

CYCLIC CHLORINATION REACTIONS INDUCED BY VISIBLE LIGHT WITH CHLOROCOPPER(II) COMPLEXES AS MEDIATORS*

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Summary

When CuCl_2 is dissolved in aprotic solvents with excess LiCl it forms a photocatalytic system in which the $\text{Cl}_2^{\cdot-}$ transient, generated together with copper(I) by blue light, is able to promote chlorination reactions of various organic substrates. The copper(I) is reoxidized by oxygen and Cl^- is regenerated by the solid lithium salt. The photoproducts were determined using gas-liquid chromatography. With toluene the major photoproduct is benzyl chloride which is formed with an absolute quantum yield Φ of 5.8×10^{-3} mol einsteins $^{-1}$; the isomers *o*-, *m*- and *p*-chlorotoluene are also formed. A chlorohexene is formed from 1-hexene with $\Phi = 15 \times 10^{-3}$, together with 1- and 2-chlorohexane as secondary products. With tetrahydrofuran (THF) the primary photoproduct is the corresponding α -chloro ether, which can be scavenged to a large extent by oxygen radicals. Hydrogen abstraction appears to be the dominant reaction mode of $\text{Cl}_2^{\cdot-}$. With 1-hexene and THF (but not with toluene) water is also formed during aerobic irradiations, indicating that oxygen radicals can enter into oxidative reactions with these two organic substrates. Nevertheless, no oxidation products of such substrates appear distinctly in the chromatograms, as the only peaks which are evident are those formed via $\text{Cl}_2^{\cdot-}$.

1. Introduction

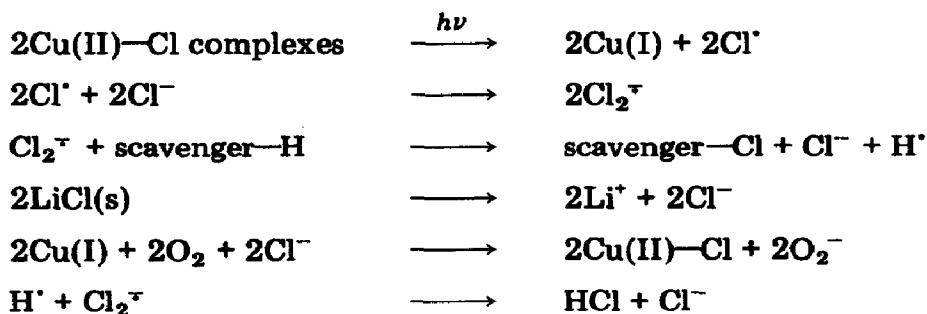
Some years ago Professor G. Sartori foresaw the importance of transition metal complexes as photocatalysts and encouraged us, as his assistants, to proceed in this new route of research. The study of the photochemistry of these compounds was then, and still is, progressing rapidly and the need for unconventional sources of energy was imminent. At the present time some interesting photocatalytic systems have already been qualitatively described, using both UV [1] and visible light [2].

*Dedicated to Professor Guido Sartori on the occasion of his 71st birthday.

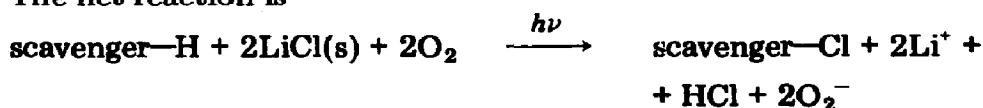
We shall restrict our attention to the second case which allows the use of sunlight. The most desirable aim is, of course, the photodecomposition of water [3]. Solar energy storage could also be accomplished by the photosynthesis of highly energetic molecules other than hydrogen, such as norbornadiene [4]. There are, however, other less ambitious uses of sunlight and one of these is simply to promote kinetically slow [5] or thermally unrealizable reactions by means of the photoproduction of reactive transients. We have moved in this direction to the extent that recently we have found an easy way of producing chloro radicals.

Chlorocopper(II) complexes absorb visible light well up to 500 nm ($\epsilon_{500} \approx 400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and their irradiation in the first part of the visible range leads to the formation of Cl^\cdot with quantum yields of about $10^{-1} - 10^{-2}$ depending on the $[\text{Cu(II)}]/[\text{Cl}^-]$ ratio. The active transient is actually Cl_2^\cdot which is formed by the association of Cl^\cdot with Cl^- present in the solution. This chloro radical anion is a powerful oxidizing ($E_0 = 2.3 \text{ V}$) [6] and chlorinating agent [7].

Thus, we generated Cl_2^\cdot in acetonitrile solutions containing toluene and 1-hexene, and also in tetrahydrofuran solutions (THF), in the presence of an excess of LiCl. The aim was to realize a photocatalytic cycle in which the photoproduced copper(I) and Cl^\cdot were oxidized by oxygen and scavenged by the organic substrate respectively. The presence of LiCl has the function of renewing the reacted Cl^- ion. The scheme is



The net reaction is



In all three cases definite evidence was obtained for chloro derivatives and other secondary products. These results will be described.

2. Experimental

2.1. Materials

Anhydrous CuCl_2 was prepared by drying $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ for 3 h at 120°C under a stream of hydrogen chloride. Water-free acetonitrile (Uvasol

for spectroscopy) and p.a. LiCl were obtained from Merck. Benzyl chloride, toluene, *o*-, *m*- and *p*-chlorotoluene, isooctane, xylene and THF were supplied by C. Erba. Ethylbenzene and 1-hexene were obtained from Aldrich.

2.2. Apparatus and procedures

The irradiations were performed with a high pressure 1045 Beckman xenon arc lamp (XB0 450 W Osram) or with a high pressure water-cooled mercury capillary arc lamp (AH6-1 1000 W PEK). The light was filtered through either GS 3-75 + 7-51 (passing band centred at 404 nm, transmittance 3.3%, halfwidth 9 nm) or 3-72 + 5-60 (peak at 467 nm, transmittance 19%, halfwidth 40 nm) Corning glasses. The incident light intensities were about 2.5×10^{-8} einsteins s^{-1} at 404 nm for the mercury lamp and ranged from 6×10^{-8} to 3×10^{-7} einsteins s^{-1} at 467 nm for both these light sources. The actinometry was performed with the Reinecke salt [8]. The irradiated volume was 3.2 or 15.5 cm^3 . The sample cuvettes were kept in circulating water at room temperature during the irradiation.

Removal of atmospheric oxygen from the acetonitrile or THF solutions was achieved by bubbling thoroughly dried and purified nitrogen gas. For the aerobic irradiations the solutions were bubbled or kept under pressure (3 - 4 Torr) with air or pure oxygen. The gases were always saturated with acetonitrile or THF.

Spectrophotometric measurements in the visible were performed with a Varian 635 D spectrometer. IR spectra were obtained with a Perkin-Elmer 580 apparatus. Electron spin resonance spectra were recorded at liquid nitrogen temperature and at room temperature with a Varian E-9 spectrometer at X-band frequencies. Gas-liquid chromatograms were obtained at temperatures up to 200 °C with a Perkin-Elmer 3920 gas chromatograph equipped with stainless steel columns 4 m long and 2 mm in diameter. These were filled with SP 1000 Supelco (2-nitrophthalic acid added to a polyethylene glycol resin) on Carbopack C 80 - 100 mesh (0.38 wt.%). In other experiments the absorbent was 5% Apiezon L on Chromosorb P 800 - 1000 mesh and the temperature was 120 °C.

3. Results

When $CuCl_2$ is dissolved in aprotic solvents it gives rise to a series of chlorocopper(II) complexes [9]. Suitable chloro radical organic scavengers and an excess of LiCl were added to the cupric solutions. The scavengers toluene, 1-hexene and THF were chosen for the study of the action of $Cl_2^{\cdot-}$ on different kinds of hydrocarbons. Toluene and 1-hexene were added to acetonitrile since this solvent has a very poor tendency to react with the photoproducted chloro radicals [10, 11]. With THF the photoreaction was carried out in bulk since the inorganic salts are easily soluble therein. The THF and 1-hexene systems were carefully studied under both aerobic and

anaerobic conditions, because they produce water in oxygenated solutions but not in deoxygenated solutions. For all the scavengers used, distinct peaks were observed in all chromatograms. The chromatograms of the THF and 1-hexene systems obtained under aerobic conditions also exhibited some small bumps along the tails of the acetonitrile and THF peaks. In addition, for the three scavengers all the products obtained from the aerobic and anaerobic irradiations were completely stable in air.

3.1. Toluene

Since toluene mixes well with acetonitrile in all proportions, its concentration was adjusted to 20 vol.% as a workable compromise. The presence of toluene reduces the solubility of LiCl. The higher the $[\text{Cu(II)}]/[\text{Cl}^-]$ ratio, the higher is the amount of the photoproducted copper(I) that is not reoxidized by oxygen and this reduces the effectiveness of copper(II) as a catalyst. However, the lower this ratio, the lower is the copper(I) quantum yield and hence the chloro radical formation, and this of course would diminish the overall quantum yield of the scavenger chloro products (see ref. 12 and Table 1).

In order to establish the efficiency of the catalyst for chlorination reactions, the quantum yield of Cl^\cdot has to be known and must have the same value as that of copper(I) for anaerobic irradiations [11]. Therefore we determined the copper(I) anaerobic quantum yield $\Phi_{\text{Cu(I)}}$ in the presence of the scavenger. The presence of excess LiCl keeps the composition of the system substantially invariant during the irradiation, even though the $[\text{Cu(II)}]$ diminishes. The amounts of copper(I) were then calculated from the simple decrease in the optical density of the solution at the end of the irradiation, assuming the absorbance due to the copper(I) species to be zero. The range of the initial $[\text{Cu(II)}]$ was from 10^{-3} to 5×10^{-3} mol dm $^{-3}$ and the amount of photoreduction was from 10% to 40%. As previously observed [12], there is a slight decrease in $\Phi_{\text{Cu(I)}}$ with the irradiation time because of the partial reoxidation of copper(I) to copper(II) by the chloro radicals. The anaerobic $\Phi_{\text{Cu(I)}}$ values obtained in the presence of toluene are listed in Table 1.

Since toluene appeared to scavenge the chloro radicals (see later), the irradiations were performed in the presence of oxygen (pure or mixed with nitrogen) to reoxidize the copper(I) and thus to have a catalyst which also continually renews itself. The toluene-derived products were identified and were quantitatively determined using gas-liquid chromatography. The only photoproducts appeared to be benzyl chloride and, to a lesser degree, *o*-, *m*- and *p*-chlorotoluene. The benzyl chloride quantum yield was determined by adding to the irradiated solution a suitable internal standard which was, in our case, ethylbenzene, previously calibrated with benzyl chloride itself. The retention times of the *o*- and *m*-chlorotoluenes were so similar that their peaks could not be resolved. The quantum yield for *o*- plus *m*-chlorotoluene and that for the *p* isomer were calculated relative to the benzyl chloride band area. No other species were detected even when the irradiations were

TABLE 1

Absolute quantum yields for copper(I) and substrate chloro derivatives at 467 nm^a

Solvent and/or substrate	$[Cu(II)]^b$ $[Cl^-]^b$	Irradiation	Quantum yields $\times 10^3$	
			Cu(I)	Chloro derivatives
Acetonitrile	1:15	Aerobic	≈ 0	Acetonitrile chloro derivatives
		Anaerobic	8.3	≈ 0
			4.0 ^c	≈ 0
10% toluene in acetonitrile ^d	$\approx 1:13^e$	Anaerobic	22	
20% toluene in acetonitrile ^d	1:7	Aerobic	1.7	Benzylchloride
		Aerobic	0.18 ^f	<i>o</i> - + <i>m</i> -Chlorotoluene
		Anaerobic	38	<i>p</i> -Chlorotoluene
20% 1-hexene in acetonitrile ^d	1:7	Aerobic	35	2-Chlorohexane
		Anaerobic	71	1-Chlorohexane
			2	Chlorohexene
THF	1:7	Aerobic	2	α -Chloro-THF
		Anaerobic	280	α -Chloro-THF oxygen derivatives
			0	

^a Conditions: CuCl₂ dissolved in the presence of LiCl; temperature, 15 - 20 °C.^b Determined by titration with aqueous AgNO₃ and/or by weight.^c Irradiation performed at 404 nm.^d Saturated in LiCl.^e Estimated from the absorption spectral shape.^f By bubbling pure oxygen.

carried out for up to 100 h, so the Φ values should be no higher than 10^{-6} . No formation of water was found using the IR technique.

3.2. 1-Hexene

The experiments on this scavenger were carried out with the same procedure as that used for toluene. *o*-Chlorotoluene and isooctane were used as internal standards. The concentration in acetonitrile was again adjusted to 20%. The aerobic quantum yields of the chloro derivatives are about twice those with toluene (see Table 1). The main difference is that water forms; this is shown by the fact that dissolved copper chloride hydrolyses to a basic oxychloride which during irradiation precipitates as a pale-green powder at the point where the light enters the cell. Three main peaks and five or six small bumps appeared in the chromatograms obtained under aerobic conditions. When oxygen was removed, the bumps disappeared but the peaks observed were still the same three, having the same retention times as before although with some difference in their absolute and relative areas. The identification of these photoproducts was performed in the following way. Gaseous hydrogen chloride was bubbled into pure 1-hexene which was then examined in the gas chromatograph. Two major peaks were observed which were coincident with the first two of the three peaks just described. Therefore these two peaks were attributed to 2-chlorohexane (boiling point 122 °C) and 1-chlorohexane (boiling point 134 °C) respectively. Their relative amounts obtained from both aerobic and anaerobic irradiations are also consistent with the Markovnikov rule. The presence of these monochlorohexanes implies the production of hydrochloric acid (HCl) during the irradiation which adds to the double bond of the scavenger. This acid can only have been created by hydrogen abstraction by $\text{Cl}_2^{\cdot-}$ on the original 1-hexene to give a chlorohexene. This hypothesis is also supported by the fact that under aerobic conditions this chlorohexene appeared to have been formed with a quantum yield close to the sum of the quantum yields of the two chlorohexanes. In the aerobic irradiation this sum was smaller but it is possible that HCl does not add quantitatively to the 1-hexene double bond because it is partially scavenged by the basic superoxide radicals present or by some 1-hexene oxygen derivatives. The chlorine atom is probably on the sixth carbon atom of the 1-hexene chain because the retention time of the peak observed indicates a boiling point around 130 - 140 °C. Production of 1,2-dichlorohexane is ruled out since the boiling point of this dichloro derivative is 173 °C. To eliminate the possibility that some other 1-hexene chloro derivatives were hidden under the acetonitrile peak, this solvent was almost fully extracted with water; however, no peaks other than the sharp peaks of the 1-hexene and its three chloro derivatives appeared.

3.3. Tetrahydrofuran

The copper chloride concentrations were in the range 10^{-2} - 10^{-3} mol dm⁻³. The internal standards were the same as those for the 1-hexene system. The anaerobic irradiations gave only one peak but those performed

under aerobic conditions gave two. The first of these has the same retention time as that obtained anaerobically and, according to a previous assignment made by Kochi [10] who studied a system similar to ours, this first peak should be α -chloro-THF. The quantum yield of this compound is reduced from 4.0×10^{-3} to 0.7×10^{-3} under aerobic conditions (see Table 1), *i.e.* it is not stable under the action of oxygen radicals. The oxidation product should be represented by the second aerobic peak since the sum of the quantum yields of the two aerobic peaks is very similar to that of the anaerobic peak. This chloro-THF oxygen derivative has a retention time (3 min) which is longer than that of its parent ether (2 min) under our experimental conditions.

It was observed that water was also formed in the presence of oxygen, since the solutions became more and more opalescent as they were irradiated. Even though THF and water are miscible as pure liquids, they are not miscible in the presence of salts. The opalescence produced after 5 h of irradiation roughly corresponds to that obtained by direct addition of 10 μ l of water to 3 ml of a non-irradiated solution (blank). The presence of water indicates strong oxidative processes by oxygen radicals on the original THF. Similar to the 1-hexene system, some small bumps are present in the chromatograms obtained under aerobic conditions, indicating that a variety of decomposition products are formed.

3.4. pH measurements

To test for the presence of free HCl, the solutions after irradiation were diluted 5 - 10 times with water. This necessary operation leads, however, to the precipitation of the basic cupric oxychloride. This hydrolysis modifies the acidity of the irradiated solution in such a way that a comparison of the acidities of the irradiated solutions with that of the blank was not very reliable. The pH values were measured both with a potentiometer and using acid-base titrations. The values obtained were somewhat erratic in that two identical systems differed by even as much as 1 pH unit. Thus, only with toluene can it be definitely stated that the irradiated solutions were more acidic than the blank, the pH of the blank being about 4.5 - 5.5.

4. Discussion

Chlorocopper(II) complexes are able to promote photocatalysed reactions with various substrates and therefore the chlorocupric catalyst described here may, in principle, be used for a variety of chlorination reactions which can allow solar-to-chemical energy conversions.

This system is, however, only speculative at the present time because of the relatively low chloro derivative quantum yield and because the system cannot work for an infinite number of cycles, since the copper(I) is not completely reoxidized by oxygen.

Although the scavengers chosen belong to the saturated, the unsaturated and the aromatic series of hydrocarbons, the reaction mode of Cl_2^\cdot appears to be always the same, *i.e.* it reacts via hydrogen abstraction. The efficiency of Cl_2^\cdot as a chlorinating agent can be estimated from the ratio of the chloro derivative quantum yield to the anaerobic copper(I) quantum yield $\Phi_{\text{Cu(I)}}$; it is about 15% for toluene, 25% for 1-hexene and 1% - 2% for THF. The Cl_2^\cdot quenching rate constants with toluene, 1-hexene and THF must therefore be about $3 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively, since the analogous value for the competing reaction with copper(II) is $1.7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [12] (it is assumed that the reaction $\text{Cu(II)} + \text{Cl}_2^\cdot$ occurs at the same rate in THF as in acetonitrile). These values are in accordance with the rate constant values for hydrogen abstraction reactions of the Cl_2^\cdot radical with saturated aliphatic compounds found by Hasegawa and Neta [7]. However, according to them the strongly preferred reaction of Cl_2^\cdot on the olefinic compounds should be that of addition to the double bond, whereas, as pointed out earlier, the only reaction occurring with 1-hexene is that of hydrogen abstraction. Two monochlorohexanes are in fact produced together with a monochlorohexene, and no evidence of 1,2-dichlorohexane was found. Neither direct oxidation nor addition reactions promoted by Cl_2^\cdot were observed with toluene, although these kinds of reactions with aromatic molecules have also been considered [7] to be faster than hydrogen abstraction.

The radicals involved in these reactions are Cl_2^\cdot and O_2^\cdot . Cl_2^\cdot is produced at the same rate as anaerobic copper(I), whereas O_2^\cdot is produced at a lower rate than that for Cl_2^\cdot because some of the copper(I) is not reoxidized to copper(II). A direct reaction of chloro radicals with oxygen radicals to give Cl^- and oxygen cannot occur to a significant extent since the aerobic and anaerobic overall quantum yields for the chloro derivatives are substantially similar.

The fraction of chloro radical anions which are able to chlorinate produces chloro derivatives and HCl in equimolar amounts. The HCl remains free in the case of toluene and adds to the double bond of 1-hexene. A smaller part of the HCl produced by toluene and 1-hexene can be scavenged by the oxygen radicals. This scavenging reaction must be complete or almost complete for THF since in this case the oxygen radicals created are much more numerous than with toluene or 1-hexene, as indicated by the large difference between the anaerobic and aerobic copper(I) quantum yields. The larger fraction of the Cl_2^\cdot that does not chlorinate is scavenged by copper(II) [12] to give copper(III) which, in turn, should be scavenged by competing reactions with oxygen radicals and, to give a variety of products, with the organic substrates.

The dioxygen (or superoxide) radical anion clearly ends up as water. This is also supported by the fact that, when water is added to THF to reproduce the opalescent effects obtained under aerobic irradiations, the results qualitatively correspond to those expected stoichiometrically on the

basis of the anaerobic copper(II) quantum yields. However, α -chloro-THF appears to resist attack by the oxygen radicals better than THF does. The longer retention time of the chloro-THF oxygen derivative with respect to that of chloro-THF indicates that the oxidized molecule does not break apart.

In the case of toluene no water is formed and no bumps or peaks other than those due to the chloro derivatives of toluene are observed; this aromatic molecule appears not to be attacked by $O_2^{\cdot -}$. Another scavenging route must therefore be considered for the oxygen radicals. The rate constants for $O_2^{\cdot -}$ oxidized by copper(II) [13] and quenched by acetonitrile [14] have similar values, about $10^9 \text{ mol}^{-1} \text{ s}^{-1}$, so the scavenging of $O_2^{\cdot -}$ by copper(III) will occur without doubt at a faster rate. Thus, part of the superoxide ions are destroyed together with free $Cl_2^{\cdot -}$ via copper(II) [12] and the remaining part will be scavenged by the acetonitrile.

For the 1-hexene system, where acetonitrile was also present, the formation of water indicates that the 1-hexene molecules precede those of acetonitrile in scavenging the superoxide ions. Nevertheless, with the exception of the chloro-THF oxygen derivative, oxidation products with distinct peaks have never been observed for any of the three systems studied. These more-or-less oxidized products are probably formed in large numbers but none has an appreciable quantum yield.

Various chlorinated copper(II) species originate when $CuCl_2$ dissolves in acetonitrile. However, we can state that the actual cupric catalyst is not in the $CuCl_4^{2-}$ form. This flattened tetrahedral anion [15] is practically photoinert towards metal reduction compared with other chlorinated copper(II) complexes. Tetrachlorocuprate(II) ions form in large quantities at low $[Cu(II)]/[Cl^-]$ ratios. The concentration of $CuCl_4^{2-}$ (or its absorption peak at 404 nm) is a maximum in pure acetonitrile when the absence of the scavenger allows the maximum $[Cl^-]$ value; the band at 467 nm, due to other chlorinated copper(II) species, is reduced to a shoulder. In this situation, if the apparent anaerobic $\Phi_{Cu(I)}$ values at 404 and 467 nm are weighted, using simple deconvolution, for the light absorbed by this peak and shoulder, it is found that the $\Phi_{Cu(I)}$ value for $CuCl_4^{2-}$ is only about 1×10^{-3} .

This is the main reason why $\Phi_{Cu(I)}$ at 467 nm decreases regularly with the ratio $[Cu(II)]/[Cl^-]$, so that with this decrease the $CuCl_4^{2-}$ contribution to the light absorption becomes more significant. When toluene or 1-hexene are 20% of the solution volume, the two bands have about the same intensity ($[Cu(II)]/[Cl^-] = 1:7$) and those chlorinated species which are different from $CuCl_4^{2-}$ absorb a significant portion of the light at 467 nm. (Series of absorption spectra of chlorocopper(II) complexes are given in refs. 9, 12, 15 and 16.)

The differences between the energy values for $CuCl_4^{2-}$ and those for all the other chlorinated species, with respect to the lowest charge transfer bands and with respect to the d-d bands, are 3100 and 4000 cm^{-1} . These shifts in energy should indicate that the structure of all the other chlorinated

species is different from the flattened tetrahedron. Unfortunately the geometry of these species cannot be established from the electron spin resonance spectra. However, if the ratio $[\text{Cu(II)}]/[\text{Cl}^-]$ is decreased from 1:3 (predominant species being the solvated CuCl_3^- ion) to 1:7 (predominant species being the tetracoordinated CuCl_4^{2-} ion) no isosbestic points or new bands are observed in the absorption spectra. Therefore at least a third species must participate in the step formation equilibria between the solvated CuCl_3^- ion and the tetracoordinated CuCl_4^{2-} ion; this unknown species should have the same shape as the solvated CuCl_3^- ion.

It follows that this unknown species must have a fourth chlorine in the coordination sphere and as such, together with CuCl_3^- , is a photocatalyst of the reactions via Cl_2^\mp described here.

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