Inorganica Chimica Acta, 25 (1977) 157–158
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A CNDO Insight to the Alcoholysis of N-Sulphinylamines in Ethanol, Using Copper(II) Chloride as Catalyst

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Received April 13, 1977

Using the CNDO/2 method, the electron densities in p-NO_2, p-*Cl, and* p-*H N-Sulphinylanilines were computed. The electron densities at sulphur were found to be proportional to the Hammett σ-values of the substituents and also to log* k_c *for the alcoholysis. The activation energy, Arrhenius factor and* $\Delta S^{\ddagger}$ *values for the system copper(II) chloride, ethanol and N-sulphinylaniline are reported.*

Introduction

In previous papers [1, 2], the reaction

$$RC_6H_4NSO + EtOH \xrightarrow{CuCl_2} CuCl_2 \cdot 2RC_6H_4NH_2 + (OEt)_2\,S{=}O$$

has been studied kinetically (R = *p*-H, *p*-NO_2, *p*-Cl). A first order rate law with respect to the N-sulphinylamine was followed, and the observed rate constant (k_{obs}) was directly proportional to the concentration of copper(II) chloride catalyst. When $[\log(k_{obs}/[CuCl_2])]$ was plotted against the Hammett σ value of the *para*-substituent of these compounds, a linear relationship was found. The positive value of ρ (0.93) determined from this plot indicated that the reaction is accelerated by electron withdrawing substituents on the ring.

The temperature variation of the catalyzed reaction of N-sulphinylaniline in ethanol with copper(II) chloride has now been completed, together with a CNDO calculation of electron densities in the N-sulphinylamines previously studied. These results supplement and support our former conclusions [1, 2] as to the mechanism of these reactions.

Experimental

N-sulphinylaniline, ethanol and copper(II) chloride were prepared as previously [1, 2]. The decrease in the π → π* band of the amine (band maximum found at 325nm) was observed on the time-drive setting of a Perkin Elmer 402 instrument, equipped with a specially constructed thermostatted cell compartment. Concentrations of 14.13 × 10^{-4} *M* of copper(II) chloride and 12.27 × 10^{-5} *M* of N-sulphinylaniline were reacted in teflon stoppered cells at four different temperatures in the range 30–40 °C. Reproducible results (±3%) were obtained for all runs at a particular temperature, and least-squares procedures were used to evaluate data on an IBM 360/50 computer.

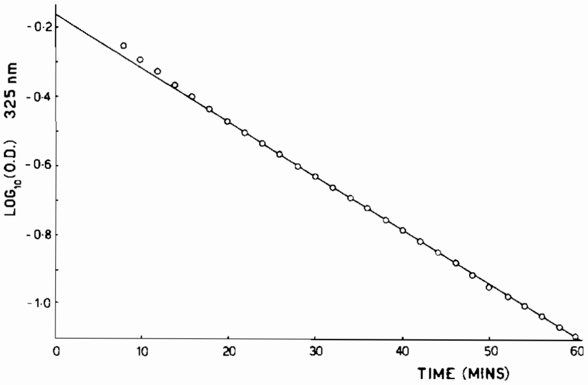

Figure 1. An example of a first-order rate plot for the copper(II) chloride, N-Sulphinylaniline, ethanol system. $[CuCl_2]$ = 14.3 × 10^{-4} *M*. Temperatures is 30.3 °C.

Results and Discussion

A deviation from first-order kinetics was noticed at the beginning of the reaction in all runs. A typical run is shown in Figure 1. As previously [1], this may be attributed to the presence in the system of a small amount of water (or other impurity) which reacts at a very fast rate with N-sulphinylaniline. No deviation from first-order kinetics at the end of the reaction was observed, as had been formerly found [1, 2]. This may be due to the fact that a large excess (*ca.* 12 fold) of cupric chloride was used. Aniline produced in the reaction immediately reacts with copper(II) chloride, effectively removing catalyst from the system and decreasing the rate. With a large enough

TABLE I. Charge Densities (ρ) in Electron Units for the N-Sulphinylamines Studied (a positive sign indicates electron deficiency), together with the Hammett Constant (σ_p) of the *p*-Substituent.

p-Substituent	Charges in Electron Units				Hammett Constant
	ρ_C (adjacent N)	ρ_N	ρ_S	ρ_O	
NO_2	0.156	−0.284	0.313	−0.128	+0.78
Cl	0.207	−0.051	0.270	−0.315	+0.23
H	0.195	−0.066	0.256	−0.301	0.0

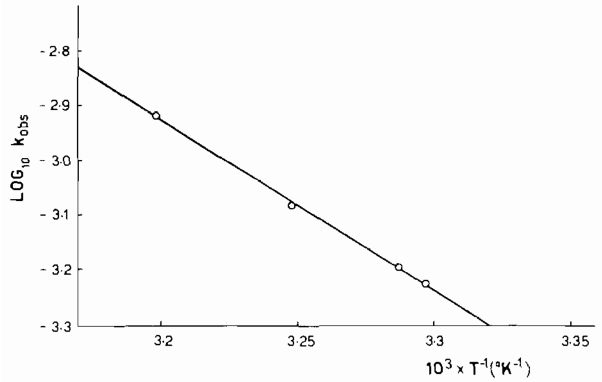

Figure 2. Arrhenius plot for the reaction of ethanol and N-sulphinylaniline catalysed by copper(II) chloride.

concentration of copper(II) chloride, the decrease in rate will not be noticeable. Again, the monitoring of the reaction at 325nm avoids a possible contribution from the "tail" of the aniline product.

A plot of $\log_{10}k_{obs}$ against T^{-1} is shown in Fig. 2. The activation energy was found to have the value 14.25 ± 1.5 Kcal mol^{-1}. This value is close to that obtained for the reaction of N-sulphinylaniline and ethanol, catalysed by triethylamine [3]. $CuCl_2$ would be expected to behave as a Lewis Acid, and triethylamine as a base.

The above activation energies have the same order of magnitude as some typical hydrolysis reactions. For instance, Swan and Scott [4] studied the kinetics of the hydrolysis of acetyl chloride, benzoyl chloride and benzene sulphonyl chloride in a water–acetone mixture and obtained activation energies of 13.9, 14.3 and 18.8 Kcal mol^{-1} respectively. This suggests that the rate-determining step involves an ethanolysis reaction, and supports the idea that the catalyst activates the ethanol converting it to a more effective nucleophile which then attacks the electron-defficient sulphur atom in N-sulphinylaniline. The Arrhenius factor for the copper(II) chloride reaction obtained by a plotting of log ($k_{obs}/[CuCl_2]$) against T^{-1} is 8.0×10^9, compared with an Arrhenius factor of 2.83×10^{10} for the triethylamine catalysed reaction [3].

On the basis of transition state theory, this ethanolysis has a $\Delta S^{\ddagger}$ value of −15.3 ± 2.3 eu. Long [5] *et al.* have proposed the use of $\Delta S^{\ddagger}$ as a criterion of the mechanism of hydrolysis reactions. In the bimolecular case (A-2, S_nII), a water molecule is considered bound in the activation complex. Typical values of $\Delta S^{\ddagger}$ for A-2 type ester hydrolyses are −15 to −30 eu.

The dependence of log k_c on the Hammett σ constant indicates that the nucleophilic attack of alkoxide ion species on electron deficient sulphur is the rate determining factor in the alcoholysis.

The charge densities were calculated using the CNDO/2 method of Pople *et al.* [6]. Bond distances and bond angles for the X–NSO entity were taken as X–N = 1.40Å, N–S = 1.51Å, S–O = 1.45Å, $\widehat{XNS}$ = 122°, $\widehat{NSO}$ = 121°, and a *trans*-conformer was assumed. The geometry of the substituted phenyl was obtained from Sutton's compilation [8]. Calculated values for the charge densities are compiled in Table I.

A plot of the electron density at sulphur (ρ_S) against the Hammett constant (σ_p) is linear: $\rho_S = 0.074\ \sigma_p + 0.255$, with a standard deviation of the slope of 0.0039. When log k_c is plotted against ρ_S, the equation $\log k_c = 12.601\ \rho_S - 3.880$ is obeyed, the standard deviation of the slope being 0.857. These results clearly support our previous suggestion that the rate determining step is attack at the sulphur atom of the N-Sulphinylaniline.

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