

# Mechanism of One-Electron Reactions of Copper(I) Chloride Complexes with Chlorohydrocarbons

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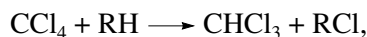
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**Abstract**—The reactivity of chlorohydrocarbons with different electron affinities ( $A_e$ ) and C–Cl bond dissociation energies ( $E_{C-Cl}$ ) in the oxidation of copper(I) chloride complexes was studied. The rate of oxidation depends only on  $A_e$ . Chain initiation, involving Cu(I), occurs by an electron-transfer mechanism.

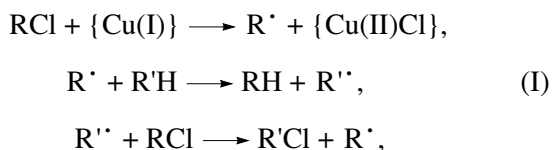
One important way of activating low-reactivity molecules is to involve them in radical chain processes. In catalytic reactions, chain initiators are regenerated in subsequent steps. Such mechanisms are inherent in hydrocarbon cracking [1], olefin polymerization [2, 3], and addition of polyhalogenated alkanes to multiple bonds (the Kharash reaction) [4–6]. However, it is widely believed that a high rate and selectivity are difficult to attain simultaneously in radical processes. Indeed, an increase in the rate of chain initiation leads to acceleration of chain termination and, accordingly, to by-products buildup [7]. On the contrary, high-selectivity catalytic reactions are generally described by non-radical mechanisms. In this case, substrates are mainly converted in the coordination sphere of metal complexes [8]. If the reactants (for example, hydrocarbons or their halogenated derivatives) have a low coordination ability, then platinum metal complexes or transition metal complexes having polydentate ligands, several metal ions, etc., are used as catalysts [9]. However, the above methods of activation of halohydrocarbons are often ineffective [9].

The metathesis of the C–Cl bond, which consists in the exchange of halogen and hydrogen atoms between a polyhalogenated derivative and an alkane,



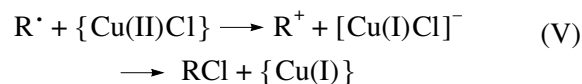
provides an example of a high-selectivity catalytic reaction.

It has recently been discovered that, in the presence of copper chloride complexes, the exchange reaction gives hexachloroethane or other products of chain termination in very small amounts [10]. Nevertheless, this process was shown to be radical chain in nature. Its key steps are redox reactions involving Cu(I) and Cu(II) ions [11]:

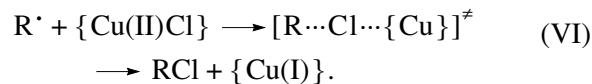


Reaction (I) produces free radicals. When reactions (II) and (III) proceed at high rates, they are quite competitive with bimolecular chain termination (IV) and are, therefore, responsible for the disappearance of free radicals. At the same time, reactions (II) and (III) yield either the original reagent or the desired product of alkane halogenation (IV), making the process highly selective.

In one-electron reactions (I), (II), and (III), the oxidation state of the metal changes by unity, and species with an unpaired electron appear or disappear. The mechanisms of reactions between radicals and Cu(II) (reactions (II) and (III)) compounds are studied in detail. These reactions can be of two types, namely, electron transfer,

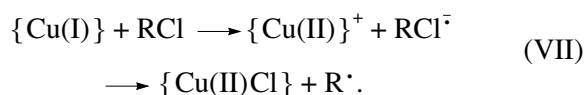


and atom transfer,

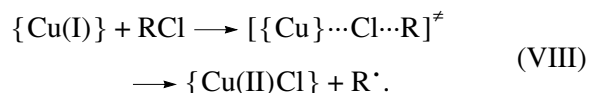


Depending on the mechanism, the above reactions differ substantially in rate (by several orders of magnitude) and in the composition of by-products [12, 13].

Unfortunately, no detailed mechanism of the interaction between Cu(I) and halohydrocarbons can be found in the literature. It is believed that the outer-sphere transfer of an electron from Cu(I) to the hydrocarbon takes place, giving an radical anion [14–16]. Subsequent abstraction of the halide anion produces a radical:



However, no conclusive evidence for this mechanism was obtained. By analogy with reverse reaction (II), one may assume that chain initiation occurs by a ligand-transfer mechanism via a bridged intermediate:



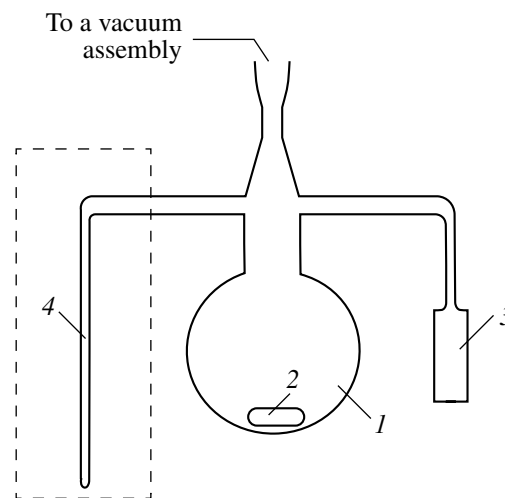
In the electron-transfer mechanism, an increase in the electron affinity of the halohydrocarbon leads to a decrease in the activation energy of the reaction [15, 17]. In the case of the atom-transfer mechanism, the lower the C–Cl bond dissociation energy the lower the activation energy of ligand transfer (according to the Polanyi–Semenov rule). Understanding of the mechanism of radical formation in the reactions of halohydrocarbons with copper(I) complexes allows one to control the catalytic activity of these complexes. The composition and structure of the best catalysts for the free-radical conversion of halogen derivatives can also be predicted.

The purpose of this work is to establish a mechanism of radical generation in the reactions of chlorohydrocarbons with Cu(I) chloride complexes.

## EXPERIMENTAL

Copper(I) chloride was obtained by reduction of  $\text{CuCl}_2$  with sodium sulfite according to a procedure described in [18]. Tributylbenzylammonium chloride (TBBAC) was synthesized as described in [19]. Chlorohydrocarbons were prepared by standard procedures [20] and dried over molecular sieves (4 Å). Chlorobenzene from Merck (reagent grade) was distilled in flowing argon and stored in an argon atmosphere over molecular sieves (4 Å).

Samples to be studied were obtained by dissolving  $\text{CuCl}$ , TBBAC, and a chlorohydrocarbon in chlorobenzene at room temperature. To avoid Cu(I) oxidation before the beginning of the reaction, the samples were prepared under anaerobic conditions using a setup presented in Fig. 1. This setup consists of a dissolution vessel (1) with a magnetic bar (2), a soldered molybdenum-glass spectrophotometric cell (3), and several ampoules (4). A mixture of  $\text{CuCl}$  and TBBAC was placed in the vessel, the device was pumped to  $10^{-4}$  Torr, chlorobenzene and the chlorohydrocarbon were recondensed, and the device was sealed off. The mixture was stirred until  $\text{CuCl}$  dissolved completely and chlorocuprites formed [20]. Next, the solution was transferred to the cell and ampoules, which were unsoldered. The initial concentrations of the reactants were the following (mol/l):  $[\text{CuCl}] = 3 \times 10^{-3}$ ,  $[\text{TBBAC}] = 6 \times 10^{-3}$ , and  $[\text{RCl}] = 0.5$ . The cell and ampoules were



**Fig. 1.** Setup for preparing solutions of Cu(I) chloride complexes: (1) dissolution vessel, (2) magnetic bar, (3) spectrophotometric cell, and (4) ampoule.

placed in a thermostat ( $T = 423$  K; the temperature was maintained to within 1 K). The cell was rapidly cooled to room temperature at intervals, and an electronic spectrum was recorded. The ampoules were unsealed, and the solution was analyzed by GLC.

The electronic spectra of solutions were recorded on UV-2401PC and C-160 Shimadzu spectrophotometers at 280–1100 nm. The concentration of Cu(II) ions was derived from absorbance at a wavelength of 454 nm, which corresponds to the isobestic point in the spectra of various forms of chlorocuprates in chlorobenzene. At this point, the extinction coefficient was  $(7.2 \pm 0.2) \times 10^{-2} \text{ l mol}^{-1} \text{ cm}^{-1}$  [21].

Chromatographic analysis was performed on a model 3700 chromatograph with a flame ionization detector using a column 1.5 m in length and 5% SE-30 on Chromaton as a stationary phase. For better separation of the reaction products, we used linear temperature programming. The products were identified by comparison with standard substances. To perform quantitative measurements, the detector was calibrated against mixtures of known composition.

## RESULTS AND DISCUSSION

The relative reactivity of halohydrocarbons in the reactions with Cu(I) chloride complexes was determined for the following series of compounds: tetrachloromethane, hexachloroethane, benzyl chloride, 3,4-dichlorobutene, and allyl chloride. In this series, the electron affinity ( $A_e$ ) and the C–Cl bond dissociation energy ( $E_{\text{C-Cl}}$ ) decrease (table) [22].

It is well known that Cu(I) chloride complexes absorb light below 330 nm [23]. In view of this, the initial solutions of Cu(I) chloride complexes are colorless. As the reactive solutions containing tetrachloromethane were heated to 423 K, three absorption

Electron affinity ( $A_e$ ) and C–Cl bond dissociation energy data ( $E_{C-Cl}$ ) for chlorohydrocarbons and the apparent rate constants ( $k_{ox}$ ) of the oxidation of Cu(I) chloride complexes

Chlorohydrocarbon	$A_e$ , eV	$E_{C-Cl}$ , kJ/mol	$k_{ox}$ , s <sup>-1</sup>
CCl <sub>4</sub>	2.1*	307*	$(3.3 \pm 0.4) \times 10^{-3}$
C <sub>2</sub> Cl <sub>6</sub>	1.3*	308*	$(1.69 \pm 0.04) \times 10^{-3}$
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	-0.7**	291*	$<10^{-5}$
CH <sub>2</sub> =CHCH <sub>2</sub> Cl	$<0$ ****	285****	$<10^{-5}$
CH <sub>2</sub> =CH-CH(Cl)-CH <sub>2</sub> Cl	$<0$ ****	—****	$<10^{-5}$

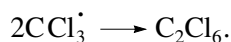
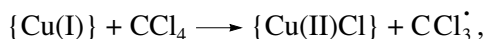
\* [22].

\*\* [27].

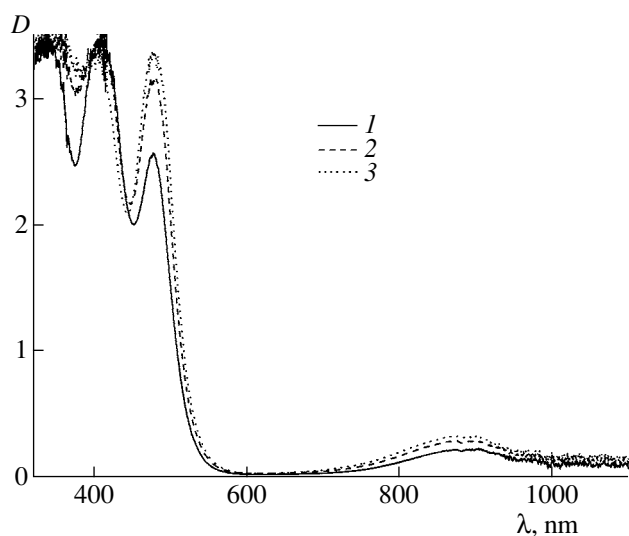
\*\*\* Estimated as in [28].

\*\*\*\* This value is close to the corresponding value for benzyl chloride.

bands appeared very soon and grew over a few minutes in the visible region, peaking at 410, 480, and 880 nm (Fig. 2). They can be assigned to electronic transitions in the Cu(II) chloro complexes CuCl<sub>4</sub><sup>2-</sup> and Cu<sub>2</sub>Cl<sub>6</sub><sup>2-</sup> [18, 24, 25]. According to chromatographic data, these transitions are accompanied by the formation of hexachloroethane. This fact points to the generation of CCl<sub>3</sub><sup>•</sup> radicals, which recombine to give C<sub>2</sub>Cl<sub>6</sub> in the absence of other reagents:



Hexachloroethane oxidizes Cu(I) chloride complexes as well, as is evidenced by the appearance of absorption bands due to chlorocuprates in the UV and visible regions (Fig. 3). The intensity of these bands grows with time.

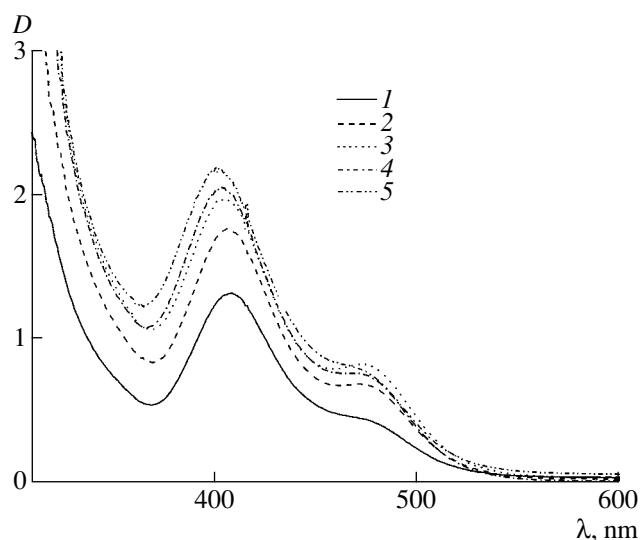


**Fig. 2.** Electronic spectra of a chlorobenzene solution of CuCl-TBBAC-CCl<sub>4</sub> held at 423 K for (1) 7, (2) 14, and (3) 58 min;  $l = 1.0$  cm.

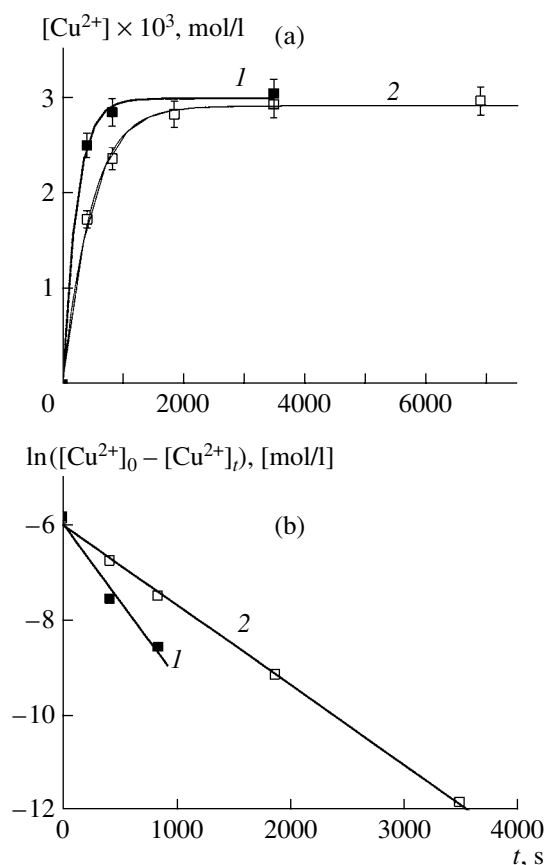
Figure 4 shows the copper(I) buildup curves and their linear anamorphoses on the coordinates of the first-order rate equation. The apparent rate constants of copper(I) oxidation by tetrachloromethane and hexachloroethane ( $k_{ox}$ ) derived from these data are  $(3.3 \pm 0.4) \times 10^{-3}$  and  $(1.69 \pm 0.04) \times 10^{-3}$  s<sup>-1</sup>, respectively. Thus, tetrachloromethane, which has a greater electron affinity than hexachloroethane, is a more powerful oxidant.

When added to Cu(I) complexes, 3,4-dichlorobutene-1 produces no copper oxidation products. On being heated, this chlorohydrocarbon yields 1,4-dichlorobutene-2. In this case, the rate of olefin isomerization is considerably lower than that observed in the presence of other metal complexes [26].

When solutions of CuCl and TBBAC were kept in allyl chloride (CH<sub>2</sub>=CHCH<sub>2</sub>Cl) or benzyl chloride (C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>Cl) at 423 K for 24 h, neither Cu(I) ion oxidation nor chlorohydrocarbon conversion was detected.



**Fig. 3.** Electronic spectra of a chlorobenzene solution of CuCl-TBBAC-C<sub>2</sub>Cl<sub>6</sub> held at 423 K for (1) 7, (2) 14, (3) 31, (4) 58, and (5) 115 min;  $l = 0.5$  cm.



**Fig. 4.** (a) Accumulation curves for the product of copper(I) oxidation in the presence of (1)  $\text{CCl}_4$  and (2)  $\text{C}_2\text{Cl}_6$ ; (b) their linear anamorphoses on the coordinates of the first-order equation.

Thus, the reaction of Cu(I) chloro complexes with chlorohydrocarbons, which have a negative electron affinity, does not occur under the experimental conditions examined, despite the fact that the C–Cl bond dissociation energy in these compounds is considerably lower than that in  $\text{CCl}_4$  or  $\text{C}_2\text{Cl}_6$ . The observed relationship between the oxidizing capacity of the chlorohydrocarbons and  $A_e$  and its independence of  $E_{\text{C-Cl}}$  values suggests an electron-transfer mechanism for Cu(I) oxidation, the process responsible for chain initiation in the reactions involving halohydrocarbons.

#### ACKNOWLEDGMENTS

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