Redox Transfer. Part IX.[1] Chlorination of Olefins by Copper(II) Chloride

By **Amos Or (Orochov)**, **Moshe Levy**, **Meir Asscher**,* and **David Vofsi**, Department of Plastics Research, The Weizmann Institute of Science, Rehovot, Israel

Evidence for a homolytic interaction between copper(II) chloride and olefins is obtained from the products of the thermal reaction with cyclohexene and with but-2-ene. The initially formed chlorobutyl radical reacts with further copper(II) chloride to give 2,3-dichlorobutane in a completely non-stereospecific fashion. The feasibility of this kind of radical generation is discussed. Styrene gives 1,2-dichloroethylbenzene in a reaction which is first order in both reactants, with E_a 23 kcal mol^{-1}, and k 2·75 × 10^{-5} for $CuCl_3^-$ and 4·7 × 10^{-6} l mol^{-1} s^{-1} for $CuCl_4^{2-}$, at 70°. Chloride ion retards the reaction progressively, until all copper(II) ion has been converted into $CuCl_4^{2-}$. The rates are correlated with a shift in the half wave-potential of the Cu^I–Cu^{II} couple towards less positive values.

THE chlorination of olefins by copper(II) chloride is a reaction of great technical importance, and the oxychlorination of ethylene to vinyl chloride is based on it. Also, the concomitant formation of copper(I) chloride initiates † chain reactions which are catalysed by copper chloride (*e.g.* the addition of carbon tetrachloride, chloroform, sulphonyl chlorides,[4] and other halogen-containing substrates [5] to olefins). Hence our interest in the process. The reaction has been studied several times [6-9] (for a bibliography, see ref. 8), but under such disparate conditions as to make a common reaction mechanism very unlikely.

The present work deals with the homogeneous, thermal reaction of styrene, but-2-ene, and cyclohexene with copper(II) chloride in acetonitrile at temperatures far below the decomposition point of copper(II) chloride.

EXPERIMENTAL

Materials.—Acetonitrile, anhydrous copper(II) chloride, and triethylammonium chloride were as specified in ref. 10. Lithium chloride (Fisher Analytical) and tetraethylammonium chloride (Eastman White Label) were dried at 110° during 24 h. Tetrabutylammonium perchlorate was from G. F. Smith. Styrene was distilled twice under argon, and each time only the middle fraction was collected, b.p. 40° at 1 mmHg, and used immediately. Cyclohexene (Fluka puriss) was distilled, and then passed through alumina before use. 1,2,4-Trichlorobenzene (B.D.H.) was redistilled, b.p. 53—54° at 1 mmHg. *cis*- and *trans*-But-2-ene were Matheson C.P., 1-, 3-, and 4-chlorocyclohexene and *trans*-1,2-dichlorocyclohexane were from K and K Laboratories, and a mixture of ±- and *meso*-2,3-dichlorobutane was from Chemical Samples Co. These compounds were used for identification by g.l.c.

G.l.c.—This was carried out on a Hewlett–Packard 7620 thermal conductivity model with an electronic integrator.

Half-wave Potentials.—These were measured on a Beckman Electroscan 30 apparatus, with a rotating platinum electrode and a silver–silver chloride reference electrode. The supporting electrolyte was tetrabutylammonium perchlorate.

U.v. Spectroscopy.—This was carried out on a Cary 15 instrument. A solution of 5 × 10^{-4}M-copper(II) chloride in acetonitrile and the appropriate amount of styrene to render the solution 1M in styrene were degassed separately by repeated freeze–thaw cycles under high vacuum in a vessel connected to an optical cell of 1 cm pathlength. After sealing the vessel, the liquids were mixed, the cell filled, sealed off in turn, and the absorption maximum at 467 nm was recorded.

Since diffuse light was found to accelerate rapidly the reaction between styrene and copper(II) chloride, special care was taken to exclude it either by shutting off the light of the spectrophotometer, or by wrapping the cell in aluminium foil between measurements. A solution of 5 × 10^{-4}M-copper(II) chloride in acetonitrile was used to calibrate the absorption to zero at 600 nm.

Reaction of Copper(II) *Chloride with Styrene* (*Kinetics*).—(a) *Below* 80°. A round-bottom flask (100 ml), fitted with a magnetic stirrer and with a side-arm closed by a self-sealing gasket, was filled with argon, and then charged with deaerated acetonitrile (50 ml) containing 0·08M-copper(II) chloride and varying amounts of triethylammonium chloride. Degassed styrene was injected through the septum after the copper(II) chloride solution had reached the bath temperature. The flask was shielded from light by aluminium foil. At intervals two samples (each *ca.* 0·5 ml) were withdrawn and added to a mixture of methylene chloride (1 ml) and water (1 ml). The mixture was shaken, and the organic (lower) layer analysed for dichlorostyrene by g.l.c., using 1,2,4-trichlorobenzene as an internal standard, on an 8 ft × 1/8 in stainless steel column packed with 10% W-98 silicone gum rubber on Chromosorb W, DMSC and programmed from 120 to 150° at 4° min^{-1}. This procedure was followed for three identical runs. Each point in Figure 1 thus represents an average of six determinations.

(b) *Above* 80°. For reactions above the b.p. of acetonitrile, a stock solution of styrene, copper(II) chloride, and triethylammonium chloride was degassed on the vacuum line, and then divided among 10 small ampoules which

---

† In related redox chain reactions, namely the copper chloride catalysed decomposition of diazonium chlorides and their reaction with olefins (the Sandmeyer and Meerwein reaction respectively), the solvent (acetone) is chlorinated on treatment with copper(II) chloride.[2] This has led to the now prevailing view [3] that copper(I) chloride is the true catalyst. We prefer [4] to regard this reduction as a chain initiation, without assigning the status of ' true ' catalyst to any particular oxidation state.

[1] A. Or, M. Asscher, and D. Vofsi, *J.C.S. Perkin II*, 1973, 1000.

[2] J. K. Kochi, *J. Amer. Chem. Soc.*, 1955, **77**, 5090; S. C. Dickerman, K. Weiss, and A. K. Ingberman, *J. Org. Chem.*, 1956, **21**, 380.

[3] (*a*) D. C. Nonhebel, *Chem. Soc. Special Publ.*, 1970, **24**, 411; (*b*) C. Walling, ' Free Radicals in Solution,' Wiley, New York, 1957, p. 520; (*c*) C. S. Rondestvedt, *Org. Reactions*, 1960, **11**, 189.

[4] M. Asscher and D. Vofsi, *J. Chem. Soc.*, (*a*) 1963, 1887, 3921; (*b*) 1964, 4962.

[5] S. Murai, N. Sonoda, and S. Tsutsumi, *J. Org. Chem.*, 1964, **29**, 2104.

[6] Ref. 3*a*, p. 428; D. Mosnaim and D. C. Nonhebel, *Tetrahedron*, 1969, **25**, 1591.

[7] R. P. Arganbright and W. F. Yates, *J. Org. Chem.*, 1962, **27**, 1205; P. P. Nicholas and R. T. Carroll, *ibid.*, 1968, **33**, 2345.

[8] W. L. Baird, J. H. Surridge, and M. Buza, *J. Org. Chem.*, 1971, **36**, 3324.

[9] T. Koyano, *Bull. Chem. Soc. Japan*, 1970, **43**, 3501.

[10] M. Asscher and D. Vofsi, *J. Chem. Soc.* (*B*), 1968, 947.

were sealed off, wrapped in aluminium foil, and placed in a thermostat. At intervals two of the ampoules were rapidly cooled, opened, and treated as above.

Reaction of Copper(II) *Chloride with Cyclohexene.*—A solution of cyclohexene (1·54 g, 0·02 mol), copper(II) chloride (1·34 g, 0·01 mol), and triethylammonium chloride (2·06 g, 0·015 mol) in acetonitrile (50 ml) was divided between two Pyrex ampoules (wall thickness 2 mm) which were degassed by freeze–thaw cycles and sealed. One was wrapped in aluminium foil and heated at 110°, and the other was irradiated at room temperature by a sun-lamp (275 W) at 25 cm, both during 24 h. The contents of the tubes were analysed by g.l.c., using an 8 ft × 1/4 in stainless steel column packed with 10% Carbowax 20 M on Chromosorb Z,AW, programmed from 80 to 160° at 10° min^{-1}.

Reaction of Copper(II) *Chloride with But-2-ene.*—A degassed solution of *cis*- or *trans*-but-2-ene (1·5 g, 0·027 mol), copper(II) chloride (270 mg, 2 mmol), and triethylammonium chloride (275 mg, 2 mmol), in acetonitrile (10 ml) was heated in a sealed ampoule wrapped in aluminium foil at 80° during 20 h. After cooling, the gas over the solution was checked by g.l.c. for possible *cis–trans*-isomerization (32·8 ft × 1/4 in copper column kept at 0° and packed with 15% ethyl hexyl tetrachlorophthalate on Chromosorb W). The composition of the products (*meso* and ±-2,3-dichlorobutane) was determined with a 23 ft × 1/4 in column packed with 20% Ucon oil LB 550 X on Chromosorb P at 150°.

RESULTS

Reaction with Styrene.—(a) *Reaction order.* The reaction with styrene follows first-order kinetics with respect to both reactants. The rate of process (1) can be expressed as

$$2CuCl_2 + PhCH{=}CH_2 \longrightarrow 2CuCl + PhCH(Cl)CH_2Cl \quad (1)$$

$r = k[CuCl_2]^p[Styrene]^n$, which reduces to $r = k'[CuCl_2]^p$ for a large excess of styrene ($k' = k[Styrene]^n$). The concentration of copper(II) chloride was deduced from the amount of dichlorostyrene formed according to equation (1). Good straight lines were obtained on plotting log[$CuCl_2$] against time (see Figure 1), thus establishing that p in the rate equation is 1.

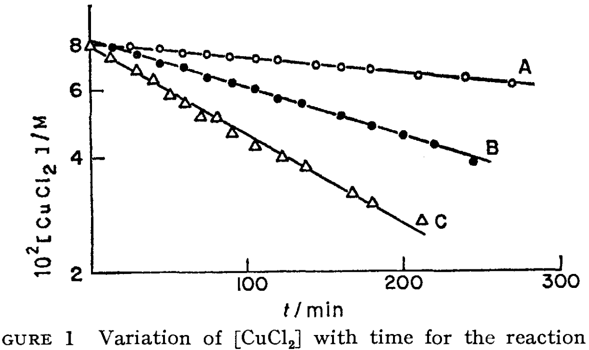


FIGURE 1 Variation of [$CuCl_2$] with time for the reaction of copper(II) chloride with styrene in acetonitrile at 70°: [$CuCl_2$]$_0$ = 0·08M; [Cl^-] (as triethylammonium chloride TEAC) = 0·12M; [Styrene] = A, 1·0, B, 1·5, C, 2·6M

A plot of log k against log[Styrene] gave a straight line with a slope of 1·12, showing that the reaction is first order with respect to styrene to a good approximation. An average of six runs at 70° gave k 1·48 × 10^{-5} l mol^{-1} s^{-1} (Table 1). Since under our particular conditions, the reacting copper(II) species is a mixture of $CuCl_3^-$ and $CuCl_4^{2-}$, this value is a weighted average of the rate constants for these chloro-complexes.

TABLE 1

Reaction of styrene and copper(II) chloride in acetonitrile at 70°

[$CuCl_2$]$_0$ = 0·08M	[TEAC] * = 0·12M
[Styrene]$_0$/M	10^5k/l mol^{-1} s^{-1}
2·60	1·57
2·00	1·50
1·75	1·47
1·50 †	1·48
1·00	1·44
0·04	1·43

* Triethylammonium chloride. † [$CuCl_2$]$_0$ = 0·04M.

Several runs with lithium or tetraethylammonium chloride as the source for additional chloride ion gave identical results.

(b) *Energy of activation.* Reaction constants were determined between 50 and 100°. A plot of log k against $1/T$ according to the Arrhenius equation gave a straight line from which the energy of activation was calculated (E_a = 23 kcal mol^{-1}). The values for 10^6k at 50, 60, 70, 85, and 100° were 1·8, 4·8, 14·2, 60·0, and 202·0 l mol^{-1} s^{-1}, respectively (see Figure 2), and, as for the energy of activation calculated from them, apply to a mixture of $CuCl_3^-$ and $CuCl_4^{2-}$ as the chlorinating agent.

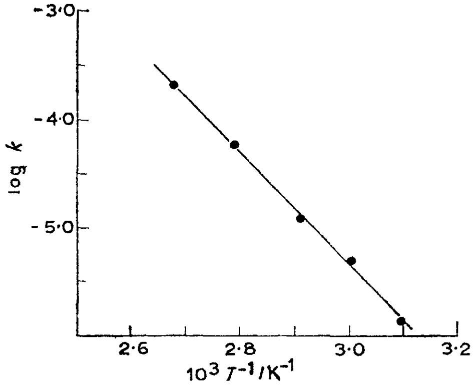


FIGURE 2 Arrhenius plot for the reaction of copper(II) chloride with styrene: [Styrene]$_0$ = 1·75; [$CuCl_2$]$_0$ = 0·08; [TEAC] = 0·12M

(c) *Effect of chloride ion.* In agreement with the findings of Baird *et al.*,[8] chloride ion strongly retarded the reaction up to a ratio Cl^- : $CuCl_2$ = 2, when the rate of chlorination was 1/8 of that with $CuCl_2$ alone. Beyond this point, which for our particular concentrations corresponds to a 95% conversion of $CuCl_2$ into $CuCl_4^{2-}$,[11] there was no further decrease. The sudden break at this ratio is illustrated by Figure 3. Under the conditions of Figure 3, the values for the rate constant are 10^5k l mol^{-1} s^{-1} = 3·75, 2·75, 1·48, 0·82, 0·50, 0·45, and 0·46 for [Cl^-] : [$CuCl_2$]$_0$ = 0·5, 1·0, 1·5, 1·75, 2·0, 3·0, and 4·0, respectively; k can be assigned to $CuCl_3^-$ when [Cl^-] : [$CuCl_2$] = 1, and to $CuCl_4^{2-}$ when this ratio is 2—4, but is an average value for the intermediate ratios.

(d) *Spectroscopy.* On mixing degassed solutions of cupric chloride with styrene (5 × 10^{-4}M-$CuCl_2$; 1M-styrene) at room temperature, the absorption maximum was found

[11] S. E. Manahan and R. T. Iwamoto, *Inorg. Chem.*, 1965, **4**, 1409.

to shift from 460 to 467 nm, with an increase in extinction coefficient, which reached a maximum after 4 h, and then very slowly diminished (see Figure 4). After 6 days the absorbance was still 55% of the maximum, or 82% of the initial value and after 12 days still 46% of the maximum. In contrast, the extinction coefficient of solutions which contained one or two equivalents of chloride ion (as triethylammonium chloride) did not increase, nor change with time after addition of styrene. The maximum was again shifted slightly (to 472 nm).

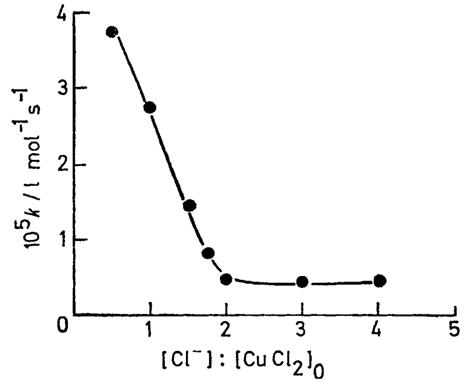


FIGURE 3 Effect of [Cl$^-$] (as TEAC) on the reaction of copper(II) chloride with styrene: [CuCl$_2$]$_0$ = 0·08; [Styrene] = 1·75M; temp. = 70°

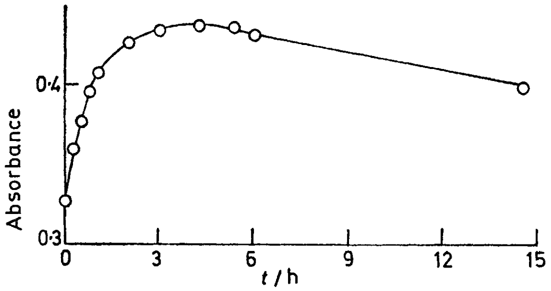


FIGURE 4 Variation in the absorbance at 467 nm with time for the reaction of 5 × 10^{-4}M copper(II) chloride and 1M-styrene in acetonitrile

Solutions containing styrene and copper(II) chloride, with or without added chloride, were completely bleached over a few hours in diffuse light, and did not reoxidize on admittance of air, in light or in the dark.

Reaction with Cyclohexene.—The dark reaction between cyclohexene and copper(II) chloride at 110° afforded the stereoisomeric 1,2-dichlorohexanes, chlorocyclohexane, and hydrogen chloride. From the presence of the latter, initial formation of 3-chlorocyclohexene was inferred, since this chloride eliminated hydrogen chloride in the presence of copper(I) chloride at 110°. Chlorocyclohexane most probably arose from the copper(I) chloride assisted addition of hydrogen chloride to cyclohexene, since cyclohexane was completely inert towards copper(II) chloride. Assuming that all the 3-chlorocyclohexene eventually appears as chlorocyclohexane, the ratio of the former to dichlorocyclohexane was *ca.* 1 : 3.

Irradiation at room temperature gave, apart from the above products, 4-chlorocyclohexene, confirming Poutsma's results,[12] and indicating photolysis of copper(II) chloride. Under these conditions toluene and cumene were reported [13] to be chlorinated in the side chain. In the dark reaction at 110° we found them to be completely inert.

Reaction with But-2-ene.—The dark reaction at 80° of both *cis*- and *trans*-but-2-ene yielded identical mixtures of *meso*- and ±-2,3-dichlorobutane, in a ratio of 61 : 39. The reaction is thus completely non-stereospecific. Control experiments established that the butenes and the dichlorobutanes were not isomerized during the reaction. (At 220—300°, and in a heterogeneous system, both Arganbright and Yates and Nicholas and Carroll [7] found the reaction to be stereospecific. We believe this to be due to the formation of molecular chlorine at these high temperatures.)

Half-wave Potentials.—The potential of the couple Cu$^{\text{I}}$–Cu$^{\text{II}}$ shifted to considerably less positive values with increasing [Cl$^-$] in acetonitrile, again only up to [Cl$^-$] : [CuCl$_2$] = 2 [for copper(II) perchlorate, $E_{1/2}$ = 1·0 V (*vs.* s.c.e.)].[14] In aqueous acetone, the shift was in an opposite direction (see Table 2), and continued to much higher [Cl$^-$] : [CuCl$_2$] ratios.

TABLE 2

Effect of chloride ion on the half-wave potential of Cu$^{\text{I}}$–Cu$^{\text{II}}$ (*vs.* silver–silver chloride electrode)

Cl$^-$ = tetraethylammonium choride
Supporting electrolyte 0·1M-tetrabutylammonium perchlorate

[Cl$^-$] : [CuCl$_2$]	$E_{1/2}$/V (in acetonitrile) *	$E_{1/2}$/V (in 4 : 1 v/v acetone-water) †
0	0·51	0·34
1	0·44	0·34
2	0·40	0·345
3	0·40	
4		0·385
10		0·43

* [CuCl$_2$] = 5 × 10^{-5}M. † [CuCl$_2$] = 5 × 10^{-4}M.

DISCUSSION

There can be little doubt that copper(II) chloride itself is the chlorinating agent in the dark reactions: they occur far below its decomposition temperature; toluene, cumene, and cyclohexane are completely inert, and no 4-chlorocyclohexene is formed from cyclohexene. Poutsma [12] found the latter product to be characteristic of chlorine-atom attack, and identified it among other compounds when a solution of copper(II) chloride and cyclohexene in acetonitrile was irradiated.

The question then arises, how chlorine is transferred from copper(II) chloride to the olefin. If dichloroalkane were formed in a concerted process, involving two copper(II) chloride molecules for each olefin, the reaction could not be first order in copper. Moreover, such a process should be stereospecific.

Another possibility is chloronium ion transfer in one form or another. If this were taking place, as postulated in refs. 7 and 9, the reaction between olefin and copper(II) chloride in aqueous or methanolic solution should give the corresponding chlorohydrin or its methyl ether as important by-products. Actually, the dichlorides are formed exclusively.[9,15]

---

[12] M. L. Poutsma, *J. Amer. Chem. Soc.*, 1965, **87**, 2161.

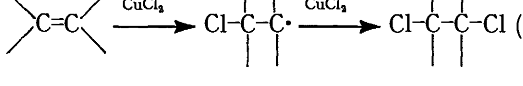
[13] J. K. Kochi, *J. Amer. Chem. Soc.*, 1962, **84**, 2121.

[14] R. C. Larson and R. T. Iwamoto, *J. Amer. Chem. Soc.*, 1960, **82**, 3239.

[15] M. L. Spector, H. Heinemann, and K. D. Miller, *Ind. Eng. Chem., Process Design and Development*, 1967, **6**, 327.

Complete lack of stereospecificity, as apparent in the reaction with but-2-ene, highlights the difference with copper(II) bromide,[8] where molecular bromine is always present, and again strongly argues against initial chloronium ion transfer, a highly improbable process in any case, in view of the valency changes involved.

Exclusive formation of dichlorides (see above), and non-stereospecificity is good evidence for a radical intermediate, which equilibrates among its conformers before going over into the final product [reaction (2)].

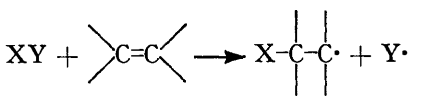


(2)

The copper chloride catalysed addition of carbon tetrachloride is likewise non-stereospecific, and in this case there can be no doubt about the radical intermediates.[1,4a] The insensitivity of the chlorination of carbonyl compounds by copper(II) chloride towards benzoquinone has been taken [16] as evidence against radical intermediates. Since we are obviously dealing with a non-chain process, this argument is invalid. Moreover, as pointed out by Lorenzini and Walling,[17] copper(II) chloride is a much better radical trap than benzoquinone.

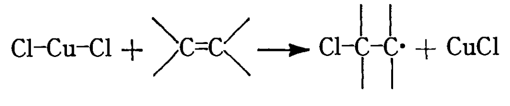
The product-forming step in (2) is well documented.[18] We will therefore concern ourselves only with the formation of the radical.

Generation of Radical Intermediates. Formal Considerations.—Formation of radicals by atom transfer from one stable compound to another appears to be energetically possible, when the bond to be cleaved is relatively non-polar and weak, and the newly formed bond strong and polar.[19] Examples can be found in the chlorination of olefins in non-polar media,[12] in the reaction of hypochlorites with styrene and acetylenes,[20] and in the fluorination of organic compounds.[21] Radical formation can then be depicted schematically as reaction (3) or (4). Formally, one can write an analogous radical generation with copper chloride [reaction (5) or (6)].



(3)

$$\mathrm{XY + H{-}R \longrightarrow X\cdot + HY + R\cdot} \qquad (4)$$



(5)

$$\mathrm{Cl{-}Cu{-}Cl + H{-}R \longrightarrow CuCl + HCl + R\cdot} \qquad (6)$$

Several striking differences with the systems cited above are immediately apparent. (*a*) Initial radical formation in the above cases [12,20,21] is followed by a rapid chain process. This cannot happen in the chlorination by cupric chloride, and one can be reasonably sure that identified products arise from 'primary' radicals. (*b*) The copper(II)–chlorine bond, although weak,* is far from being non-polar. This will vary for different $\mathrm{Cu^{II}}$–chloride complexes. (*c*) In processes such as (3) and (4) two radicals are being formed, while in (5) and (6), one of them is replaced by the stable copper(I) chloride. Thus, whereas (*b*) detracts from the energetic feasibility of processes like (5) or (6), (*c*) operates in their favour. The outcome of these opposing factors appears to be a slow process with a relatively high energy of activation, as measured for the case of styrene. Aliphatic olefins react still more slowly, since an unstabilized radical is being formed. Bridging ligands would seem to be essential, and without going into details about copper(II) chloride–olefin or –carbonyl complexes as possible intermediates (see below), reactions such as (5) and (6) may explain why other copper(II) salts (*e.g.* acetate [17]) are unreactive.

Copper(II) chloride appears to be capable of abstracting allylic hydrogen atoms in cyclohexene (formation of 3-chlorocyclohexene; see Results section) in a reaction such as (6), although toluene and cumene are inert.

Effect of Chloride Ion.—The strongly retarding effect of chloride ion on the reaction of olefins with copper(II) chloride, as reported by Baird *et al.*[8] and confirmed by us (Figure 3), is in striking contrast to its influence on the reaction of carbonyl compounds with copper(II) chloride in aqueous acetone or propan-2-ol,[16,17] where chloride ion accelerates the reaction. The sharp drop in the reaction rate with increasing $[\mathrm{Cl^-}]$, the sudden levelling-out at $[\mathrm{Cl^-}] : [\mathrm{CuCl_2}] = 2$ (Figure 3), and the corresponding changes in the half-wave potential (Table 2) are all manifestations of the large formation constants of the chlorocopper(II) complexes in acetonitrile, which for $\mathrm{CuCl^+}$, $\mathrm{CuCl_2}$, $\mathrm{CuCl_3^-}$, and $\mathrm{CuCl_4^{2-}}$ are $10^{9\cdot7}$, $10^{7\cdot9}$, $10^{7\cdot1}$, and $10^{3\cdot7}$ respectively.[11] The corresponding constants in water are 1, 0·2, 0·04, and 0·01,[22] and this explains why the changes in the half-wave potential in aqueous acetone are much more gradual, and continue far beyond the ratio $[\mathrm{Cl^-}] : [\mathrm{CuCl_2}] = 2$ (Table 2).

The shift in the half-wave potential of the $\mathrm{Cu^I}$–$\mathrm{Cu^{II}}$ couple with increasing $[\mathrm{Cl^-}]$, towards less positive values in acetonitrile and more positive ones in aqueous acetone or propan-2-ol (Table 2), is thus reflected in the rates of chlorination in these media.

In an oxidation–reduction reaction such as (5), a shift

---

* The extremely fast ligand transfer reactions, $\mathrm{R\cdot + CuCl_2 \longrightarrow RCl + CuCl}$, indicate a weak $\mathrm{Cu^{II}}$–Cl bond. (See ref. 18 and literature cited there).

[16] J. K. Kochi, *J. Amer. Chem. Soc.*, 1956, **78**, 1228, 4815; 1957, **79**, 2942; E. M. Kosower, W. J. Cole, G. S. Wu, D. E. Cardy, and G. Meisters, *J. Org. Chem.*, 1963, **28**, 630; E. M. Kosower and G. S. Wu, *ibid.*, p. 633.

[17] A. Lorenzini and C. Walling, *J. Org. Chem.*, 1967, **32**, 4008.

[18] C. L. Jenkins and J. K. Kochi, *J. Org. Chem.*, 1971, **36**, 3095; J. K. Kochi and D. M. Mog, *J. Amer. Chem. Soc.*, 1965, **87**, 522.

[19] For reviews see, (*a*) F. S. Dyachkovskii and A. E. Shilov, *Russ. Chem. Rev.*, 1966, **35**, 300; (*b*) G. B. Sergeev and I. A. Leenson, *ibid.*, 1972, **41**, 726.

[20] C. Walling, L. Heaton, and D. D. Tanner, *J. Amer. Chem. Soc.*, 1965, **87**, 1715.

[21] W. T. Miller, jun., *J. Amer. Chem. Soc.*, 1940, **62**, 341; W. T. Miller, jun., and A. L. Dittman, *ibid.*, 1956, **78**, 2793; W. T. Miller, jun., S. D. Koch, jun., and F. W. McLafferty, *ibid.*, p. 4992.

[22] J. Bjerrum, *Kem. Maanedsblad*, 1945, **26**, 24.

of 100 mV in acetonitrile is more than adequate to explain an eightfold drop in reaction rate (Figure 3). If complex formation between copper(II) chloride and olefin (or enol) were a pre-requisite for the reaction, a strong competitor for copper(II) chloride such as chloride ion should always have a retarding effect, without regard to the solvent. Moreover, one would expect the retarding effect of chloride to continue beyond $[Cl^-] : [CuCl_2] = 2$, since chloride ion has to be displaced from $CuCl_4^{2-}$ by styrene for complex formation [reaction (7)]. In the lower chloro-complexes, acetonitrile, which solvates copper(II) ion only weakly,[11] must be displaced.

$$CuCl_4^{2-} + C_8H_8 \rightleftarrows CuCl_3(C_8H_8)^- + Cl^- \quad (7)$$

The results given in Figure 3 could also arise from a progressively diminishing equilibrium concentration of an olefin–copper(II) chloride complex by increasing $[Cl^-]$, until, when $[Cl^-] : [CuCl_2] = 2$, the co-ordinatively saturated, tetrahedral $CuCl_4^{2-}$ is the only copper(II) species reacting with styrene without prior complex formation. Our spectral data indicate some sort of interaction between styrene and copper(II) chloride, which is absent in the higher chlorocopper(II) complexes (see Results section). It is therefore possible that a reaction through an olefin complex and a direct process occur side by side, up to saturation of Cu^{II} by chloride ion. [Until now, labile olefin–copper(II) complexes have only been recorded in the case of hexafluoroacetylacetonatecopper(II), a strong Lewis acid.[23]]

In summary, while at intermediate $[Cl^-] : [CuCl_2]$ ratios a reaction through an olefin–copper(II) chloride complex remains a distinct possibility, the retarding effect of chloride ion can also be explained on the basis of redox potentials alone.

Our results with cyclohexene, and especially with but-2-ene, clearly implicate chloroalkyl radicals as intermediates. The overall mechanism as illustrated by reaction (2) resembles in many respects that suggested earlier by Nonhebel [6] and by Lorenzini and Walling [17] for quite different substrates and reaction conditions.

We thank Mrs. M. Moshitzky and S. Margel for help in the spectral measurements and the polarographic work, respectively.

[3/2236 *Received*, 31*st October*, 1973]

---

[23] R. A. Zelonka and M. C. Baird, *J. Organometallic Chem.*, 1971, **33**, 267.