Chlorination of Cyclohexene by Copper(II) Chloride

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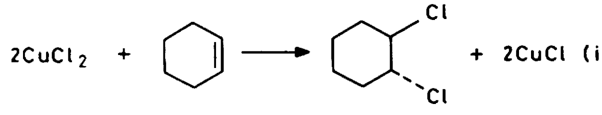
Evidence is presented which indicates that $CuCl^+$ is the reactive species in the chlorination of cyclohexene by copper(II) chloride in acetonitrile. The reaction is retarded by an excess of chloride ion and by copper(I) salts, and accelerated by aluminium trichloride. A kinetic scheme which accounts for these observations is suggested.

The chlorination of olefins by copper(II) chloride in a variety of solvents has been studied by Baird *et al.*[1] They demonstrated that acetonitrile is a particularly efficient solvent for this reaction, possibly because it stabilises copper(I) relative to copper(II). They noted that the reaction was inhibited by an excess of chloride ion but did not carry out any rate measurements. Cyclohexene was chlorinated to give *trans*-1,2-dichlorocyclohexane with only traces of the *cis* isomer; no other products were reported [reaction (i)].



(i)

In the present study, the rate of reaction of cyclohexene with copper(II) chloride in refluxing acetonitrile has been measured over a wide range of concentrations of the major reagents. A quantitative study of the effect of copper(I) and of the ratio of copper(II) to chloride ion has been carried out. The effect of aluminium chloride on the reaction has been briefly studied.

Experimental

Reagents.—Cyclohexene (reagent grade) was washed with iron(II) sulphate to remove peroxides and dried over anhydrous sodium sulphate. It was found to contain less than 0.01% water.

Acetonitrile as received contained variable quantities of two unidentified oxidisable species and water. A standard solvent was obtained by refluxing the acetonitrile over anhydrous copper(II) chloride and distilling prior to use. This gave material containing <0.1% water.

Anhydrous copper(II) tetrafluoroborate (Alfa Inorganics) was always wet and could not be obtained really dry without decomposition. When this was used to complement $CuCl_2$ the water content of the reacting system was measured.

Analytical Procedures.—The reaction could be followed either by estimating the 1,2-dichlorocyclohexane or the copper(I) produced, or by spectrophotometric determination of the copper(II) consumed. The results of all three methods agreed within experimental error. Chromatographic analysis of 1,2-dichlorocyclohexane was carried out on a Perkin-Elmer F11 instrument using 15% Carbowax 20M on Chromosorb W at 110 °C. This confirmed that *trans*-1,2-dichlorocyclohexane was produced with less than 2% of the *cis* isomer. The copper(I) analysis was carried out using the method described by Vogel.[2] For spectrophotometric analysis of copper(II) the band at 310 nm was monitored continuously.[3]

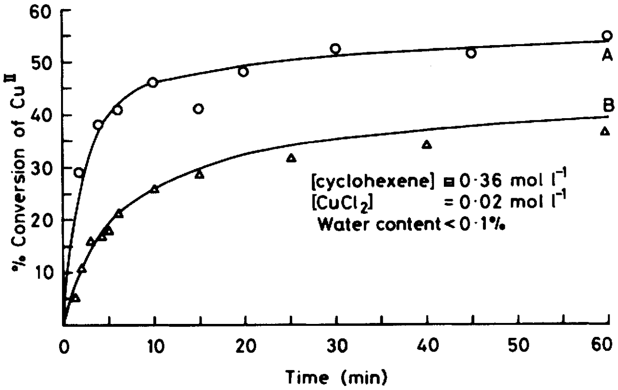


Figure 1. Reactions of (A) cyclohexene with $CuCl_2 + AlCl_3$ and (B) cyclohexene with $CuCl_2$; curves are calculated from the rate equation, points are experimental

Kinetic Measurements.—Reactions were carried out in refluxing acetonitrile at 81 °C. The initial reagent conditions were set up and the cyclohexene was injected into the mixture. Samples were withdrawn for chromatographic or titrimetric analysis, and quenched by rapid cooling. Spectrophotometric analysis was carried out by circulating the reacting solution through the cell. A few runs were checked by all three methods but most of the work was done by chromatographic analysis. The initial reaction rates are markedly influenced by traces of water, but the shape of the overall reaction curve is changed but little if the water content is below 3%. In all runs recorded the water content was <1.5%.

Results and Discussion

A typical reaction plot is shown as curve A of Figure 1. A fast initial reaction of copper(II) up to about 20% conversion is followed by a much slower reaction which eventually becomes very slow between 35 and 40% conversion but does not entirely stop. This pattern of reaction was always observed with only relatively small differences over a range of initial copper(II) to cyclohexene ratios, copper(II) to chloride ion ratios, and copper(I) to copper(II) ratios, despite very wide variations in the absolute rate at which the reaction commenced. The stoicheiometry of the reaction shows that as the reaction proceeds the ratio of Cu^I to Cu^{II} progressively increases. In addition the ratio of chloride ion to copper(II) also increases, as one copper(II) atom is reduced for each covalent carbon–chlorine bond formed. The retardation of the reaction with increasing conversion of copper(II) into copper(I) could therefore be a consequence of either or both of these factors. Neither factor would influence the initial rate for a fixed ratio of Cu^{II} to Cl^- with no Cu^I present. Accordingly experiments were carried out to establish the order of reaction with respect to $CuCl_2$ and cyclohexene, for the initial rate.

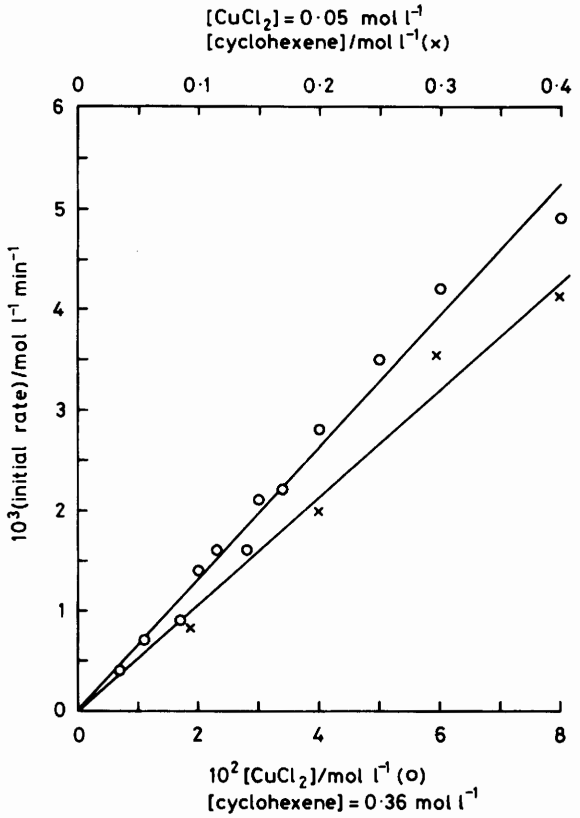


Figure 2. Initial rate against [$CuCl_2$], [cyclohexene]

Table 1. Effect of the ratio of chloride ion to copper(II) *

[Cl]/[Cu^{II}]	0.5	0.75	1.0	1.5	2.0	2.5	3.0
10^3(initial rate)/ mol l^{-1} min^{-1}	1.7	2.5	2.6	2.4	1.1	0.3	0.06
10^2[$CuCl^+$]/ mol l^{-1}	5.4	8.7	11.0	8.6	5.7	3.0	0.6

* Water content 1.4%; [cyclohexene] = 0.36 mol l^{-1}; [Cu^{II}] = 0.1 mol l^{-1}.

The results are shown in Figure 2. The initial reaction is first order in both reagents with a rate constant of 0.17 l mol^{-1} min^{-1} [equation (ii)].

$$\text{initial rate} = k[CuCl_2][C_6H_{10}] \qquad \text{(ii)}$$

In order to study the effect of the ratio of chloride ion to copper(II) the initial rates for a series of mixtures of Cu[BF_4]$_2$ and $CuCl_2$ were studied to give ratios of [Cl] to [Cu^{II}] in the range 0.5—2. In addition ratios in the range 2—3 were studied using tetraethylammonium chloride as the source of the additional chloride ion. The results are given in Table 1 and plotted in Figure 3. There is a pronounced maximum at a [Cl]/[Cu^{II}] ratio of 1 : 1, and when this ratio reaches 3 : 1 the reaction is very slow.

The chloro-complexes of copper(II) and copper(I) in acetonitrile have been studied by spectrophotometric and electrochemical methods by Manahan and Iwamoto.[3] They estimate that the stepwise formation constants for chloro-complexes in acetonitrile are $K(CuCl^+) = 10^{9.7}$, $K(CuCl_2) = 10^{7.9}$, $K(CuCl_3^-) = 10^{7.1}$, $K(CuCl_4^{2-}) = 10^{3.7}$ l mol^{-1} for copper(II) species and $K(CuCl) = 10^{4.9}$, $K(CuCl_2^-) = 10^{5.9}$ l mol^{-1} for copper(I) species. These figures are formal formation constants and do not take account of ion-pair formation; they are used here with this in mind. Thus reference to a species such as $CuCl^+$ does not imply that this simple formula is correct but merely that we are dealing with a cationic copper species at the reaction site.

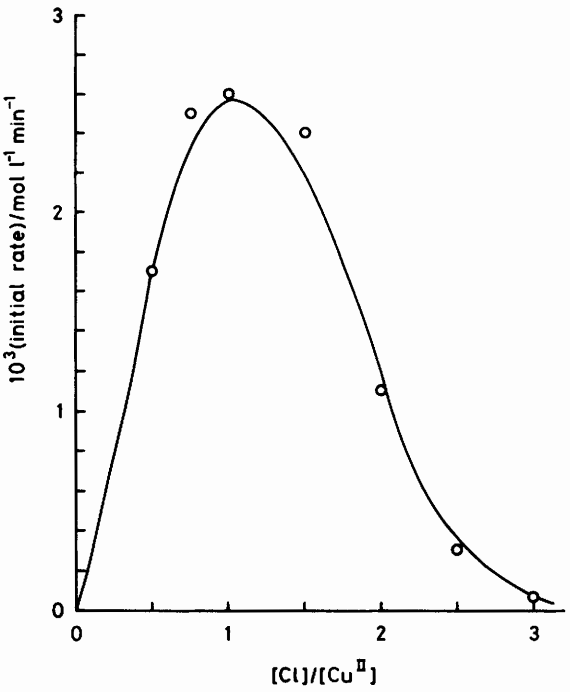


Figure 3. Effect of varying [Cl]/[Cu^{II}]

By using these formation constants it can be seen that below 50% conversion of Cu^{II} into Cu^I, [Cu^I] has little effect on the chloro-complexes of Cu^{II}. It also follows that in the range of concentrations used nearly all the Cu^I is present as Cu^+, with [CuCl] less than 5% of total Cu^I.

The calculated concentration of $CuCl^+$ as a function of [Cl]/[Cu^{II}] [3] gives a curve of very similar shape to Figure 3. This is confirmed by the plot (Figure 4) of initial rate against [$CuCl^+$], which is linear, strongly suggesting that the key species in the reaction of copper(II) chloride with cyclohexane in acetonitrile is $CuCl^+$. This also explains the effect of added water on the initial reaction rate: the water would react with $CuCl^+$ as in reaction (iii). This is supported by the marked

$$CuCl^+ + H_2O \longrightarrow Cu^{2+}\cdot H_2O + Cl^- \qquad \text{(iii)}$$

reduction in the intensity of the absorption band at 296 nm attributed by Manahan and Iwamoto [3] to $CuCl^+$.

In order to discover the effect of copper(I) on the reaction, it is necessary to employ initial conditions with the same [Cl]/[Cu^{II}] ratio. This was done by preparing a series of solutions from Cu[BF_4]$_2$, CuCl, and NEt_4Cl with a [Cl]/[Cu^{II}] ratio of 2 : 1 and with [Cu^I]/[Cu^{II}] varying from 0 to 2. Although there was a large reduction in initial rate as the copper(I) content increased the shape of the reaction curves was very similar to that normally observed. The initial rates are given in Table 2.

The main features of the reaction are now clear. First the initial rate is proportional to [$CuCl^+$] and [cyclohexene]. Secondly, the reaction is inhibited by Cu^I. It remains to explain the course of an individual reaction.

A very simple kinetic model is given in the Scheme. The rate constant k_1 cannot be identified with the rate constant k

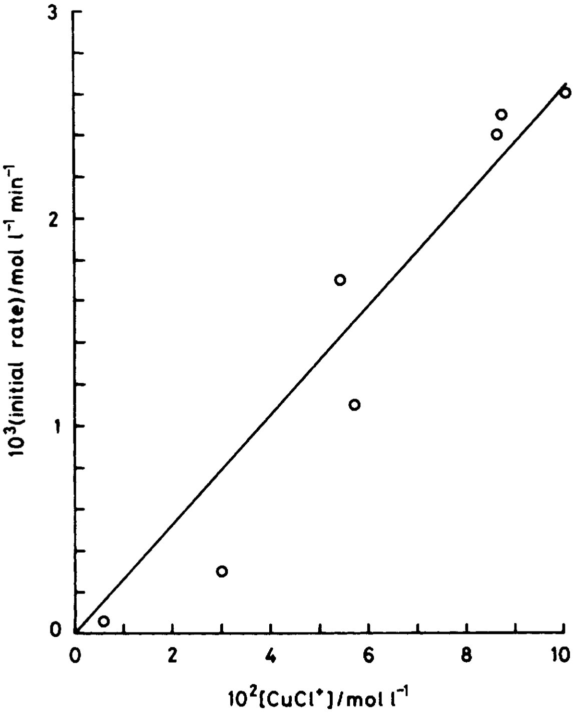


Figure 4. Initial rate against calculated [CuCl$^+$]

Table 2. Effect of [Cu^I] on initial rate *

[Cu^I]/[Cu^{II}]	0	0.5	1	1.5	2
10^4(initial rate)/ mol l^{-1} min^{-1}	12.5	3.4	2.1	1.5	1.1
$D = 1 + 3$ ([Cu^I]/ [CuCl$^+$])	1	4	7	10	13
10^4(initial rate) × D/ mol l^{-1} min^{-1}	12.5	13	15	15	14

* Water content <0.1%; [cyclohexene] = 0.36 mol l^{-1}; [Cu^{II}] = 0.02 mol l^{-1}.

$$\mathrm{CuCl^+ + C_6H_{10} \xrightarrow{k_1} CuCl^+{\cdot}C_6H_{10}} \qquad \text{(iv)}$$

$$\mathrm{CuCl^+{\cdot}C_6H_{10} + CuCl^+ \xrightarrow{k_2} 2Cu^+ + C_6H_{10}Cl_2} \qquad \text{(v)}$$

$$\mathrm{CuCl^+{\cdot}C_6H_{10} + Cu^+ \xrightarrow{k_3}} \text{ unreactive intermediates} \qquad \text{(vi)}$$

Scheme.

Table 3. Formation curve for *trans*-1,2-dichlorocyclohexane production from cyclohexene *

10^{-3}[1,2-dichlorocyclohexane]/ mol l^{-1}	1.5	2.1	2.8	2.8
% Conversion of Cu^{II}	12	18	26	27
Time (min)	2	4	8	10
10^{-3}[1,2-dichlorocyclohexane]/ mol l^{-1}	3.2	3.2	3.5	3.9
% Conversion of Cu^{II}	31	33	36	38
Time (min)	15	30	45	60

* Initial [CuCl$_2$] = 0.02 mol l^{-1}; water content <0.1%; for 0.02 mol dm^{-3} CuCl$_2$, 10^{-3} mol l^{-1} product ≡ 10% conversion of Cu^{II}.

Table 4. Variation of $F = 1 + 3$ ([Cu$^+$]/[CuCl$^+$]) as reaction proceeds

% Conversion of Cu^{II}	0	20	30	40	45
F	1	4	7	22	48

obtained previously for the initial rates as a function of [CuCl$_2$][cyclohexene] until the [CuCl$^+$] corresponding to a [Cu^{II}] to [Cl] ratio of 1 : 2 is evaluated. When this is done a value of $k_1 = 0.35$ l mol^{-1} min^{-1} is obtained. The first two reactions are straightforward. While it is interesting to speculate on the reaction of Cu$^+$ with the intermediate complex, the experimental evidence here allows no conclusion to be drawn, except that the products eventually revert to species already present (no product other than 1,2-dichlorocyclohexane is produced).

$$k_1[\mathrm{CuCl^+}][\mathrm{C_6H_{10}}] = k_2[\mathrm{CuCl^+{\cdot}C_6H_{10}}][\mathrm{CuCl^+}] + k_3[\mathrm{Cu^+}][\mathrm{CuCl^+{\cdot}C_6H_{10}}] \qquad \text{(vii)}$$

$$[\mathrm{CuCl^+{\cdot}C_6H_{10}}] = \frac{k_1[\mathrm{CuCl^+}][\mathrm{C_6H_{10}}]}{k_2[\mathrm{CuCl^+}] + k_3[\mathrm{Cu^+}]} \qquad \text{(viii)}$$

$$\frac{\mathrm{d}[\mathrm{C_6H_{10}Cl_2}]}{\mathrm{d}t} = k_2[\mathrm{CuCl^+}][\mathrm{CuCl^+{\cdot}C_6H_{10}}] = \frac{k_1[\mathrm{CuCl^+}][\mathrm{C_6H_{10}}]}{1 + (k_3/k_2)([\mathrm{Cu^+}]/[\mathrm{CuCl^+}])} \qquad \text{(ix)}$$

If now it is assumed that the complex CuCl$^+$·C$_6$H$_{10}$ is a reactive intermediate the formation and destruction rates of which are equal, one can write equations (vii) and (viii). The rate of formation is given by equation (ix). This is consistent with the observation that initial rates are proportional to [CuCl$^+$] and [C$_6$H$_{10}$] and with the inhibition by [Cu^I].

This expression cannot be simply integrated to give a curve of product formation against time owing to the complexity of the behaviour of [CuCl$^+$]. It can, however, be approximated by stepwise integration on a computer. This is done by calculating [CuCl$^+$] and hence the rate and multiplying by time for a small interval. The new Cu^{II} to Cl$^-$ ratio enables a new value of [CuCl$^+$] to be obtained; the other concentrations are then adjusted and the operation is repeated. The time interval needed is 0.1 min in the early stages of the reaction where [CuCl$^+$] is changing rapidly, increasing to 5 min in the later stages. In order to test this expression a run was carried out in which the reaction was followed by monitoring product formation and copper(II) decay. The results are shown in Table 3 and in Figure 1 (curve A), where the experimental points are superimposed on the line generated by taking $k_1 = 0.33$ l mol^{-1} min^{-1} and $k_3/k_2 = 3$. Given the assumptions made, this is in good agreement with the values of k_1 obtained for the initial rate data.

The kinetic scheme can be applied to all our results. There is a fair scatter of values of k_1, due to the effect of water on the initial rate between groups of kinetic runs. With any one batch of stock solutions, however, the value is consistent. The value of k_3/k_2 appears to be little affected.

The computer integration program can print out values of $1 + 3$([Cu$^+$]/[CuCl$^+$]); these are shown in Table 4 for an initial [CuCl$_2$] of 0.02 mol l^{-1}. Clearly this function increases very steeply with decay of Cu^{II}; this explains the sharp fall of rate above 30% reaction of copper(II). It also shows why the reaction pattern is relatively little changed by water even though initial rates are quite sensitive, as in the later stages of the reaction a small change in k_1 has much less effect than the rapid change in [Cu$^+$]/[CuCl$^+$].

The third row of Table 2 also gives the values of this function when Cu^{I} is added to the reaction mixture before the cyclohexene. If the kinetic expression is correct, (initial rate) × $\{1 + 3([Cu^+]/[CuCl^+])\}$ should be constant for this series, as [CuCl] and [cyclohexene] are identical for all experiments. The fourth row of Table 2 shows that this product is approximately constant. These data also permit another estimate of k_1. The value so obtained is 0.36 l mol^{-1} min^{-1}. As the assumption that $[CuCl^+]$ is independent of $[Cu^{I}]$ must be less valid as $[Cu^{I}]$ increases, this is in reasonable agreement with the previous values.

By carrying out the reaction at temperatures between 60 and 80 °C an estimate can be made for the change in initial rate. From this the variation of k_1 with temperature can be obtained. This leads to an estimated $\Delta H^* = -22$ kcal mol^{-1} (cal = 4.184 J) and $\ln A = 24$. The value of k_2/k_3 would not be expected to change much over a small temperature range, and this appears to be the case as the full reaction curves over this temperature range are fitted by the changing values of k_1 with k_2/k_3 unchanged.

These results contrast strongly with the chlorination of ethylene by aqueous copper(II) chloride studied by Spector *et al.*[4] They show that reaction rate is a maximum when the mole fraction of Cu^{II} is about 0.9, and suggest that $Cu^+ \cdot C_2H_4$ is an intermediate. It has been shown, in a brief investigation using polarographic oxidation of Cu^{I} to Cu^{II} in the presence and absence of ethylene, that Cu^+ forms a stable ethylene complex in water [5,6] but not in acetonitrile. This is consistent with the much stronger interaction of acetonitrile than water with Cu^{I}. Given this difference in copper(I)–olefin interaction, and the different stability constants of Cu^{I} and Cu^{II} with chloride ion in water [7] and acetonitrile,[3] a difference in reaction mechanism would be expected.

If the reactive species in solution is $CuCl^+$, the addition of a Lewis acid such as $AlCl_3$ should lead to the equilibrium (x).

$$\mathrm{CuCl_2 + AlCl_3 \rightleftharpoons CuCl^+ + AlCl_4^-} \qquad \text{(x)}$$

This would be expected to lead to much higher conversions of Cu^{II} into Cu^{I} before the reaction was slowed by the denominator in the rate equation. That this is the case is shown in curve B of Figure 1. A quantitative explanation would need a knowledge of the equilibria in $CuCl_2$–$AlCl_3$ solutions. However, if the simplistic assumption is made that the free Cl^- is captured by the $AlCl_3$ as $CuCl_2$ is converted into $CuCl^+$ then the calculated reaction curve in Figure 1(curve B) is obtained. This is fairly close to the observed behaviour.

Kinetic models of this type are a notoriously poor guide to reaction mechanism in the absence of evidence about actual intermediates. However, the close agreement of initial rates with $[CuCl^+]$ is probably significant. The suggested mechanism of inhibition by Cu^{I} is plausible, but cannot be regarded as proved.

References

1 W. C. Baird, J. H. Surridge, and M. Buzi, *J. Org. Chem.*, 1971, **36**, 3324.
2 A. I. Vogel, ' A Textbook of Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1979, p. 323.
3 S. E. Manahan and R. T. Iwamoto, *Inorg. Chem.*, 1965, **4**, 1409.
4 M. L. Spector, H. Heinemann, and D. Miller, *Ind. Eng. Chem., Process Des. Dev.*, 1967, **6**, 327.
5 O. N. Temkin, A. G. Ginzburg, and R. M. Flid, *Kinet. Katal.*, 1964, **5**, 221.
6 T. Ogura, *Inorg. Chem.*, 1976, **15**, 2301.
7 M-J. Schwing-Weill, *Bull. Soc. Chim. Fr.*, 1973, 823.

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