

PHOTOCHEMISTRY

Photochemistry of Tetraalkylammonium Tetrachlorocuprates in Low-Temperature Matrices

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Received January 22, 2009

Abstract—The product composition and the principles of photochemical transformations of tetrahexylammonium tetrachlorocuprate $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ ($\text{RH} = \text{C}_6\text{H}_{13}$) in 2-chlorobutane at 77 K have been found out by ESR spectroscopy. It has been shown that the photolysis of $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ results in the formation of alkyl radicals (R^\bullet), presumably, anions $[\text{Cu}^{\text{I}}\text{Cl}_3]^{2-}$ and organic copper(II) compounds $\{\text{Cu}^{\text{II}}\text{R}\}$. A reduction in the quantum yield of primary photolysis products during the reaction, nonequivalence of the quantum yield of the buildup of paramagnetic photolysis products to that of $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ consumption, and a decrease in the total number of paramagnetic particles in the system during the photolysis have been revealed. A photolysis mechanism involving both photochemical and thermal processes is proposed.

DOI: 10.1134/S0018143909050099

Copper(II) chloride complexes are used as precursors of catalysts for transformations of chlorinated hydrocarbons. Earlier it was shown [1–3] that particles similar to the intermediates of catalytic reactions in structure can be obtained by photolysis of $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ tetrachlorocuprates, where RH is an alkyl (C_4H_9 , C_6H_{13} , C_8H_{17}) and/or benzyl (PhCH_2), at the $\text{Cl} \rightarrow \text{Cu}$ charge-transfer band ($\lambda_{\text{max}} = 405\text{--}415$ nm) in the matrices of frozen, non-complexing, vitrifiable (2-chlorobutane, toluene–chloroform mixture), and crystallizing (chlorobenzene, chloroform) solvents at 77 K. The $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ photolysis products are the organic radicals (R^\bullet) produced via hydrogen atom abstraction from the alkyl substituents of the quaternary ammonium cation. Evidence for the formation of new, presumably, organometallic copper(II) complexes $\{\text{Cu}^{\text{II}}\text{R}\}$ was obtained by spectral methods during continuous and flash photolyses of solutions of copper(II) chloride complexes in dimethylformamide (DMF), ethanol, and chlorinated organic solvents [2, 4]. It is with these complexes that the appearance of a new absorption band at $\lambda_{\text{max}} = 436$ nm in the electronic absorption spectra of the photolysis products, which can be referred to $\text{Cl}^- \rightarrow \text{Cu}^{\text{II}}$ charge transfer typical of mixed-ligand complexes $[\text{Cu}^{\text{II}}\text{LCl}_3]^-$ (L is a ligand), is associated [5]. The spin Hamiltonian parameters $g_1 = 2.082 \pm 0.003$, $g_2 = 2.033 \pm 0.001$, $g_3 = 2.024 \pm 0.001$, resulted from EPR spectrum simulation for one of the products, are also typical of asymmetrical copper(II) complexes with weak ligands [6], for example, alkyl fragments. Another photolysis product of tetrachlorocuprates, by analogy with their thermal reduction [7], can be the $[\text{Cu}^{\text{I}}\text{Cl}_3]^{2-}$ chlorocuprite anion.

The stability of a number of $\{\text{Cu}^{\text{II}}\text{R}\}$ complexes, such as $[\text{Cu}^{\text{II}}\text{RCl}_3]^{2-}$, where $\text{R} = \text{CH}_3$ or $i\text{-C}_3\text{H}_7$, was confirmed by quantum-chemical calculations with the unrestricted DFT method (exchange-correlation functional PBE) [8]. According to the calculations, the Cu–C bond dissociation energy in these complexes is on average 90 kJ/mol. Several ways of the degradation of $\{\text{Cu}^{\text{II}}\text{R}\}$, including those in reactions with similar complexes, alkyl radicals, hydrogen chloride, etc., were proposed. The calculated values for the energies of these reactions, which were at least 200 kJ/mol, confirmed the high reactivity of $\{\text{Cu}^{\text{II}}\text{R}\}$, thereby seemingly explaining that it is impossible to observe these complexes in solutions at room temperature. On the contrary, it is unlikely that the degradation of $\{\text{Cu}^{\text{II}}\text{R}\}$ follows the monomolecular mechanism at low temperatures because of quite a high Cu–C bond strength.

A scheme of the main steps in the photochemical transformations of $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$, which includes the dehydrochlorination of the excited complex, as well as secondary thermal processes involving the photolysis products $\{\text{Cu}^{\text{II}}\text{R}\}$, R^\bullet , $[\text{Cu}^{\text{I}}\text{Cl}_3]^{2-}$, HCl, and initial tetrachlorocuprate $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ both at 77 K and during further heating, was proposed [1]. However, the detailed mechanism of the reactions remained an open question. For example, the reasons for the decrease in the total number of paramagnetic particles in the sample during the photolysis and further heating were unclear [1]. In this context, we found it reasonable to reveal the dependence of the composition of the products and intermediates, the quantum yield, and other characteristics of $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ photolysis upon the initial complex concentration in a low-temperature matrix.

The aim of this work was to determine the effect of the concentration of an anionic copper(II) chloride complex, taking $[(C_6H_{13})_4N^+]_2[Cu^{II}Cl_4]^{2-}$ as an example, on the product composition and the kinetic characteristics of photochemical transformations in the glassy matrix of frozen 2-chlorobutane.

EXPERIMENTAL

Anhydrous copper(II) chloride was prepared from $CuCl_2 \cdot 2H_2O$ via azeotropic dehydration with benzene [9] followed by vacuum pumping at 10^{-3} torr. Tetrahexylammonium chloride $(C_6H_{13})_4N^+Cl^-$ from Sigma-Aldrich (Switzerland) was used without additional purification. 2-Chlorobutane from Merck (Germany) was purified by distillation over phosphoric anhydride.

The solutions of $[(C_6H_{13})_4N^+]_2[Cu^{II}Cl_4]^{2-}$ were prepared by successive dissolution of an excess of preliminarily evacuated $(C_6H_{13})_4N^+Cl^-$ and $CuCl_2$ in freshly distilled 2-chlorobutane. The copper concentration was varied from 1.7×10^{-3} to 1.0×10^{-2} mol/l. The ratio $[(C_6H_{13})_4N^+Cl^-] : [CuCl_2] = 6 : 1$ ($[Cl^-]_{\Sigma} : [Cu^{II}]_{\Sigma} = 8 : 1$) was maintained constant in all the solutions in order to preclude the formation of bi- and polynuclear chlorocuprates [10]. The concentration of tetrachlorocuprate solutions and their purity were monitored by spectrophotometry [11]. The electronic absorption spectra of the solutions were recorded at 20°C on a Shimadzu UV-2401PC spectrophotometer in quartz cells with an optical path length of 1 mm.

The photolysis of the samples was carried out at 77 K in ESR cylindrical quartz ampoules of 4 mm inner diameter. The ampoules were preliminarily calcined at 500 K and freed of adsorbed water by connecting to a vacuum line of 10^{-3} torr. Each ampoule was filled with 0.13 ml of solution with a certain copper(II) concentration, subjected to three freezing–pumping (10^{-3} torr)–thawing cycles, and then sealed off. The photolysis was carried out with light from a DRSh-250 high-pressure mercury lamp equipped with a glass filter for isolation of the line at $\lambda = 405$ nm ($T_{\max} = 27\%$, $\Delta\nu_{1/2} = 2400$ cm^{-1}). The light intensity was determined with a ferrioxalate actinometer. The dependence of the amount of initial tetrachlorocuprate and photolysis products upon the absorbed light dose and the corresponding quantum yields were determined according to the procedure described in [12]. The correction for light absorption by the photolysis products at the photolysis wavelength was introduced with allowance for the molar absorption coefficients of the $\{Cu^{II}R\}$ copper complexes produced [13].

Warming the samples from 77 to 200 K after photolysis was performed with a special facility comprising a Dewar flask filled with liquid nitrogen and equipped with a heating coil to induce nitrogen boiling. A sample was placed in a stream of vapor over boiling nitrogen. The ampoule was held at a predetermined temperature for 5 min in the nitrogen stream; then, thermostating

was interrupted, the sample was held at 77 K over 5 min, and its ESR spectra were recorded. It was found that the required sample temperature inside the ampoule in the range of 77–130 K was established within no more than 4 min.

The ESR spectra were recorded on a Varian-E3 X-band radiospectrometer (100 kHz magnetic field modulation) at 77 K. The measurement was performed under conditions that ruled out both saturation and modulation broadening of the signal. The *g*-factor was determined with the use Mn^{2+} -doped MgO as a standard. The spin Hamiltonian parameters were calculated as recommended in [14]. The invariability of the recording conditions in the resonator cavity was controlled via the simultaneous recording of the spectrum of a test sample and a certain component of the spectrum of ruby (Al_2O_3 containing Cr^{3+}) single crystal as an internal standard. The number of paramagnetic centers in the test samples was determined with respect to the standard $CuCl_2 \cdot 2H_2O$ single crystal with a known number of paramagnetic centers. The concentration of $[Cu^{II}Cl_4]^{2-}$ was also estimated from the amplitude value of the parallel component of the ESR spectrum, since the spectral line shape remained unchanged during the photolysis. The relative accuracy in determination of the concentration of paramagnetic particles was $\pm 10\%$.

RESULTS AND DISCUSSION

Tetrahexylammonium tetrachlorocuprate $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ ($RH = C_6H_{13}$) in 2-chlorobutane has an intense $Cl \rightarrow Cu^{II}$ charge transfer band at $\lambda_{\max} = 414$ nm at room temperature. The position of the band maximum does not depend on the concentration of the solution in the range of 1.7×10^{-3} – 1.0×10^{-2} mol/l. Similar electronic absorption spectra characterize the $[CuCl_4]^{2-}$ anions in other weakly polar solvents and in polar media [1–3]. It is believed that 2-chlorobutane molecules do not enter into the first coordination sphere of the copper(II) ion, which is composed of the chloride anions only [15].

The optical density of the solution at the absorption band maximum is linearly related to the concentration in accordance with the Beer–Lambert–Bouguer law in the examined range of $[(RH)_4N^+]_2[Cu^{II}Cl_4]^{2-}$ concentrations in 2-chlorobutane at room temperature. The molar absorption coefficient was calculated to be $\epsilon_{414} = (2.4 \pm 0.2) \times 10^3$ l mol^{-1} cm^{-1} . Freezing the solutions to 77 K results in a hypsochromic shift by 8 nm in the maximum of the charge transfer band. The frozen solutions form transparent glasses; however, the background absorption of the samples in the UV range is enhanced at a concentration of 5×10^{-3} mol/l, thereby suggesting the association of the complexes. Indeed, it is known that the association of quaternary ammonium salts with the formation of aggregates of 10 or more particles takes place at room temperature even at a concentration of $\sim 10^{-2}$ mol/l in weakly polar solvents [16].

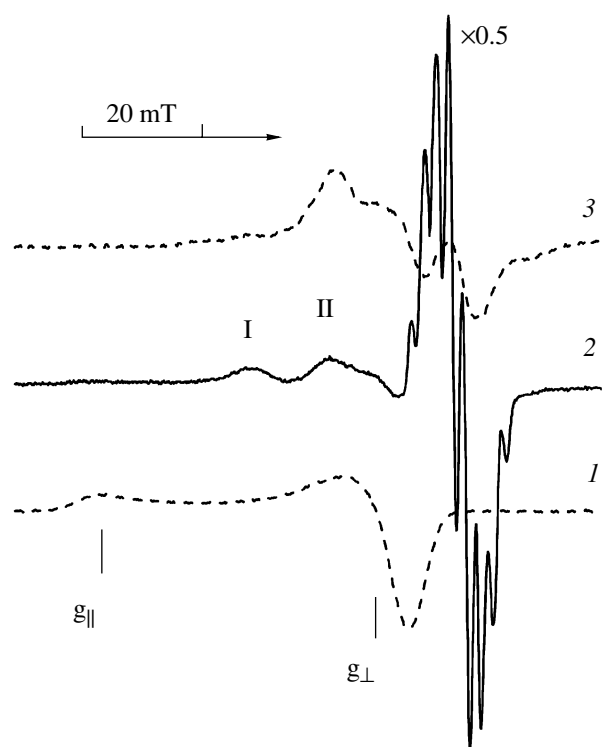


Fig. 1. The ESR spectra of the $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ sample (4.2×10^{-3} mol/l) in the matrix of 2-chlorobutane at 77 K (1) before the photolysis, and after (2) the 12 h photolysis and (3) subsequent heating to 110 K.

The ESR spectrum of $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ in the low-temperature matrix of 2-chlorobutane is characterized by axial anisotropy of the g -tensor and the absence of a hyperfine structure (Fig. 1). The effective values of parallel and perpendicular g -tensor components were $g_{\parallel} = 2.458 \pm 0.001$ and $g_{\perp} = 2.055 \pm 0.001$, respectively. The absence of a hyperfine structure can be due to the strong dipole–dipole interaction, which appears in the case of association of tetrachlorocuprate anions in frozen solutions. Another reason can be a superposition of the spectra of equilibrium complexes with different geometries (e.g., different Cl–Cu–Cl angles), which results in a considerable change in the g -tensor [6, 17]. The ESR spectral line shape and the magnetic resonance parameters remain unchanged when the concentration of $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ is increased from 1.7×10^{-3} to 1.0×10^{-2} mol/l. The number of paramagnetic centers independently calculated from the electronic absorption (295 K) and ESR spectra (77 K) coincides within a 10% accuracy. In addition, the intensity of the parallel component of the $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ signal linearly depends on the total number of copper(II) ions, thereby making it possible to use this value in the calculation of the amount of $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ during the photolysis and subsequent heating.

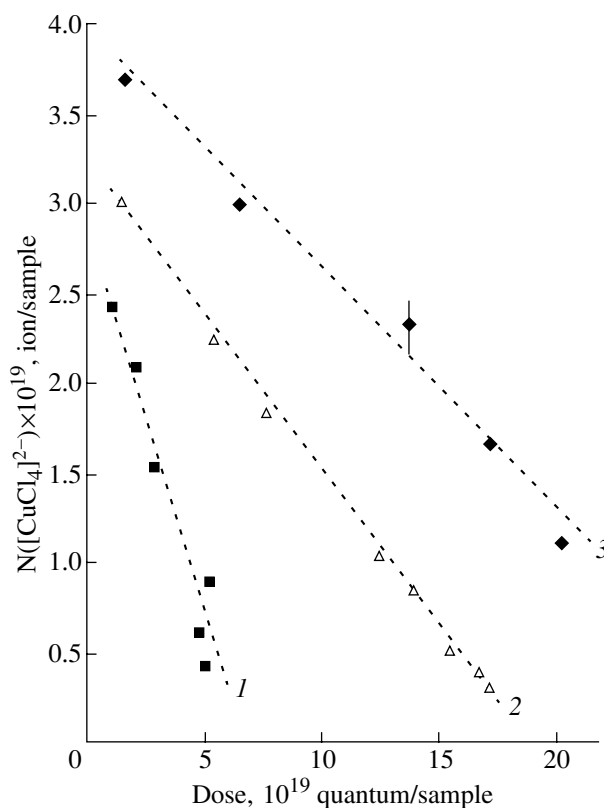


Fig. 2. The dependence of the amount of $[\text{CuCl}_4]^{2-}$ having an initial concentration of (1) 3.1×10^{-3} , (2) 4.2×10^{-3} , or (3) 5.2×10^{-3} mol/l in the low-temperature matrices of 2-chlorobutane upon the absorbed light dose during photolysis.

As in the cases described earlier [1, 2], a reduction in the intensity of the tetrachlorocuprate lines in the ESR spectra and the appearance of lines corresponding to a mixture of new copper complexes (components I and II) [2] and alkyl radicals (Fig. 1) are observed during the photolysis at the charge transfer band of $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ in 2-chlorobutane at 77 K. In this system, alkyl radicals can be formed exceptionally via hydrogen atom abstraction from the hexyl substituents on the ammonium cation. We estimated their mole fraction in the product mixture at 10–15% at the most.

The dependences of the consumption of $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ and the buildup of the paramagnetic products $\{\text{Cu}^{\text{II}}\text{R}\}$ and R^{\bullet} upon the absorbed light dose are illustrated in Figs. 2 and 3, respectively. The data in Fig. 2 show that the tetrachlorocuprate photoreduction efficiency increases with a decrease in the $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ concentration in the low-temperature matrix. The dose dependences of $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ consumption are linear up to conversions of 80–90% independently from the $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ concentration. At the same time, the dependence of the $\{\text{Cu}^{\text{II}}\text{R}\}$ and R^{\bullet} buildup on the absorbed light dose is nonlinear, that is, the effective quantum yield of the accumulation of these products decreases during the photolysis (Fig. 3). We believe that

this is associated with secondary thermal reactions of the photolysis products leading to the formation of diamagnetic compounds. For example, such a reaction can be the recombination of radicals. We have established that neither photolysis at $\lambda = 405$ nm nor irradiation at a wavelength close to the absorption maximum of $\{\text{Cu}^{\text{II}}\text{R}\}$ (436 nm) results in the secondary photochemical reactions of the $\{\text{Cu}^{\text{II}}\text{R}\}$ complex [13].

The $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ consumption and the $\{\text{Cu}^{\text{II}}\text{R}\}$ and R^\bullet buildup quantum yields calculated from the respective dose dependences are given in the table. For the samples with an initial $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ concentration of 5.2×10^{-3} mol/l, the $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ photoreduction quantum yield coincides with the quantum yield of the formation of $\{\text{Cu}^{\text{II}}\text{R}\}$ and R^\bullet , thus suggesting the 90–95% conversion of $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ into $\{\text{Cu}^{\text{II}}\text{R}\}$ and R^\bullet . At lower concentrations (3.1×10^{-3} and 4.2×10^{-3} mol/l), the initial value of the quantum yield of the products $\{\text{Cu}^{\text{II}}\text{R}\}$ and R^\bullet remains constant and close to the corresponding value for the $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ consumption at the maximum concentration of $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$. However, as the concentration of $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ decreases, the quantum yield of its consumption increases by a factor of 2.5. These samples are also characterized by the greatest drop in the total number of paramagnetic particles (ξ) (see the table).

The decrease in the total number of paramagnetic particles in the matrices subjected to irradiation is observed for all the of test systems. The effect is enhanced with a reduction in the initial tetrachlorocuprate concentration and can reach 40%. It likely that this enhancement, as the difference between the quantum yields of the $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ consumption and the formation of $\{\text{Cu}^{\text{II}}\text{R}\}$ and R^\bullet , is due to the secondary thermal processes involving the photolysis products.

As noted above, the accumulation of $\{\text{Cu}^{\text{II}}\text{R}\}$ during the photolysis manifests itself as two new components (I and II) in the ESR spectrum, whereas the high-field part of the signal is distorted by the absorption of alkyl radicals (Fig. 1). The amplitudes of components I and II increase symbatically during the photolysis (Fig. 4). When the nonlinearity of the dose dependence for the yield of the photolysis products becomes noticeable, the concentration of the new copper complexes stops

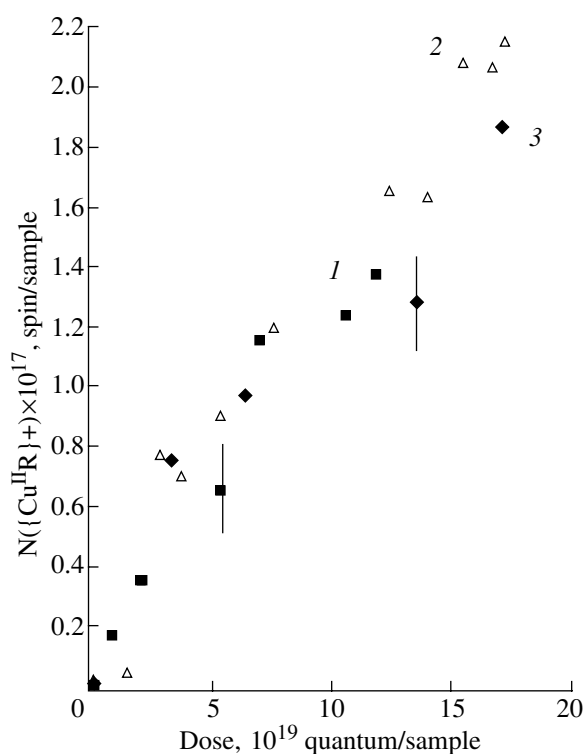


Fig. 3. The dependence of the amount of $\{\text{Cu}^{\text{II}}\text{R}\}$ and R^\bullet produced during the photolysis of $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ with initial concentrations of (1) 3.1×10^{-3} , (2) 4.2×10^{-3} , and (3) 5.2×10^{-3} mol/l in 2-chlorobutane matrices at 77 K upon the absorbed light dose.

increasing at $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ conversions of about 50%, thereby suggesting their further transformations.

After heating the mixture to 100 K and subsequent cooling to 77 K, the spectrum of alkyl radicals vanishes and the high-field portion of the spectrum of the complexes becomes detectable [2, 3]. The intensity of the spectral components attributed to the copper complexes varies with a rise in the temperature (Fig. 1). Low-field component I vanishes, whereas the amplitudes of the other components assigned to the copper complexes increase. We believe that the temperature changes observed in the ESR spectra indicate the formation of at least two types of the $\{\text{Cu}^{\text{II}}\text{R}\}$ complex resulting

The quantum yields of $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ consumption and $\{\text{Cu}^{\text{II}}\text{R}\}$ and R^\bullet buildup and the degree of reduction in the total number of paramagnetic particles in the low-temperature matrix, depending on the initial $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ concentration

$c([\text{Cu}^{\text{II}}\text{Cl}_4]^{2-})_0 \times 10^3$, mol/l	$\Phi([\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}) \times 10^4$	$\Phi(\{\text{Cu}^{\text{II}}\text{R}\} + \text{R}^\bullet)_0 \times 10^4$	$\xi_{1/2}$	ξ_∞
3.1	3.6 ± 0.2	1.5 ± 0.2	0.30 ± 0.10	0.40 ± 0.10
4.2	1.9 ± 0.2	1.5 ± 0.2	0.15 ± 0.10	0.30 ± 0.10
5.2	1.5 ± 0.2	1.5 ± 0.2	0.05 ± 0.10	0.20 ± 0.10

Note: $c([\text{Cu}^{\text{II}}\text{Cl}_4]^{2-})_0$ is the initial $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ concentration in the matrix before the photolysis; $\Phi([\text{Cu}^{\text{II}}\text{Cl}_4]^{2-})$ is the quantum yield of $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ consumption; $\Phi(\{\text{Cu}^{\text{II}}\text{R}\} + \text{R}^\bullet)_0$ is the initial quantum yield of the buildup of the $\{\text{Cu}^{\text{II}}\text{R}\}$ and R^\bullet paramagnetic photolysis products; $\xi_{1/2}$ and ξ_∞ are the degrees of reduction in the total number of paramagnetic particles in the matrix during the photolysis over the kinetic half-life and the complete consumption of $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$, respectively; $\xi = (N_t - N_0)/N_0$, where N is the number of paramagnetic particles in the matrix; and t is the transformation (photolysis) time.

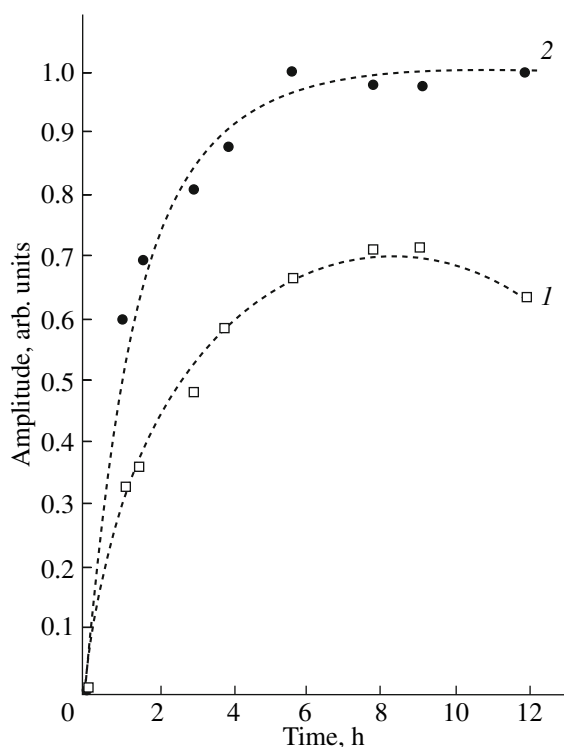
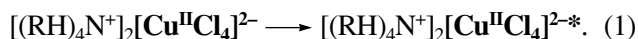


Fig. 4. Change in the amplitude of components (1) I and (2) II of the ESR spectrum of $\{\text{Cu}^{\text{II}}\text{R}\}$ complexes during the photolysis of $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ with the initial concentration of 4.2×10^{-3} mol/l in 2-chlorobutane matrices at 77 K.

from the photolysis. Component I seems to correspond to the less stable structure transforming into the more stable complex on heating, which produces component II in the ESR spectrum. In the range 100–110 K, the line shape of the spectrum remains unchanged. An increase in the sample temperature to 110 K results in the disappearance of the ESR lines of the photolysis products. The heating of the sample to room temperature does not result in the recovery of the initial signal of the tetrachlorocuprate anion.

These results are in general consistent with the earlier proposed mechanism for the photochemical transformations of $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ in low-temperature matrices based on the synchronous cleavage of the Cu–Cl and C–H bonds in the excited complex [1]. Its first step is the formation of the excited $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-*}$ complex by photolysis at the ligand-to-metal charge transfer band:



Hereinafter, paramagnetic complexes are given in bold. The second step is the dehydrochlorination of the excited complex, which can result in different products of its phototransformation, primarily, organic copper(II) compounds, as well as single radicals and trichlorocuprate anions (in writing stoichiometric equations, the formula $[(\text{RH})_4\text{N}^+][(\text{RH})_3\text{N}^+\text{R}-\text{Cu}^{\text{II}}\text{Cl}_3]^{2-}$ will

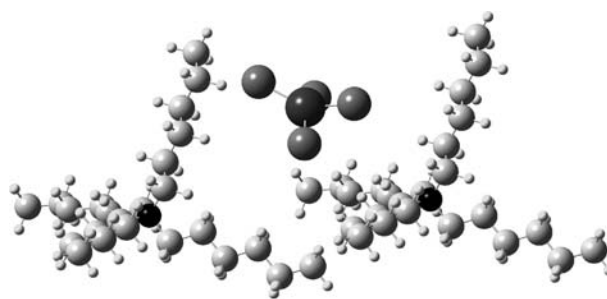
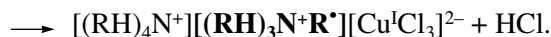
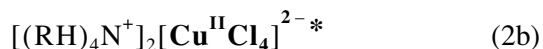
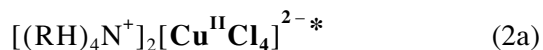


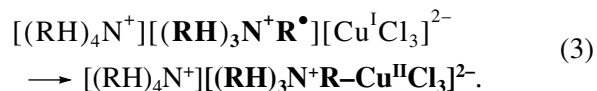
Fig. 5. The structure of the $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ coordination complex.

be ascribed to the product organic copper compound $\{\text{Cu}^{\text{II}}\text{R}\}$).



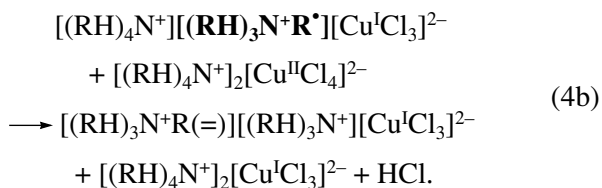
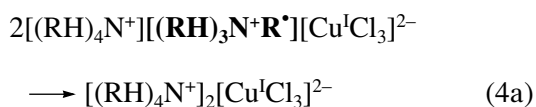
We believe that a sterically favorable arrangement of copper atoms in the tetrachlorocuprate anion and the carbon atoms in the alkyl substituent on the counterion is necessary to form the $[(\text{RH})_4\text{N}^+][(\text{RH})_3\text{N}^+\text{R}-\text{Cu}^{\text{II}}\text{Cl}_3]^{2-}$ compound via reaction (2a) (Fig. 5). When the Cu–C distance is much longer than the bond length, alkyl radicals and, apparently, $[\text{Cu}^{\text{I}}\text{Cl}_3]^{2-}$ anions are generated during the photolysis. In this case, route 2b offers a higher probability of occurrence for the subsequent thermal reactions, resulting in the decay of the free valence (decrease in the a number of paramagnetic particles), which indeed happens during the photolysis of frozen solutions at a lower concentration (table).

Photochemical processes are accompanied by thermal transformations of the resultant complexes. For example, the $[(\text{RH})_4\text{N}^+][(\text{RH})_3\text{N}^+\text{R}^{\bullet}][\text{Cu}^{\text{I}}\text{Cl}_3]^{2-}$ complex can convert into the complex having the Cu–C σ -bond:

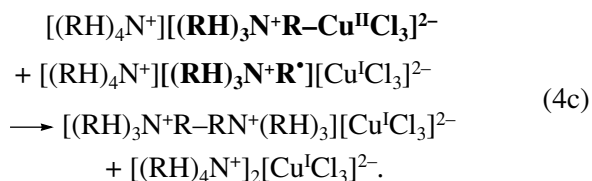


Thus, $\{\text{Cu}^{\text{II}}\text{R}\}$ can be formed concurrently both in the primary photochemical event (2a) and consecutive reactions (2b) and (3) during the photolysis.

The reactions described above do not result in free valence decay. The paramagnetism can be lost as a result of the reaction between two alkyl radicals, in particular, involving hydrogen atom tunneling [18], for example, with the formation of the hexenyl moiety (the symbol (=) denotes the presence of the C=C bond) via the transfer of the vicinal hydrogen atom from one radical to another (4a) or the synchronous detachment of the vicinal hydrogen atom from the radical and the chlorine atom from the chlorocuprate anion (4b):

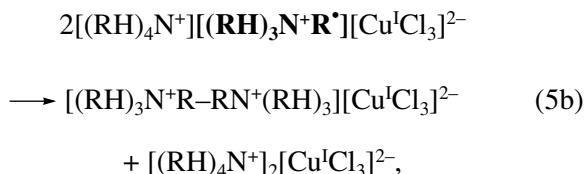
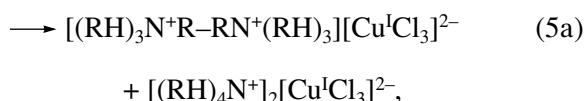


The decay of paramagnetic centers can also be due to the interaction of the bound and free radicals:

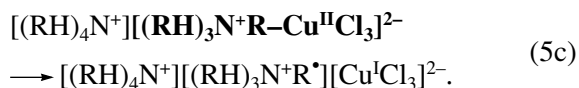


Processes (4a)–(4c) can take place in the 2-chlorobutane matrix even at 77 K, thereby resulting in the disappearance of paramagnetic centers observed during photolysis.

Warming the samples creates conditions for the occurrence of diffusion-controlled reactions (5a) and (5b):

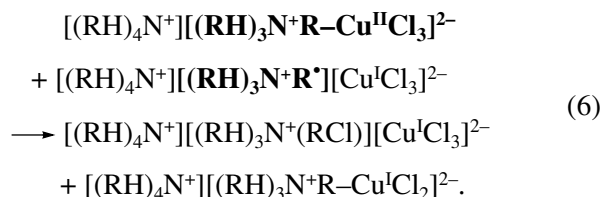


Here, reaction (5a) is the step of the bimolecular decay of the organocopper complex and (5b) is the coupling process of alkyl radicals. According to quantum-chemical calculations [8], the unimolecular degradation of the organic copper complex (5c) has a substantially lower probability:



The abstraction of a chlorine atom in the tetrachlorocuprate-anion by the alkyl radical (reaction (6)), resulting in the formation of organic copper(I) compounds,

which are undetectable by ESR and electronic absorption spectroscopy in the visible range, is also possible:



The proposed mechanism agrees with the basic principles of the photolysis of quaternary ammonium tetrachlorocuprates. However, it is difficult to explain the concentration dependence of the $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ consumption quantum yields in terms of this mechanism: the quantum yield changes from 1.4×10^{-3} to 3.6×10^{-3} in quite a small range concentration of $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ (~1.5-fold), as well as the rate of loss of paramagnetism. The failure can be associated with the fact that the most concentrated solutions are close to the saturation limit ($\sim 10^{-2}$ mol/l) and the association effects can occur in them, unlike the case of dilute systems. Note that substantial portion of $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ ion pairs is unassociated and the $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ packing in the matrix is looser for the samples with a $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ concentration of 3.1×10^{-3} mol/l. In contrast, tetrahexylammonium tetrachlorocuprate in the samples with a $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ concentration of 5.1×10^{-3} mol/l exists mainly as ordered associates. It is likely that probably, a part of the closely arranged copper atoms in the tetrachlorocuprate anion and carbon atoms in the alkyl substituent increases in such systems (Fig. 5), thus facilitating the formation of the $[(\text{RH})_4\text{N}^+][(\text{RH})_3\text{N}^+\text{R}-\text{Cu}^{\text{II}}\text{Cl}_3]^{2-}$ organocopper compound. Hence, it follows that prone to photochemical transformations are primarily systems in which reaction (2a) is sterically favored.

CONCLUSIONS

Thus, in the present work the mechanism of the photochemical transformation of tetrahexylammonium tetrachlorocuprate in the low-temperature matrix of a weakly polar solvent has been formulated. It has been found that the photochemical transformations are accompanied by thermal processes even at 77 K. The presence of the thermal steps is responsible for the decrease in the quantum yield of the primary photolysis products at high degrees of conversion and its discrepancy, in some cases, with the quantum yield of $[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ consumption, which is accompanied by a decrease in the total number of paramagnetic particles in the system. It has been shown that a change in the $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ concentration in solutions close to saturation substantially affects the quantum yield and the composition of its photochemical transformation products. It is assumed that the reason for different concentration-dependent $[(\text{RH})_4\text{N}^+]_2[\text{Cu}^{\text{II}}\text{Cl}_4]^{2-}$ behaviors in the photochemical process is the difference in the degree of its association in the frozen solvent matrix.

ACKNOWLEDGMENTS

The authors are grateful to Professor A. Kh. Vorob'ev for kindly providing the computer programs for the processing of ESR spectra and V. I. Pergushov for fruitful discussions.

The work was supported by the Russian Foundation for Basic Research, project no. 09-03-00406.

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