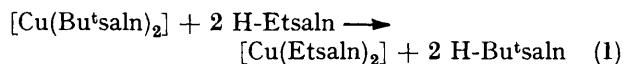


## Kinetics of Ligand Substitution in Bis(*N*-*t*-butylsalicylideneiminato)-copper(II): Aprotic Organic Solvents as Media

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Stopped-flow spectrophotometry has been used to study the kinetics of ligand substitution in the title complex [Cu(Bu<sup>t</sup>saln)<sub>2</sub>] with *N*-ethylsalicylideneimine in a variety of aprotic organic solvents. The rate of substitution follows a two-term rate law, rate = ( $k_0 + k_{\text{ligand}}[\text{ligand}]$ )[complex], with the substitution of the first ligand being rate controlling. It is shown that the ligand-independent rate term  $k_0$  represents the sum of the genuine solvent contribution  $k_s$ , of a water contribution ( $k_{\text{H}_2\text{O}}^{\text{I}}[\text{H}_2\text{O}] + k_{\text{H}_2\text{O}}^{\text{II}}[\text{H}_2\text{O}]^2$ ), and of contributions caused by protic admixtures such as methanol, e.g.  $k_{\text{MeOH}}[\text{MeOH}]$ . The investigation of the dependence  $k_0 = f([\text{H}_2\text{O}])$  reveals that for toluene and carbon tetrachloride  $k_s = 0$ . The  $k_s$  values obtained for the aprotic solvents dimethylformamide, dimethylacetamide, tetramethylurea, dimethyl sulphoxide, acetonitrile, nitromethane, and pyridine lie in the range  $10^{-4}$ – $10^{-2}$  s<sup>-1</sup>. Their correlation with solvent parameters such as dielectric constant, donor or acceptor number, fluidity, or Reichardt's  $E_T$  (30) value is unsatisfactory, whereas the activation energy for the  $k_0$  path correlates reasonably well with the heat of vaporization of the solvents. The size of  $k_{\text{ligand}}$ ,  $k_{\text{MeOH}}$ , and especially  $k_{\text{H}_2\text{O}}^{\text{I}}$  varies with the type of aprotic solvent, the reactivity of water,  $k_{\text{H}_2\text{O}}^{\text{I}}$  being 2 000-fold greater in toluene than in dimethylformamide. Admixtures of 2,4-dimethylpentan-3-ol and 3-ethylpentan-3-ol to carbon tetrachloride act as water scavengers and suppress the water contribution to  $k_0$ . The mechanism of the various substitution pathways induced by the solvent, by water, and by the incoming ligand is discussed.

LIGAND substitution in bis(*N*-*t*-butylsalicylideneiminato)copper(II), [Cu(Bu<sup>t</sup>saln)<sub>2</sub>], according to (1) (H-Etsaln = *N*-ethylsalicylideneimine) as studied in alcoholic media<sup>1</sup> follows rate law (2). The ligand-



$$\text{Rate} = k_{\text{obs.}}[\text{Cu}(\text{Bu}^t\text{saln})_2] = (k_s + k_{\text{H-Etsaln}}[\text{H-Etsaln}])([\text{Cu}(\text{Bu}^t\text{saln})_2]) \quad (2)$$

dependent contribution  $k_{\text{H-Etsaln}}[\text{H-Etsaln}]$  (*i.e.* the ligand path) was found to be very small compared to the dominating contribution  $k_s$ , which represents the alcohol-induced reaction channel and is therefore called the solvent path.<sup>1</sup> It was shown that  $k_s$  can be correlated with the solvent polarity parameter  $E_T$  (30),<sup>2</sup> *i.e.* with the hydrogen-bond donor property of the alcohols, and also with their acid strength.<sup>1</sup>

The present investigation was undertaken to study the question of whether aprotic solvents are also able to offer a solvent path for substitution reaction (1). This reaction implies proton transfer from the entering to the leaving ligand. One would expect, therefore, that any protic solvent (and any protic species present in a solvent) would be much more efficient in initiating a solvent path than an aprotic one. On the other hand, it might well be possible that highly polar aprotic media allow the formation of ionic species able to open a ligand-independent reaction channel. These considerations led us to carry out reaction (1) in a variety of aprotic organic solvents, to establish the corresponding rate law, and to investigate thus the existence of any genuine solvent path in these media. It is obvious that in such a study the kinetic effects caused by any water present in the system have to be rigorously controlled and accounted for with care.

### EXPERIMENTAL

*N*-Ethylsalicylideneimine and bis(*N*-*t*-butylsalicylideneiminato)copper(II) were obtained as described previously.<sup>1,3</sup> The elemental analyses agreed with calculated data. Heptan-1-ol (Merck-Schuchardt, Darmstadt), 2,4-dimethylpentan-3-ol (EGA, Steinheim), and 3-ethylpentan-3-ol (Fluka, Neu-Ulm) were fractionated under reduced pressure and dried statically over 4-Å molecular sieves.

Carbon tetrachloride and toluene (both reagent grade; Merck, Darmstadt) were dried dynamically with 4-Å molecular sieves. Pyridine (py), dimethylformamide (dmf), acetonitrile, dimethyl sulphoxide (dmsO), and propylene carbonate (all reagent grade; Merck) as well as *N,N*-dimethylacetamide (dma), tetramethylurea (tmu), and nitromethane (all Merck-Schuchardt) were purified by fractional distillation under reduced pressure according to procedures described in the literature.<sup>4</sup> They were dried dynamically over 3-Å molecular sieves. The solvents were stored over the appropriate molecular sieves in the dark. Their water content (see Table 1) was determined by automatic Karl-Fischer titration using Karl-Fischer reagents A and B (Merck).

Kinetic measurements were performed with a modified<sup>1</sup> Durrum D110 stopped-flow apparatus in combination with an Aminco DASAR storage oscilloscope. The absorbance-time data obtained at 600 nm under pseudo-first-order conditions (excess of entering ligand) were fitted to an exponential function with a computer program.

### RESULTS AND DISCUSSION

*Kinetic Data.*—As found for alcoholic media,<sup>1</sup> the change in absorbance with time observed for reaction (1) can be described by just one exponential function for all aprotic solvents studied. The transient formation and decay of a mixed-ligand complex [Cu(Bu<sup>t</sup>saln)-(Etsaln)] could not be detected. The substitution of the first ligand is therefore rate determining, the substitution of the second being a fast consecutive step.

TABLE 1  
Kinetic parameters for reaction (1) as studied in aprotic solvents at 25 °C<sup>a</sup>

| Solvent                         | 10 <sup>3</sup> k <sub>0</sub> /s <sup>-1</sup> | E <sub>a</sub> (k <sub>0</sub> ) <sup>b/</sup><br>kJ mol <sup>-1</sup> | 10 <sup>2</sup> k <sub>HL</sub> /<br>dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> | ΔH <sup>‡</sup> (k <sub>HL</sub> ) <sup>b/</sup><br>kJ mol <sup>-1</sup> | -ΔS <sup>‡</sup> (k <sub>HL</sub> ) <sup>b/</sup><br>J K <sup>-1</sup> mol <sup>-1</sup> | 10 <sup>2</sup><br>[H <sub>2</sub> O] <sup>c/</sup><br>mol dm <sup>-3</sup> |
|---------------------------------|---|--|--|--|--|---|
| dmf                             | 1.59 ± 0.25                                     | 75 ± 2.3   | 0.40 ± 0.084   | 40 ± 1.0   | 155 ± 3.2  | 0.035   |
| dma                             | 0.41 ± 0.047                                    | 88 ± 4.8   | 0.50 ± 0.017   | 26 ± 3.4   | 200 ± 11   | 0.17  |
| tmu <sup>d</sup>                | <0.6  |  | 11.8 ± 2.1   |  |  | 0.23  |
| dmso                            | 2.14 ± 0.15                                     | 70 ± 6.6   | 0.20 ± 0.054   |  |  | 1.7–3.5 <sup>e</sup>  |
| CH <sub>3</sub> CN              | 1.46 ± 0.047                                    |  | 0.135 ± 0.018  |  |  | 0.1   |
| CH <sub>3</sub> NO <sub>2</sub> | 12.1 ± 0.6                                      | 49 ± 4   | 6.34 ± 0.21  | 26 ± 3.2   | 180 ± 10   | 0.14  |
| py                              | 5.27 ± 0.18                                     | 49 ± 2.2   | 1.04 ± 0.065   | 39.5 ± 2.6   | 150 ± 8  | 0.31  |
| Propylene carbonate             | 0.433 ± 0.042                                   | 55 ± 8.4   | 0.287 ± 0.016  | 67 ± 9.4   | 70 ± 30  | 1.0   |
| PhMe <sup>f</sup>               | 2.25 ± 1.3                                      |  | 12.3 ± 0.50  |  |  | 0.079   |
|                                 | 13.7 ± 1.4                                      |  | 12.2 ± 0.55  |  |  | 1.64  |
| CCl <sub>4</sub>                | 2.73 ± 0.20                                     |  | 1.15 ± 0.066   |  |  | 0.075   |

<sup>a</sup> [Cu(Bu<sup>t</sup>saln)<sub>2</sub>]<sub>0</sub> = 5 × 10<sup>-4</sup> mol dm<sup>-3</sup>; [H-Etsaln]<sub>0</sub> = 0.01–0.5 mol dm<sup>-3</sup>. <sup>b</sup> From measurements at five or six temperatures in the range 25–50 °C. <sup>c</sup> [H<sub>2</sub>O] determined by Karl–Fischer titration (estimated error: 5–10%). <sup>d</sup> Rate law (4) is observed; k<sub>HL</sub>' = 8.8 ± 2 dm<sup>3</sup> mol<sup>-1</sup> at 25 °C. <sup>e</sup> [H<sub>2</sub>O] was determined after each kinetic run. <sup>f</sup> From ref. 5.

Variation of the concentration of the entering ligand (0.01–0.5 mol dm<sup>-3</sup>) led to the well known relation (3).

$$k_{\text{obs.}} = k_0 + k_{\text{H-Etsaln}}[\text{H-Etsaln}] = k_0 + k_{\text{HL}}[\text{HL}] \quad (3)$$

The data obtained for k<sub>0</sub> and k<sub>HL</sub> at 25 °C are compiled in Table 1 together with the activation parameters for some of the solvents studied and the concentration of residual water.

Only for tmu as solvent was the observed ligand dependence curved. This can be more accurately described by equation (4) (HL = H-Etsaln).

$$k_{\text{obs.}} = (k_0 + k_{\text{HL}}[\text{HL}])/(1 + k_{\text{HL}}'[\text{HL}]) \quad (4)$$

The ligand-independent rate contribution k<sub>0</sub> in (3) and

Table 2 together with the maximum water concentrations studied.

It has been shown for toluene<sup>5</sup> and it follows for pyridine from Table 2 that the water content does not affect the value of k<sub>HL</sub>. In propylene carbonate, however, k<sub>HL</sub> increases linearly with [H<sub>2</sub>O] (see Table 3).

$$k_{\text{HL}} = k_{\text{HL}}^0 + k_{\text{HL}}''[\text{H}_2\text{O}] \quad (7)$$

Knowing the separate contributions from the ligand path [see equation (3)] and from the 'water paths' [see equation (6)] to the observed rate constant k<sub>obs.</sub>, one can calculate the rate constant k<sub>s</sub> for the solvent path by subtraction, assuming that water is the only kinetically effective impurity in the solvent. Subtraction of either

TABLE 2

Rate constants for the water-induced ligand substitution according to reaction (1) as studied in aprotic solvents at 25 °C  
{[Cu(Bu<sup>t</sup>saln)<sub>2</sub>] = 5 × 10<sup>-4</sup> mol dm<sup>-3</sup>}

| Solvent                         | 10 <sup>2</sup> k'/s <sup>-1</sup> | 10 <sup>2</sup> k <sub>H<sub>2</sub>O<sup>I</sup>}/<br/>dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup></sub> | 10 <sup>2</sup> k <sub>H<sub>2</sub>O<sup>II</sup>}/<br/>dm<sup>6</sup> mol<sup>-2</sup> s<sup>-1</sup></sub> | [H-Etsaln] <sup>b/</sup><br>mol dm <sup>-3</sup> | [H <sub>2</sub> O] <sub>max.</sub> <sup>c/</sup><br>mol dm <sup>-3</sup> |
|---------------------------------|------------------------------------|--|---|--|--|
| dmf                             | 0.238 ± 0.043                      | 0.035 ± 0.029  | 0.0376 ± 0.0028   | 0.01   | 11   |
| dma                             | 0.0207 ± 0.0084                    | 0.192 ± 0.012  | n.o.  | 0.01   | 1.1  |
| tmu                             | 0.206 ± 0.013                      | 0.0922 ± 0.022   | n.o.  | 0.01   | 1  |
| dmso                            | 0.271 ± 0.019                      | 0.315 ± 0.029  | n.o.  | 0.01   | 1.2  |
| CH <sub>3</sub> CN              | 1.14 ± 0.52                        | 4.34 ± 0.81  | 1.43 ± 0.19   | 0.1  | 4.9  |
| CH <sub>3</sub> NO <sub>2</sub> | 1.56 ± 0.22                        | 3.2 ± 1.3  | 15.4 ± 1.4  | 0.01   | 0.9  |
| py                              | 0.46 ± 0.11                        | 6.86 ± 0.18  | n.o.  | 0.01   | 1.1  |
|                                 | 1.17 ± 0.065                       | 7.25 ± 0.11  | n.o.  | 0.5  | 1.1  |
| Propylene carbonate             | 0.056 ± 0.025                      | 0.87 ± 0.14  | 1.41 ± 0.15   | 0.01   | 0.9  |
| PhMe <sup>d</sup>               | <0.1                               | 70.7 ± 1.6   | n.o.  | 0.001  | 0.016  |
| CCl <sub>4</sub>                | —                                  | ca. 2 000  | —   | 0.4  | 0.005  |

<sup>a</sup> See equation (6). n.o. = Not observed. <sup>b</sup> Concentration of the incoming ligand. <sup>c</sup> Maximum water concentration studied. <sup>d</sup> From ref. 5.

(4) may be the sum of rate contributions stemming from the solvent, from residual water, and from any other kinetically effective solvent impurity.

To characterize the water contribution to k<sub>obs.</sub>, the dependence k<sub>obs.</sub> = f([H<sub>2</sub>O]) was studied in detail at [H-Etsaln] = constant. At low water concentrations relation (5) is found, whereas at high water concentrations relation (6) is more meaningful for some of the solvents.

$$k_{\text{obs.}} = k' + k_{\text{H}_2\text{O}^{\text{I}}}[\text{H}_2\text{O}] \quad (5)$$

$$k_{\text{obs.}} = k' + k_{\text{H}_2\text{O}^{\text{I}}}[\text{H}_2\text{O}] + k_{\text{H}_2\text{O}^{\text{II}}}[\text{H}_2\text{O}]^2 \quad (6)$$

The rate constants k', k<sub>H<sub>2</sub>O<sup>I</sup></sub>, and k<sub>H<sub>2</sub>O<sup>II</sup></sub> are listed in

(k<sub>H<sub>2</sub>O<sup>I</sup></sub>[H<sub>2</sub>O] + k<sub>H<sub>2</sub>O<sup>II</sup></sub>[H<sub>2</sub>O]<sup>2</sup>) from k<sub>0</sub> or k<sub>HL</sub>[HL] from k' leads to two sets of k<sub>s</sub> values (see Table 4).

Considering the experimental difficulties associated

TABLE 3

Effect of water on k<sub>0</sub> and k<sub>HL</sub> in propylene carbonate at 25 °C

| [H <sub>2</sub> O]/<br>mol dm <sup>-3</sup> | 10 <sup>3</sup> k <sub>0</sub> /<br>s <sup>-1</sup> | 10 <sup>2</sup> k <sub>HL</sub> /<br>dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> |
|---|---|--|
| 0.01  | 0.433 ± 0.042                                       | 0.287 ± 0.016  |
| 0.11  | 1.56 ± 0.052  | 0.55 ± 0.020   |
| 0.33  | 5.28 ± 0.17   | 0.674 ± 0.057  |
| 0.44  | 6.64 ± 0.55   | 1.07 ± 0.19  |
| 0.55  | 9.31 ± 0.49   | 1.36 ± 0.19  |

TABLE 4  
Solvent path  $k_S$  at 25 °C

| Solvent                         | Relative contribution (%) <sup>a</sup> of water to $k_0$ | $10^3 k_S$ (from $k_0$ )/ $s^{-1}$ | Relative contribution (%) of $k_{HL}[HL]$ to $k'$ | $10^3 k_S$ (from $k'$ )/ $s^{-1}$ |
|---------------------------------|--|------------------------------------|---|-----------------------------------|
| dmf                             | <1   | $1.58 \pm 0.25$                    | 1.7   | $2.34 \pm 0.43$                   |
| dma                             | <1   | $0.404 \pm 0.047$                  | 24  | $0.16 \pm 0.084$                  |
| tmu                             | <1   | <0.6                               | 57  | $0.88 \pm 0.25$                   |
| dmsu                            | 3.5  | $2.06 \pm 0.15$                    | <1  | $2.69 \pm 0.19$                   |
| CH <sub>3</sub> CN              | 3  | $1.42 \pm 0.05$                    | 1.2   | $11.3 \pm 5.2$                    |
| CH <sub>3</sub> NO <sub>2</sub> | <1   | $12.1 \pm 0.6$                     | 4.1   | $15.0 \pm 2.2$                    |
| py                              | 4  | $5.06 \pm 0.18$                    | 2.2   | $4.5 \pm 0.11$ <sup>b</sup>       |
| Propylene carbonate             | 20   | $0.346 \pm 0.044$                  | 44  | $6.5 \pm 0.73$ <sup>c</sup>       |
| PhMe                            | 25   | $1.7 \pm 1.3$ <sup>d</sup>         | 5.1   | $0.53 \pm 0.25$                   |
|                                 | 85   | $2.1 \pm 1.4$ <sup>e</sup>         | >10   | <1                                |
| CCl <sub>4</sub>                | >100 <sup>f</sup>  | <i>ca.</i> 0                       | —   | —                                 |

<sup>a</sup> Calculated according to equation (5) or (6). <sup>b</sup> [H-Etsaln] = 0.01 mol dm<sup>-3</sup>, <sup>c</sup> [H-Etsaln] = 0.5 mol dm<sup>-3</sup>. <sup>d</sup> [H<sub>2</sub>O] =  $7.9 \times 10^{-4}$  mol dm<sup>-3</sup>. <sup>e</sup> [H<sub>2</sub>O] = 0.0164 mol dm<sup>-3</sup>. <sup>f</sup> The water contribution is slightly greater than  $k_0$ .

with kinetic studies in aprotic solvents at low water concentrations and the indirect procedure for the evaluation of  $k_S$ , the agreement between the two  $k_S$  values obtained for a given solvent is in general very good. In the case of pyridine, for example, the three values obtained are 0.005 06, 0.0045, and 0.0065 s<sup>-1</sup> (see Table 4). For the solvents toluene and carbon tetrachloride the  $k_S$  values are small and the limits of error exceed 50%. It is concluded, therefore, that these solvents do not give rise to a genuine solvent path. The question of whether propylene carbonate opens a solvent path cannot be answered conclusively. The large difference between the two  $k_S$  values obtained for acetonitrile points to an experimental error (impurity in CH<sub>3</sub>CN?) in the determination of  $k'$ .

The size of the  $k_S$  values and their relatively small limits of error for the solvents dmf, dma, tmu, dmsu, CH<sub>3</sub>NO<sub>2</sub>, and py substantiates the existence of a genuine solvent path in these media. There are, however, still at least two objections to be made, namely (i) that undetected protic impurities simulate a solvent path and (ii) that linear extrapolation to [H<sub>2</sub>O] = 0 on the basis of equations (5) and (6) might be wrong in the sense that very small amounts of water are more reactive than predicted by (5) and (6).

Both objections are hard to disprove unambiguously. One would expect that the latter one could be tested by studying reaction (1) at very low water concentrations. At these concentrations, however, one approaches the situation where [Cu(Bu<sup>t</sup>saln)<sub>2</sub>]<sub>0</sub> ≈ [H<sub>2</sub>O], *i.e.* the pseudo-first-order condition is no longer fulfilled. An experimental indication for this lies in the finding that at such low water concentrations in some of the solvents studied the observed absorbance against time curves are sigmoidal at the lowest ligand concentrations of 0.01 mol dm<sup>-3</sup>. This effect is most pronounced in the solvent CCl<sub>4</sub> where  $k_{H_2O}$ <sup>1</sup> is greatest (see Table 2).

In a series of kinetic runs, reaction (1) was studied in CCl<sub>4</sub> at low ligand concentration and in the presence of various alcohols. In these runs the above mentioned sigmoid shape was no longer observed and pure exponential curves were obtained instead. Addition of the three

isomeric C<sub>7</sub> alcohols heptan-1-ol, 2,4-dimethylpentan-3-ol, and 3-ethylpentan-3-ol at constant ligand concentration led to kinetically different results (see Figure 1).

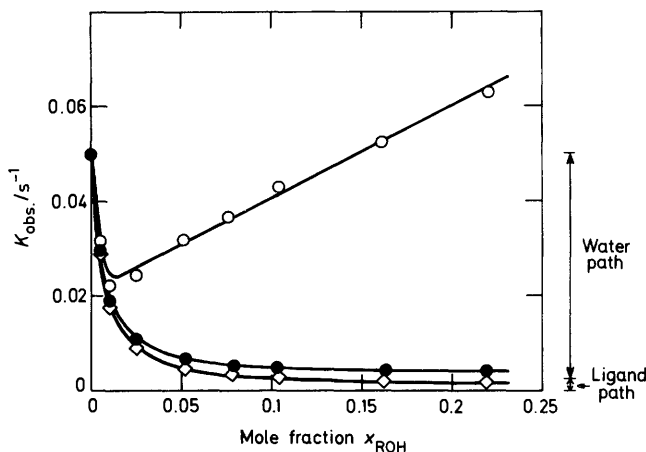


FIGURE 1 Kinetic effect of heptan-1-ol (○), 2,4-dimethylpentan-3-ol (●), and 3-ethylpentan-3-ol (◇) on reaction (1) as studied in CCl<sub>4</sub> at 25 °C ([H<sub>2</sub>O] ≈  $2 \times 10^{-3}$ , [H-Etsaln] = 0.2 mol dm<sup>-3</sup>)

In the case of heptan-1-ol the rate of ligand substitution first decreases sharply and then increases linearly with increasing alcohol concentration, *i.e.* this alcohol gives rise to an additional heptan-1-ol initiated reaction path. Addition of the two branched heptanols, however, reduces the rate of substitution as shown in Figure 1. Obviously, these alcohols act as scavengers and catch more or less effectively the water mainly responsible for the reaction in CCl<sub>4</sub> at [H<sub>2</sub>O] ≈  $2 \times 10^{-3}$  mol dm<sup>-3</sup> and [H-Etsaln] = 0.2 mol dm<sup>-3</sup>. The most probable explanation for this effect is that sterically hindered 2,4-dimethylpentan-3-ol and 3-ethylpentan-3-ol are no longer able to form oligomers according to the 1-2-4 model;<sup>6</sup> they are still able, however, to form adducts with small hydrogen-bond donors such as water. As a consequence, the water molecules are trapped and the rate decreases to the limiting value due to  $k_{HL}[HL]$ .

*Mechanism of the Solvent Path.*—There is general agreement<sup>7</sup> that the mechanism of the solvent path for

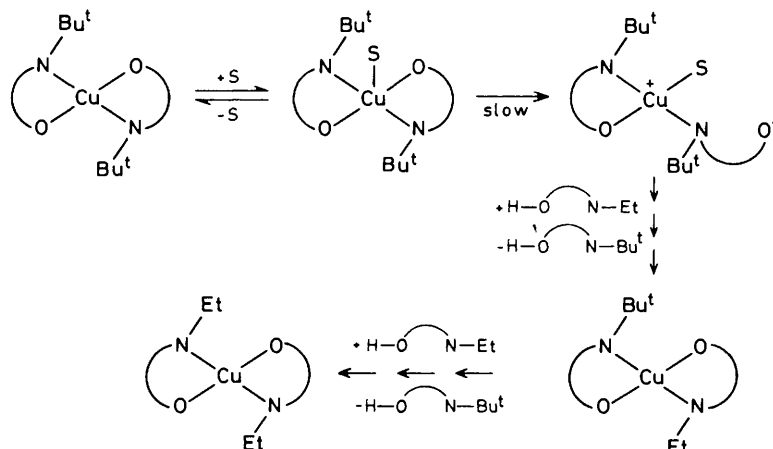
ligand substitution in square-planar  $d^8$  complexes is associative. It is assumed that the first step is a Lewis acid-base reaction in the sense that the electron-pair-donating solvent molecule attacks or is co-ordinated at the electron-deficient  $d^8$  metal.

We have shown previously<sup>1,8</sup> that this interpretation is not valid for the solvent path of ligand substitution in four-co-ordinate bis(*N*-alkylsalicylideneiminato)-complexes of copper(II) and nickel(II) as studied in alcoholic media. Although in toluene these complexes

cleavage of the Cu-N bond could be a reasonable alternative.

Scheme 1 implies that the solvent can form an adduct with the complex (fast pre-equilibrium) and that it is also able to facilitate the formation of charged intermediates. It is not surprising, therefore, that non-polar or weakly polar solvents such as carbon tetrachloride and toluene do not open a solvent path.

The  $k_s$  values obtained for the various aprotic solvents do not differ a great deal (see Table 4). The fact that the



SCHEME 1 Mechanism of the solvent path in aprotic solvents S

add one or two molecules of pyridine at the metal<sup>8,9</sup> and can therefore be classified as Lewis acids, they also possess Lewis-base centres at the phenolic oxygen-donor atoms. So, the alcohol molecule obviously attacks as an electrophile at the donor oxygen through hydrogen bonding, thus initiating a mechanistically unusual solvent path. The general conclusion with respect to solvent-initiated substitution pathways is, therefore, that the type and site of solvent-substrate interaction depends on both the acid and base properties of the substrate relative to those of the solvent.

With the exception of nitromethane, the aprotic solvents studied here cannot interact with the basic oxygen-donor atoms of  $[\text{Cu}(\text{Bu}^t\text{saln})_2]$  through hydrogen bonding and cannot provide a proton for the leaving ligand  $\text{H-Bu}^t\text{saln}$ . Therefore, they behave as nucleophiles and interact with the copper atom as a weak Lewis-acid centre.<sup>9</sup> This type of interaction induces a solvent path which is much less effective. The proton-induced solvent path is clearly preferred, the ratio  $k_s(\text{alcohol})/k_s(\text{aprotic dipolar solvent})$  being of the order of  $10^2$  to  $10^3$  (see Table 4 and ref. 1).

As shown in Scheme 1 it is necessary to invoke charged species for the mechanistic interpretation of the solvent path in aprotic solvents. All steps following the rate-determining breaking of the Cu-O bond are thought to be fast. It is concluded from substituent effects on rate<sup>10</sup> that in protic media the metal-oxygen bond is broken first, although in aprotic solvents the rate-determining

$k_s$  value for nitromethane is exceptionally high is probably a consequence of the relatively strong CH acidity of this solvent. This again demonstrates the high sensitivity of reaction (1) to protic species.

On the basis of Scheme 1, one would expect the size of  $k_s$  for aprotic media to depend on their donor properties as well as on their capability to allow the formation and solvation of charged species as shown in Scheme 1. In agreement with this expectation any attempt to correlate the  $k_s$  values of Table 4 with single solvent properties such as dielectric constant ( $\epsilon$ ), donor number (DN), acceptor number, fluidity, or the polarity parameter  $E_T(30)$  was more or less unsuccessful. A somewhat better result is obtained (see Figure 2) when  $k_s$  is correlated with both the donor and dielectric properties of the solvent on the basis of relation (8).

$$\log k_s = a\text{DN} + b[(\epsilon - 1)/(2\epsilon + 1)] + c \quad (8)$$

It has been shown<sup>11</sup> for the formation of nickel(II) complexes in non-aqueous media that the heat of vaporization of the solvent correlates with  $\Delta H^\ddagger$ , the enthalpy of activation. This indicates the significance of the energy necessary to separate a single solvent molecule from its neighbourhood in the bulk. Taking the activation energy  $E_a(k_0)$  (see Table 1) as measure for  $\Delta H^\ddagger(k_s)$  one can demonstrate (see Figure 3) that this parallelism exists for the ligand substitution of the present study as well. This does not contradict the mechanism shown in Scheme 1.

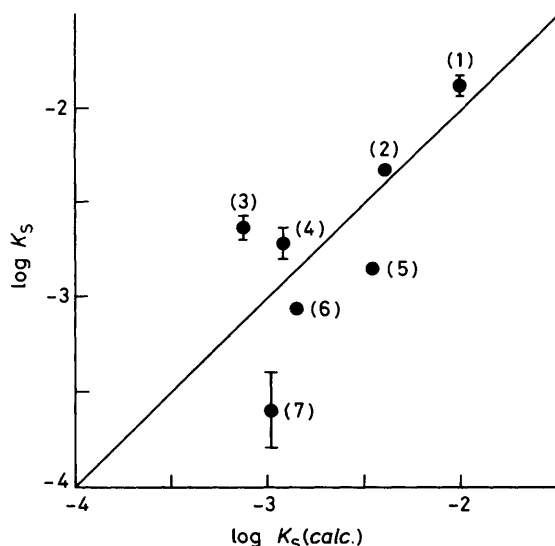


FIGURE 2 Correlation of  $\log k_s$  with the donor number and dielectric constant of the solvents [ $\text{CH}_3\text{NO}_2$  (1), py (2), dmsO (3), dmf (4),  $\text{CH}_3\text{CN}$  (5), tmu (6), dma (7)] according to  $\log k_s(\text{calc.}) = -0.04\text{DN} - 20[(\epsilon - 1)/(2\epsilon + 1)] + 8$ . The error bars are given by the two different  $k_s$  values of Table 4

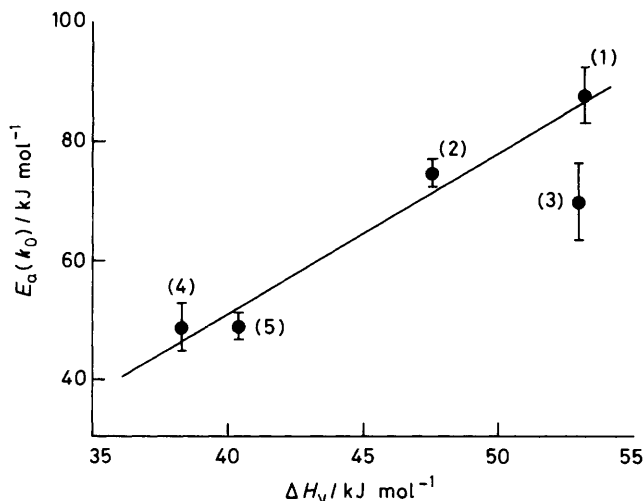


FIGURE 3 Correlation of the activation energy  $E_a$  ( $k_0$ ) with the heat of vaporization  $\Delta H_v$  of the solvents dma (1), dmf (2), dmsO (3),  $\text{CH}_3\text{NO}_2$  (4), and py (5)

**Reactivity of Water and Methanol in Aprotic Media.**—The kinetic contribution of water and methanol, respectively, to  $k_{\text{obs}}$ , is described by equations (5) and (9). It is

$$k_{\text{obs.}} = k' + k_{\text{MeOH}}[\text{MeOH}] \quad (9)$$

surprising to see that both water and methanol contribute linearly up to concentrations of at least  $1 \text{ mol dm}^{-3}$  (see Tables 2 and 5). Further support for the similarity in kinetic behaviour between water and methanol is reflected by the fact that  $k_{\text{H}_2\text{O}}/k_{\text{MeOH}}$  varies only slightly and that the condition  $k_{\text{H}_2\text{O}} \geq k_{\text{MeOH}}$  is fulfilled (see Table 5).

A mechanistic interpretation of the linear rate contribution  $k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]$  in equation (5) is given in Scheme 2.

It follows closely the mechanism suggested for alcohol-induced ligand substitution in nickel(II) and copper(II) bis(*N*-alkylsalicylideneiminato)-complexes.<sup>8</sup> Again, all

TABLE 5

Rate constants  $k_{\text{H}_2\text{O}}$  and  $k_{\text{MeOH}}$  at 25 °C in various solvents

| Solvent                  | $10^2 k_{\text{H}_2\text{O}}/$<br>$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ | $10^2 k_{\text{MeOH}}/$<br>$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ | $[\text{MeOH}]_{\text{max.}}/$<br>$\text{mol dm}^{-3}$ |
|--------------------------|---|--|--|
| MeOH                     | $9.5 \pm 0.48^b$  | $4.2 \pm 0.1^b$  | 24.6   |
| EtOH                     | $9.0 \pm 0.29^b$  | $2.30 \pm 0.04$  | 5.0  |
| 2-BuOH                   | —   | $1.43 \pm 0.08^c$  | 5.0  |
| 2-Me-2-BuOH              | $2.76 \pm 0.055^b$  | $0.81 \pm 0.06^c$  | 2.5  |
| dmsO                     | $0.315 \pm$<br>$0.029^b$  | $0.344 \pm$<br>$0.013^b$   | 1.5  |
| $\text{CH}_3\text{CN}$   | $4.34 \pm 0.81$   | $3.77 \pm 0.11^b$  | 24.6   |
| $\text{CH}_3\text{NO}_2$ | $3.2 \pm 1.3$   | $5.55 \pm 0.36$  | 12.5   |
| py                       | $6.86 \pm 0.18$   | $3.23 \pm 0.14$  | 2.5  |
| PhMe                     | $70.7 \pm 1.6^d$  | $16 \pm 0.4^e$   | 1.0  |

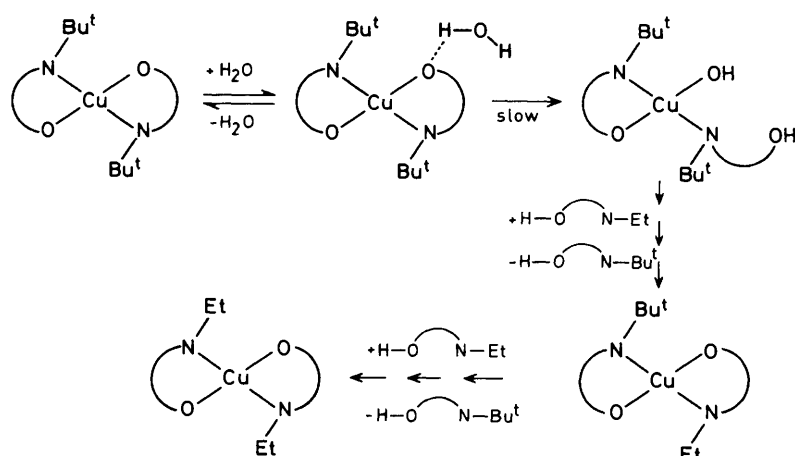
<sup>a</sup> Maximum concentration of MeOH up to which equation (9) was found to be valid. <sup>b</sup> From ref. 1. <sup>c</sup> H. Elias, H. Muth, B. Niedernhöfer, and K. J. Wannowius, *J. Chem. Soc., Dalton Trans.*, 1981, 1825. <sup>d</sup> From ref. 5. <sup>e</sup> From ref. 8.

steps following the rate-determining formation of the hydroxo-intermediate with a singly bonded H-Bu<sup>t</sup>saln ligand are thought to be fast.

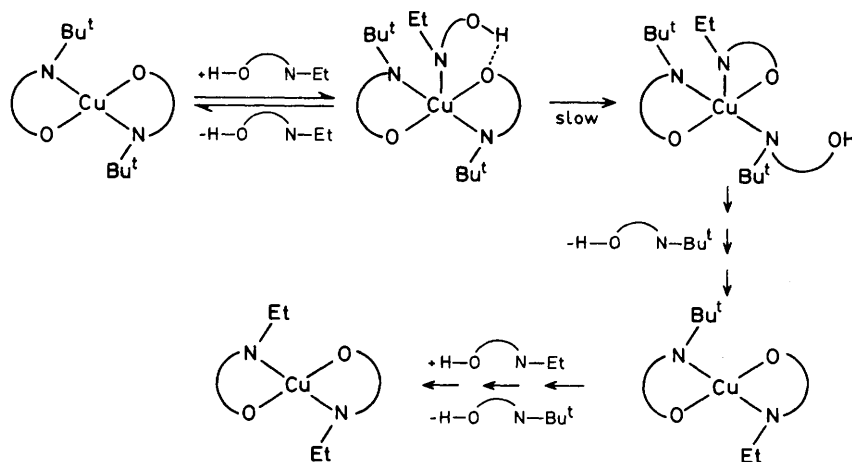
It is most interesting to see that the reactivity of water in aprotic solvents as characterized by  $k_{\text{H}_2\text{O}}$  differs enormously (see Table 2);  $10^2 k_{\text{H}_2\text{O}}$  is greatest for the non-polar solvent  $\text{CCl}_4$  (ca.  $2000 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) and smallest for the dipolar solvent dmsO ( $0.035 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). It is obvious that the polarity of the solvent cannot be the only parameter responsible for this difference of several orders of magnitude. Probably the internal structure of the solvent and its capability to interact efficiently with water have to be considered. A simple approach to explain the solvent-dependent reactivity of water is to assume that there is competition between the bulk solvent and the complex  $[\text{Cu}(\text{Bu}^t\text{saln})_2]$  to interact with the highly polar water molecules. The relative strength of the interactions, complex-water on the one hand, and solvent-water on the other, decides how effective the water is in opening a reaction channel. The types of interaction will be manifold and include polarity, as well as the possibility of hydrogen-bond formation and other parameters.

It is clear that this interpretation of competitive interaction of the substrate and of the solvent with water applied to other admixtures such as MeOH, other alcohols, and the entering ligand as well. Figure 1 presents convincing proof for this.

The fact that for some solvents the quadratic (6) is necessary for an adequate description at water concentrations exceeding  $0.5\text{--}1 \text{ mol dm}^{-3}$  and that the water affects even the ligand path [see equation (7)] reflects that the formation of water clusters begins to interfere, *i.e.* that water begins to cause medium effects. For the solvent propylene carbonate the effect of water on several physical solvent parameters such as viscosity, fluidity, vapour pressure, and enthalpy of mixing has been studied in detail.<sup>12</sup> From these studies non-linear water effects like those in equation (6) are not unexpected.



SCHEME 2 Mechanism of water-induced ligand substitution



SCHEME 3 Mechanism of the ligand path

**Mechanism of the Ligand Path.**—Due to the small Lewis acidity of the complex  $[\text{Cu}(\text{Bu}^t\text{saln})_2]$ <sup>9</sup> there is no ligand path to be observed in most alcohols.<sup>1</sup> It has been pointed out previously<sup>8</sup> for various nickel(II) complexes  $[\text{Ni}(\text{Rsaln})_2]$  ( $\text{R} = \text{alkyl}$ ) that there are convincing arguments for a mechanism of the ligand path in which the ligand attacks at the metal. The ligand path found for  $[\text{Cu}(\text{Bu}^t\text{saln})_2]$  in the aprotic solvents of this study is assumed to follow the same pattern (see Scheme 3). The  $k_{\text{HL}}$  values obtained (see Table 1) vary within two orders of magnitude. The following order is found:  $\text{CH}_3\text{CN} < \text{dmso} < \text{propylene carbonate} < \text{dmf} < \text{dma} < \text{py} \approx \text{CCl}_4 < \text{CH}_3\text{NO}_2 < \text{tmu} < \text{PhMe}$ . The high reactivity of the ligand in toluene is not unexpected; it is, however, not paralleled by a correspondingly high  $k_{\text{HL}}$  value in  $\text{CCl}_4$ . The high  $k_{\text{HL}}$  value in tmu as well as the curved dependence on the ligand concentration observed for this solvent [see equation (4)] are not understood.

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

[1/1177 Received, 24th July, 1981]

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