Some Studies of the Alcoholysis of *p*-Nitro- and *p*-Chloro-*N*-sulphinylaniline in Ethanol using Copper(II) Chloride as Catalyst

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Kinetic studies of the title *N*-sulphinylanilines in ethanolic solution showed that a first-order rate law with respect to the *N*-sulphinylamine was obeyed. The observed rate constant (k_{obs}) was directly proportional to the catalyst concentration. A linear relationship was found when log (k_{obs}/[$CuCl_2$]) was plotted against the Hammett σ value of the *para*-substituent for the compounds. The increase in k_c as the electron-withdrawing capacity of the ring substituent increases implies that an [RNSO:$CuCl_2$] complex is not involved in the reaction mechanism. Contrary to PhN:S:O, an uncatalysed reaction with the solvent was observed for the substituted *N*-sulphinylanilines.

IN a previous paper,[1] the alcoholysis (1) of *N*-sulphinylaniline in pure ethanol was investigated. Copper(II)

$$PhN{:}S{:}O + 2EtOH \longrightarrow PhNH_2 + (EtO)_2S{:}O \quad (1)$$

chloride was used as a catalyst and the reaction was followed by monitoring the $\pi \longrightarrow \pi^*$ band of *N*-sulphinylaniline (log ε *ca.* 4·0) at 315 nm. The reaction was found to be subject to autocatalysis and inhibition. Characteristic deviations from an integral kinetic order

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[1] N. C. Collins and W. K. Glass, *J. Chem. Soc.* (*B*), 1971, 887.

occurred at the beginning and end of a rate measurement, and the effect that predominated depended on the relative concentrations of reactants and products, and the nature of the solvent. Both effects could be wholly or partly suppressed by the use of relatively high concentration ratios (up to 17 : 1) of copper(II) chloride. It was evident that a substantially first-order rate law was followed with respect to *N*-sulphinylaniline. Observed rate constants (k_{obs}) were evaluated from the central linear portion of the pseudo-first-order plots. When plotted against the concentration of copper(II) chloride, values of k_{obs} showed a direct proportionality to the catalyst concentration in the range 6·75—71·5 × 10^{-5}M, the *N*-sulphinylaniline concentration being 4·05 × 10^{-5}M. The line passed through the origin, and thus $k_{obs} = k_c[CuCl_2]$. No spontaneous reaction of *N*-sulphinylaniline in the absence of catalyst could be detected.

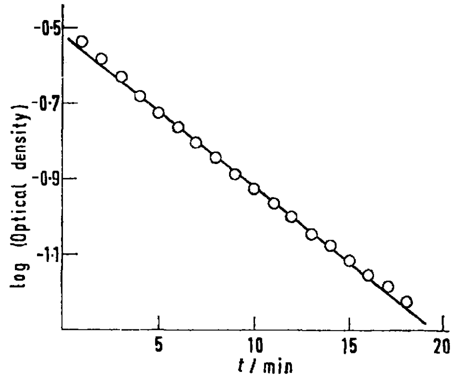
Two types of mechanism were considered for the reaction, one in which a complex of copper(II) chloride and *N*-sulphinylaniline reacted with the solvent, the other in which a solvent molecule in the solvation–coordination sphere of Cu^{II} was ionized (to EtO^-,$CuCl_2$) and then attacked the uncomplexed sulphinylaniline. Both mechanisms would be expected to have the kinetic form observed for the reaction, and although no evidence for the formation of an *N*-sulphinylanilinecopper(II) chloride complex, the essential feature distinguishing between the mechanisms, could be found by u.v. or i.r. measurements, it remained possible that it was present at concentration too low for spectroscopic detection but high enough to be of kinetic significance.

In this paper, we attempt to distinguish the two mechanisms by extending the kinetic study to *p*-chloro- and *p*-nitro-*N*-sulphinylaniline to ascertain if any relationship exists between k_c and the electron-withdrawing power of the substituent group. Electron withdrawal must inhibit the formation of an *N*-sulphinylaniline–metal complex and, almost certainly, would increase the energy of a transition state arising either from attack of a neutral (solvent) molecule on the complex or from subsequent reaction of the complex solvent adduct. Therefore, if electronegative substituents lead to an *increase* in k_c, it can reasonably be inferred that a sulphinylanilinecopper(II) chloride complex does not lie on the reaction path.

RESULTS

Copper(II) *Chloride*-N-*Sulphinylaniline–Ethanol System.*—Data were obtained in precisely the same manner as previously,[1] except that the initial concentration of PhNSO was 3·0 × 10^{-4}M and that ($CuCl_2$) varied from 8·21 to 4·10 × 10^{-3}M. Good first-order results were obtained. A typical plot of log (Optical density) against time for the system is shown in the Figure. A plot of [$CuCl_2$] against k_{obs} (utilizing the results in Table 1) gave a straight line which passed through the origin. The value of k_c was 0·217 l mol^{-1} s^{-1}. The root mean square deviation (r.m.s.d.) was 0·005, the standard error of estimate (s.e.e.) 0·0001, and the correlation coefficient (*r*) 0·9882.

p-*Chloro*-N-*sulphinylaniline–Copper*(II) *Chloride–Ethanol System.*—This system was followed by observing the decrease in optical density of the $\pi \longrightarrow \pi^*$ transition at 325 nm as the reaction progressed. The initial concentration of *p*-ClC_6H_4NSO was 3·10 × 10^{-4}M, and the copper(II) chloride concentration varied from 1·93 to 7·76 × 10^{-3}M. The first-order plots displayed little evidence of the complicating features observed in the case of *N*-sulphinylaniline. The plot of k_{obs} against [$CuCl_2$], using the results in Table 1, gave a k_c value of 0·345 l mol^{-1} s^{-1}, and an intercept of 0·56 × 10^{-3} s^{-1}. For these data, r.m.s.d. was 0·0025, s.e.e. 0·0001, and *r* 0·9844.



A typical kinetic run of the PhN:S:O–$CuCl_2$–EtOH system. All runs in each system studied were reproducible to better than ±5%. In this case [$CuCl_2$] = 7·18 × 10^{-3}M and [PhNSO] = 3·0 × 10^{-4}M. The reaction was followed to the completion of its second half-life

TABLE 1

Kinetic data for the *N*-sulphinylanilines studied

[PhNSO] = 3·0 × 10^{-4}M		[*p*-ClC_6H_4NSO] = 3·1 × 10^{-4}M		[*p*-$NO_2C_6H_4NSO$] = 3·1 × 10^{-4}M	
$10^3[CuCl_2]$/M	10^3k_{obs}/s^{-1}	$10^3[CuCl_2]$/M	10^3k_{obs}/s^{-1}	$10^3[CuCl_2]$/M	10^3k_{obs}/s^{-1}
8·21	1·69	6·76	2·92	7·95	9·72
7·18	1·56	5·79	2·41	6·96	8·98
6·16	1·36	4·83	2·34	5·96	6·97
5·13	1·11	3·86	2·02	3·32	4·02
4·10	0·80	2·90	1·46	1·66	2·79
		1·93	1·22	1·11	1·93
				0·55	1·32

TABLE 2

Values of k_0, k_c, and Hammett σ for the three *N*-sulphinylanilines RC_6H_4NSO studied

R	σ	k_0/s^{-1}	k_c/l mol^{-1} s^{-1}
H	0·0	0	0·217
p-Cl	0·23	0·56 × 10^{-3}	0·345
p-NO_2	0·78	0·64 × 10^{-3}	1·14

p-*Nitro*-N-*sulphinylaniline–Copper*(II) *Chloride–Ethanol System.*—Since at 375 nm *p*-nitro-*N*-sulphinylaniline absorbs in the same region as the product *p*-nitroaniline, the variation of optical density with time was treated using the first-order equation (2) where *D* is the optical density of the

$$\log [(D_0 - D_\infty)/(D - D_\infty)] = kt/2{\cdot}303 \qquad (2)$$

solution at time *t*, D_0 is the initial optical density, and D_∞ is the optical density at the end of the reaction. The initial concentration of *p*-nitro-*N*-sulphinylaniline was 3·10 × 10^{-4}M, which corresponds to D_0 and D_∞ having values of 0·105 and 0·497 respectively. First-order rate constants were obtained graphically by plotting log $[(D_0 - D_\infty)/(D - D_\infty)]$ against time, and evaluating the slope. Excellent first-order rate plots, with no evidence of inhibition or autocatalysis, were observed. The plot of k_{obs} against [$CuCl_2$], using the results of Table 2, gave a straight line with intercept k_0 of $0{\cdot}64 \times 10^{-3}$ s^{-1}, and a slope, k_c, of 1·14 l mol^{-1} s^{-1}. For these data, r.m.s.d. was 0·0013, s.e.e. 0·0003, and r 0·9957.

DISCUSSION

Before considering the substituent effects on the copper(II) chloride catalysed reaction of *N*-sulphinylaniline, it is necessary to consider in what way they may be affected by the autocatalysis and inhibition that complicate kinetic behaviour.

For *N*-sulphinylaniline, the main features of the catalysis and inhibition were summarized above, and have been discussed in more detail in a previous paper. It is likely that autocatalysis arises from participation of the product (aniline) in the reaction. Basic amines, such as triethylamine, accelerate the reaction and it is notable that autocatalysis is observable only for substrates yielding a sufficiently basic product. For *p*-nitro-*N*-sulphinylaniline, which gives *p*-nitroaniline as a product, no autocatalysis can be detected.

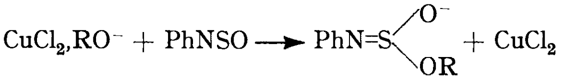
As described previously, this ' self-catalysis ' may be virtually suppressed by having copper(II) chloride in excess. The reason for this is presumably that the product is deactivated by formation of a dianiline-copper(II) chloride complex. At moderate copper(II) chloride concentrations the main disturbance to the first-order kinetics comes from self-inhibition, as may be clearly seen from the Figure, which shows the small but definite downward drift in first-order rate constant as the concentration of *N*-sulphinylaniline decreases. The most reasonable explanation of this behaviour is that it is due to catalysis by the *N*-sulphinylaniline itself acting as a base; the sulphinylaniline concentration decreases as the reaction progresses, and so the rate constant falls. However, because of the low basicity of the sulphinylaniline, the catalysis is quite weak; it is also diminished by electron-withdrawing substituents, and for *p*-nitro-*N*-sulphinylaniline it was not observed at all.

In order to diminish any contribution to *para*-substituent effects on the copper(II) chloride catalysed reaction, care was taken to compare rate constants for the substituted and unsubstituted substrates using the same initial *N*-sulphinylaniline concentration. This expedient was also employed in a study of isocyanate alcoholysis [2] using trisacetylacetonatoiron(III) as catalyst. However, inspection of the Figure suggests that even in the case of *N*-sulphinylaniline the discrepancy is not large, and care was taken to avoid the use of electron-donating substituents to ensure that no larger effect was introduced. It should be emphasized that the observed departures from first-order behaviour were systematic and could be reproduced to ±5%.

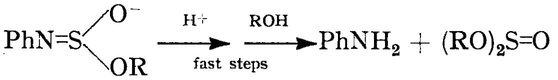
The rate constants for the catalysed reaction of the substituted *N*-sulphinylanilines are shown in Table 1. For the reasons given above, we believe that the variation in rate constants represents a substituent effect upon the copper(II) chloride reaction. That the kinetic complications for unsubstituted *N*-sulphinylaniline and the *p*-chloro-derivative did not have any substantial effect is corroborated by the excellent correlation with Hammett substituent constant obtained when values of k_c are plotted with that for the *p*-nitro-derivative.

The magnitude of ρ found from the plot is 0·93, and its positive value [3] clearly indicates that the reaction is accelerated by electron-withdrawing substituents and therefore that, as discussed above, a sulphinylaniline-copper(II) chloride complex is unlikely to be an intermediate. It follows that the role of copper(II) chloride must be in facilitating attack of the solvent, and the most likely possibility would seem to be ionization of an ethanol molecule in its solvation shell, followed by rate-determining attack at the sulphur atom of the *N*-sulphinylaniline [reactions (3) and (4)].

$$CuCl_2,ROH \rightleftharpoons CuCl_2,RO^- + H^+ \qquad (3)$$



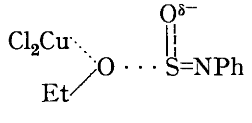
$$CuCl_2,RO^- + PhNSO \longrightarrow PhN{=}S\begin{matrix}O^-\\OR\end{matrix} + CuCl_2 \qquad (4)$$



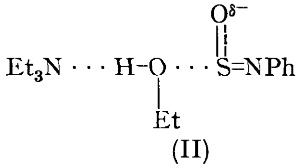
$$PhN{=}S\begin{matrix}O^-\\OR\end{matrix} \xrightarrow[\text{fast steps}]{H^+} \xrightarrow{ROH} PhNH_2 + (RO)_2S{=}O \qquad (5)$$

The transition state (I) for reaction (4) would be consistent with the moderate magnitude of ρ and the absence of strong conjugative interactions implied by the satisfactory correlation of the *p*-nitro-group by the normal Hammett substituent constant σ_p rather than σ_p^-.

Also consistent with the reaction involving catalysed nucleophilic attack at sulphur is the observation of an uncatalysed reaction with solvent when the *N*-sulphinylaniline has electron-withdrawing substituents. Rate constants for the solvent reaction determined from the intercept of the plots of k_{obs} against [$CuCl_2$] are also listed in Table 2. As expected, the rate constant for *p*-nitro-*N*-sulphinylaniline is greater than that for the *p*-chloro-derivative. The lower selectivity between *p*-chloro and *p*-nitro than for the faster catalysed reaction is unexpected; this may reflect a relatively large error (±25%) in the rate constants for uncatalysed reaction, as they are obtained by an extrapolation to zero copper(II) chloride concentration.



(I)



(II)

The observed variation of k_c with initial concentration of *N*-sulphinylaniline is surprising in view of the good first-order plots. At *N*-sulphinylaniline concentrations of 30·0, 12·27, and $4{\cdot}05 \times 10^{-5}$M, k_c values of *ca.* 0·22,

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[2] R. S. Bruenner and A. E. Oberth, *J. Org. Chem.*, 1966, **31**, 887.

[3] A. Liberles, ' Introduction to Theoretical Organic Chemistry,' Macmillan, London, 1968.

0·42, and 0·95 mol^{-1} l s^{-1} were recorded. Thus the catalysing power of copper(II) chloride appears to decrease with increasing concentration of *N*-sulphinylaniline. In a study of the ethanolysis of *N*-sulphinylaniline using triethylamine as catalyst,[4] a similar though not as pronounced an effect was observed. At *N*-sulphinylaniline concentrations of 25·6, 12·8, and 6·4 × 10^{-5}M, the values of k_c ($k_c = k_{obs}/[NEt_3]$) were 1·42, 1·73, and 1·96 mol^{-1} l s^{-1} and it was suggested that the catalyst was inhibited by a compound which accumulated with time during the course of reaction, in proportion to the initial concentration of *N*-sulphinylaniline. It is evident that triethylamine has superior catalysing powers to copper(II) chloride in this ethanolysis. It is unlikely that at the low concentrations of *N*-sulphinylaniline used in our studies, dielectric effects alone would be sufficient to account for the observed changes in k_c. The fact that the runs at higher concentration exhibited freedom from the primary complications of those at lower concentration may well be significant {the commencement of the central straight line portion of the plot occurred after *ca.* 3 min of reaction with [PhNSO] 30·0 × 10^{-5}M, whereas at [PhNSO] 4·05 × 10^{-5}M, the central plot occurred after 14 min with roughly the same relative concentrations of copper(II) chloride}. The only significant ' impurity ' in the system is residual traces of water (the ethanol was purified to contain at most 10 p.p.m. of water); PhNSO can undergo nucleophilic attack with water, and we earlier proposed this [1] as an explanation of the deviation at the beginning of the kinetic first-order plots.

It is possible that the final component in the observed reactions, the catalysis by amines,[4] arises from ionization of the solvent to give the more nucleophilic ethoxide ion. The expected effectiveness of ethoxide as a nucleophile was shown qualitatively by the fact that reaction was too fast for measurement in the presence of even very small concentrations of ethoxide ion. However, it is also possible that the amine is present in the transition state (II), acting as a general base catalyst for nucleophilic attack. This is more obviously consistent with catalysis by such weak bases as the *N*-sulphinylanilines themselves and is analogous to the established mode of base catalysis for the attack of weak nucleophiles at a carbonyl group.[5] Again with respect to copper(II) chloride catalysis, it seems intuitively reasonable that copper(II) chloride, although playing a very different role from the base should also act upon the nucleophilic group in the transition state.

EXPERIMENTAL

A least-squares procedure was used to evaluate data on an I.B.M. 360/50 computer. The reaction goes to completion with all the *N*-sulphinylanilines studied. Diethyl sulphite, b.p. 44°, was recovered in *ca.* 75% yield, and the bisaniline product in >90% yield for the reaction using preparative scale conditions.

N-Sulphinylaniline was prepared using Michaelis and Hertz's method.[6] *p*-Chloro-*N*-sulphinylaniline was made by adding thionyl chloride to *p*-chloroaniline in benzene solution, refluxing for 6 h, followed by fractional distillation.[7] *p*-Nitro-*N*-sulphinylaniline was prepared similarly. Friedman and Wetter's method [8] was used to purify thionyl chloride. Anhydrous copper(II) chloride was produced by treating hydrated copper(II) chloride with thionyl chloride. Ethanol was dried by the method in ref. 1. All materials were stored under dry nitrogen, and, whenever possible, handling operations were carried out in a dry-box. The reactions were initiated by pipetting the required amounts of the *N*-sulphinylanilines in heptane into ethanol solutions of $CuCl_2$.

A Unicam SP 500 spectrophotometer, equipped with a thermostatted sample compartment (25°) was used for monitoring purposes. The temperature was controlled to 0·03° by means of a Townson and Mercer TU3 thermostatted unit. The 1 mm. far-u.v. cells (Thermal Syndicate) had Teflon stoppers.

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