

Photochemistry of copper(II) polyfluorocarboxylates and copper(II) acetate as their hydrocarbon analogues

E.M. Glebov^{a,*}, V.F. Plyusnin^a, V.P. Grivin^a, S.A. Krupoder^b, T.I. Liskovskaya^b, V.S. Danilovich^b

^a Institute of Chemical Kinetics and Combustion, 630090 Novosibirsk, Russia

^b Institute of Inorganic Chemistry, 630090 Novosibirsk, Russia

Received 13 January 2000; accepted 13 February 2000

Abstract

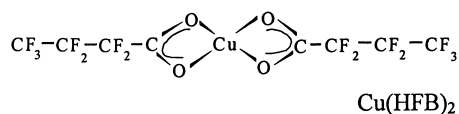
Photochemistry of copper(II) acetate and polyfluorocarboxylates in liquid and frozen alcohol solutions has been investigated. The photolysis of copper(II) acetate leads to the metal copper as a final product. The mechanism of photolysis, including the intramolecular electron transfer as the initial stage of process, has been proposed. ESR spectra of free radicals were registered at the low-temperature (77 K) photolysis of copper(II) acetate in isopropanol solution, being the indirect evidence for the validity of proposed mechanism. Photochemical transformations of copper(II) perfluorocarboxylates have been found to occur in two stages. The first one includes the changes in the coordination sphere of Cu(II) ion. The second stage results in the reduction process, leading to metal copper and the precipitate CuF. The 'dark' contact of the precipitate with methanol solution, obtained after irradiation, yields the complex Cu(PFC)×2CH₃OH, where PFC is the perfluorocarboxylate anion. The mechanisms for the observed photochemical and dark reactions have been proposed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Copper(II) polyfluorocarboxylates; Copper(II) acetate; Photochemistry; Kinetics and mechanism

1. Introduction

The complexes of copper(II) with the carbon [1] and polyfluorocarbon [2] acids and the hydrates of fluorosubstituted ketoacids [3] in alcoholic media are known to undergo the photoreduction to yield metal copper. But as concerned the cited works [1–3], the detailed mechanism of photolysis had not been established. The similar photochemical transformations have been found to occur for related compounds — copper(II) and nickel(II) β-diketonates [4]. The mechanism of photoreduction process for β-diketonates was proposed in [5].

The preliminary information concerning the photolysis of one of the representatives of perfluorocarboxylates — copper(II) heptafluorobutyrate (further — Cu(HFB)₂) — is given in our previous work [6].



According to data presented in [6], the mechanism of photolysis seems to be more complicated with respect to cop-

per(II) β-diketonates. It involves two stages. The first, being reversible in the presence of oxygen, consists the changes in the coordination sphere of Cu(II) ion. The second stage has substantially lower quantum yield and consists of the reduction of copper(II). The observed products were identified as the metal copper and the black precipitate, presumably the copper(II) oxide. The maintaining of that precipitate in the dark under solution has been found to lead to its transformation into the pale-blue form, being identified as copper(II) fluoride complex with methanol [6]. The latter conclusion seems now to be corrected in the light of the data, obtained in this work.

The present work considers the photolysis of some representatives of copper(II) perfluorocarboxylates and their hydrocarbon analogues — copper(II) acetate in alcohol solutions. The main purpose of the undertaken investigation consisted in generalization and more detailed validation of the mechanism of photolysis, proposed in [6] on the basis of newly obtained experimental data.

2. Experimental

The photochemical investigation was carried out using dioxane complexes of copper(II) acetate and per-

* Corresponding author.

fluorocarboxylates, obtained by the method described in [7]. As follows from the elemental analysis data, molecular formula of initial compounds corresponds to $(\text{CH}_3\text{COO})_2\text{Cu} \times \text{C}_4\text{H}_8\text{O}_2$ for acetate (Ac) [7] and $2[(\text{R}_f\text{COO})_2\text{Cu}] \times \text{C}_4\text{H}_8\text{O}_2$ for polyfluorocarboxylates ($\text{R}_f = \text{CF}_3$ for trifluoroacetate (TFA) [7], C_2F_5 for pentafluoropropionate (PFP), $n\text{-C}_3\text{F}_7$ for heptafluorobutyrate (HFB) [6], respectively). The acetate and relative chelate copper(II) complexes are known to exist in crystalline state as dimers. The distance between copper atoms in the copper(II) acetate monohydrate dimer is equal to 2.64 Å [8].

Spectrally pure alcohols were used as solvents. If necessary, argon was bubbled through the solutions to remove the dissolved oxygen. The electronic absorption spectra were recorded using Specord UV–VIS and Specord M40 (Carl Zeiss) spectrophotometers. The stationary photolysis was carried out using the radiation of high-pressure mercury lamp with the set of glass filters to cut the light of required wavelength or of excimer XeCl (308 nm) and KrF (248 nm) lasers. The experiments on laser flash photolysis (308 nm) were carried out using experimental device described elsewhere [9]. IR spectra of solid products of photolysis were recorded using Specord 75 IR spectrometer. The content of copper was determined by the standard method of trilonometric titration [10].

3. Results and discussion

3.1. The state of the complexes in solution and the electronic absorption spectra

The typical electronic absorption spectrum for the alcohol solutions of dioxane complexes of copper(II) perfluorocarboxylates (PFC) is presented in Fig. 1a for the example of $\text{Cu}(\text{HFB})_2$. The spectrum consists of charge-transfer (LMCT) band with the maximum at 235–245 nm and weak d–d band of Cu(II) with the maximum at 750 nm. From our point of view, the solvation of the dioxanates in methanol leads to the cleavage of the coordination bonds between Cu^{2+} ions and dioxane ligands resulting in the existence of $\text{Cu}(\text{PFC})_2$ molecules in solution. Therefore, the values of extinction coefficients on Fig. 1a are given as calculated for isolated molecules $\text{Cu}(\text{HFB})_2$.

The indirect argument for such solvolysis can be found in the fact, that the addition of perfluorocarboxylic acids to the methanol solutions of copper(II) perchlorate (ClO_4^- anion does not form the complex with Cu^{2+} ions [11]) gives the solutions with the UV spectra completely coinciding with those for the methanol solutions of the dioxane compounds of Cu^{2+} perfluorocarboxylate salts of the same acids (Fig. 1b). The addition of the small quantities of water (up to 3%) to the alcohol solutions should be noticed to lead to substantial transformation of the optical spectrum, probably connected with the appearance of the aquated ions $\text{Cu}_{\text{aq}}^{2+}$, being in equilibrium with $\text{Cu}(\text{PFC})_2$. The wavelengths for

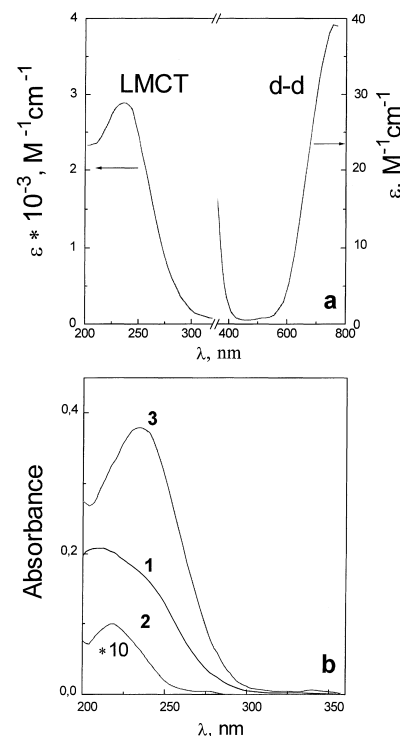


Fig. 1. Optical absorption spectra of complexes in methanol. (a) $\text{Cu}(\text{HFB})_2$ obtained by dissolution of $2\text{Cu}(\text{HFB})_2 \times \text{C}_4\text{H}_8\text{O}_2$. (b) $\text{Cu}(\text{HFB})_2$ obtained by mixing of $\text{Cu}(\text{ClO}_4)_2$ and $\text{H}(\text{HFB})$. Curve 1 — spectrum of $1.25 \times 10^{-3} \text{ M}$ $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$; curve 2 — spectrum of $2.8 \times 10^{-2} \text{ M}$ $\text{H}(\text{HFB})$; curve 3 — spectrum of solution containing $1.25 \times 10^{-3} \text{ M}$ $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $2.8 \times 10^{-2} \text{ M}$ $\text{H}(\text{HFB})$ after subtraction of the spectrum of the rest of free $\text{H}(\text{HFB})$. Cuvette thickness is 1 mm.

maxima in electronic absorption spectra and the values of extinction coefficients are presented in the Table 1.

Table 1 contains also the data of UV spectra for the methanol solution of hydrocarbon analogue of considered perfluorocarboxylates — $\text{Cu}(\text{Ac})_2$. The LMCT band of this complex is shifted to long-wave region. Unlike the case of perfluorocarboxylates, the spectrum of solution of this compound cannot be reproduced by the mixing of the alcohol solution of $\text{Cu}(\text{ClO}_4)_2$ with acetic acid.

The characteristic peculiarity for the optical spectra of solutions of copper(II) carboxylates consists in the presence of the weakly exposed band (or shoulder) at approximately 375 nm with the typical extinction coefficient ca. $100 \text{ M}^{-1} \text{ cm}^{-1}$. That band indicates the presence of dimeric

Table 1

The parameters of electronic absorption spectra of copper(II) acetate and perfluorocarboxylates in methanol

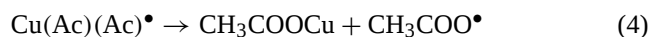
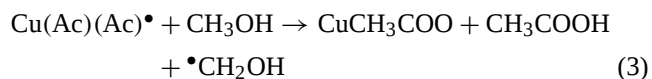
Compound	LMCT band		d–d band	
	λ_{max} (nm)	ϵ_{max} ($\text{M}^{-1} \text{ cm}^{-1}$)	λ_{max} (nm)	ϵ_{max} ($\text{M}^{-1} \text{ cm}^{-1}$)
$\text{Cu}(\text{TFA})_2$	235	2840	787	26
$\text{Cu}(\text{PFP})_2$	236	2750	789	24.5
$\text{Cu}(\text{HFB})_2$	238	2920	789	24
$\text{Cu}(\text{Ac})_2$	247	3250	709	75.6

form of carboxylates in solution [12,13]. In the case of the solutions of polyfluorocarboxylates such band is lacking in the spectra (see Fig. 1). Hence, these compounds can be supposed to exist in alcohol solutions mainly as monomers.

3.2. Photoreduction of copper(II) acetate in the alcohol solution

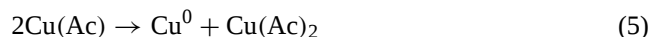
The authors of [1] described the photochemical formation of metallic copper from the alcohol solutions of $\text{Cu}(\text{Ac})_2$ in the presence of benzophenone and proposed the mechanism of that reaction. In our work the precipitation of copper under the conditions of direct photolysis of copper(II) acetate was also observed. The irradiation of oxygen-free alcohol solution of $\text{Cu}(\text{Ac})_2$ by light of high-pressure mercuric lamp (313 nm) or XeF laser (308 nm) has been found to lead to the formation of metallic copper. Besides, some quantity of black precipitate, being presumably copper(II) oxide, has been obtained. The acetic acid also was observed as one of the products. The quantum yield of photolysis for methanol solution under irradiation with $\lambda=308$ nm, determined by the decrease of optical density in the maximum of LMCT band for initial compound (247 nm), is equal to $(8\pm1)\times10^{-3}$. The analogous value for the irradiation of solution of $\text{Cu}(\text{Ac})_2$ in isopropanol, being also accompanied by the formation of copper, is equal to $(2.5\pm0.3)\times10^{-2}$. The process of photolysis does not occur at all in the case of solutions, containing oxygen even in natural amounts.

The mechanism of photoreduction of $\text{Cu}(\text{Ac})_2$ in alcohol solutions can be assumed to be the same as for copper(II) β -diketonates [5] and $\text{Cu}(\text{HFB})_2$ [6]. The absorption of light quantum promotes the intramolecular electron transfer from the π -system of one of ligands to the central ion. As a result, Cu^{2+} ion transforms to Cu^+ and the ligand turns into radical complex, being coordinated to copper ion by only one oxygen atom. The radical complex $\text{Cu}(\text{Ac})(\text{Ac})^\bullet$ has to transform further to the non-radical complex of copper(I). This transformation can occur via interaction with the solvent molecule (Eq. (3)) or by monomolecular decomposition via intermediate formation of $\text{CH}_3\text{COO}^\bullet$ radical (Eq. (4)):



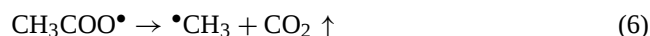
The reaction similar to those described by Eq. (3), is usually postulated in the investigations of photochemistry of copper(II) β -diketonates [4,5]. The Eq. (4) is analogous to those used in [6] for explanation of the mechanism of photoreduction of $\text{Cu}(\text{HFB})_2$. The lack of registration of the radical species in all of the cited works should be noticed. The intermediate complex of monovalent copper, formed in

the reactions (3) and (4), can undergo the reduction to Cu^0 as a result of bimolecular reaction of disproportionation (5), explaining the formation of copper ‘mirror’:

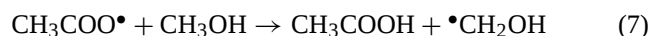


Hydroxyalkyl radicals, being in oxygen-free solutions, are able to fast recombination. The rate constant for recombination of hydroxymethyl radicals at the room temperature is found to be equal to $1.4\times10^9 \text{ M}^{-1} \text{ s}^{-1}$ [14].

The carboxyl radicals $\text{CH}_3\text{COO}^\bullet$ can disappear by two possible routes. First of all they are known to be able to fast decarboxylation (the rate constant for the aliphatic series is about $5\times10^8 \text{ s}^{-1}$ at 20°C [15]):



The second route consists in the elimination of H atom from the methanol molecule to form acetic acid and new hydroxyalkyl radical



The rate constant for that reaction is not available in literature. To be effectively concurrent with the decarboxylation process, the reaction (7) should have the rate constant value $\geq 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

The methyl radical, in turn, can attack the molecule CH_3COOCu with the simultaneous oxidation of $\text{Cu}(\text{I})$ to $\text{Cu}(\text{II})$



The reaction (8) is obviously the concurring one to the process of elimination of hydrogen atom from the molecule of solvent by the methyl radical. The rate constant for this reaction is known to be small ($2.2\times10^2 \text{ M}^{-1} \text{ s}^{-1}$ at 293 K [16]).

The attempt to register the intermediate products of photolysis of $\text{Cu}(\text{Ac})_2$ by the laser flash photolysis with excitation at 308 nm and registration in the range 300–700 nm was unsuccessful. That fact indicates either the absence of intermediates, or too low values of extinction coefficients. Therefore, we tried to register the radical products at the low-temperature (77 K) photolysis of $\text{Cu}(\text{Ac})_2$ in the isopropanol solution.

Unlike methanol, isopropanol forms the transparent glassy matrix without addition of water (water decomposes the initial complex). The quantum yield of low temperature (77 K) photolysis is high enough to register the appearance of the spectra of radicals and the changes in optical spectra. At the same time the photolysis of copper(II) acetylacetonate or perfluorocarboxylates in alcohol matrices under similar conditions has been found not to occur: there were no either spectral changes or the ESR signals after a number of hours of experiment.

The ESR spectrum of the product of photolysis in the isopropanol matrix is shown in Fig. 2. This spectrum coincides with that of the radical of matrix $(\text{CH}_3)_2\bullet\text{COH}$ (see [17–21]). The photolysis of copper(II) acetate can lead to the formation of hydroxyalkyl radical by several routes. These

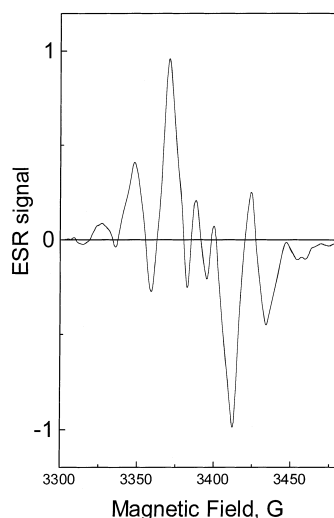


Fig. 2. Change in the ESR spectrum on the photolysis (308 nm) of copper(II) acetate in isopropanol matrix (77 K). Initial concentration is 0.001 M; time of irradiation is 20 min.

can be the reactions (3) and (7) or the direct elimination of hydrogen atom from the matrix molecule by the methyl radical. The observed radical $(\text{CH}_3)_2\text{COH}\cdot$ can be considered as the secondary product of the photolysis of $\text{Cu}(\text{Ac})_2$. The primary one — the radical complex $\text{Cu}(\text{Ac})(\text{Ac})\cdot$ — was not revealed in the ESR spectra, probably, because of very fast transformations by the reactions (3) or (4,5) even at the temperature of liquid nitrogen. The same can be mentioned also about carboxy radical $\text{CH}_3\text{COO}\cdot$ in the case of its formation as a result of reaction (4) it undergoes fast disappearance by the reactions of (6) or (7) type.

As it has been mentioned above, the presence of oxygen dissolved in methanol acts as an inhibiting factor towards the photolysis. This effect can be probably connected with the oxidation of the intermediate complex of copper(I) into initial $\text{Cu}(\text{PFC})_2$ in the presence of O_2 and HPFC.

3.3. Photochemistry of copper(II) perfluorocarboxylates in alcohol solutions

3.3.1. The first stage of photolysis

The photochemical transformations of oxygen-free alcohol solutions of perfluorinated copper(II) carboxylates were studied in our previous work [6] using methanol solutions of $\text{Cu}(\text{HFB})_2$. The process was found to occur in two stages [6]. The first one is accompanied by changes in LMCT bands in UV spectra of solutions (Fig. 3). But the isosbestic point presents in all cases, disappearing only at the time of irradiation, exceeding the characteristic time of formation of the new band. That fact permits (in frames of supposition for initial compounds to undergo the complete transformation) to evaluate extinction coefficients for the appearing bands and quantum yields of the first stage of photolysis. The corresponding data are presented in Table 2.

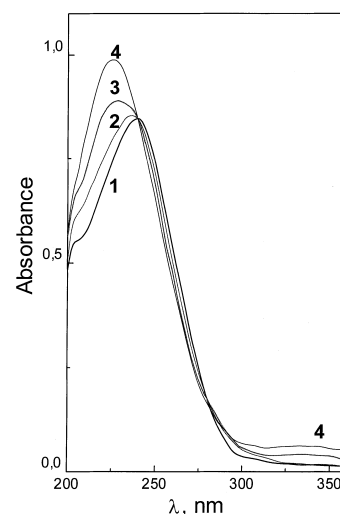


Fig. 3. Change in the optical absorption spectrum of $\text{Cu}(\text{HFB})_2$ (2.9×10^{-3} M) in deaerated methanol solution (295 K) in photolysis at 248 nm (KrF laser; pulse energy, 3.5 mJ; cuvette thickness, 1 mm). Curves 1–4 denote 0, 200, 600, 1200 pulses, respectively.

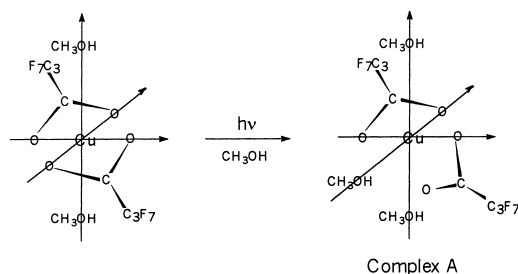
The first stage of photolysis does not practically lead to the changes in the region of d–d bands of copper(II). So, the central ion remains in the bivalent state. The addition of free ligand up to tenfold exceeding of the concentration of initial carboxylate has no influence on the photolysis rate, therefore, the process probably cannot be considered as photosolvation. Two possible mechanisms of photoprocesses can be proposed (see also [6]) on the example of $\text{Cu}(\text{HFB})_2$ in methanol solution.

The first of them begins from the generation of copper(I) — containing radicals by the equations, similar to (1) and (2). The vacant place in the coordination sphere of copper ion is occupied by the molecule of solvent. Afterwards the electron transfers from Cu(I) ion back to π -system of radical with the simultaneous restoration of the molecular form of ligand. But as in the case of the radical, the coordination of ligand takes place by only one oxygen atom. The resulting complex of copper(II) (further — complex A) can be responsible for the increase of absorption in 221 nm region. Scheme 1 provides the example of such a reaction for the case of $\text{Cu}(\text{HFB})_2$.

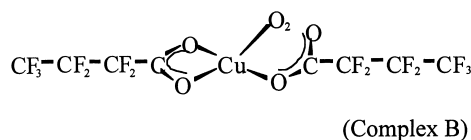
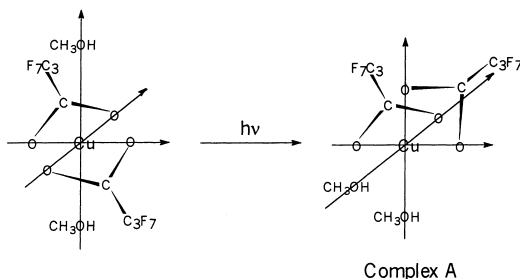
Table 2
The results of the first stage of photolysis of perfluorocarboxylates in methanol^a

Compound	λ_{max} (nm)	ε_{max} ($\text{M}^{-1} \text{cm}^{-1}$)	λ_{iso} (nm)	φ_1	φ_2
$\text{Cu}(\text{TFA})_2$	206	2640	221	0.16	0.7×10^{-3}
$\text{Cu}(\text{PFP})_2$	220	3440	236	0.11	1.3×10^{-3}
$\text{Cu}(\text{HFB})_2$	224	3480	241	0.10	4×10^{-3}

^a λ_{max} — maximum of the new absorption band; ε_{max} — extinction coefficient; λ_{iso} — isosbestic point; φ_1 — quantum yield of the first stage (248 nm, KrF laser); φ_2 — quantum yield of disappearance of Cu(II) d–d band (irradiation of high pressure mercury lamp, $\lambda < 370$ nm, full absorption).



Scheme 1.



Scheme 2.

Another mechanism of phototransformation can be considered as the isomerization of initial complex. In that case both oxygen atoms of ligand in the complex A coordinate with Cu^{2+} ion and the difference between this structure and the initial complex consists in the non-planar coordination center of four oxygen atoms (Scheme 2).

The mentioned photoreactions occur only in oxygen-free solutions. The influence of the dissolved oxygen can be explained on the basis of the Scheme 1 by the addition of O_2 molecule to the radical $\text{Cu}(\text{HFB})(\text{HFB})^\bullet$ with the further transformation to the complex $\text{Cu}(\text{HFB})(\text{HFB})(\text{O}_2)$ — complex B. Its structure is presented below.

3.3.2. The second stage of photolysis

The second stage of photolysis of oxygen-free solutions of $\text{Cu}(\text{PFC})_2$ is accompanied by the photoreduction of the central ion, leading to the formation of the black precipitate and copper 'mirror'. The quantum yields of reduction process for Cu^{2+} ion, determined by the decrease in the maxima of d-d bands, are presented in Table 2. The value of quantum yield increases from $\text{Cu}(\text{TFA})_2$ to $\text{Cu}(\text{HFB})_2$.

Table 3 shows the content of copper in the black precipitate, obtained as a result of photolysis of the investigated compounds. In the case of photolysis of $\text{Cu}(\text{TFA})_2$ this value is close to the corresponding value for CuF (77.0 wt.%), being the rather probable product, and differs from those for CuO (79.9 wt.%). In the other cases (see Table 3), the con-

Table 3

The content of copper (in wt.%) in the products of photolysis of copper(II) perfluorocarboxylates

Compound	Black precipitate	Pale-blue precipitate	Required for $\text{Cu}(\text{PFC}) \times 2\text{CH}_3\text{OH}$
$\text{Cu}(\text{TFA})_2$	76.6	26.0	26.4
$\text{Cu}(\text{PFP})_2$	62.4	22.5	21.9
$\text{Cu}(\text{HFB})_2$	68.1	19.3	18.7

tent of copper does not correspond to any reasonable formula. But the black precipitate for these compounds can be most probably assigned to the mixture of copper(I) fluoride with the products of the dark reactions, described below.

After the end of irradiation the black precipitate, remained in contact with the solution, has been found to undergo slow transformation in dark into the pale-blue substance, practically insoluble in methanol. The content of copper in these substances (see Table 3) corresponds satisfactory to the copper(I) perfluorocarboxylate complex with methanol, possessing the composition $\text{Cu}(\text{PFC}) \times 2\text{CH}_3\text{OH}$ and probably the polymeric structure.

This composition is also in accordance with the IR spectra of pale-blue precipitates. Fig. 4 presents the IR spectrum of that precipitate for the case of $\text{Cu}(\text{TFA})_2$ with the assignment of the principal bands taken presumably from [22]. The wide band in the region of $2700\text{--}3600\text{ cm}^{-1}$ results from the vibrations of C–H and O–H groups (the last are connected with the intramolecular H-bonds). The band in the region of 1650 cm^{-1} is characteristic for the carbonyl group. The twin peak in the region of $1100\text{--}1200\text{ cm}^{-1}$ belongs to the vibrations of CF_3 group. Finally, the band in the region of 700 cm^{-1} most likely belongs to the Cu–O vibration, because this band presents in the spectrum of copper(II) oxide. So, both content of copper and IR spectra confirm the supposed composition of pale-blue product.

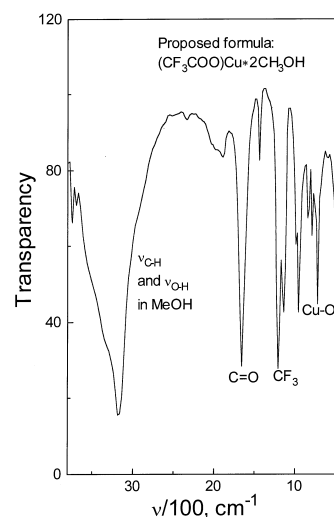
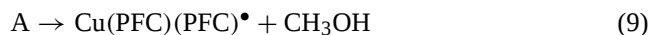


Fig. 4. IR spectrum of the final product (pale-blue precipitate) of the photolysis of $\text{Cu}(\text{TFA})_2$ in methanol solution.

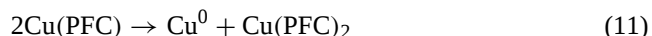
The mechanism of photoreduction of copper in methanol solutions of $\text{Cu}(\text{PFC})_2$ presumably includes the intramolecular electron transfer with the formation of the radical complex. The difference with the case of the photolysis of $\text{Cu}(\text{Ac})_2$ consists in the absorption of the light quantum by the methanol-containing complex A but not by the initial compound



The radical complex $\text{Cu}(\text{PFC})(\text{PFC})^\bullet$, besides the reverse transformation into complex A (or the initial compound $\text{Cu}(\text{PFC})_2$), can decompose with the formation of the unstable perfluorocarboxyl radical $\text{PFC}^\bullet$ ($\text{R}_f\text{COO}^\bullet$)



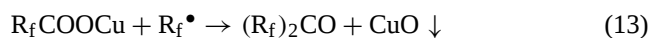
The copper(I) perfluorocarboxylate, formed in the reaction (10), can disproportionate (Eq. (11)), explaining the observed appearance of the copper ‘mirror’



The perfluorocarboxyl radical $\text{R}_f\text{COO}^\bullet$ has two most probable routes of transformations. By the first one, it can attack the molecule of methanol to give the corresponding acid R_fCOOH and hydroxymethyl radical $^\bullet\text{CH}_2\text{OH}$:

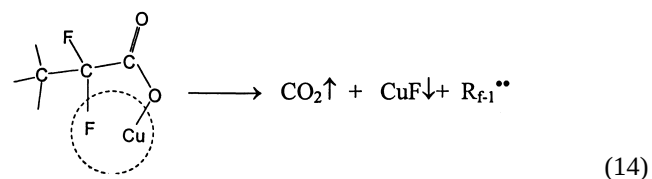


By the second, it can undergo decarboxylation to generate perfluoroalkyl radicals $\text{R}_f^\bullet$, possessing the electrophilic properties and in principle being able to attack the $\text{Cu}(\text{PFC})$ molecule by C–O bond with the simultaneous oxidation of $\text{Cu}(\text{I})$ to $\text{Cu}(\text{II})$



Nevertheless, the composition of black precipitate, presented in Table 3, makes the presence of CuO in it rather unbelievable. The more real product seems to be copper(I) fluoride.

The formation of CuF under the irradiation of the relative compounds — copper(II) perfluoro- β -diketonates — in gas phase has been observed in [23] and confirmed by mass-spectra. Its formation was considered as the result of simple elimination, facilitated by the convenient conformation of β -diketonate molecule, permitting the necessary spatial proximity of Cu and F atoms. The same situation can also be realized for the considered copper(II) perfluorocarboxylates in the intermediate complex R_fCOOCu , formed by Eq. (10):

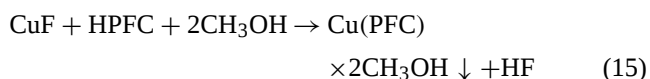


The decomposition of the complex of copper(I) by Eq. (14) leads to carbon dioxide, observed copper(I) fluoride and the

perfluorocarbene species, easily transforming into volatile perfluoroolephines.

The same elimination reaction, leading to copper(I) fluoride, can occur also in complex A (Scheme 1). The ligand, bonded with copper atom by only one oxygen, can rotate about C–C and C–O single bonds to make possible the required spatial contact between copper and fluorine atoms.

So, the formation of the resulting product of ‘dark’ reactions — pale-blue complex $\text{Cu}(\text{PFC}) \times 2\text{CH}_3\text{OH}$ can be explained by the reaction of copper(I) fluoride (black precipitate) with perfluorocarbonic acid, presenting in methanol solution as a product of reaction (12)



The complex, obtained in reaction (15), presumably has the polymeric structure (either with Cu–O, or with Cu–Cu bonds), being characteristic for copper(I) complexes. The similar situations are known in literature for β -diketonates [24].

4. Conclusions

The present work confirms the general tendency for copper(II) chelate complexes to undergo photochemical reduction to yield the metal copper. The mechanism of photolysis, as has been demonstrated above for polyfluorocarboxylates, can be rather complicated, including a number of photochemical and dark stages. Nevertheless, the main primary process for all analogous systems seems to consist in the intramolecular electron transfer.

To prove the nature of mechanisms of photolysis (as proposed in the present work, as known from literature), the registration of the intermediate products of photolysis by direct methods is necessary. As a rule, the experimental conditions do not facilitate the registration process because of low quantum yields and small extinction coefficients for intermediates. In the present work we have found the system (copper(II) acetate in the frozen isopropanol matrix), providing the substantial experimental progress in this direction.

Acknowledgements

The financial support of the Russian Foundation for Fundamental Research (Grant No 99-03-32272) and Russian Federal Program ‘Integration’ (Grant No. 274) is gratefully acknowledged.

References

- [1] K. Takeda, Y. Iwakura, Bull. Chem. Soc. Jpn. 41 (1968) 268.
- [2] I.A. Piterikh, V.I. Saloutin, K.I. Pashkevich, I.Ya. Postovsky, Zh. Obshch. Khim. 51 (1981) 706 (in Russian).

- [3] V.I. Saloutin, K.I. Pashkevich, I.A. Piterskikh, I.Ya. Postovsky, *Izv AN SSSR, Ser. Khim.* 10 (1981) 2379 (in Russian).
- [4] B. Marchiniak, G.E. Buono-Core, *J. Photochem. Photobiol. A: Chem.* 52 (1990) 1.
- [5] H.D. Gafney, R.L. Lintvedt, *J. Am. Chem. Soc.* 93 (1972) 1623.
- [6] E.M. Glebov, V.F. Plyusnin, V.P. Grivin, V.S. Danilovich, S.A. Krupoder, T.I. Liskovskaya, V.F. Trounova, *Zh. Strukt. Khim.* 38 (1997) 665 (in Russian).
- [7] S.A. Krupoder, V.S. Danilovich, A.O. Miller, G.G. Furin, *J. Fluor. Chem.* 73 (1995) 13.
- [8] J.N. van Niekerk, F.R. Schoening, *Acta Cryst.* 6 (1953) 227.
- [9] V.P. Grivin, I.V. Khmelinski, V.F. Plyusnin, I.I. Blinov, K.P. Balashev, *J. Photochem. Photobiol. A: Chem.* 51 (1990) 167.
- [10] H. Flashka, *Mikrochemie* 39 (1952) 38.
- [11] H. Remy, *Treatise on Inorganic Chemistry*, Elsevier, Amsterdam, Vol. 1, 1956, p. 809.
- [12] R. Tsuchida, Sh. Yamada, *Nature* 176 (1955) 1171.
- [13] Sh. Yamada, H. Nakamura, R. Tsuchida, *Bull. Chem. Soc. Jpn.* 30 (1957) 953.
- [14] D.W. Johnson, G.A. Salmon, *Can. Chem. J.* 55 (1977) 2030.
- [15] W. Braun, L. Rajbenbach, F.R. Eirich, *J. Phys. Chem.* 66 (1962) 1591.
- [16] G. Bullock, R. Cooper, *Trans. Faraday Soc.* 66 (1970) 2055.
- [17] M. Fujimoto, D.J.E. Ingram, *Trans. Faraday Soc.* 54 (1958) 1304.
- [18] R.S. Alder, T.H. Anderson, L.A. Welb, *J. Chem. Phys.* 30 (1959) 695.
- [19] V.A. Roginski, A.G. Kotov, C.Ya. Przezecki, *Zh. Fiz. Khim.* 50 (1966) 51 (in Russian).
- [20] J.E. Bennett, B. Mile, A. Thomas, *J. Chem. Soc. A* (1967) 1399.
- [21] S.A. Dzyuba, A.M. Raitsimring, Yu.D. Tsvetkov, *Teor. Eksp. Khim.* 15 (1979) 541 (in Russian).
- [22] L.J. Bellami, *The Infra-Red Spectra of Complex Molecules*, Methuen, London, Wiley, New York, 1958, p. 590.
- [23] D.S. Talaga, J.I. Zink, *Inorg. Chem.* 35 (1996) 5050.
- [24] Y.L. Chow, G.E. Buono-Core, *Can. J. Chem.* 61 (1983) 795.