

Mechanistic Information on Solvent Initiated Ligand Substitution from Kinetic Solvent Effects and their Correlation with the Solvent Polarity Parameter $E_T(30)$

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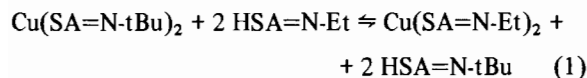
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Introduction

There is general agreement [1] that the mechanism of ligand substitution in square-planar d^8 complexes is associative for both the solvent path and the reagent path forming the observed two-term rate law. It is assumed that solvent attack as well as ligand attack occurs at the d^8 metal centre.

Ligand substitution in pseudo tetrahedral bis(N-t-butylsalicyl-aldiminato)copper(II) ($\cong \text{Cu}(\text{SA}=\text{N-tBu})_2$) by N-ethylsalicyl-aldimine ($\cong \text{HSA}=\text{N-Et}$) according to (1), as studied in various alcohols by stopped-flow spectrophotometry, follows two-term rate law (2), as it is typically observed for planar d^8 complexes.



$$\text{rate} = (k_S + k_{\text{HSA}=\text{N-Et}} [\text{HSA}=\text{N-Et}]) [\text{Cu}(\text{SA}=\text{N-tBu})_2] \quad (2)$$

It is found [2], however, that for most alcohols applied as solvent the ligand dependent reagent path $k_{\text{HSA}=\text{N-Et}} [\text{HSA}=\text{N-Et}]$ is negligibly small. So, the substitution according to (1) occurs predominantly through the solvent path and $\text{rate} = k_S [\text{complex}]$. The system is therefore well suited for the study of solvent effects on the rate of ligand substitution in the pseudo tetrahedral complex $\text{Cu}(\text{SA}=\text{N-tBu})_2$. The present contribution reports on a mechanistically interesting correlation existing between the solvent path rate constant k_S and Reichardt's solvent polarity parameter $E_T(30)$ [3].

Experimental

The preparation of $\text{Cu}(\text{SA}=\text{N-tBu})_2$ and $\text{HSA}=\text{N-Et}$ has been described elsewhere as well as the procedure for carrying out the stopped-flow measurements

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[2]. The various alcohols (reagent grade) were dried over molecular sieves. The parameter $E_T(30)$ was determined as described earlier [4].

Results and Discussion

Rate constant k_S varies strongly with the type and structure of alcohol applied as solvent [2], e.g., $k_S(\text{MeOH}) = 1.03 \text{ s}^{-1}$ and $k_S(2\text{-methyl-butanol-2}) = 0.0011$ at 25°C . Figure 1 demonstrates that there is a close linear correlation between $\log k_S$ and $E_T(30)$ for the group of the non-substituted aliphatic alcohols 1–10. In the case of the substituted alcohols 11–15 not all fall on the same line.

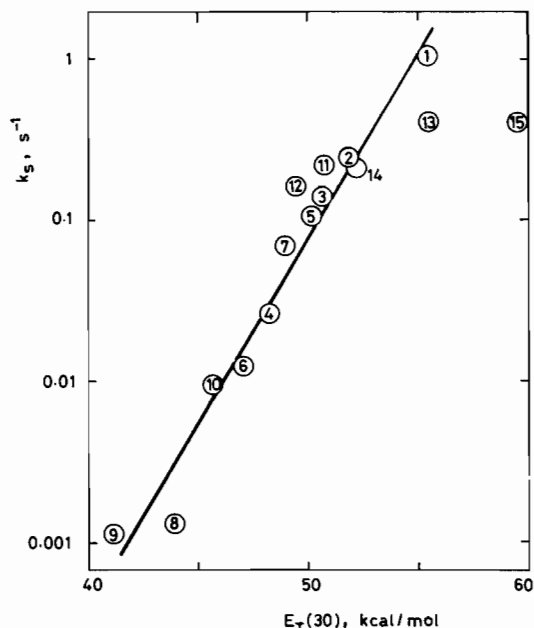
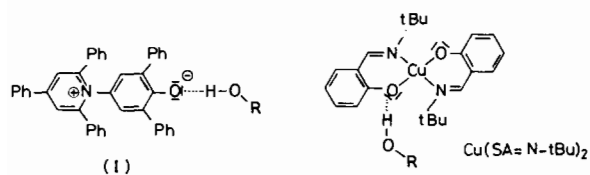


Fig. 1. Correlation of rate constants k_S with Reichardt's $E_T(30)$ values (1: methanol; 2: ethanol; 3: propanol-1; 4: propanol-2; 5: butanol-1; 6: butanol-2; 7: 2-methyl-propanol-1; 8: 2-methyl-propanol-2; 9: 2-methyl-butanol-2; 10: pentanol-3; 11: benzyl alcohol; 12: 2-phenyl-ethanol; 13: 2-chloro-ethanol; 14: 2-methoxy-ethanol; 15: 2-cyano-ethanol).

Most of the k_S values are similar to those reported earlier [2]. The value of $k_S(\text{pentanol-3})$ was determined as part of this study and was found to be $0.0095 \pm 0.0001 \text{ s}^{-1}$ [5]. The $E_T(30)$ values were taken from the literature [3], except for $E_T(30)(2\text{-chloro-ethanol}) = 55.5 \text{ kcal/mol}$ and $E_T(30)(2\text{-cyano-ethanol}) = 59.6 \text{ kcal/mol}$. These values had to be determined [4] according to Reichardt's procedure. The reported value of $E_T(30)(2\text{-methyl-butanol-2}) = 41.9$ [3] was found to be 41.1 kcal/mol upon re-determination [4].

As pointed out by Reichardt [3] the $E_T(30)$ values of protic solvents reflect primarily the HBD (hydrogen-bond donor) properties and, hence, the electrophilicity of these solvents. This is a consequence of the structure of the solvatochromic betaine dye(I) applied for the determination of $E_T(30)$ values and its specific charge distribution. The most favourable site for an alcohol molecule ROH to interact with the dye is its phenolic oxygen, the type of interaction being hydrogen bonding as indicated in the following scheme:



The close correlation between $\log k_S$ for reaction (1) and $E_T(30)$ can be taken as a strong indication for an analogous interaction initiating the solvent path of (1). Two of the donor atoms in the substrate $\text{Cu}(\text{SA}=\text{N}-t\text{Bu})_2$ are also phenolic and the ROH molecule will attack at these most basic and easily accessible oxygen sites through hydrogen bonding, as shown in the scheme above. Proton transfer from an associated ROH molecule to the phenolic oxygen is followed by breaking of the Cu–O bond and transient coordination of the RO^- group.

In support of this interpretation it is found [6] for a given solvent that (i) sterically demanding groups such as the *t*-butyl group in *ortho* position to the phenolic oxygen in $\text{Cu}(\text{SA}=\text{N}-\text{R})_2$ reduce the size of k_S due to shielding and (ii) increasing tetrahedral distortion of planar complexes $\text{Cu}(\text{SA}=\text{N}-\text{R})_2$ makes the donor oxygen atoms more accessible and, therefore, increases the size of k_S .

The fact that for solvents such as 2-chloro-ethanol (13) and 2-cyano-ethanol (15) the correlation between $\log k_S$ and $E_T(30)$ becomes worse is probably due to another functional group being present in these alcohol molecules. The HBD properties of such 'biphilic' solvents and their ability to initiate reaction (1) are obviously rather different.

In conclusion, for ligand substitution in a 4-coordinate *trans*- N_2O_2 copper(II) complex in alcohol media strong evidence is provided for the solvent path to be mechanistically unusual in the sense that solvent attack does not occur at the metal but at the donor oxygen, through hydrogen bonding.

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