N{-}tBu)_2$ + HSA=N–Et	0.0079 ± 0.0013	4.3 ± 0.1	5.0 ± 0.1	0.95 ± 0.02	0.86	2.5	3.2	2.7
(II)	$Cu(SA{=}N{-}tBu)_2$ + HSA=N–iPr	0.051 ± 0.007	2.4 ± 0.1	2.8 ± 0.2	0.88 ± 0.06	0.86	1.5	2.2	1.7
(III)	$Cu(SA{=}N{-}iPr)_2$ + HSA=N–Et	0.012 ± 0.002	0.26 ± 0.02	2.2 ± 0.3	0.11 ± 0.01	0.12	1.5	1.0	1.3

[a] k_{obs} according to equation (4) in the absence of additional leaving ligand HA; $[HB]_o$ = 0.01–0.5 *M*. [b] From equilibrium studies [3].

TABLE II. k_{obs} for Reaction I Obtained in the Presence of Additional Leaving Ligand HSA=N–tBu at a Constant Ratio [HSA=N–Et]/[HSA=N–tBu] = 0.0033 [$(Cu(Sa{=}N{-}tBu]_2)$ = 5 × 10^{-5} *M*; T = 25 °C).

[HSA=N–tBu] (*M*)	[HSA=N–Et] (*M*)	k_{obs} (s^{-1})
0.15	0.0005	0.0213
0.15	0.0005	0.0216
0.30	0.0010	0.0214
0.45	0.0015	0.0221
0.60	0.0020	0.0206
0.60	0.0020	0.0215
		$\bar{k}_{obs} = (0.0214 \pm 0.05)^{-1}$

Results and Discussion

The rate constants k_s obtained under normal conditions (*i.e.*, without addition of the leaving ligand HA) are compiled in column 5 of Table I. In support of rate law (4) the condition $k_{obs}(I) = k_{obs}(II)$ is fulfilled within the limits of error. The complex $Cu(SA{=}N{-}iPr)_2$ (reaction III) reacts approx. 8 times slower than the t-butyl complex in I and II.

When the substitution of ligands in reaction I is studied in the presence of the leaving ligand HSA=N–tBu, the rate of substitution decreases. For a ratio of [HB]/[HA] = [HSA=N–Et]/[HSA=N–tBu] = 0.0033 the value of k_{obs} drops from 0.95 to 0.021 s^{-1}. It is interesting to see, however, that this decrease in rate does not follow the concentration of the leaving ligand [HA] as such, but obviously the ratio [HB]/[HA]. Table II demonstrates this very convincingly for a relatively wide range of concentrations.

Figure 1 proves that in all three reactions k_{obs} does indeed depend on the size of the ratio [HB]/[HA]. The double logarithmic plot of k_{obs} *vs.* $[HB]_o/[HA]_o$ results in S-shaped curves with limiting values for k_{obs} at small and at large values of the concentration ratio. The rate reducing effect of additional leaving ligand HA is most pronounced for the t-butyl complex $Cu(SA{=}N{-}tBu)_2$ reacting with the ethyl ligand HSA=N–Et (reaction I).

The dependencies shown in Fig. 1 follow the linear three parameter function (7) ($x \equiv [HB]_o/[HA]_o$):

$$k_{obs} = \frac{k' + k''\cdot x}{1 + k'''\cdot x} \tag{7}$$

Computer fitting of the data results in values for k′, k″, and k‴ which are compiled in Table I.

The observed mass-law retardation (7) is an indication of solvent induced dissociative steps being involved in reaction (3). As far as the rate controlling steps are concerned the following reaction scheme appears to be kinetically adequate (charges, solvation and

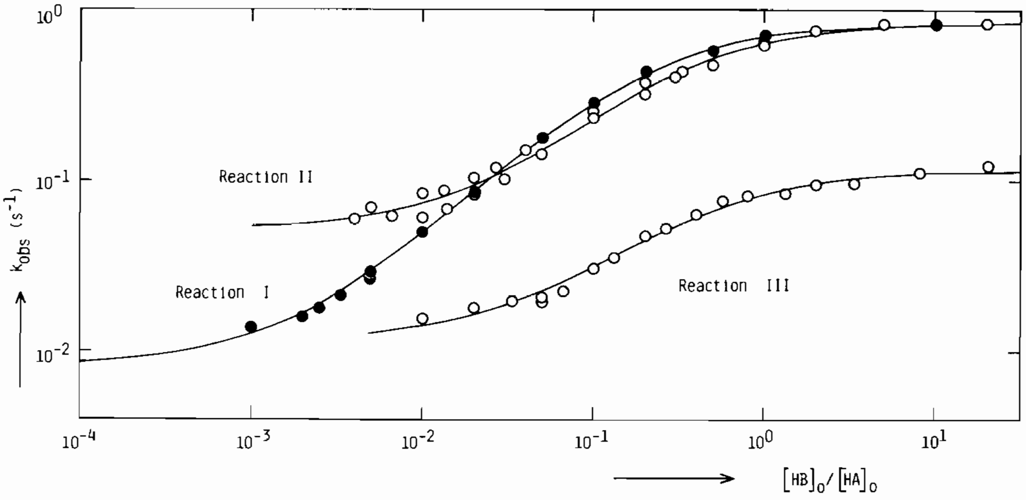


Fig. 1. Double logarithmic plot of k_{obs} *vs.* $[HB]_0/[HA]_0$ for Reactions I–III (solid lines: calculated by computer fitting).

proton balance are neglected; see discussion below):

$$MA_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MA + HA \tag{8}$$

$$MA + HB \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MAB \tag{9}$$

Assuming that k_1 is the slowest step of the forward reaction ($MA_2 \rightarrow MB_2$) and k_{-2} the slowest step of the reverse reaction ($MB_2 \rightarrow MA_2$), the overall rate of reaction (3) corresponds to the rate of the formation of MAB. On the basis of a steady state treatment for the species MA and the conditions $[MA_2]_o \ll [HA]_o$, $[HB]_o$, and $[MA_2]_o = [MA_2] + [MAB]$ eqn. (10) is obtained:

$$d[MAB]/dt = \alpha - \beta \cdot [MAB] \tag{10}$$

$$\alpha = \frac{k_1 \cdot k_2 [HB]_o [MA_2]_o}{k_{-1}[HA]_o + k_2 [HB]_o} \tag{11}$$

$$\beta = \frac{k_{-2} + (k_1 \cdot k_2/k_{-1})([HB]_o/[HA]_o)}{1 + (k_2/k_{-1})([HB]_o/[HA]_o)\ )} \tag{12}$$

The parameter β corresponds to the experimental rate constant k_{obs} and equation (12), in comparison with eqn. (7), leads to the following relations:

$$k' = k_{-2}; k''/k''' = k_1; k''/k''/k' = K_1 \tag{13}$$

For large values or small values of $[HB]_o/[HA]_o$ equation (12) reduces to $\beta = k_{obs} = k_1$ or to $\beta = k_{obs} = k_{-2}$. This implies that (*i*) for the upper limit the rate is determined by the dissociation of MA_2 and (*ii*) for the lower limit the rate of equilibration is given by the dissociation of MAB.

The data in Table I prove that the agreement between $k''/k''' = k_1$ (column 6) and $k_{obs} = k_1$ (column 5) is indeed good. On the other hand the ratio k''/k' (column 9) corresponds satisfyingly to K_1 (column 7), as determined with a relatively large error from equilibrium studies [3].

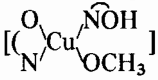
The fact that k_1 for $Cu(SA{=}N{-}tBu)_2$ is approx. 7 times greater than k_1 for $Cu(SA{=}N{-}iPr)_2$ parallels the smaller thermodynamic stability of the t-butyl complex [3] due to strong tetrahedral distortion [5]. As far as the reactivity of the three mixed ligand complexes MAB is concerned, it follows from the corresponding k_{-2} values (Table I), as obtained by extrapolating to $[HB]_o/[HA]_o \rightarrow 0$, that the complex $[Cu(SA{=}N{-}tBu)(SA{=}N{-}iPr)]$ tends to dissociate most easily, which again could be due to the degree of tetrahedral distortion.

The dissociation of MA_2 into MA + HA necessitates the transfer of a proton from a methanol molecule to the bidentate anion A^- to allow the formation of the very weak acid HA. Therefore, the species MA, postulated in (8) and (9), is supposedly a neutral species with four-coordinate copper(II), two of the coordination sites being occupied by the bidentate anion A^- ($\hat{=} N\ O^-$), one by a methoxide anion, CH_3O^-, and the fourth by methanol. The formation of MA by dissociation of MA_2 or MAB in methanol should therefore be described more properly by eqns. (8a) and (9a) instead of (8) and (9):

$$MA_2(solv.) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [MA(CH_3O)(CH_3OH)] + HA \tag{8a}$$

$$[MA(CH_3O)(CH_3OH)] + HB \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MAB\,(solv.) \tag{9a}$$

The methanolysis of MA_2 and MAB according to (8a) and (9a) and the coordination of the formed methoxide anion is not unusual since it is well known that upon heating of transition metal chelate complexes in alcohols alkoxide bridged solvolysis products are fomred [6].

The ligands A and B represent bidentate anions of the $\widehat{NO}^-$-type. One could argue, therefore, that possibly the 'dissociation' of MA_2 consists in the formation of a species containing one half bound chelate ligand, namely  $[(\genfrac{}{}{0pt}{}{O}{N})Cu(\genfrac{}{}{0pt}{}{\widehat{NO}H}{OCH_3})]$. If so, the addition of similar monodentate N-ligands such as N-t-butylbenzaldimine and N-ethylbenzaldimine should also produce rate effects for reaction (3). This is not the case, however [2b]. In contrast, when the corresponding 4-hydroxybenzaldimines are added instead of the leaving ligand, reaction (3) becomes slightly faster [2b].

Ligand substitution in square planar complexes of d^8-metals follows a two-term rate law. It is generally accepted that the rate controlling step of the ligand independent solvent path is the solvolysis of the complex, *i.e.*, the formation of the 'solvento' complex [7]. The present contribution gives strong support to this interpretation by demonstrating that in the reaction studied a solvento complex is formed and – as a consequence – mass-law retardation is observed. Interestingly enough, the reaction of the nickel complex $Ni(SA{=}N{-}tBu)_2$ with HSA=N–Et in methanol, for which only a solvent pathway according to (4) is observed, is also retarded by addition of the leaving ligand HSA=N–tBu. The reaction of $Ni(SA{=}N{-}iPr)_2$ with HSA=N–Et, however, which takes place predominantly through a ligand pathway $k_2[HSA{=}N{-}Et]\cdot[Ni(SA{=}N{-}iPr)_2]$, is not subject to mass-law retardation [8].

Acknowledgment

The authors thank the Deutsche Forschungsgemeinschaft and the Verband der Chemischen Industrie e.V. for support. Salicylaldehyde was kindly provided by Bayer AG, Leverkusen.

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