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Kinetics of Ligand Substitution in Bis(N-alkylsalicylideneiminato)copper(II) Complexes as Studied in Solvent Mixtures

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Stopped-flow spectrophotometry has been used to study the kinetics of ligand substitution in three bis(N-alkylsalicylideneiminato)copper(II) complexes $[Cu(Rsaln)_2]$ *(R = Et, Pr*^{i}*, and Bu*^{t}*) with N-ethylsalicylideneimine (H-Etsaln) in a variety of solvent mixtures, especially mixtures of methanol with protic, polar aprotic and non-polar aprotic co-solvents. The experimental conditions were such that the rate of substitution follows a simple rate law, namely rate = k[complex]. The observed dependence* $k = f(x_{MeOH})$ *(*$x_{MeOH} \equiv$ *mole fraction of methanol) can be mathematically described by power series for most of the solvent mixtures studied. The kinetic effects caused by the co-solvents and also activation parameters are discussed in terms of solvent-solvent and solvent-substrate interactions.*

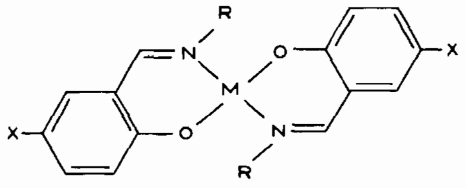
Introduction

The kinetics of ligand substitution in bis(N-alkylsalicylideneiminato)metal(II) complexes **I** by N-ethylsalicylideneimine according to (i) has been studied in our laboratory for M = Cu(II) and Ni(II) in a variety of protic and aprotic organic solvents [1–3].

$$M(Rsaln)_2 + 2H\text{-}Etsaln \rightleftharpoons M(Etsaln)_2 + 2H\text{-}Rsaln \qquad (i)$$

The observed rate law (ii) is made up of two terms, a ligand-independent 'solvent path' and a 'ligand path':

$$\text{rate} = (k_s + k_{H\text{-}Etsaln}[H\text{-}Etsaln])[M(Rsaln)_2] \qquad (ii)$$



I $\hat{=}$ ML_2 $\hat{=}$ $M(Rsaln)_2$

	R	X
(1) $[Cu(Bu^tsaln)_2]$	Bu^t	H
(2) $[Cu(Pr^isaln)_2]$	Pr^i	H
(3) $[Cu(Et\text{-}msaln)_2]$	Et	Me

For alcohol solvents k_s parallels fairly well the hydrogen bond donor properties of the alcohol as characterized by its $E_T(30)$-value [4]. Presumably the solvent attack occurs through hydrogen bond formation at the donor oxygen as the most basic site in the complex. Since the accessibility of the phenolic oxygen is greater in a tetrahedral than in a square-planar ligand arrangement the solvent path k_s grows upon increasing distortion of the substrate [2].

In solvent mixtures of 2-BuOH and MeOH there is a parallelism between the extent of solvation of a tetrahedral substrate such as (1) and the size of k_s, which is less pronounced for the pseudotetrahedral substrate (2) and for the square-planar substrate (3) [5]. For (2) and (3) adduct formation has to be considered. The conclusions which can be drawn from a comparison of kinetic data and $E_T(30)$-values obtained in solvent mixtures [6] are on the same line.

In the present contribution we report a more detailed study of kinetic solvent effects in organic solvent mixtures. Aliphatic alcohols differing in acidity and size of the alkyl group as well as aprotic solvents were mixed with methanol and these solvent mixtures were applied as media for reaction (i) with ML_2 being (1), (2), and (3). Special attention

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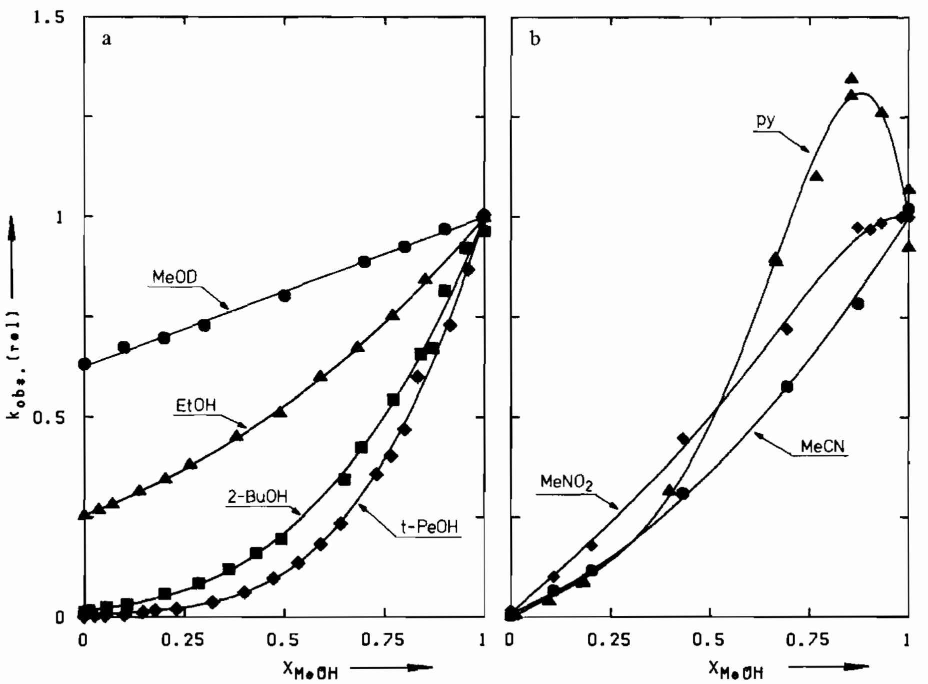

Fig. 1. The dependence of the relative rate constant k_{obs} (rel) $\equiv k_{obs}/k_{MeOH}$(calc) on the mole fraction x_{MeOH} for the reaction of the tetrahedral complex (1) with H-Etsaln according to (i) in mixtures of MeOH with alcohol co-solvents (see 1a) and with aprotic co-solvents (see 1b).

was given to the effects observed for the MeOH-rich part of the mixtures.

Experimental

The ligand H-Etsaln [1] and the complexes were prepared as described previously [1, 7]. Their purity was controlled by elemental analysis.

The solvents methanol (MeOH), propan-2-ol (2-PrOH), butan-2-ol (2-BuOH), 2,4-dimethylpentan-3-one (Pr^iCOPr^i), pyridine (py), toluene (PhMe) [all reagent grade; Merck, Darmstadt] and ethanol (EtOH) [reagent grade; Roth, Karlsruhe] as well as methanol-d_1 (MeOD) [99% D Merck, Darmstadt] and 2,2-dimethylpropan-1-ol (neo-PeOH) [reagent grade; EGA, Steinheim] were applied without further purification. Diisopropyl ether (Pr^iOPr^i) [reagent grade] and tert-butyl methyl ether (Bu^tOMe) [both Merck, Darmstadt] were stored over KOH and fractionated prior to use. 2-Methylbutan-2-ol (t-PeOH) [Merck, Darmstadt], 2,4-dimethylpentan-3-ol (2,4 Me_2-3-PeOH) [EGA], 3-ethylpentan-3-ol (3-Et-3-PeOH) [Fluka, Neu Ulm], decan-1-ol (1-DeOH) [Merck], acetonitrile (MeCN) [reagent grade, Merck], isobutyronitrile (2-PrCN) [Merck], pivalonitrile (Bu^tCN) [EGA], 2,2,2-trifluoroethanol [Merck], 2-(2-hydroxyethyl)pyridine [Merck], and 2-(hydroxymethyl)pyridine [Merck] were fractionated twice at reduced pressure over a 30-cm-Vigreux column. 2,6-Lutidine (Lut) [EGA] was dried with KOH and fractionated twice. All solvents were dried dynamically or statically with 3 or 4 Å molecular sieves. Their water content was controlled by automatic Karl-Fischer-titration ($[H_2O] = 10^{-3}$–10^{-2} *M*). 2-Hydroxypyridine [Merck] was recrystallized several times from a mixture of petroleum ether (b.p. <40 °C)/chloroform.

The kinetic measurements were carried out with a modified [1] DURRUM D110 stopped-flow spectrophotometer in the visible range under pseudo-first-order conditions ($[\text{complex}] \ll [\text{H-Etsaln}]$).

Results and Discussion

The substitution of the first ligand in the copper complexes (1)–(3) studied is rate determining, as it follows from the simple exponential decay of absorbance with time and from the fact that the change in absorbance observed covers the complete conversion $Cu(Rsaln)_2 \rightarrow Cu(Etsaln)_2$. The experimental rate law is given by (ii). In the present study the ligand concentration was kept low (mostly 0.04 *M*) so that the contribution of the ligand-dependent term in (ii) could be neglected, *i.e.*, $k_{obs} \equiv k_s$.

Reaction (i) requires the transfer of a proton from the incoming to the leaving ligand. In one of the two

TABLE I. Rate Coefficients a_i for the Description of the Dependence $k_{obs} = f(x_{MeOH})$ According to (iii) for Reaction (i) Studied with Complex (1) ([complex] = $5 \cdot 10^{-4}$ *M*) at 25 °C.

No.	Solvent Mixture	Rate Coefficients a_i/s^{-1}						Δx_{MeOH}[a]	k_{MeOH} (calc.)[b] s^{-1}	slope at $x_{MeOH} = 1$
		a_0	a_1	a_2	a_3	a_4	a_6			
1	MeOH/MeOD	0.6196	0.367					0–1	0.9866	0.367
2	MeOH/EtOH	0.2362	0.3634	0.2507	0.07695			0–1	0.9272	1.10
3	MeOH/2-BuOH	0.01595	0.09724	0.2531	0.5774			0–1	0.9435	2.34
4	MeOH/t-PeOH	0.0011	0.1483	−0.5402	1.3552			0–1	0.9614	3.13
5	MeOH/neo-PeOH		−2.087	7.223	−4.221			0.77–1	0.913	≈0
6	MeOH/2.4-Me_2-3-PeOH		6.620	−14.950	9.272			0.84–1	0.942	4.54
7	MeOH/3-Et-3-PeOH		−2.890	3.847				0.97–1	0.957	4.80
8	MeOH/1-DeOH		9.832	−21.505	12.59			0.87–1	0.922	4.59
9	MeOH/MeCN	0.00939	0.3824	0.5203				0–1	0.9121	1.42
10	MeOH/2-PrCN		−1.483	2.408				0.77–1	0.9252	3.33
11	MeOH/Bu^tCN		4.482	−10.096	6.553			0.80–1	0.9389	3.95
12	MeOH/Bu^tOMe		2.751	−6.839	5.027			0.82–1	0.9387	4.15
13	MeOH/Pr^iOPr^i		5.032	−11.914	7.826			0.84–1	0.9445	4.68
14	MeOH/Pr^iCOPr^i		−5.213	13.551	−7.422			0.84–1	0.9151	≈0
15	MeOH/PhMe	0.00529[d]	1.611	−2.2904	1.6420			0–1	0.9681	1.96
16	MeOH/$MeNO_2$	0.01056	0.8486	0.0515		0.7245	−0.6733	0–1	0.9622	≈0
17	MeOH/py	0.0018	0.4633	0.02561		4.325	−3.882	0–1	0.9293	−5.48
18	EtOH/CF_3CH_2OH	0.2344	0.772					0–0.71[c]	–	–

[a] Validity range. [b] k_{obs} calculated for $x_{MeOH} = 1$. [c] $\Delta x_{CF_3CH_2OH}$. [d] This value of a_0 does not correspond to a toluene induced solvent path [3].

TABLE II. Rate Coefficients b_i for the Description of the Dependence $k_{obs} = f(x_{MeOH})$ According to (iv) for Reaction (i) Studied with Complexes (2) and (3) at 25 °C ([complex] = $5 \cdot 10^{-4}$ *M*).

Complex	Solvent Mixture	Rate Coefficients b_i				Δx_{MeOH}[a]
		b_0	b_1	b_2	b_3	
(2)	MeOH/MeOD	−1.131	0.191			0–1
(2)	MeOH/2-BuOH	−2.932	2.238	−0.2632	25.862	0–1
(3)	MeOH/MeOD	−2.078	0.121			0–1
(3)	MeOH/EtOH	−2.877	1.096	−0.2037	3.543	0–1
(3)	MeOH/2-PrOH	−3.154	1.913	−0.7466	12.36	0–1
(3)	MeOH/2-BuOH	−3.006	2.607	−1.954	3.627	0–1
(3)	MeOH/t-PeOH	−3.247	3.007	−1.899	8.710	0–1

[a]Validity range.

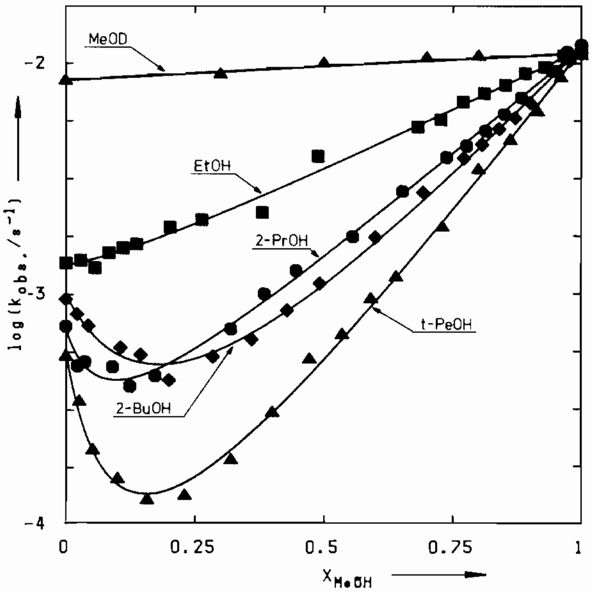

Fig. 2. The dependence of rate constant k_{obs} on the mole fraction x_{MeOH} for the reaction of the planar complex (3) with H-Etsaln according to (i) in mixtures of MeOH with alcohol co-solvents.

pathways described by rate equation (ii) this is accomplished by the direct bimolecular interaction of the weakly acidic entering ligand H-Etsaln with the complex (ligand path). Considering the ligand-independent contribution k_s, *i.e.*, the so-called solvent path, one has to differentiate between a variety of possible reaction initiating species, namely the solvent molecules as such, traces of water, solvated protons, or any other protic trace impurities present in the organic solvent. It has been shown recently [3] that the effect of water can be suppressed by addition of suitable catcher molecules. On the other hand one can never be sure with organic solvents to have eliminated all reactive impurities, and the role of solvated protons in reactions such as (i) can hardly be overestimated.

Substitution in complexes (1)–(3) according to (i) was followed in a variety of solvent mixtures. The dependence $k_{obs} \equiv k_s = f(x_{MeOH})$ observed (x_{MeOH} = mole fraction of MeOH) was in most cases non-ideal, *i.e.*, non-linear. The data obtained were therefore fitted to a power series of the general form (iii) by a least squares procedure.

$$k_{obs} = a_o + a_1 x_{MeOH} + a_2 x^2_{MeOH} + \cdots = \sum_{i=0}^{n} a_i x^i_{MeOH} \qquad \text{(iii)}$$

For the majority of the systems studied 3 or 4 terms in (iii) were sufficient for a proper description of the function $k_s = f(x_{MeOH})$.

Table I presents the fitting parameters a_i for the k_{obs} values obtained upon reacting the tetrahedral copper complex (1) with H-Etsaln according to (i) in 18 different solvent mixtures. In those cases where the validity range extends to $x_{MeOH} = 0$ the coefficient a_o corresponds to the rate constant k_s for the pure co-solvent mixed with MeOH.

Figure 1 gives some examples of the type of curvature observed for alcohol mixtures 1–4 (Fig. 1a) and for mixtures of MeOH with aprotic solvents such as acetonitrile (No. 9), nitromethane (No. 16), and pyridine (No. 17) (Fig. 1b). The mixture MeOH/MeOD (No. 1) is the only one for which a linear dependence of k_{obs} on x_{MeOH} is observed. When pyridine is admixed to MeOH (mixture No. 17) k_{obs} passes even through a maximum at $x_{MeOH} \approx 0.85$. The difference between k_{MeOH} and $k_{co\text{-}solvent}$, which in some cases is rather drastic, has been dealt with earlier [1].

The function $k_{obs} = f(x_{MeOH})$ clearly depends on the stereochemical properties of the substrate CuL_2. So, the curve obtained with the tetrahedral complex (1) $\hat{=}$ $Cu(Bu^tsaln)_2$ in a mixture of MeOH

TABLE III. Rate Coefficients a_i for the Description of the Dependence $k_{obs} = f(x_{MeOH})$ According to (iii) for Reaction (i) Studied with Complexes (1)–(3) (at $5 \cdot 10^{-4}$ *M*).

Complex	Solvent mixture	Rate Coefficients a_i/s^{-1}					Δx_{MeOH}[a]	k_{MeOH} (calc)[b]/s^{-1}
		a_1	a_2	a_3	a_4	a_6		
(1)	MeOH/py	−13.266	34.195	−19.834			0.77–1	1.095
(2)	MeOH/py	−4.896	13.311	−8.285			0.75–1	0.130
(3)	MeOH/py	−1.369	3.364	−1.983			0.78–1	0.0121
(1)	MeOH/Lut[c]				0.1954	0.7373	0.81–1	0.933
(2)	MeOH/Lut[c]				−0.0592	0.1830	0.81–1	0.124
(3)	MeOH/Lut[c]				−0.00421	0.01553	0.78–1	0.0113

[a] Validity range. [b] k_{obs} calculated for $x_{MeOH} = 1$. [c] Lut ≡ 2,6-dimethylpyridine.

and t-PeOH (see Fig. 1a) differs significantly from the one obtained with the planar complex (3) ≙ Cu(Et-msaln)$_2$] in the same mixture (see Fig. 2). As a matter of fact, the k_{obs} data obtained for complexes (2) and (3) reacting according to (i) appear to be more properly described by equation (iv) instead of (iii):

$$\log k_{obs} = b_o + b_1 x_{MeOH} + \frac{b_2 b_3 x_{MeOH}}{1 + b_3 x_{MeOH}} \qquad \text{(iv)}$$

Again, b_o corresponds to log k_{ROH} for the pure co-solvent ROH admixed to MeOH, *i.e.*, for $x_{MeOH} = 0$.

The results obtained for the alcohol mixtures MeOH/ROH (see Tables I and II) can be best interpreted by taking into account the proton acceptor and donor properties of the two components of the mixture, the internal structure of the bulk solvents and the size and structure of the hydrophobic group R in the alcohols ROH. The linear increase in k_{obs} observed for MeOH/MeOD mixtures is due to the greater proton acidity of MeOH only. The limiting slope at $x_{MeOH} = 0$ drops in the series MeOH > EtOH > 2-BuOH > t-PeOH and appears to be paralleled by increasing proton acceptor properties of the co-solvent ROH according to (v):

$$MeOH_2^+ + ROH \rightleftharpoons MeOH + ROH_2^+ \qquad \text{(v)}$$

On the other hand, at $x_{MeOH} \rightarrow 1$ the limiting slope *increases* in the same order, *i.e.*, the curves become steeper. This means that even small amounts of the co-solvent ROH admixed to methanol cause a significant decrease in rate, presumably by occupying solvated protons $MeOH_2^+$ according to (v). If only solvent structure were to be responsible for the decrease in rate, one would expect ideal behaviour around $x_{MeOH} \approx 1$. The linear dependence of k_{obs} on $x_{CF_3CH_2OH}$ observed for the solvent mixture EtOH/CF$_3$CH$_2$OH (No. 18) is in agreement with this interpretation.

Table I also presents some data on solvent mixtures with alcohols ROH carrying branched alkyl groups R. As far as the slope of the curves on the methanol-rich side is concerned, β-branching (such as in neo-PeOH, No. 5) has no effect, whereas α-branching (such as in 2-BuOH, t-PeOH) makes the curves rather steep. This is especially true for diisopropylcarbinol (No. 6) and triethylcarbinol (No. 7). The finding that the primary alcohol 1-decanol (No. 8) is as effective as the α-branched alcohols is surprising and points to the important role played by the nature of R and its effect on solvent structure.

Running reaction (i) with the planar copper complex (3) instead of (1), the tetrahedral one, leads to minima in rate at $x_{MeOH} \approx 0.2$ for mixtures with the α-branched alcohols 2-PrOH, 2-BuOH, and especially t-PeOH (see Fig. 2 and Table II). The planar complex (3) is the stronger Lewis acid as compared to its tetrahedral analogue (1), possibly explaining why the interaction between the solvent and complex (3), *i.e.*, its solvation, is more sensitive to changes in solvent composition and hence in solvent structure.

When aprotic solvents such as acetonitrile and nitromethane are mixed with MeOH, the rate constant k_{obs} for the reaction of complex (1) according to (i) varies almost linearly with x_{MeOH} (see Fig. 1b). Admixing of pyridine, however, creates a distinct maximum at $x_{MeOH} \approx 0.85$, which is not readily understood and which probably has to be associated with the good hydrogen bond acceptor properties of this solvent. Nitriles and ethers (see mixtures No. 10 + 11 and 12 + 13 respectively in Table I) are very effective in reducing the rate even at small concentrations, whereas diisopropyl ketone (No. 14, see Table I) I) causes no great change in k_{obs} around $x_{MeOH} \approx 1$.

The solvent mixture MeOH/toluene (No. 15, see Table I) is interesting in the sense that the aprotic and almost non-polar component toluene obviously interacts only slightly with the methanol, since

TABLE IV. Rate Constants for Ligand Substitution in Complex (1) by H-Etsaln According to (i) as Studied in Pyridine at 25 °C in the Presence of Biphilic Compounds.[a]

Compound admixed	[compound]·10^4/M	$k_{obs}\cdot 10^2/s^{-1}$	$k_{ad}/M^{-1}\cdot s^{-1}$
2-Hydroxypyridine	0	2.07	84.9 ± 1.3
	0.5	2.37	
	2.5	3.92	
	5.0	6.07	
	12.5	12.6	
2-Hydroxymethylpyridine	0.5	0.868	2.8 ± 1.2
	2.5	0.878	
	5.0	0.917	
	7.5	1.17	
	10	1.05	
2-(2-Hydroxyethyl)pyridine	0.5	0.839	<0.1
	2.5	0.802	
	5.0	0.820	
	7.5	0.713	
	10	0.697	
	12.5	0.726	
	25	0.771	
	50	0.816	
	100	0.827	

[a] [complex] = $5\cdot 10^{-4}$ M, [H-Etsaln] = 0.5 M, [H_2O] = 0.003–0.01 M.

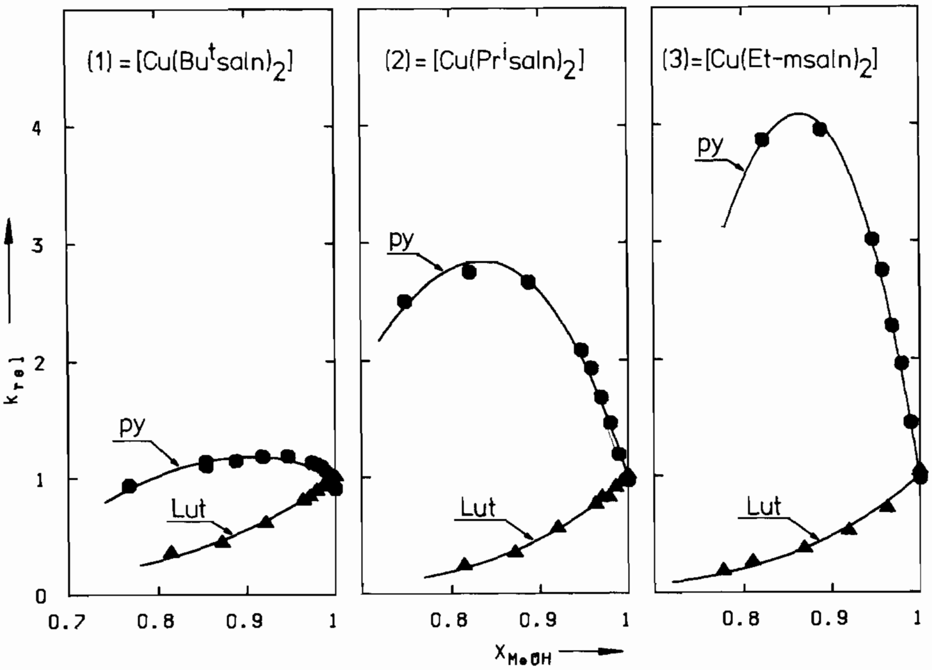

Fig. 3. The relative rate constant $k_{rel} \equiv k_{obs}/k_{MeOH}$ plotted *vs.* mole fraction of MeOH for complexes (1)–(3) reacting according to (i) in mixtures MeOH/py and MeOH/Lut (Lut ≡ 2,6-dimethylpyridine).

k_{obs} decreases almost linearly with decreasing x_{MeOH} values (interesting additional information comes from the mixture toluene/pyridine, in which from $x_{py} \geqslant 0.1$ on k_{obs} remains constant and corresponds to the k_{obs} value obtained in pure pyridine [3]).

The above mentioned solvent mixture MeOH/py (No. 17, see Table I) was studied in further detail

TABLE V. Activation Parameters for Reaction (i) as Studied with Complex (1)[a] in the Solvent Mixtures Methanol/Pyridine, Methanol/Toluene, and Methanol/Acetonitrile.

Solvent Mixture	x_{MeOH}	[MeOH]/M	$-\delta\Delta H^\ddagger$/(kJ/mol)	$-T\delta\Delta S^\ddagger$/(kJ/mol)	$\delta\Delta G^\ddagger$/(kJ/mol)
MeOH/py	0	0	19.1 ± 2.1	31.7 ± 2.1	13.0
	0.095	1.23	5.9 ± 2.1	13.4 ± 2.1	7.9
	0.181	2.46	4.8 ± 2.6	10.7 ± 2.5	6.1
	0.398	6.15	7.3 ± 2.9	10.0 ± 2.8	3.0
	0.665	12.3	11.2 ± 2.1	11.3 ± 2.1	−0.1
	0.768	15.4	5.5 ± 3.4	5.2 ± 3.3	0.2
	0.855	18.45	9.3 ± 2.2	8.5 ± 2.1	−0.5
	0.933	21.5	7.1 ± 1.8	6.2 ± 1.8	−0.6
	1	24.6	0 ± 2.6[b]	0 ± 2.5[c]	0.3
MeOH/MeCN	0	0	15.4 ± 3.0	26.8 ± 2.9	10.1
	0.1072	1.23	11.6 ± 2.1	18.3 ± 2.0	7.1
	0.2023	2.46	5.1 ± 1.4	10.5 ± 1.4	5.7
	0.4320	6.15	4.5 ± 1.3	7.6 ± 1.3	3.3
	0.6953	12.3	1.3 ± 1.1	2.8 ± 1.1	1.8
	0.8731	18.45	1.0 ± 1.6	1.8 ± 1.6	0.8
	1	24.6	0 ± 1.5[b]	0 ± 1.5[c]	0.3
MeOH/PhMe	0	0	19.3 ± 1.6	30.9 ± 1.5	12.6
	0.0129	0.123	20.2 ± 2.5	29.7 ± 2.4	9.6
	0.0628	0.615	13.0 ± 1.1	18.5 ± 1.0	5.7
	0.121	1.23	5.9 ± 1.1	10.2 ± 1.0	4.4
	0.225	2.46	3.2 ± 0.8	6.4 ± 0.8	3.3
	0.466	6.15	2.6 ± 1.5	4.6 ± 1.5	2.1
			1.4 ± 1.1	3.5 ± 1.1	2.1
	0.723	12.3	−4.9 ± 1.5	−3.4 ±1.5	1.3
			−2.0 ± 1.7	−0.7 ± 1.7	1.3
	0.887	18.45	−2.1 ± 1.5	−1.5 ± 1.5	0.6
			−2.0 ± 0.9	−1.3 ± 0.8	0.6
	1.0	24.6	0 ± 0.7[b]	0 ± 0.7[c]	0
			0.7 ± 2.0	0.7 ± 2.1	0

[a] [complex] = $5 \cdot 10^{-4}$ *M*; [H-Etsaln] = 0.04 *M*; ΔT = 25–50 °C; [b] $\Delta H^\ddagger$ = 60.7 kJ mol^{-1} for $X_{MeOH} = 1$; [c] $T\Delta S^\ddagger = -12.5$ kJ mol^{-1} for $X_{MeOH} = 1$.

because of the maximun in k_{obs} observed for complex (1) reacting with H-Etsaln. The results are compiled in Table III. It turns out that for complexes (2) and (3) the maximum in k_{obs} becomes even more pronounced. In Fig. 3 the relative change in rate (as compared to pure MeOH) is plotted as $k_{rel} = k_{obs}/k_{MeOH} = f(x_{MeOH})$ for the MeOH-rich side of the MeOH/py mixtures. The more planar the complex is, the more the rate of substitution according to (i) is enhanced upon admixing pyridine at a mole fraction of approximately 0.1–0.2. This is explained best by assuming Lewis acid/base interactions between pyridine and the substrates (1)–(3), among which (3) is the strongest Lewis acid. This interpretation is supported by the finding (see Fig. 3) that addition of the sterically hindered base 2,6-dimethylpyridine has no such effect.

Further evidence for the participation of bases such as pyridine in substitution reaction (i) comes from the results obtained for the system complex (1)/H-Etsaln/py in the presence of 'biphilic' partners such as 2-hydroxypyridine, 2-hydroxymethylpyridine and 2-(2-hydroxyethyl)pyridine (see Table IV). In the concentration range studied the rate increases linearly with the concentration of the compounds admixed, so that $k_{obs} = k_s + k_{ad}$[compound]. The values obtained for the bimolecular rate constant k_{ad} follow the order:

2-(2-hydroxyethyl)pyridine < 2-hydroxymethylpyridine < 2-hydroxypyridine

This order follows the proton acidity of the compounds and can be taken as a strong indication for both the pyridine nitrogen and the hydroxylic hydrogen or proton being cooperatively involved in the reaction.

Measuring of the temperature dependence of reaction (i) for complex (1) led to the activation parameters $\delta\Delta H^\ddagger$ and $\delta\Delta S^\ddagger$ listed in Table V for the mixtures MeOH/py, MeOH/PhMe, and MeOH/MeCN. It has been found [5] for mixtures of MeOH and 2-BuOH that the observed variation in $\delta\Delta G^{\ddagger}$ is fully determined by a corresponding variation in $\delta\Delta H^{\ddagger}$. This is not so for the mixtures of MeOH with the aprotic solvents pyridine, acetonitrile, and toluene. Here the parameters $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$ change simultaneously, large entropy effects partly being compensated by changes in enthalpy. So, this again reflects the different type of interaction existing in mixtures MeOH/ROH and in mixtures MeOH/aprotic solvent.

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