complexes, and it seems relevant to discuss some of them here.

The infrared spectrum of $[Ru(bpy)_2(Cl)N(O)OC_2H_5]^{2+}$ includes bands assignable to ν(NO) and ν(O-R) modes at $\sim$1500 cm^{-1} (partially hidden by bpy ligand bands) and 930 cm^{-1}, respectively. The shift of the MLCT band to lower energy (λ_{max} = 417 nm) for $[Ru(bpy)_2(Cl)N(O)OC_2H_5]^+$ compared to the pyridyl complex is consistent with the effect of a chloro group compared to a back-bonding pyridyl ligand. The effect is also seen in the much lower potential for oxidation of Ru(II) to Ru(III) as seen by cyclic voltammetry ($E_{p,a}$ = +1.24 V). Exhaustive electrolysis of an acetonitrile solution containing $[Ru(bpy)_2(Cl)N(O)OC_2H_5]^+$ at 1.3 V gave an n value of 0.9. The only product observed by cyclic voltammetry was $[Ru(bpy)_2(Cl)NO]^{2+}$, and the competitive solvation reaction shown in the scheme for the pyridyl complexes must be slow, at least in a relative sense, for the chloro complexes. The Ru product and n value close to 1.0 suggest that the oxidative chemistry of $[Ru(bpy)_2(Cl)N(O)OC_2H_5]^+$ is similar to that found for the analogous pyridyl complex.

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Registry No. $[Ru(bpy)(py)N(O)OCH_3](PF_6)_2$, 72709-12-7; $[Ru(bpy)(py)N(O)OC_2H_5](PF_6)_2$, 72709-10-5; $[Ru(bpy)(py)N(O)O\text{-}n\text{-}C_4H_9](PF_6)_2$, 72709-08-1; $[Ru(bpy)(py)N(O)O\text{-}i\text{-}C_3H_7](PF_6)_2$, 72709-06-9; $[Ru(bpy)_2(Cl)N(O)OC_2H_5]^+$, 72709-04-7; $[Ru(bpy)_2(Cl)N(O)O\text{-}i\text{-}C_3H_7]^+$, 72709-03-6; $[Ru(bpy)_2(Cl)NO](PF_6)_2$, 29102-12-3; $[Ru(bpy)_2(py)NO](PF_6)_3$, 29241-00-7.

Contribution from Anorganische Chemie III,
Eduard-Zintl-Institut der Technischen Hochschule Darmstadt, D-6100 Darmstadt, Federal Republic of Germany

Kinetics of Ligand Substitution in Bis(*N*-*tert*-butylsalicylaldiminato)copper(II) in Various Alcoholic Media: Mechanism of the Solvent Path

HORST ELIAS,* UWE FRÖHN, ARVED VON IRMER, and KLAUS J. WANNOWIUS*

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Stopped-flow spectrophotometry has been used to investigate the kinetics of ligand substitution in bis(*N*-*tert*-butylsalicylaldiminato)copper(II) (Cu(SA=*N*-*t*-Bu)$_2$) with *N*-ethylsalicylaldimine (HSA=*N*-Et) in various alcohols (ROH) according to Cu(SA=*N*-*t*-Bu)$_2$ + 2HSA=*N*-Et $\rightleftharpoons$ Cu(SA=*N*-Et)$_2$ + 2HSA=*N*-*t*-Bu (K_{298} = 1.7 × 10^5 in MeOH). The rate of ligand substitution follows a two-term rate law, namely, rate = (k_{ROH}[ROH] + $k_{HSA=N\text{-}Et}$[HSA=*N*-Et])[Cu(SA=*N*-*t*-Bu)$_2$], although for most alcohols the ligand path $k_{HSA=N\text{-}Et}$[HSA=*N*-Et] cannot compete with the solvent path k_{ROH}[ROH]. In the presence of water an additional linear term contributes, namely, k_{H_2O}[H_2O][Cu(SA=*N*-*t*-Bu)$_2$]. It is concluded from spectrophotometric equilibrium studies that the mechanism of the solvent path is made up of the following steps: (i) fast equilibrium Cu(SA=*N*-*t*-Bu)$_2$ + ROH $\rightleftharpoons$ Cu(SA=*N*-*t*-Bu)$_2$·ROH; (ii) fast proton transfer from bound ROH to the phenolic oxygen of the coordinated *tert*-butyl ligand; (iii) rearrangement in the coordination sphere with breaking of the Cu-OH(ligand) bond; and (iv) stepwise but fast substitution of the two-*tert*-butyl ligands by the ethyl ligands. Rearrangement step (iii) is presumably rate determining. It follows from the kinetic data that the intermediate Cu(SA=*N*-*t*-Bu, SA=*N*-Et) reacts faster than Cu(SA=*N*-*t*-Bu)$_2$. The observed order in k_{ROH} is MeOH > EtOH > 1-PrOH ≈ 1-BuOH > 2-Me-1-PrOH > 2-PrOH > 2-BuOH > 2-Me-2-PrOH > 2-Me-2-BuOH for the nonsubstituted alcohols ROH, whereas for substituted alcohols the differences in k_{ROH} are small. Attempts to correlate k_{ROH} with solvent parameters like fluidity, heat of vaporization, dielectric constant, pK^a_{ROH}, and σ_R*(Taft) are described. For Me_2SO/ROH mixtures the correlation of $k^{Me_2SO}_{ROH} \sim K^{Me_2SO}_{ROH}$ is very satisfying ($K^{Me_2SO}_{ROH}$ = acid dissociation constant of ROH in Me_2SO). It follows, therefore, that the acidity of the coordinated ROH molecules is kinetically significant. The ligand path $k_{HSA=N\text{-}Et}$[HSA=*N*-Et] can be described as a bimolecular reaction between Cu(SA=*N*-*t*-Bu)$_2$ and HSA=*N*-Et. Activation parameters as determined with a commercial stopped flow apparatus are critically analyzed and compared to those obtained with a properly thermostated device.

Introduction

In a previous contribution we reported[1] that ligand substitution in copper(II) salicylaldimines as studied by isotopic exchange in toluene follows a two-term law with $k_{obsd} = k_S + k_{ligand}$[ligand] and resembles that observed for square-planar complexes. It was shown, however, that the apparent solvent path k_S is due to residual water and that it can only be described by $k_S = k_{H_2O}$[H_2O]. Hence, the coordinating properties of the nonpolar aprotic solvent toluene are obviously not sufficiently strong to initiate a solvent path.

The solvent path in classical square-planar substitution reactions has been studied predominantly in water, although there are data also with methanol as solvent.[2] It appeared very promising to us to extend the measurements on ligand substitution in copper(II) salicylaldimines by introducing a greater variety of solvents ranging from aprotic nonpolar ones like toluene to protic polar and aprotic polar ones like methanol and Me_2SO, respectively. This extension of the measurements aims, of course, at the collection of data which might allow a stepwise extrapolation of solvent rate constants k_S from nonreacting media like toluene and from moderately reacting ones to finally water as the most widely applied solvent. Since the complex under study is a copper(II) chelate system, other interesting aspects are additionally involved such as the formation and chemical nature of "solvento" intermediates with partially bonded chelate ligands and the question of how fast four-coordinate copper(II) complexes react in water-like media such as methanol as compared to the extremely fast reacting Cu^{2+} ions in water.

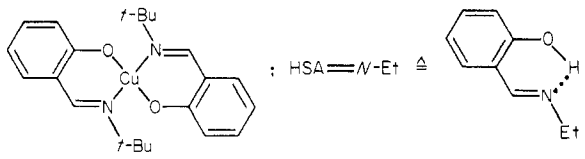
In the present contribution we present kinetic data obtained by stopped-flow measurements on the ligand substitution of complex I according to

Cu(SA=*N*-*t*-Bu)$_2$ + 2HSA=*N*-Et $\rightleftharpoons$
Cu(SA=*N*-Et)$_2$ + 2HSA=*N*-*t*-Bu

(1) Voss, H.,; Wannowius, K. J.; Elias, H. *Inorg. Chem.* **1979**, *18*, 1454.
(2) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967.

0020-1669/80/1319-0869$01.00/0

I ≙ Cu(SA=*N*-*t*-Bu)$_2$ ≙



Fourteen aliphatic alcohols, ROH, differing in the size and structure of R, were used as solvent.

Experimental Section

Ligands and Complexes. Bis(*N*-*tert*-butylsalicylaldiminato)copper(II) was prepared as described earlier;[3] mp 188 °C. Anal. Calcd: C, 63.52; H, 6.78; N, 6.73. Found: C, 63.08; H, 6.79; N, 6.68.

N-Ethylsalicylaldimine was prepared by adding 0.15 mol of ethylamine to a solution of 0.1 mol of salicylaldehyde in 300 mL of ethanol. The solvent was evaporated in vacuo. The residual yellow oil was dissolved in dichlormethane and dried over Na_2SO_4. The solvent was evaporated in vacuo, and the product was fractionated at reduced pressure in a 30-cm Vigreux column: yellow oil, bp 128 °C (15 mmHg) (lit. 129 °C (20 mmHg)[4]). Anal. Calcd: C, 72.46; H, 7.46; N, 9.39. Found: C, 72.48; H, 7.48; N, 9.13.

N-Ethyl-4-hydroxybenzaldimine (II), *N*-*tert*-butyl-4-hydroxybenzaldimine (III), *N*-ethylbenzaldimine (IV), and *N*-*tert*-butylbenzaldimine (V) were synthesized by the following method: to a solution of the aldehyde in ethanol the appropriate amine (20% excess; dissolved in ethanol) was added dropwise. The mixture was refluxed for 1 h and the solvent evaporated in vacuo. Compounds II and III were recrystallized twice from ethanol. II: yellow crystals, mp 113–115 °C. Anal. Calcd: C, 72.46; H, 7.43; N, 9.39. Found: C, 72.51; H, 7.48; N, 9.23. III: yellowish crystals, dec pt 170 °C. Anal. Calcd: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.38; H, 8.61; N, 7.76. Compounds IV and V were fractionated in a 30-cm Vigreux column at reduced pressure. IV: yellowish oil, bp 72–74 °C (6 mmHg) (lit. 73–74 °C (9–10 mmHg)[5]). V: yellowish oil, bp 81 °C (6 mmHg) (lit. 90–92 °C (11 mmHg)[6]).

Solvents. Methanol, methanol-d_1, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, benzyl alcohol, and ethylene glycol monomethyl ether (all reagent grade, Merck, Darmstadt) were dried dynamically over 3- or 4-Å molecular sieves. 2-Methyl-2-butanol, 2-phenylethanol, 2-chloroethanol, 2-hydroxypropionitrile, and *m*-cresol were fractionated (at least twice) in a 30-cm Vigreux column at reduced pressure prior to drying with molecular sieves. Dimethyl sulfoxide (reagent grade, Merck, Darmstadt) was fractionated three times at reduced pressure in a 30-cm Vigreux column and then dried over 3-Å molecular sieves. The water content of the solvents was determined by automatic Karl-Fischer titration (Methrom, Herisau). The results are given in Tables II and III. Since Me_2SO is very hygroscopic,[7] its water content was determined after each kinetic run.

Kinetic Measurements. The kinetic measurements were done with a Durrum D110 stopped-flow spectrophotometer in combination with an Aminco-DASAR storage oscilloscope. It turns out that the Durrum system is not properly suited for measurements with solvents of low viscosity. Furthermore, the temperature within the cuvette cannot be controlled, and there is a considerable temperature gradient between the drive syringes and the cuvette for temperatures deviating from room temperature by more than 5 °C. This temperature gradient causes artifacts with a duration of approximately 1 s superimposing on the kinetic signals. Therefore, the mechanical part of the commercial device had to be reconstructed.

Hamilton gastight syringes (5.000 μL) were used as drive and stop syringes. All connections were made with PTFE tubes and fittings. Thermostating was achieved by bedding the cuvette and the drive syringes into an aluminum plate and by putting the latter between two aluminum plates through which thermostating water was circulating in many channels. This construction allowed control of the temperature in the cuvette near the mixing chamber and at the two ends of the drive syringes with a thermocouple. After thermostating no temperature gradient could be detected.

Pressure artifacts caused by the pressure drop immediately after operation of the pneumatic cylinder are greater in size in organic solvents than in water. Depending on the time scale necessary for the observation of a reaction, these artifacts can be shifted to time periods that are lying before or after the observation time. The shifting is done with a variable time switch for the magnetic valve controlling the operation of the pneumatic cylinder. A further advantage of this new device is that any contact between water and the nonaqueous solutions in the syringes is made impossible.

The kinetic runs were done under pseudo-first-order conditions (at least 20-fold excess of ligand over complex). The change in absorbance was followed at a wavelength in the 575–625-nm range. Only such runs which could be reproduced at least twice were evaluated with a computer program. A total of 200 data points were fitted to an exponential function using the least-squares method. In all cases the deviations from ideal first-order kinetics were much smaller than 1%.

Equilibrium Constants. The equilibrium constants were determined by absorption spectrophotometry and evaluated with a computer program described previously.[8]

Table I. Equilibrium Constants for Adduct Formation with Pyridine[a] and Methanol According to Equations 3 and 4

complex	K_{py}^{298}, M^{-1}	K_{MeOH}^{293}, M^{-1}
Cu(SA=*N*-*t*-Et)$_2$	0.54 ± 0.023	0.17 ± 0.03
Cu(SA=*N*-*t*-Bu)$_2$	0.31 ± 0.089	0.24 ± 0.05

[a] Ewert, A.; Wannowius, K. J.; Elias, H. *Inorg. Chem.* **1978**, *17*, 1691.

Results and Discussion

Properties of the Complexes in Solution. X-ray diffraction studies[9] have shown that the bis(salicylaldiminato)copper(II) complexes possess coordination geometries that range between nearly planar and almost tetrahedral depending on the N-alkyl group R. The pseudotetrahedral distortion is reflected in a red shift of the dd bands in the reflectance spectra of crystalline samples.[10] The same behavior is found in solution (toluene, chloroform), where the ligand field bands are shifted to longer wavelengths in the series Cu(SA=*N*-Et)$_2$ < Cu(SA=*N*-*i*-Pr)$_2$ < Cu(SA=*N*-*t*-Bu)$_2$ as a result of increasing pseudotetrahedral distortion.

The internal strain within the complexes with branched N-alkyl groups is also reflected in the overall equilibrium constants K_{298} for the ligand substitution reactions (eq 1 and 2). In methanol as solvent the equilibrium constants have

Cu(SA=*N*-*t*-Bu)$_2$ +

2HSA=*N*-Et $\overset{K_1}{\rightleftharpoons}$ Cu(SA=*N*-*t*-Bu,SA=*N*-Et) +

HSA=*N*-Et + HSA=*N*-*t*-Bu $\overset{K_2}{\rightleftharpoons}$ Cu(SA=*N*-Et)$_2$ + 2HSA=*N*-*t*-Bu (1)

Cu(SA=*N*-*i*-Pr)$_2$ +

2HSA=*N*-Et $\overset{K_1}{\rightleftharpoons}$ Cu(SA=*N*-*i*-Pr,SA=*N*-Et) +

HSA=*N*-Et + HSA=*N*-*i*-Pr $\overset{K_2}{\rightleftharpoons}$ Cu(SA=*N*-Et)$_2$ + 2HSA=*N*-*i*-Pr (2)

been determined spectrophotometrically:[11] $K_{298} = K_1K_2 = (2.9 \times 10^2)(1.5 \times 10^3) = (4.4 \pm 0.8) \times 10^5$ for reaction 1 and $K_{298} = K_1K_2 = 34 \times 9.1 = 310 \pm 90$ for reaction 2. The corresponding changes in the free enthalpy $\Delta G°_{298}$ are −32 kJ/mol and −14 kJ/mol for reactions 1 and 2, respectively.

If one assumes that the contributions of the free ligands to the free energy change cancel each other, the $\Delta G°_{298}$ values can be taken as a rough measure for the internal strain within

(3) Voss, H.; Wannowius, K. J.; Elias, H. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1404.
(4) *Beilstein, 3rd Suppl.*, **1969**, *8*, 150.
(5) Maginnity, P. M. *J. Am. Chem. Soc.* **1951**, *73*, 49.
(6) Emmons, W. D. *J. Am. Chem. Soc.* **1957**, *79*, 5739.
(7) Riddick, J. A.; Bunger, W. A. *Tech. Chem. (N.Y.)* **1970**, *2*.
(8) Ewert, A.; Wannowius, K. J.; Elias, H. *Inorg. Chem.* **1978**, *17*, 1691.
(9) Holm, R. H.; O'Connor, M. J. *Prog. Inorg. Chem.* **1971**, *14*, 241.
(10) Sacconi, L.; Ciampolini, M. *J. Chem. Soc.* **1964**, 276.
(11) Reiffer, U.; Schumann, M.; Wannowius, K. J., Elias, H. *Transition Met. Chem.*, in press.

Table II. Ligand Substitution According to Equation 1 as Studied in Nonsubstituted Alcohols at 298 K

no.	solvent	k', s^{-1}	$10^2 k_{ROH}$, M^{-1} s^{-1}	$10^2 k_{H_2O}$, M^{-1} s^{-1}	$10^2 k_{HSA=N\text{-}Et}$, M^{-1} s^{-1}	σ^* [c]	$1/\epsilon$ [b]	$10^3 \times$ [H_2O], [f] M
1	MeOH	1.03 ± 0.024	4.2 ± 0.10	9.5 ± 0.48	*e*	0.000	0.0306	10
2	EtOH	0.236 ± 0.0061	1.39 ± 0.036	9.0 ± 0.29	*e*	−0.100	0.0407	0.38
3	1-PrOH	0.138 ± 0.0036	1.04 ± 0.027		*e*	−0.115	0.0492	3.7
4	2-PrOH	0.0261 ± 0.00046	0.201 ± 0.0035	9.0 ± 0.36	*e*	−0.190	0.0502	1.2
5	1-BuOH	0.105 ± 0.0020	0.97 ± 0.018		*e*	−0.130	0.0571	1.0
6	2-BuOH	0.0122 ± 0.00025	0.113 ± 0.0023		0.44 ± 0.088	−0.210	0.0604	0.56
7	2-Me-1-PrOH	0.069 ± 0.0013	0.64 ± 0.012		*e*	−0.125	0.0558	0.80
8	2-Me-2-PrOH	0.00129 ± 0.000057	0.0122 ± 0.00054		0.21 ± 0.020	−0.300	0.0802	0.34
9	2-Me-2-BuOH	0.00166 ± 0.000086	0.0031 ± 0.0015[d]	2.76 ± 0.055[d]	0.16 ± 0.060[d,g]	−0.320[a]	0.1718	1.8

[a] Estimated: σ^*(2-Me-2-Bu) = σ^*(2-Me-2-Pr) − σ^*(2-Pr) + σ^*(2-Bu). [b] ϵ values from Riddick, J. A.; Bunger, W. A. *Tech. Chem. (N.Y.)* 1970, *2*. [c] Taft, R. W., Jr. In "Steric Effects in Organic Chemistry", Newman, M. S., Ed.; Wiley: New York, 1965. [d] Results from fit to the rate law $k_{obsd} = k_{ROH}[ROH] + k_{H_2O}[H_2O] + k_{HSA=N\text{-}Et}[HSA=N\text{-}Et]$. [e] No ligand dependence observed. [f] Residual water content in the solvent determined by Karl-Fischer titration with an error of 5–10%. [g] Water content [H_2O] = 0.037–0.042 M as determined in each run.

Table III. Ligand Substitution According to Equation 1 as Studied in Substituted Alcohols at 298 K

no.	solvent	k', s^{-1}	$10^2 k_{ROH}$ M^{-1} s^{-1}	σ^* [a]	$1/\epsilon$ [b]	10^3[H_2O], [e] M
10	$PhCH_2OH$	0.220 ± 0.0070	2.28 ± 0.073	0.215	0.0763	2.0
11	$PhCH_2CH_2OH$	0.16 ± 0.014	1.9 ± 0.17	0.080		4.3
12	$ClCH_2CH_2OH$	0.404 ± 0.0029	2.72 ± 0.020	0.385	0.0388	45
13	$CH_3OCH_2CH_2OH$	0.207 ± 0.0034	1.64 ± 0.027	0.19[c]	0.0591	1.0
14	$NCCH_2CH_2OH$	0.40 ± 0.018	2.7 ± 0.12	0.48[c]		3.0
15	CH_3OD	0.619 ± 0.0045	2.60 ± 0.019			10
16	3-CH_3PhOH	0.22 ± 0.044[d]	2.3 ± 0.46		0.0847	0.34

[a] Taft, R. W., Jr. In "Steric Effects in Organic Chemistry", Newman, M. S., Ed.; Wiley: New York, 1965. [b] Riddick, J. A.; Bunger, W. A. *Tech. Chem. (N.Y.)* 1970, *2*. [c] Estimated from σ^* ($NCCH_2$) = 1.300 and σ^* (CH_3OCH_2) = 0.520, respectively; insertion of a $-CH_2$ group reduces σ^* by a factor of approximately 2.7 (cf. footnote *a*). [d] Observed rate law $k_{obsd} = (k' + k''[HSA=N\text{-}Et])/(1 + k'''[HSA=N\text{-}Et])$: $k'' = 8.9 \pm 0.79$ M^{-1} s^{-1}, $k''' = 1.4 \pm 0.27$ M^{-1}. [e] Residual water content in the solvent determined by Karl-Fischer titration with an error of 5–10%.

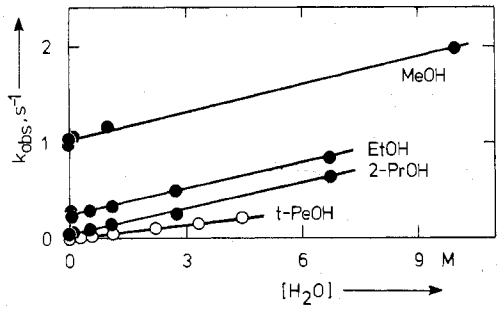


Figure 1. Effect of water on k_{obsd} at constant ligand concentration ([Cu(SA=*N*-*t*-Bu)$_2$] = 5×10^{-4} M; [HSA=*N*-Et] = 0.02 M (MeOH), 0.01 M (EtOH, 2-PrOH), 0.005 M (*t*-PeOH = tert-pentyl alcohol = 2-methyl-2-butanol); T = 298 K).

the complexes (the changes due to the solvation of the complexes in methanol may be neglected on the basis of the very similar values of K_{MeOH} as presented in Table I). The bis(salicylaldiminato)copper complexes exhibit pronounced Lewis acidity toward donor molecules such as pyridine.[8] In toluene as solvent only one pyridine molecule is added (3). The

$$Cu(SA{=}N\text{-}R)_2 + py \underset{}{\overset{K_{py}}{\rightleftharpoons}} Cu(SA{=}N\text{-}R)_2{\cdot}py \quad (3)$$

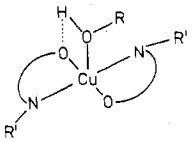
equilibrium constant K_{py} is only slightly dependent on the coordination geometry of the complexes[8] (see Table I).

In this work the addition of the donor methanol to Cu(SA=*N*-R)$_2$ was studied. Although the differences in the absorption spectra in toluene and methanol are very small (MeOH causes a slight red shift and intensity increase), the equilibrium constant could be evaluated (see Table I). The existence of isosbestic points in the system Cu(SA=*N*-*t*-Bu)$_2$/py is taken as support for the interpretation of only one MeOH molecule being coordinated to Cu(SA=*N*-R)$_2$ (see eq 4). Although for R = Et the spectra do not intersect, the

$$Cu(SA{=}N\text{-}R)_2 + MeOH \underset{}{\overset{K_{MeOH}}{\rightleftharpoons}} Cu(SA{=}N\text{-}R)_2{\cdot}MeOH \quad (4)$$

spectral changes are in good agreement with this 1:1 stoichiometry for the adduct.

The equilibrium constants K_{MeOH} are very similar for Cu(SA=*N*-Et)$_2$ and Cu(SA=*N*-*t*-Bu)$_2$ but slightly smaller than the corresponding K_{py} values. For an alcohol coordinated by Cu(SA=*N*-R)$_2$ according to (4) one has to consider that hydrogen bonding between the OH proton and the electron-rich site of the donor atoms occurs in addition to the Cu–ROH interaction (VI). In a similar fashion the addition of chloroform to Cu(acac)$_2$ has been explained.[12]



VI

It follows from the K_{MeOH} values (see Table I) that in pure methanol Cu(SA=*N*-*t*-Bu)$_2$ as well as Cu(SA=*N*-Et)$_2$ are present predominantly in the form Cu(SA=*N*-R)$_2$·MeOH.

It might be that the magnitude of K_{MeOH} is subject to solvent effects. It is impossible, however, to prove this because the spectral changes are observed only at very high MeOH concentrations (approximately 10 M corresponds to ~50 mol % MeOH in toluene). For the kinetic discussion immediately following, it is important to keep in mind that the solvation of Cu(SA=*N*-R)$_2$ by MeOH can be specific with respect to type, strength, and extent of interaction. It can be concluded that other alcohols possess similar solvation properties like methanol.

Kinetic Results. The rate of reaction 1 was studied kinetically in various alcohol solvents. In Table II the data for a first group of nonsubstituted aliphatic alcohols ranging from MeOH to 2-Me-2-BuOH are compiled. In all cases pseudo-

(12) Burgess, J. M. A. "Metal Ions in Solution"; Ellis Horwood: Chichester, England, 1978; p 95.

first-order conditions were maintained ([Cu(SA=*N*-*t*-Bu)$_2$] ≪ [HSA=*N*-Et]). The absorbance decreased exponentially during the reaction, starting with the value for pure Cu(SA=*N*-*t*-Bu)$_2$ and ending at the absorbance characteristic for pure Cu(SA=*N*-Et)$_2$. The trace on the oscilloscope could be fitted to a single exponential function with an accuracy greater than 99%. Hence, any slow consecutive reaction is ruled out, and the conclusion is that the substitution of the first chelate ligand is slow compared to that of the second one ($k_1 \leq 0.1k_2$ in eq 5). This result was also observed in toluene

$$\mathrm{Cu(SA{=}\mathit{N}\text{-}\mathit{t}\text{-}Bu)_2} \xrightarrow[\substack{+\mathrm{HSA{=}\mathit{N}\text{-}Et}\\ -\mathrm{HSA{=}\mathit{N}\text{-}\mathit{t}\text{-}Bu}}]{k_1} \mathrm{Cu(SA{=}\mathit{N}\text{-}\mathit{t}\text{-}Bu,SA{=}\mathit{N}\text{-}Et)} \xrightarrow[\substack{+\mathrm{HSA{=}\mathit{N}\text{-}Et}\\ -\mathrm{HSA{=}\mathit{N}\text{-}\mathit{t}\text{-}Bu}}]{k_2} \mathrm{Cu(SA{=}\mathit{N}\text{-}Et)_2} \quad (5)$$

as solvent and is somewhat unexpected. In toluene solutions, however, which were "enriched" in Cu(SA=*N*-*t*-Bu,SA=*N*-Et) (by addition of some ligand HSA=*N*-Et prior to the stopped-flow measurement) the observed oscilloscope signal was composed of two exponential functions with $k_2 \gtrsim 10k_1$. Similar experiments in methanol as solvent failed to prove the existence of two exponential functions which is probably due to the protic nature of methanol.

The rate of the reaction is given by eq 6. The variation

$$-\mathrm{d[Cu(SA{=}\mathit{N}\text{-}\mathit{t}\text{-}Bu)_2]}/\mathrm{d}t = k_{\mathrm{obsd}}[\mathrm{Cu(SA{=}\mathit{N}\text{-}\mathit{t}\text{-}Bu)_2}] \quad (6)$$

of the ligand concentration ([HSA=*N*-Et] = 0.01–0.5 M) reveals that for most alcohols (MeOH, EtOH, 1-PrOH, 2-PrOH, 1-BuOH, and 2-Me-1-PrOH) the pseudo-first-order rate constant k_{obsd} is independent of ligand concentration ($k_{\mathrm{obsd}} = k'$). For some of the higher alcohols (2-BuOH, 2-Me-2-PrOH, and 2-Me-2-BuOH) a ligand-dependent term is observed leading to rate law

$$k_{\mathrm{obsd}} = k' + k_{\mathrm{HSA=\mathit{N}\text{-}Et}}[\mathrm{HSA{=}\mathit{N}\text{-}Et}] \quad (7)$$

The kinetic parameters are compiled in Table II. The reaction was studied at five temperatures ranging from 25 to 45 °C. From the temperature dependence, values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined (see Table VII). The observed rate expression (7) is in agreement with the typical rate law observed for ligand substitution reactions in square-planar d^8 complexes in aqueous solution.[13] This analogy suggests, therefore, that the reaction proceeds via two pathways, namely, the solvent path (k') and the reagent path ($k_{\mathrm{HSA=\mathit{N}\text{-}Et}}$[HSA=*N*-Et]). Rate expression 7 reduces to $k_{\mathrm{obsd}} = k'$ for the limiting condition of $k_{\mathrm{HSA=\mathit{N}\text{-}Et}}[\mathrm{HSA{=}\mathit{N}\text{-}Et}] \ll k'$.

The reagent path clearly stands for the biomolecular reaction between the ligand and the complex, whereas the solvent path needs some further consideration. In aqueous solution the solvent path mechanistically occurs by water molecules attacking the complex and forming a labile aquo intermediate. When the solvent water is replaced by an organic medium, one has to be aware of the following: (i) as compared to water, the donor properties and the reactivity of the organic solvent may be much smaller and, hence, (ii) trace amounts of a polar and reactive species like water present in a weakly polar and nonreactive solvent such as toluene can be of great kinetic significance. On the other hand, the kinetic effects of traces of water present in a comparatively water-like solvent such as methanol will be much less pronounced. Returning to rate equation 7, one has to consider, therefore, any "reactive" species present in the alcohol solvents to be capable of initiating a solvent path k'.

(13) Wilkins, R. G. "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, 1974; Chapter 4.

Table IV. Ligand Exchange in MeCN/MeOH Mixtures[a]

[MeOH], M	k_{obsd}, s^{-1}	[MeOH], M	k_{obsd}, s^{-1}
0[b]	0.0034	12.3	0.526
1.23	0.0607	18.4	0.714
2.46	0.107	24.6	0.930
6.15	0.283		

[a] [Cu(SA=*N*-*t*-Bu)$_2$] = 0.001 M; [HSA=*N*-Et] = 0.04 M; T = 298 K. [b] Solvent acetonitrile.

For nonaqueous solvents the main impurity which has to be considered kinetically is residual water. In toluene as solvent[1] the so-called solvent path k' could be fully ascribed to the effect of water: $k' = k_{\mathrm{H_2O}}[\mathrm{H_2O}]$. In alcohol solvents, which are more water-like than toluene, a real participation of the solvent might occur. To reveal the contribution of water, we studied the water dependence of reaction 1 in some typical aliphatic alcohols (MeOH, EtOH, 2-PrOH, and 2-Me-2-BuOH) (see Figure 1 and Table II). The kinetic effect observed for water concentrations up to approximately 5 M could be described by eq 8. As it can be visualized from Figure

$$k' = k_{\mathrm{S}} + k_{\mathrm{H_2O}}[\mathrm{H_2O}] \quad (8)$$

1, the values obtained for $k_{\mathrm{H_2O}}$ are very similar. Hence, the reactivity of water in these alcoholic media is nearly unaffected by the specific alcohol solvent studied (see Table II).

It seems justified to assume that in the other alcohols, for which $k_{\mathrm{H_2O}}$ was not measured, water possesses a similar reactivity. Taking the concentration of water in the applied alcohols into account (see Table II), one can easily show that water cannot even partly be responsible for the observed solvent pathway k' (except in the case of 2-Me-2-BuOH).

All solvents used were reagent grade. It might be that impurities other than water were present. If so, they would contribute to the observed value for k' in a similar manner. However, it seems to be improbable that any impurities can account for the large differences in rate in the various alcohols.

In 2-Me-2-BuOH the contribution of the term $k_{\mathrm{H_2O}}[\mathrm{H_2O}]$ to the solvent path k' is appreciable. Therefore, the water content of each solution was measured separately by Karl-Fischer titration. The observed rate constants k_{obsd} were fitted to the full rate equation (9). The resulting values for $k_{\mathrm{H_2O}}$

$$k_{\mathrm{obsd}} = k_{\mathrm{S}} + k_{\mathrm{H_2O}}[\mathrm{H_2O}] + k_{\mathrm{HSA=\mathit{N}\text{-}Et}}[\mathrm{HSA{=}\mathit{N}\text{-}Et}] \quad (9)$$

and $k_{\mathrm{HSA=\mathit{N}\text{-}Et}}$ are given in Table II. In contrast to toluene as solvent,[1] alcohols obviously give rise to a "real" solvent path, i.e., an alcohol path. In the series of alcohols applied, k' decreases by nearly 3 orders of magnitude upon going from MeOH to 2-Me-2-PrOH (see Table II). Before the reasons for this decrease in rate will be discussed, additional evidence for the solvent path resulting from studies in solvent mixtures shall be presented.

The nonaqueous solvent system MeCN/MeOH is very suitable to demonstrate the effect of increasing MeOH concentration because this system shows a very regular behavior in several ways: (i) the density changes monotonously;[14] (ii) the molar polarization is linear;[14] (iii) the observed rate constants k_{obsd} for the ligand substitution according to (1) are very different in the pure solvents.

The variation of k_{obsd} with solvent composition is shown in Table IV. For the whole concentration range of MeOH the data follow relation 10. We conclude, therefore, that in pure

$$k_{\mathrm{obsd}} = k_{\mathrm{MeCN}} + k_{\mathrm{MeOH}}[\mathrm{MeOH}] \quad (10)$$

alcohols the pseudo-first-order rate constant k_{S} has to be divided by the molarity of the solvent (11). The k_{ROH} values

(14) Cunningham, G. P.; Vidulich, G. A.; Kay, R. L. *J. Chem. Eng. Data* **1967**, *12*, 336.

$$k_{ROH} = k_S/[ROH] \quad (11)$$

listed in Tables II and III were calculated on the basis of relation 11.

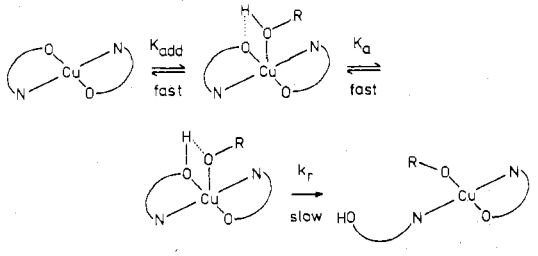
Mechanism of the Solvent Path. At moderate concentrations of the incoming ligand the contribution of the reagent path in the replacement of unidentate ligands in typical square-planar d^8 complexes is in general dominant for aqueous as well as for methanolic solutions.[15] This is not so in the present study. In most alcohols applied the solvent path is the only one to be observed, which reflects a rather poor reactivity of the chelate ligands involved as compared to that of the alcohols.

In discussing the finding that only more or less acidic species become operative in the rate law, one has to be aware of the following: (i) the Schiff-base ligands applied are weak acids; (ii) the ligands can be introduced as acids only, since the conditions for anion formation are such that the azomethine group would be destroyed; (iii) the ligand replacement according to eq 1 does involve proton transfer from the entering to the leaving ligand. It is not unexpected, therefore, that the rate of substitution is controlled by the presence and aciditiy of protic species.

As far as the solvent path in alcoholic media is concerned, the reaction initiating attack of an alcohol molecule at the complex Cu(SA=*N*-R)$_2$ will at some stage of the reaction lead to an intermediate with half bound chelate ligand (on the basis of substitutent effects on the kinetics of metal substitution in Cu(SA=*N*-R)$_2$ it is concluded[16] that the Cu–O bond is the first one to break).

The interesting question is as to when the proton transfer from the solvent to the oxygen of the leaving ligand takes place. If proton transfer is the rate-determining step, one would expect a large isotope effect when the solvent CH_3OD is used instead of CH_3OH. The result is, however, that the rate in CH_3OD is reduced by a factor of 1.6 only. This relatively small factor could be simply due to the lower acidity of CH_3OD and excludes an interpretation with proton transfer as rate-determing step.

Equation 12 presents some of the steps probably involved.



(12)

As compared to rearrangement step k_r, the constant K_{add} describes a fast equilibrium (the rate of pyridine addition is too fast for the stopped-flow time scale) and so does K_a presumably. The experimental rate constant k' is given by eq 13.

$$k' = k_{ROH}[ROH] = K_{add}K_ak_r[ROH] \quad (13)$$

In principle, the observed dependence of k' on the nature of the alcohol could be due to each of the three parameters involved in eq 13. As can be seen from Table I, however, for a given copper complex the variation of K_{add} with the nucleophiles pyridine and methanol is rather small. The equilibrium constant K_a will definitely depend on the organic group R of the alcohol as well as on the basicity of the phenolic oxygen. The rate constant k_r finally will be influenced by the organic group R of the alcohol and more strongly by the solvation power of the alcohol solvent for a singly bonded chelate ligand.

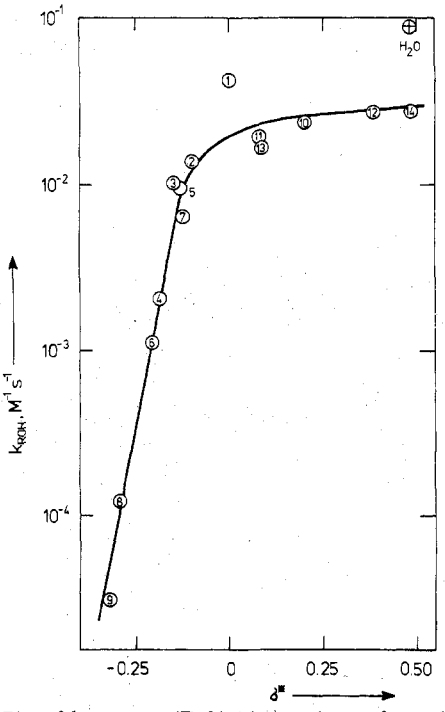


Figure 2. Plot of k_{ROH} vs. σ^*(Taft) (the numbers refer to the solvents listed in Tables II and III).

Taft's parameter σ^* for the aliphatic carbon chain of the alcohols applied is a measure for the electron density at the alcoholic oxygen. For the group of aliphatic alcohols 1–9 (see Table II) the k_{ROH} values correlate properly with σ^* according to relation 14, ρ^* being approximately +10. The positive sign

$$\log k_{ROH} = \rho^*\sigma^* + \log k_{MeOH} \quad (14)$$

of ρ^* clearly rules out that the donor strength of ROH and, hence, K_{add} are responsible for the observed variations.

Alcohols 1–9 have in common a richness in electron density at the oxygen relative to MeOH ($\sigma^* \leq 0$). To present further evidence and support, we introduced alcohols 10–14 (see Table III) with $\sigma^* > 0$ as solvents. For these solvents no ligand path is observed, so that $k_{obsd} = k'$ The Taft plot (see Figure 2) is no longer linear for these alcohols. This might indicate that (i) σ^* characterizes the kinetic behavior of single molecules and cannot be used to describe medium effects or that (ii) not only electronic but also steric effects are involved in eq 12 (the solvent structure might become important).

The phenolic solvent *m*-cresol leads to a more complicated rate law which is given in footnote *d* of Table III. Therefore, it is not discussed in detail.

Due to the very low solubility of Cu(SA=*N*-*t*-Bu)$_2$ and HSA=*N*-Et, the reaction could not be studied in water as solvent. From alcohol/water mixtures, however, k_{H_2O} was determined (see Table II). As can be seen from the Taft plot in Figure 2, k_{H_2O} ($\sigma^*_H = +0.49$)[17] does not fit into the data obtained for the other solvents. This result indicates that the linear extrapolation from ROH/H_2O mixtures to pure H_2O as solvent is probably objectionable.

The ease of separation of a single solvent molecule from the bulk solvent should be given by the "openess" of the solvent structure which itself should be reflected by the fluidity (density/viscosity) or by the enthalphy of vaporization.[18] For both plots (k_{ROH} as function of the fluidity and ΔH_{vap}, respectively) the correlation coefficient is very poor, however.

(15) See relevant literature in ref 13, p 230.
(16) Wannowius, K. J.; Voss, H.; Elias, H. *Chem. Ber.* **1976**, *109*, 3292.
(17) Taft, R. W., Jr. In "Steric Effects in Organic Chemistry"; Newman, M. S.; Ed.; Wiley: New York, 1965.
(18) Caldin, E. F.; Benetto, H. P. *J. Solution Chem.* **1973**, *2*, 217.

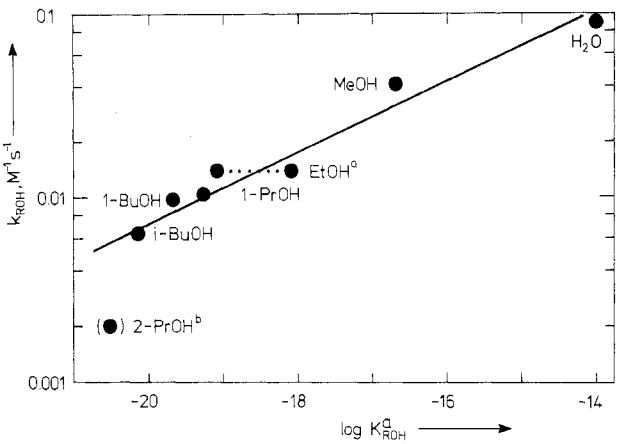


Figure 3. Double-logarithmic plot of k_{ROH} vs. K^a_{ROH} (ionic product of the alcohols = $[ROH_2^+][RO^-]$). (a) The two different values for K^a_{EtOH} are given in the literature.[19] (b) There is no plausible explanation for the deviation of $K^a_{2\text{-PrOH}}$.

Table V. Influence of Alcohols on the Rate of Ligand Exchange in Me_2SO[a]

ROH	$10^3 k^{Me_2SO}_{ROH}$, M^{-1} s^{-1}	$pK^{Me_2SO}_{ROH}$
H_2O	3.15 ± 0.29	28.1[c]
MeOH	3.44 ± 0.13	29.1[b]
EtOH	1.45 ± 0.21	29.5[b]
1-PrOH	0.74 ± 0.14	30.1[b]
2-Me-2-PrOH	≈0	31.3[b]

[a] $[Cu(SA{=}N\text{-}t\text{-}Bu)_2]$ = 0.0005 M; [HSA=*N*-Et] = 0.01 M; T = 298 K. [b] Ritchie, C. D. In "Solute-Solvent Interactions"; Dekker: New York, 1976; Vol. 2, p 229. [c] Reference 23a.

The acidity of the alochols as described by K^a_{ROH} = $[ROH_2^+][RO^-]$ should also be strongly dependent on the electron density at the oxygen: the smaller the electron density is the higher the acidity should be.

The plot of log k_{ROH} vs. log K^a_{ROH} for a limited number of alcohols[19] gives a slope of +0.2 (see Figure 3). If the self-ionization constants were a true measure of the acidity of a *coordinated* ROH molecule, one would expect a slope of 1. The observed deviation can, of course, be explained by the fact that the K^a_{ROH} values refer to the pure solvent with its intrinsic structure (it is well-known that aliphatic alcohols are composed of monomers, dimers, and higher oligomers[20]).

A reasonable approach to the acidity of coordinated alcohol molecules could be the acidity of alcohols in dilute polar media. There are data in the literature[21] on the acidity of some alcohols in Me_2SO. These $pK^{Me_2SO}_{ROH}$ values should be a better measure for the "real" acidity of an isolated ROH molecule. Therefore, ligand substitution according to eq 1 was studied in Me_2SO with increasing amounts of those alcohols where $pK^{Me_2SO}_{ROH}$ is known. As can be seen from Figure 4, k_{obsd} increases linearly with [ROH] at small alcohol concentrations ([ROH] ≤ 1 M, at higher concentrations most of the curves deviate from linearity). The limiting rate law for small alcohol concentrations takes the form of eq 15, therefore

$$k_{obsd} = k' + k^{Me_2SO}_{ROH}[ROH] \qquad (15)$$

The observed intercept k' is probably due to a Me_2SO and/or ligand pathway. The values for $k^{Me_2SO}_{ROH}$ at 298 K are tabulated in Table V and plotted vs. $K^{Me_2SO}_{ROH}$ in Figure 5.

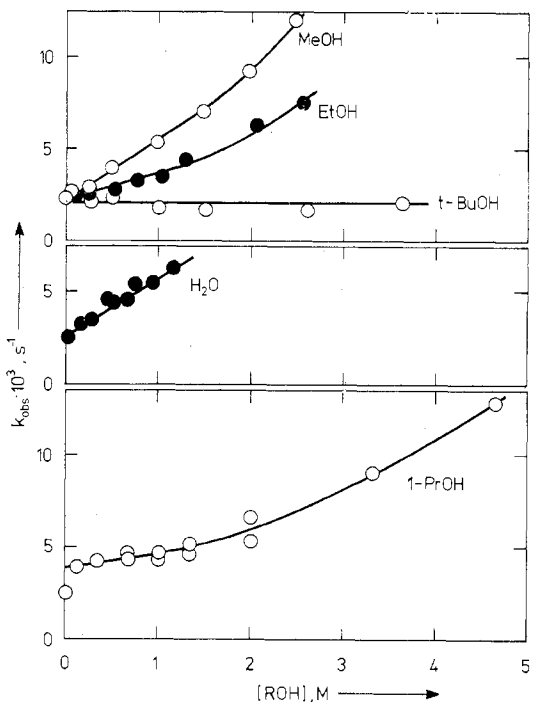


Figure 4. Effect of various alcohols and of water on k_{obsd} in Me_2SO at constant ligand concentration (T = 298 K; $[Cu(SA{=}N\text{-}t\text{-}Bu)_2]$ = 5 × 10^{-4} M; [HSA=*N*-Et] = 0.01 M (H_2O dependence), 0.1 M (alcohol dependence)).

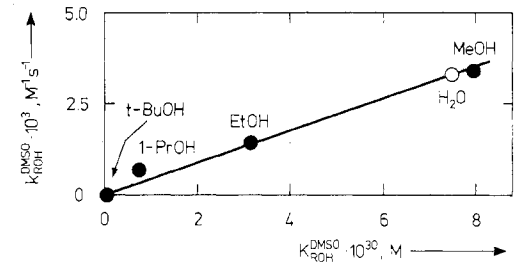


Figure 5. Plot of $k^{Me_2SO}_{ROH}$ in Me_2SO vs. $K^{Me_2SO}_{ROH}$ (acid dissociation constant of ROH in Me_2SO); $K^{Me_2SO}_{H_2O}$ results from the observed value for $k^{Me_2SO}_{H_2O}$ (see text).

The observed linearity provides good evidence for the "real" acidity of the alcohols controlling the rate of ligand substitution via the "alcohol" path, i.e., solvent path. Interestingly enough the effect of water in Me_2SO is very similar to that of MeOH (see Table V). Whereas the $pK^{Me_2SO}_{ROH}$ values applied were reported by a single group of authors,[22] several others[23] have measured $pK^{Me_2SO}_{H_2O}$ and have reported values that range from 28 to 33. Figure 5 leads to $pK^{Me_2SO}_{H_2O}$ = 29.1 which appears to be very resonable.

In going from one solvent to another one has to keep in mind that the individual attacking species and the medium are changed simultaneously. Medium effects on rate can often be described on the basis of the dielectric properties of the medium. In Figure 6 the k_{ROH} values are plotted vs. the

(19) (a) Bell, R. P. "Proton in Chemistry"; Methuen: London, 1959; p 37. (b) Providaki-Molinou, Ioanna Ph.D. Thesis, Univeristy of Athens, 1974.
(20) See for example: Kunst, M; van Duijn, D.; Bordewijk, P. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 1073 and references therein.
(21) Ritchie, C. D. In "Solute-Solvent Interactions", Coetzee, J. F., Ritchie, C. D, Eds.; Dekker: New York, 1976; Vol 2, p 229.
(22) (a) Ritchie, C. D. In "Solute-Solvent Interactions", Coetzee, J. F., Ritchie, C. D. Eds.; Dekker: New York, 1969; Vol 2, p 233. (b) Ritchie, C. D. In "Solute-Solvent Interactions"; Coetzee, J. F., Ritchie, C. D., Eds.; Dekker: New York, 1969; Vol. 1, Chapter 4.
(23) (a) Courtot-Coupez, J.; Le Demezet, M. *Bull. Chim. Soc. Fr.* **1969**, 1033 and references therein. (b) Sorkhabi, H. A.; Halle, J.-C.; Terrier, F. *J. Chem. Res. (S)* **1978**, 108–9; *J. Chem. Res. (M)* **1978**, 1371–94 and references therein. (c) A review and critical discussion of the acidities in Me_2SO is given by Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Varnier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006.

Table VI. Rate of Substitution in the Presence of Compounds Added[a]

symbol	compd added	solvent	concn range, M	k_{add},[c] M^{-1} s^{-1}
II	*N*-ethyl-4-hydroxybenzaldimine	MeOH	0-0.4	0.40 ± 0.05
III	*N*-*tert*-butyl-4-hydroxybenzaldimine	MeOH	0-0.5	1.11 ± 0.14
IV	*N*-ethylbenzaldimine	MeOH	0-0.5	≈0
V	*N*-*tert*-butylbenzaldimine	MeOH	0-0.2	≈0
III	*N*-*tert*-butyl-4-hydroxybenzaldimine	toluene	0-0.008	9.9 ± 0.9
HSA=*N*-Et	*N*-ethyl-2-hydoxybenzaldimine[b]	toluene[b]	0.001-0.5	0.123 ± 0.005

[a] [Cu(SA=*N*-*t*-Bu)$_2$] = 0.001 M; [HSA=*N*-Et] = 0.04 M; T = 298 K. [b] Voss, H.; Wannowius, K. J., Elias, H. *Inorg. Chem.* 1979, *18*, 1454. [c] Rate expression: $k_{obsd} = k_{obsd}^{0} + k_{add}$[compound added]; k_{obsd}^{0} = observed rate constant in the absence of added compounds.

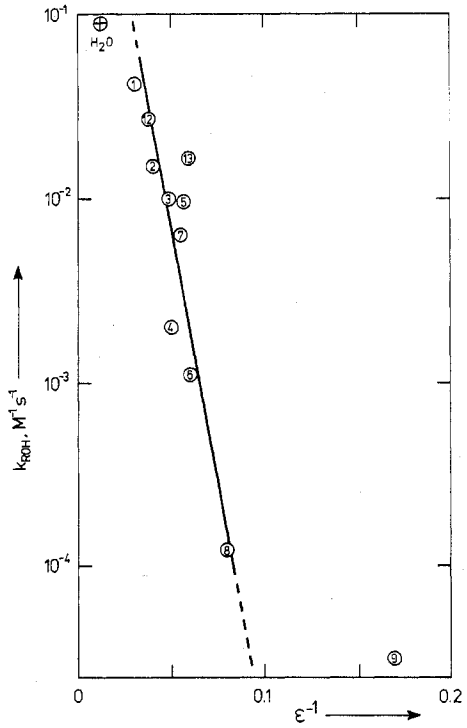


Figure 6. Plot of k_{ROH} vs. the reciprocal of the dielectric constant (the numbers refer to the solvents listed in Tables II and III).

inverse dielectric constant ϵ^{-1} (ϵ could not be found in the literature for all alcohols studied). Fitting of the data leads to a straight line with a negative slope. For media with small dielectric power, the deviations are considerable, however. The negative slope of the curve would point to polar structures being involved in the solvent pathway. Similarly, the acidity of the solvents might be related to the polarity of the solvent as characterized by ϵ.

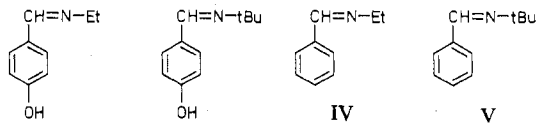
Ligand Path. A ligand path $k_{HSA=N\text{-}Et}$[HSA=N-Et] is observed for three solvents only, namely, 2-BuOH, 2-Me-2-PrOH, and 2-Me-2-BuOH (see Table II). This means that only in solvents with rather small k_S values, the ligand pathway can compete observably with the solvent pathway. The size of $k_{HSA=N\text{-}Et}$ is very much the same for all three alcohols.

Upon addition of free ligand (up to 2 M) to the corresponding complex (i.e., Cu(SA=*N*-*t*-Bu)$_2$ + HSA=*N*-*t*-Bu, Cu(SA=*N*-Et)$_2$ + HSA=*N*-Et) there were no spectral changes to be observed in the visible range of the spectrum. If, however, the size of the equilibrium constants for the addition of free ligand is similar to that observed for MeOH, spectral changes are not to be expected at these concentrations. On the other hand, one would guess that the acid strength of the ligands HSA=*N*-Et and HSA=*N*-*t*-Bu is greater than that of the alcohols applied as solvents (pK_a values are known neither for the free nor for the coordinated ligands). A possible explanation for these findings and for $k_{HSA=N\text{-}Et}$ being practically insensitive to solvent changes could be the existence of intramolecular O—H···N hydrogen bonds in HSA=*N*-Et and HSA=*N*-*t*-Bu. The mechanism of ligand substitution via the ligand path could be analogous to that suggested for the solvent path or different in the sense that it is initiated by simple bimolecular attack of the entering ligand at the complex without adduct formation. The spectroscopic studies would favor the latter interpretation. To obtain some further information on the ligand path, we studied the substitution according to eq 1 in methanol in the presence of compounds II-V (II and III are substitution isomers of HSA=*N*-Et and HSA=*N*-*t*-Bu, respectively, whereas IV and V are their OH-stripped analogues).

Table VII. Activation Parameters for the Solvent Pathway k' (ΔT = 25-50 °C)

no.	solvent	E_a,[a] kJ/mol	E_a,[b] kJ/mol	$\Delta H^{\ddagger}$, kJ/mol	$-\Delta S^{\ddagger}$, J K^{-1} mol^{-1}
1	MeOH	52.1 ± 1.1	63.2 ± 0.4	60.7 ± 0.5	41.8 ± 1.6
2	EtOH	50.3 ± 3.0	63.7 ± 1.0	61.2 ± 1.0	51.2 ± 3.3
3	1-PrOH	42.8 ± 3.5	66.5 ± 0.7	64.0 ± 0.4	46.6 ± 1.4
4	2-PrOH	52.3 ± 1.0	66.7 ± 2.7	64.1 ± 2.7	59.3 ± 8.7
5	1-BuOH	49.6 ± 1.0	67.9 ± 0.7	65.3 ± 0.4	43.1 ± 1.3
6	2-BuOH	57.3 ± 3.7	76.3 ± 1.0	73.7 ± 1.1	32.9 ± 3.5
7	2-Me-1-PrOH	56.5 ± 0.3	62.5 ± 0.8	59.9 ± 0.9	65.8 ± 3.0
8	2-Me-2-PrOH	70.4 ± 6.4	83.6 ± 5.3	81.0 ± 5.4	29 ± 17
9	2-Me-2-BuOH		78.0 ± 2.9	75.4 ± 3.0	47.7 ± 9.6
10	$PhCH_2OH$	45.1 ± 0.8	69.1 ± 1.0	66.5 ± 1.0	33.2 ± 3.3
11	$PhCH_2CH_2OH$	47.7 ± 1.5	71.9 ± 2.1	69.3 ± 2.2	29.6 ± 7.1
12	$ClCH_2CH_2OH$	45.1 ± 1.7	75.7 ± 9.4	73.1 ± 9.4	5 ± 30
13	CH_3OCH_2-CH_2OH	49.7 ± 1.5	68.0 ± 1.7	65.4 ± 1.7	39.1 ± 5.4
14	$NCCH_2$-CH_2OH	59.2 ± 6.1			
15	CH_3OD	44.6 ± 1.8			

[a] Determined with commercially available Durrum-D110. [b] Determined with modified apparatus (see Experimental Section).



II III IV V

The result (see Table VI) that there is no contribution from IV and V indicates that ligand substitution cannot be initiated by Cu-N bonding to the azomethine nitrogen of the entering ligand as the first step. On the other hand, the increase in rate observed for II and III proves again that protic species like water, alcohols, and phenols can initiate ligand substitution by proton transfer to the leaving ligand as discussed earlier. The result that the rate increasing effect of II and III can be observed even in MeOH proves that the ligand HSA=*N*-Et—possibly due to intramolecular hydrogen bonding—is much less acidic then II and III, since HSA=*N*-Et does not lead to a ligand path in MeOH. In toluene as solvent the effects observed for MeOH become more pronounced (see Table VI).

Activation Parameters. At the beginning of these studies the temperature dependence of k_{obsd} at a fixed ligand concentration was measured with a commercial Durrum D110 stopped-flow spectrophotometer. The activation parameters

derived from these measurements are compiled in Table VII. It turned out, however, that thermostating of the commercial device is very unsatisfying[24] and that a precise control of the temperature at the syringes and at the cuvette is not possible. As described in the Experimental Section, a modified thermostating device was built, and special efforts were made to provide it with good temperature control. The reinvestigation of the temperature dependence (25–50 °C) led to distinctly greater activation energies (as it can be seen from Table VII) whereas the rate constants at 25 °C were identical. Hence, at higher temperatures there is a temperature gradient in the system which leads to activation energies that are 25–30% too low. By comparing k' (Table II and III) and $\Delta H^{\ddagger}$ (Table VII), one can see that the decrease in rate constants for the solvent path is paralleled by an increase in activation enthalpy. The plot of $\Delta H^{\ddagger}$ vs. $T\Delta S^{\ddagger}$ is reasonably linear with a slope of 0.8; i.e., both enthalpy and entropy changes are equally responsible for the variation in rate.

(24) The problems associated with thermostating the Durrum-D110 stopped-flow instrument have been dealt with earlier by: Chattopadhyay, P. K., Coetzee, J. F. *Anal. Chem.* **1972**, *44*, 2117.

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Registry No. I, 36748-26-2; II, 72784-66-8; III, 72784-67-9; IV, 6852-54-6; V, 6852-58-0; HSA=*N*-Et, 5961-36-4; salicylaldehyde, 90-02-8; ethylamine, 75-04-7; $Cu(SA{=}N\text{-}Et)_2$, 26194-23-0; MeOH, 67-56-1.

Contribution from the Instituto de Quimica, Universidade de Sao Paulo, Sao Paulo, Brazil

Ligand Oxidation in Iron Diimine Complexes. 4. Temperature and Acidity Dependence of the Oxidation of Tris(glyoxal bis(methylimine))iron(II) by Cerium(IV)[1]

HELENA LI CHUM* and MARIA E. M. HELENE

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The influence of acidity and temperature on the kinetics of the oxidation of tris(glyoxal bis(methylimine))iron(II), $Fe(GMI)_3^{2+}$, by cerium(IV) was studied in the temperature range 10–30 °C and acidity 4–7 M H_2SO_4. The stoichiometry of the reaction is $Fe(GMI)_3^{2+} + Ce(IV) \rightleftharpoons Ce(III) + Fe(GMI)_3^{3+} \rightarrow 0.24Fe(GMI)_2(GA)^{3+} + 0.12Fe(GMI)_2(GH)^{2+} + 0.64Fe(GMI)_3^{2+}$; GMI = $H_3CN{=}CHCH{=}NCH_3$, GA = $H_3CN{=}CHC(OH){=}NCH$, and GH = $H_3CN{=}CHCH{=}NCH_2OH$. The primary step is the oxidation of $Fe(GMI)_3^{2+}$ by Ce(IV) to the corresponding iron(III) complex. The thermodynamic parameters for this reaction are $\Delta H = -(2.1 \pm 0.6)$ kcal/mol and $\Delta S = 5 \pm 2$ eu, in 4.0 M H_2SO_4. The equilibrium constant for this reaction increases by a factor of approximately 2 in going from 4.0 to 6.0 M H_2SO_4. The iron(III) complex undergoes ligand oxidation, yielding the products above, in a reaction which is second order with respect to the iron(III) complex. The plot of $\log k_{obsd} - H_0$ vs. $\log a_{H_2O}$ is linear within the experimental error, where H_0 is the Hammett acidity function, essentially equal to the activity of acid in the medium. The slope is 1.9 ± 0.4. Therefore, the observed rate constant can be expressed as $k_{obsd} = k[H_2O]^2/[H_3O^+]$. The mechanism proposed to explain this dependence involves the iron(III) complex $Fe(GMI)_3^{3+}$, which undergoes an intramolecular reduction with concomitant ligand oxidation. This reaction is assisted by a reversible nucleophilic attack by solvent water. The products of this reaction are an iron(III)–ligand radical (on the methine or methyl carbons) complex and H_3O^+. The iron(III)–ligand radical complex undergoes oxidation by another molecule of iron(III) complex. This step is also assisted by solvent water. The rate law derived with this scheme reproduces the experimental rate law. The disproportionation of $Fe(GMI)_3^{3+}$ was also studied as a function of temperature, holding $\log ([H_2O]^2/[H_3O^+])$ constant within 2.5%. Within the experimental error, plots of $\log k_{obsd}$ vs. T^{-1} are linear with an activation enthalpy of 10.5 ± 1 kcal/mol. The activation entropy is $-(8 \pm 2)$ eu.

Introduction

In parts 1[2] and 2[3] of this series, the stoichiometry, reaction products, and kinetics of the oxidation of tris(glyoxal bis(methylimine))iron(II), $Fe(GMI)_3^{2+}$, GMI = $H_3CN{=}CH{-}CH{=}NCH_3$, by cerium(IV) were studied at 25 °C in 4.0 M H_2SO_4. This reaction provides an example of a well-studied process in which ligand oxidation proceeds with the intermediate formation of the iron(III) complex, which then undergoes an intramolecular reduction to the iron(II) state, with concomitant oxidation of the organic ligands, yielding stable ligand-oxidized complexes. Several other examples of ligand oxidation proceeding via intermediate formation of the complex in a higher oxidation state prior to ligand oxidation are known.[4,5] More recently, ruthenium(II) derivatives[6] of ethylenediamine were shown to be oxidized to the corresponding ruthenium(II) diimine complex and then further oxidized at the ligands, via Ru(III) complexes. No detailed kinetic studies were described. The kinetics of the autoxidation of the iron diimine complex derived from biacetyl was studied in detail.[7] It has been suggested that the reaction proceeds via the iron(III) complex.[7] In part 2[3] of this series it was shown that the rate of ligand oxidation of $Fe(GMI)_3^{2+}$ by Ce(IV),

* To whom correspondence should be addressed at the Solar Energy Research Institute, Chemical and Biological Conversion Branch, Golden, CO 80401.

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