

Halocopper(II) complexes in acetic acid anhydride. III. Spontaneous redox changes of chloro- and bromocopper(II) complexes

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Redox changes occurring in the systems containing complex species $[\text{CuCl}_3\text{AA}]^-$ and $[\text{CuBr}_3\text{AA}]^-$ (AA = acetic acid anhydride) were investigated. The course of the redox changes was found to be influenced particularly by molecular oxygen. Halocopper(I) complex resulting in the spontaneous redox reaction is stable in an inert atmosphere, but in the presence of oxygen it undergoes reoxidation to halocuprate(II). The decrease of halides after complete reduction of Cu(II) to Cu(I) was in agreement with the equation of the reaction proposed



The redox changes proceed much slower in acetic acid solution than in AA solution.

Были изучены окислительно-восстановительные изменения в системах, содержащих комплексы $[\text{CuCl}_3\text{AA}]^-$ и $[\text{CuBr}_3\text{AA}]^-$ (AA = ангидрид уксусной кислоты). На ход влияет особенно молекулярный кислород. Галогенидный комплекс Cu(I), образующийся самопроизвольной окислительно-восстановительной реакцией, стабилен в инертной атмосфере, однако в присутствии кислорода обратно окисляется в галогенидный комплекс Cu(II). Убыль галогенидов при полном восстановлении Cu(II) на Cu(I) соответствует реакции



Окислительно-восстановительные реакции в растворе уксусной кислоты протекают существенно медленнее по сравнению с раствором в AA.

Spontaneous redox changes occurring in the solutions of halocopper(II) complexes are strongly affected by solvent molecules which enter the coordination sphere of Cu(II). Solvents capable to form dative π bonds with the central atom have also considerable effects [1, 2].

Acetic acid anhydride (AA) belongs to this type of solvents. It has been assumed that the Cu—AA bond can affect the Cu—halogen bond to create suitable conditions for a halogenation reaction analogous to the halogenation reaction of acetone with copper(II) chloride [3].

The spontaneous changes of absorbance observed in AA solutions of halocopper(II) complexes are caused by redox processes in which Cu(II) is reduced and AA halogenated.

The present work deals with the redox changes in the systems containing anion $[\text{CuX}_3\text{AA}]^-$ as a dominant complex [4]. In the view of the consequences of ligand interactions [1, 2] its halogenation ability should be pronounced more than that of $[\text{CuX}_4]^{2-}$ [5]. The halogenation effects of copper(II) complexes were also compared in acetic acid and its anhydride. In these solvents halocopper(II) complexes behave differently. They show differences in composition and stability [4, 6]. Differences in physical properties of the mentioned solvents (e.g. in dielectric constants) and in the type of the Cu—solvent bond may influence the halogenation effects of halocopper(II) complexes as well.

Experimental

Chemicals and equipments

The following chemicals were used: $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, prepared from copper(II) hydroxide carbonate and HClO_4 ; LiBr , prepared from Li_2CO_3 and HBr ; LiCl (anal. grade); acetic acid anhydride, the fraction with b.p. 140—141°C; acetic acid, the fraction with b.p. 119°C.

Absorption spectra in the visible region were recorded with a UV VIS 200 spectrophotometer (Zeiss, Jena).

Analytical procedures

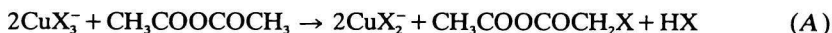
Copper in $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was determined complexometrically. Halides were determined in solutions after appropriate dilution argentometrically using potentiometric indication.

Nonionic bound halogens (present in halogen derivatives of solvents formed in the redox reaction) were determined as a difference between halide content at the beginning and at the end of the reaction.

Results

“Ageing” of the systems $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}—\text{LiCl}—\text{AA}$ and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}—\text{LiBr}—\text{AA}$ with $\text{X}^-/\text{Cu}(\text{II})$ ratios from 3 to 10 ($\text{X} = \text{Cl}, \text{Br}$) in which the complex $[\text{CuX}_3\text{AA}]^-$ predominates [4], was investigated first in the presence of air oxygen at room temperature in the c_{Cu} interval $2 \times 10^{-3}—2 \times 10^{-2} \text{ mol dm}^{-3}$. The results of spectrophotometric and argen-

tometric measurements obtained 22 days after the preparation of the solutions are summarized in Tables 1 and 2. The decrease of absorbance at 21 000 and 15 400 cm^{-1} (the regions of maximum absorbance of $[\text{CuCl}_3\text{AA}]^-$ and $[\text{CuBr}_3\text{AA}]^-$, respectively) was ascribed to the decrease of Cu(II) due to its reduction to Cu(I). In case the spontaneous redox process obeys the equation



reduction of 2 moles of Cu(II) corresponds to 1 mole decrease of halides in the final solution. Thus the spectrophotometrically determined decrease of Cu(II) was used for calculation of the decrease of X^-/Cu .

The correlation of results obtained by the two mentioned methods was not satisfactory, especially at higher X^-/Cu ratios. One of the reasons may be the presence of air oxygen.

Table 1

Decrease of chlorides in the system Cu(II)— Cl^- —AA determined spectrophotometrically and argentometrically (after 22 days at room temperature in the presence of oxygen)

$$c_{\text{Cu}} = 10^{-2} \text{ mol dm}^{-3}$$

Cl^-/Cu in the starting solution	Decrease of Cu(II) ^a %	$\Delta \text{Cl}/\text{Cu}^b$	Cl^-/Cu^c	$\Delta \text{Cl}/\text{Cu}^d$
3	71	0.355	2.62	0.38
4	69	0.345	3.56	0.44
5	66.5	0.33	4.54	0.46
10	59	0.295	9.48	0.52

a) Determined spectrophotometrically; b) calculated from spectrophotometrical measurements; c) determined argentometrically; d) calculated from argentometrical measurements.

Table 2

Decrease of bromides in the system Cu(II)— Br^- —AA determined spectrophotometrically and argentometrically (after 22 days at room temperature in the presence of oxygen)

$$c_{\text{Cu}} = 10^{-2} \text{ mol dm}^{-3}$$

Br^-/Cu in the starting solution	Decrease of Cu(II) ^a %	$\Delta \text{Br}/\text{Cu}^b$	Br^-/Cu^c	$\Delta \text{Br}/\text{Cu}^d$
3	68	0.34	2.68	0.39
4	68	0.34	3.55	0.45
5	72	0.36	4.48	0.52
10	78	0.39	9.30	0.7

Superscripts are explained in Table 1.

Therefore, we decided to repeat the experiments in the nitrogen atmosphere employing the following procedure: AA solutions with various $X^-/\text{Cu(II)}$ ratios having characteristic orange or green colour were sealed in ampules under nitrogen and then heated (100°C) until the colour had disappeared as an indication that the reduction of Cu(II) to Cu(I) was completed. The decolouration took 3–5 h in the case of chlorocopper(II) complexes and 40–60 min in the case of bromocopper(II) complexes. The decrease of halides determined argentometrically after complete reduction of Cu(II) is shown in Table 3.

Table 3

Decrease of halides in the systems $\text{Cu(II)}-\text{Cl}^-$ -AA and $\text{Cu(II)}-\text{Br}^-$ -AA after complete reduction of Cu(II) (temperature 100°C , inert atmosphere)
 $c_{\text{Cu}} = 10^{-2} \text{ mol dm}^{-3}$

X^-/Cu in the starting solution	Cl^-/Cu after reduction of Cu(II)	$\Delta\text{Cl}/\text{Cu}$	Br^-/Cu after reduction of Cu(II)	$\Delta\text{Br}/\text{Cu}$
3	2.52	0.48	2.52	0.48
4	3.53	0.47	3.51	0.49
5	4.54	0.46	4.51	0.49
10	9.53	0.47	9.52	0.48

Under identical conditions (inert atmosphere, the same concentration of Cu(II) and $\text{Cl}^-/\text{Cu(II)}$ mole ratio) the decrease of chlorides in the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}-\text{LiCl}$ -acetic acid was substantially lower. After three-month standing at room temperature no significant changes of these solutions were observed (the decrease of chlorides was 0.03 mole per 1 mole of Cu(II) in the original solution). Heating at 60°C for three months, however, led to an evident decrease of chlorides, in average 0.3 mole per 1 mole of Cu(II) in the original solution.

Discussion

Spontaneous redox processes connected with the halogenation of the CH_3 group were expected in both AA and acetic acid solutions. The experiments carried out pointed to different halogenation ability of Cu(II) complexes in the examined solvents.

The results obtained in the study of the systems $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}-\text{LiX}-\text{AA}$ in the inert atmosphere are in a good consonance with the original proposal that the redox reaction (A) takes place. The decrease of halides at all X^-/Cu ratios examined was about 0.5 mole per 1 mole of Cu(II) in the starting solution which is the value expected according to the above-quoted reaction. The results were reproducible with a relative deviation not exceeding 4% (calculated from 10 measurements).

The presence of oxygen considerably affects the reaction and consequently lowers reproducibility of results. The effect of oxygen is associated with the reoxidation of halocopper(I) complex formed in the reaction (A). The oxidation and the reduction are reversible; both processes can be repeated for several times by varying the quantity of oxygen in the system. For this reason the decrease of halides is obviously higher than the proposed value 0.5 mole per 1 mole of Cu(II) in the original solution. Therefore, the reaction has a catalytic character.

In the medium of acetic acid the reaction proceeds very slowly in comparison to that in AA. The type of the Cu—solvent bond plays here probably the decisive role. Acetic acid as a ligand is not so capable to form dative Cu—O π -bonds as AA. This fact, according to previous suggestions [1, 2], diminishes the ability of acetic acid to influence the oxidation of halogen as a consequence of ligand interactions in the Cu(II) complexes.

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