



Aliphatic bromination with tetrabromomethane on immobilized copper complexes



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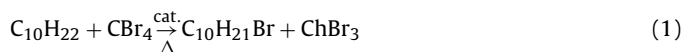
ABSTRACT

New catalytic systems with supported bromine- and chlorine-containing copper complexes for selective bromination of alkanes with tetrabromomethane have been proposed. Introduction of donor additives (e.g., low-molecular-weight alcohols) into the reaction increases the activity and stability of these catalysts. The kinetic features of the processes have been investigated. It has been shown that the dependences of the yield of bromodecanes on temperature and concentration of donor additives are both nonmonotonic in character.

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1. Introduction

Bromination of organic substrates still remains an important method for preparing a broad range of products and intermediates for organic synthesis [1–18]. This study is devoted to the design of catalytic systems with covalently attached copper complexes for bromination of alkanes with tetrabromomethane and selection of optimal conditions for these processes using the reaction of decane as an example:



In the previous publications [19,20] we reported the development of an effective method for substitutive bromination of hydrocarbons in the presence of transition metal complexes using tetrabromomethane as a source of bromine. As a result of the catalytic reaction, monobrominated derivatives of linear and cyclic alkanes, adamantane, and alkylbenzenes were synthesized with high selectivity. The catalysts were homogeneous copper complexes with a quaternary ammonium bromide or silica-grafted copper- or nickel-containing polymetallic phenylsiloxanes. Furthermore, catalysts based on aromatic amino alcohol complexes grafted on a mineral support surface showed a good result in the addition of CBr_4 to the double $\text{C}=\text{C}$ bond [21]. In that case, the

use of heterogeneous systems substantially facilitated the reaction procedure and the analysis of products.

In the last years, we proposed new promising catalytic systems based on immobilized copper complexes with quaternary ammonium bases (QAB) for chlorination of alkanes with carbon tetrachloride [22,23]. It was shown that the covalent binding of the complexes to the mineral support surface retains their activity and makes them much more stable than both their homogenous analogues and the catalysts prepared by impregnating the support with these complexes. The introduction of donor additives (in particular, low-molecular-weight alcohols) into the reaction system further increases the activity and stability of these catalysts. This study has revealed similarities and dissimilarities between aliphatic bromination and chlorination mediated by the catalytic systems proposed.

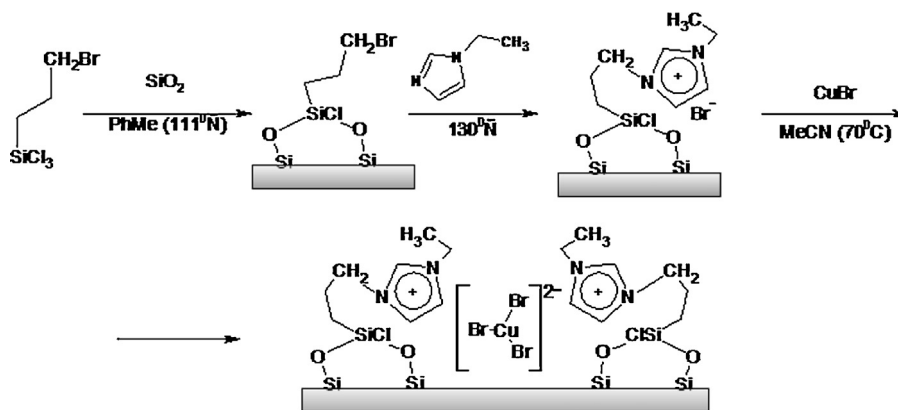
2. Experimental

2.1. Reagents and materials

The procedure for the purification of tetrabromomethane (99%, Merck) was reported previously [20]. Ethanol (rectified, 96%), anhydrous ethanol (99.9%, Merck), *n*-propanol (reagent grade for chromatography), decane (99%, Merck), ethylimidazole (99%, Aldrich), triethylamine (99.5%, Aldrich), and copper (I) bromide (analytical grade) were used without further purification. 3-Bromopropyltrichlorosilane (chemically pure grade) was distilled in vacuum (b.p. 74°C/10 Torr) immediately before being

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Scheme 1. Synthesis of catalyst (I).

used for the silica gel surface modification. Silica gel of KSK-2 brand ($S_{sp} = 300 \text{ m}^2/\text{g}$) was pretreated according to the procedures reported previously [22].

2.2. Synthesis of copper (I) bromide complexes with immobilized *N*-propyl-*N*'-ethylimidazolium and triethylpropylammonium bromides

The CuBr complex with immobilized *N*-propyl-*N*'-ethylimidazolium bromide (catalyst (I)) was synthesized by a procedure described previously for chlorine-containing complexes (see Scheme 1) [22,23]. In the first stage, 3-bromopropyltrichlorosilane (2.1 ml, 1.06×10^{-2} mol) was added to dehydrated silica gel (5 g) immersed in toluene (25 ml) in a 50 ml flask equipped with a Dean–Stark apparatus and a reflux condenser. The reaction mixture was refluxed for 6 h, then the solid phase was filtered off, washed with dry toluene (10 ml per gram of silica gel), and dried.

The reaction between ethylimidazole (1.5 ml, 1.55×10^{-2} mol) and modified silica gel (1.01 g) was carried out in an evacuated glass ampoule with stirring at 130°C for 18 h. After completion of the synthesis, the remaining ethylimidazole was washed out with ethanol. After filtering and drying at room temperature, the grafted ethylpropylimidazolium bromide sample obtained in this manner was placed into a solution containing CuBr (0.1 g) in dry acetonitrile (10 ml). The mixture was stirred for 30 min with mild heating ($\sim 50^\circ\text{C}$). Filtering off and drying the sediment resulted in a green–brown powder with a copper content of 1.2 wt.%. Elemental analysis (wt.%): C, 4.06; H, 1.10, N, 1.41.

The copper(I) bromide complex with triethylpropylammonium bonded to silica gel (catalyst (II)) was synthesized in a similar way. Elemental analysis (wt.%): C, 4.49; H, 1.60, N, 0.74, the copper content was 0.7 wt.%.

The synthesis procedures, the composition and the properties of silica gel-bonded copper(II) chloride complexes with triethylpropylammonium chloride (catalyst (III), copper content 0.5%), propylpyridinium chloride (catalyst (IV), copper content 0.5%), and *N*-propyl-*N*'-ethylimidazolium chloride (catalyst (V), copper content 1.0%) were reported previously [22,23].

2.3. Instrumental methods for catalyst analysis

The SALDI mass spectra of the compounds were recorded in the RP Pep Mix mode on a Ultraflex instrument (Bruker) equipped with a nitrogen laser with a 337 nm wavelength and a $110 \mu\text{J}$ energy. A time-of-flight mass analyzer was used. The spectra were recorded in the positive and negative ion modes. Cluster ion identification based on isotope distribution was performed using the IsoPro simulator.

The diffuse reflectance electronic spectra were measured on an HR400CG-UV-NIK Ocean Optics instrument with an integrating sphere in the range of 300–1200 nm.

The X-ray photoelectron spectra (XPS) were measured at the Shared Use Research Center “Nanochemistry and atmospheric chemistry” for unground catalyst grains on an Axis Ultra DLD spectrometer (Kratos) using monochromatized $\text{AlK}\alpha$ radiation at an X-ray tube power of 150 W. The spectra were recorded at a pass energy of 160 eV for the wide-scan spectrum and 40 eV for the spectra of separate lines. The analysis area was about $300 \times 700 \mu\text{m}$. To eliminate the sample charging effect, the spectra were recorded using a charge neutralizer. The spectra obtained were calibrated against the carbon 1s binding energy for carbon adsorbed on the surface of the specimens, which was taken to be 285.0 eV.

2.4. Catalytic experiments

The reactions were carried out in sealed evacuated glass tubes. Unless otherwise specified, the solutions with the molar ratio of $\text{C}_{10}\text{H}_{22}:\text{CBr}_4 = 10:1$ were used. The samples were held at a specified temperature in a temperature-controlled air bath equipped with a variable speed rotation device allowing for change of the tube rotation direction. The conditions of experiments ensured independence of the results from the rotation speed.

The activity of the supported catalysts was evaluated from the overall yield of the products of decane bromination with CBr_4 . The products were identified by GC/MS analysis on a THERMO TRACE DSQ II instrument (Termo Fisher Sci.) and determined by GLC on a Kristall 2000M chromatograph (Chromatec, Russia) equipped with a flame ionization detector and a 3 m long column with the non-polar phase SE-30 (5%).

3. Results and discussion

3.1. XPS analysis of the catalytic complexes¹

The wide-scan spectra of the samples of catalysts (I) and (II) (Fig. 1) exhibit oxygen, carbon, bromine, copper, nitrogen, and silicon lines (Fig. 2).

Table 1 shows the binding energies of copper, nitrogen, and bromine photoelectron lines and the corresponding chemical states of these elements.

Fig. 3 presents the Cu2p XPS spectra of the test catalysts, which are typical of cupric compounds as regards both the binding energy

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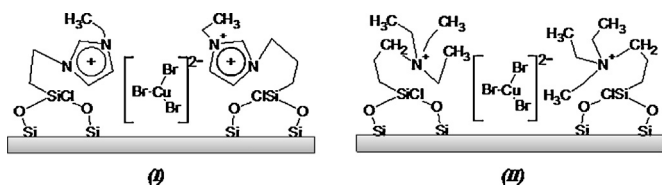


Fig. 1. The structure of the catalysts (I) and (II).

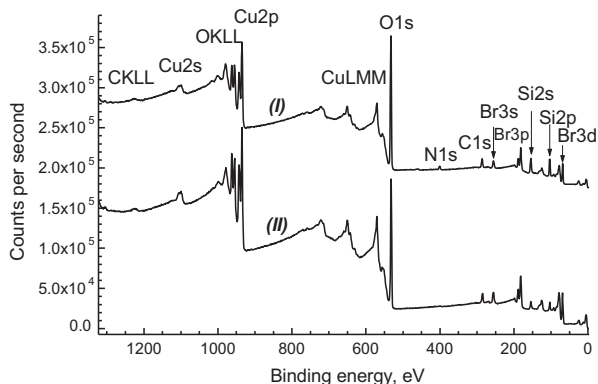


Fig. 2. Wide-scan XPS spectra of the catalysts (I) and (II).

Table 1

Binding energies (eV) of photoelectron lines of the test samples and the corresponding chemical states of the atoms. The relative fractions of each state of the elements are shown in parentheses.

Line	Catalyst		Chemical states
	(I)	(II)	
Cu2p _{3/2}	932.5 (03.2%)	932.5 (00.3%)	Cu ⁺
	935.0 (96.8%)	935.0 (99.7%)	Cu ²⁺
N1s	400.0 (47.3%)	399.8 (52.1%)	N–C
	401.7 (52.7%)	401.9 (47.9%)	N ⁺ –C
Br3d _{5/2}	68.5 (77.7%)	68.3 (70.8%)	Br [–]
	69.4 (22.3%)	69.4 (29.2%)	Br–Si

values and the line shape with an intense shake up satellite. The spectra of the samples look very similar, and the only noticeable

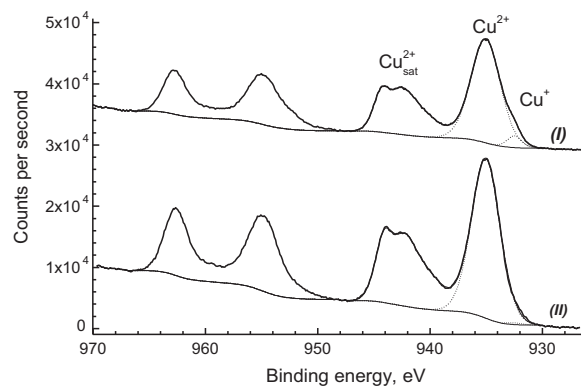


Fig. 3. Cu2p XPS spectra of the samples (I) and (II).

difference is band broadening in the Cu²⁺ spectrum of catalyst (I). This is due to the appearance of a small shoulder on the low-energy side of binding energy in the spectrum of catalyst (I), which indicates the presence of a small amount (less than 3%) of copper(I). Thus, in both cases of catalyst synthesis, copper was oxidized by oxygen in air or dissolved in the solvent; however, the oxidation process with the imidazole derivative complex that contained a greater more amount of the metal did not go to completion.

From the copper to bromine ratio, it becomes clear that the chemical state of copper is determined not only by the copper–bromine, but also copper–oxygen bonds. In the Br3d XPS spectra, the ground state of bromine is represented by a doublet with a Br3d_{5/2} binding energy of 68.3–68.5 eV, which corresponds to the bromide ion state (Br[–]). The nitrogen 1s XPS spectrum consists of two components with approximately equal intensities and the binding energies of about 400 and 402 eV, which corresponds to nitrogen atoms in organic compounds in neutral and charged states (N⁺), respectively.

These results lead to the conclusion that even short-term exposure of the both catalysts to the air resulted in oxidation of copper(I). A similar result has been observed previously in the synthesis of immobilized copper complexes with amino alcohols [24,25].

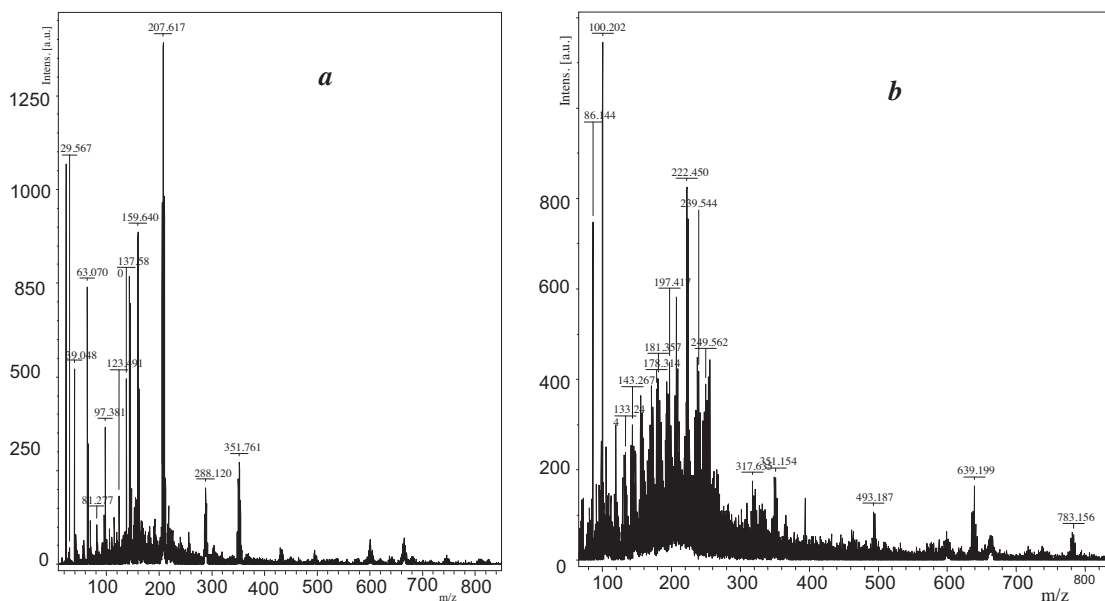


Fig. 4. The positive ion SALDI mass spectra of the bromo-containing catalysts: (a) – (I), (b) – (II).

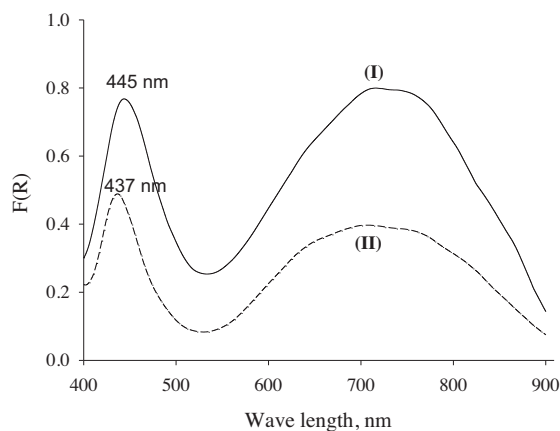


Fig. 5. Diffuse reflectance spectra of catalysts (I) and (II).

3.2. SALDI mass spectra and UV–vis spectra of the catalytic complexes

The positive-ion SALDI mass spectra are shown in Fig. 4. A comparison of Fig. 4a and b indicates that the spectra of the catalysts have same differences. Copper-mononuclear CuBr^+ ions (m/z 143) and $\text{NET}_3\text{PrBr}^+$ ions (m/z 222) can be identified in the spectrum of catalyst (II), whereas the other spectral bands are due to fragmentation of amines. In the case of catalyst (I), copper-polynuclear ions Cu_2Br^+ , Cu_2Br_2^+ , and Cu_3Br_2^+ (207, 288, 351, respectively) predominate. The organic component is represented by a band at m/z 137, which may correspond to the EtPrIm^+ ion. It is noteworthy that various cluster ions contain copper in the oxidation state +1, which is inconsistent with the XPS data at first glance. However, it is known that Cu^{2+} can be reduced to Cu^+ during SALDI ionization, as has been shown for copper chloride [26].

It should be noted that the special SALDI mass spectrometric study of catalyst (I) and (II) showed no Cu–O bond formation. On the basis of the XPS data, it would be difficult to uniquely determine the molecular form of copper complexes in (I) and (II). However, taking in account that copper reacts in the oxidation state (1+) in principal step (2) – initiation of bromination (see kinetic scheme (2)–(9) in Section 3.4) – and CuBr was initially used in the synthesis of the catalysts, we depict catalytic complexes (I) and (II) with copper(I) in this paper.

The SALDI data on diverse nuclearities of the copper bromide complexes on the silica gel surface are in good agreement with the electronic spectroscopy data (Fig. 5). Indeed, the charge transfer band at 437 nm in the diffuse reflectance spectrum of catalyst (II) is due to the copper-mononuclear bromide complex [27–30]. The shift of the similar band of catalyst (I) to longer wavelengths suggests a decrease in the distance between the ions and the formation of polynuclear structures. This trend has been well investigated for copper halide complexes [31–33]. Previously, we obtained analogous results in the study of grafted ionic liquids (IL) containing copper chloride complexes of various compositions [22,23].

Thus, mononuclear copper halide complexes are predominantly formed in the case of triethylamine-based IL, whereas the IL containing the imidazole derivative is prone to the formation of polynuclear complexes.

3.3. Decane bromination with tetrabromomethane in the absence of additives

When reaction solutions were prepared using decane of moderate purity (<95%), CBr_4 behaved as a brominating agent even without heating or addition of initiating additives to the reac-

Table 2

Results of decane bromination with CBr_4 in the absence of additives. The volume of the reaction mixture was 0.20 ml.

CBr_4 , mol $\times 10^4$	Time (h)/reaction temperature, °C	Yield of bromodecanes, (%)
1.0	Initial solution held for a week in the dark at room temperature	Traces
1.0	3/130	Traces
3.0	3/140	11
3.0	3/140	18*

Note: * The working solution was prepared using decane of 94% purity; the reaction was carried out immediately after preparation of the solution.

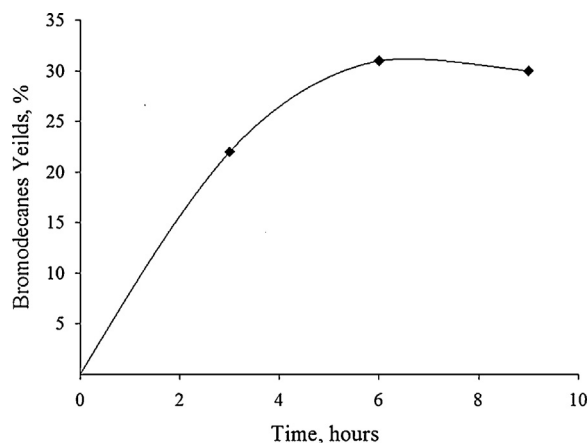


Fig. 6. Kinetic curve of accumulation of bromodecanes on catalyst (I). Initial conditions: volume of the reaction mixture 0.20 ml, $[\text{CBr}_4]_0 = 0.44$ mol/L, catalyst weight 2.5×10^{-2} g, temperature 130 °C.

tion medium. Indeed, tetrabromomethane solutions in decane of 94% purity (commercial Merck chemical) with a molar ratio of $\text{C}_{10}\text{H}_{22}:\text{CBr}_4 = 10:1$ contained up to 20% bromodecanes (with respect to CBr_4) after 24-h exposure to daylight at room temperature. This result could be due to unsaturated impurities, e.g., alkenes, present in the insufficiently pure decane. The products of decomposition by heating or irradiation of molecular complexes of unsaturated compounds with polyhalomethanes are able to induce radical processes, as it was described for halogens [34]. The use of the 99% pure alkane eliminated these effects even without its further purification.

Heating CBr_4 solutions in that sort of decane to a temperature less than 130 °C did not lead to a change in the composition of the reaction mixture, whereas noticeable amounts of bromodecanes (up to 11% at 140 °C, Table 2) were formed above this threshold temperature. This is most likely due to the thermal dissociation of the CBr_4 molecule followed by initiation and propagation of the chain bromination of decane [35].

3.4. Catalytic bromination of decane with tetrabromomethane

Copper-containing catalysts considerably increased the efficiency of the reaction of tetrabromomethane with decane. Noticeable amounts of bromination products were formed even at 100 °C, and the yield of the products at 140 °C almost doubled as compared with the non-catalyzed experiments. The reaction was selective: the yields of secondary monobrominated products were nearly quantitative (99%), with 1-bromodecane and dibromodecanes being detected in trace amounts. This product distribution is inherent in the radical reaction mechanism and complies with published data [20].

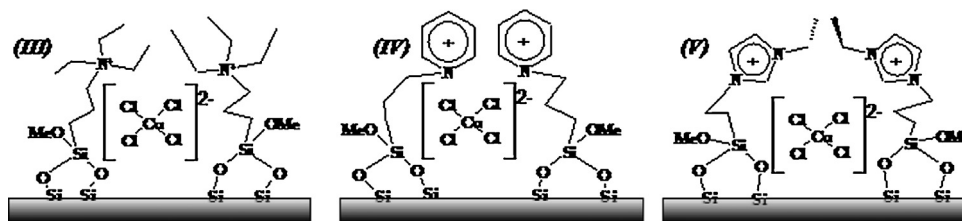


Fig. 7. The structures of the catalysts (III)–(V).

Table 3

Results of decane bromination with tetrabromomethane in the presence of bromine- and chlorine-containing catalysts (I), (II) and (III)–(V), respectively. Volume of the reaction mixture 0.20 ml, catalyst weight 2.6×10^{-2} g, reaction time 3 h.

Catalyst, amount of Cu (mol $\times 10^6$)	Reaction temperature, °C	Yield of bromodecanes, %
(I), 4.9	140	22
(I), 4.9	155	35
(II), 2.9	140	20
(II), 2.9	155	34
(III), 2.0	140	18*
(III), 2.0	155	27
(IV), 2.0	155	30
(V), 4.0	155	29

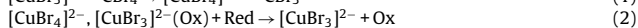
Note: * The initial concentration $[\text{CBr}_4]_0 = 1.32$ mol/L.

Fig. 6 shows the kinetic curve for accumulation of secondary monobromodecanes at 130 °C. After 5 h of the reaction, the curve reaches its maximum when a 30% conversion is attained; a further increase in the reaction time does not lead to an increase in the product yield.

Since the main product formation route is catalytic initiation (under these conditions, the contribution of thermally initiated bromination in decane is insignificant, see Section 2.2), this pattern of the rate curve can be due to either a parallel consumption of the products or catalyst deactivation.

Analysis of the reaction mixture after 9 h showed that the contribution of dibromodecanes was still minor (<1%) and olefins were found only as traces. Hence, it is most likely that the latter factor came into play. The bromination of organic ligands involved in the formation of the catalytic complex, especially when a concentration of tetrabromomethane substantially exceeds the copper concentration, can induce gradual destruction and, as a result, catalyst deactivation, as it has been found previously for tetrachloromethane [22,23].

The schematic model of radical bromination of alkanes in the presence of copper bromides was considered in our previous works and, in essence, should not be significantly different from the one proposed for chlorination with CCl_4 used as a source of chlorine [19,20,22,23]:



initiation, oxidation of copper in the initial catalytic complex
reduction of copper in the catalytic complex

chain propagation
chain propagation
chain transfer
chain transfer
chain termination
chain termination

Note: $[\text{CuBr}_3]^{2-}(\text{Ox})$ is an expression of one in every oxidized forms of copper mentioned regarding Table 1.

The resemblance of the reaction schemes follows from the similarity in the products of the both processes as well as the decane bromination efficiency of the catalysts that have been used in the reactions with CCl_4 . Comparison of the data in Table 3 confirms that there is no significant difference in activity between the bromine-

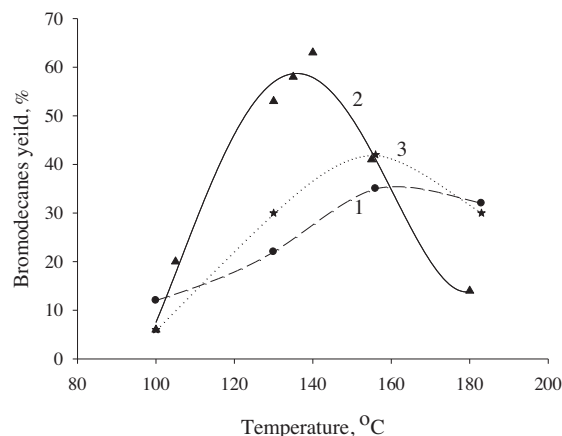


Fig. 8. Yield of bromodecanes vs. temperature in the presence of the catalyst and donor additive (*n*-propanol). Initial conditions: volume of the reaction mixture 0.225 ml, $[\text{n-PrOH}]_0 = 1.3$ mol/L, $[\text{CBr}_4]_0 = 0.44$ mol/L, reaction time 3 h, temperature 130 °C, catalyst weight 2.5×10^{-2} g. 1– $\text{C}_{10}\text{H}_{22}\text{-CBr}_4$ -catalyst (I) system, 2– $\text{C}_{10}\text{H}_{22}\text{-CBr}_4$ -catalyst (I)–*n*-propanol system, 3– $\text{C}_{10}\text{H}_{22}\text{-CBr}_4$ -*n*-propanol system. For the experiment carried out at 135 °C (system (2)), the composition of the *n*-propanol transformation products in the bromination of decane with CBr_4 was studied.

and chlorine-containing (see Fig. 7) catalysts in the reaction in question.

The difference between the bromine- and chlorine-containing catalysts is solely in the products: up to 5% chlorodecanes were formed within 3 h in the latter case.

As should be expected, the reaction with CBr_4 proceeds under milder conditions relative to chlorination: the products formed in substantial amounts even at 100–130 °C (Fig. 8, curve 1), the maximum yield (35%) was attained at 150–155 °C, whereas a similar yield in the case of chlorination was achieved at temperatures above 170 °C [23]. A further increase in temperature to 180 °C did not enhance the productivity of the bromination reaction, apparently, because of accelerated catalyst degradation and increased contribution of side processes, in particular, dehydrohalogenation

of the products [36,37]. This conclusion is supported by substantial tarring of the reaction mixture, in particular, on the surface of catalyst powder, even at 150 °C after 3 h of the reaction. Tarring was the most intense clearly during the reactions mediated by catalyst (II); therefore, only a limited number of tests were performed with it.

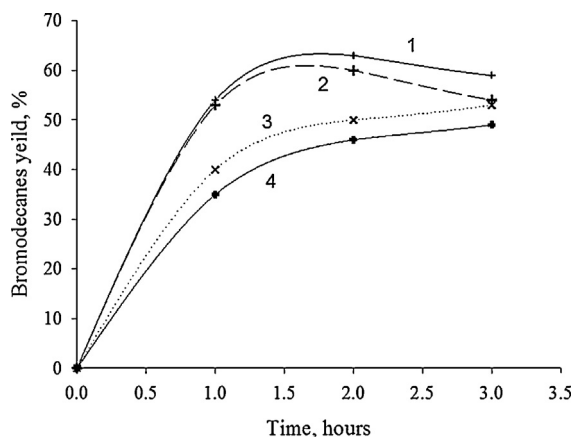


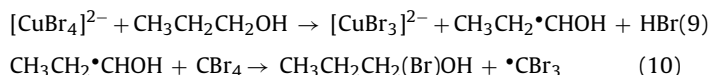
Fig. 9. Kinetics of bromination in $C_{10}H_{22}-CBr_4$ -chlorine-containing catalyst-*n*-propanol system. Initial conditions: reaction volume of 0.225 ml, $[CBr_4]_0 = 0.44$ mol/L, $[EtOH]_0 = 1.6$ mol/L, $[n-PrOH]_0 = 1.3$ mol/L, catalyst weighed 2.6×10^{-2} g: **1** – catalyst (III) + *n*-PrOH, **2** – catalyst (III) + EtOH, **3** – catalyst (IV) + EtOH, **4** – catalyst (V) + EtOH. Reaction temperature 135 °C.

3.5. Effect of alcohols on the catalytic bromination of decane with tetrabromomethane

In our previous studies of the reaction of decane with tetrachloromethane in the presence of Cu(II) chloride complexes with quaternary ammonium bases, we found that donor additives, in particular low-molecular-weight alcohols, increased the yield of the chlorination products [22,23]. Ethanol and *n*-propanol, which had exhibited the highest efficiency, considerably increased the degree of bromination in the catalytic reaction with CBr_4 as well. A comparison of the data of Table 3 with those in Figs. 8 and 9 shows that the yield of bromination products almost virtually doubled in the $C_{10}H_{22}-CBr_4$ -catalyst-donor additive system. However, this effect had some limitations, in particular, as regards the reaction temperature and the amount of added alcohol.

It is noteworthy that as in case of the reactions in the absence of alcohol (see above), there was no significant difference in activity between the bromine- and chlorine-containing catalysts (Fig. 9).

The temperature dependence of the yield of monobromodecanes in the presence of catalyst and *n*-PrOH (Fig. 8, curve 2) has a distinct extremum. Such a shape of the curve can be explained as follows: the initial increase in the yield to a maximum is due to the fact that alcohols are not only involved in the formation of mixed-ligand complexes with copper halide derivatives or/and formation of the solvation shell around the polar moiety of the catalyst, but also can directly participate in chain initiation (10) and propagation (11) [22,23]:



The alcohol bromination products (mono- and dibromopropanols) were detected by the GC/MS technique. Undergoing catalytic or/and thermal bromination, an alcohol simultaneously “shields” the organic ligands, thereby preventing the catalytic complex from degradation.

As the temperature increased, such associates with an alcohol (in particular, *n*-propanol) were destroyed, thus making the QABs fragments containing C–H bonds more accessible for an attack by free radicals. However, in the temperature range up to 130–140 °C, this factor is apparently counterbalanced by an increase in the formation rate of bromodecanes (see below). Although the alcohol itself undergoes bromination, it insignificantly competes with decane at a low or medium concentration. This conclusion is supported by an increase in the chain length of the major radical

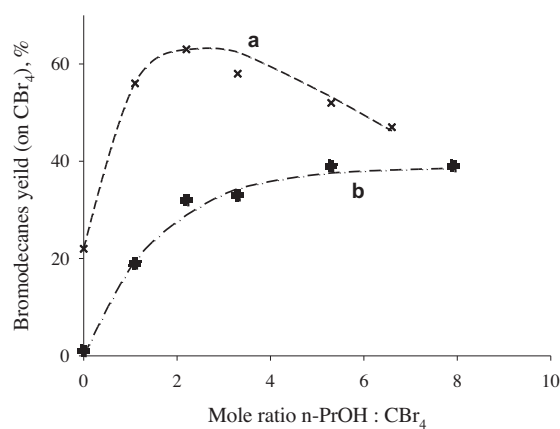


Fig. 10. Bromodecanes yield vs. tetrabromomethane to *n*-propanol ratio in the reaction of CBr_4 with decane. (a) – In the presence of the catalyst (I), 10 wt.%, (b) – without a catalyst. The molar ratio $CBr_4:C_{10}H_{22} = 1:10$, reaction temperature 135 °C.

reaction with temperature. Indeed, the reaction mixture in the experiment at 135 °C (Fig. 8, curve 2) still contained a considerable amount (15%) of *n*-propanol after the complete consumption of CBr_4 . Another piece of evidence is that the alcohol added in a moderate amount quantity in the absence of the catalyst did not change significantly the product buildup pattern (curve 3 in Fig. 8).

As the temperature was elevated above the indicated values (descending portion of curve 2 in Fig. 8), the contribution of thermally induced dissociation of CBr_4 increased. Under these conditions, the “shielding” role of alcohols decreased and gradually lost its value. Moreover, some associates can have even a detrimental effect, transferring the radical chain via the hot radicals formed in reaction (10) to the ligands of the active complex. The accelerated (catalytic or thermally initiated) consumption of the donor additive and the progressively increasing rate of catalyst deactivation (probably involving the alcohol in the process) dramatically decreased the yield of bromodecanes to values below those observed in the

An increase in the amount of the alcohol in the system resulted in higher yields of bromodecanes but only to a certain limit. This effect was observed for both catalyzed and non-catalyzed reactions. Curve b in Fig. 10, which corresponds to the latter case, shows the dependence of the yield of bromodecanes on the amount of *n*-propanol added at 135 °C. In this case, the products were formed under the conditions when the thermally initiated dissociation of tetrabromomethane did not result in a considerable change in the composition of the initial reaction system (see Table 2). The occurrence of the reaction was due to the fact that a certain amount of $\cdot Br$ and $\cdot CBr_3$ radicals was formed to have an energy sufficient to abstract the α -hydrogen atoms from alcohols (C–H bond dissociation energy is 385 kJ/mol for ethanol [38]). The radical products thus formed are capable of initiating a new chain that can involve alkane molecules as well (the C–H bond energy for secondary bonds of linear alkanes is 399–405 kJ/mol [39]). This reaction pathway was confirmed by the observed formation of the noticeable amount of the acetal $CH_3CH_2CH(OCH_2CH_2CH_3)_2$, which resulted from the reaction of propionaldehyde with *n*-propanol. The aldehyde is probably the product of the enol rearrangement of prop-1-en-1-ol, which in turn can be produced by dehydrobromination of 1-bromopropan-1-ol, a quite likely process under the given conditions. Hydrogen bromide appeared in this reaction can serve as a catalyst for the acetal formation.

The initial segment of curve b in Fig. 10 shows an increase in the yield of bromodecanes with an increase in the alcohol concentration (positive effect), which is due to increase in the number of propagation steps upon the thermal dissociation of CBr_4 , result-

ing in chain initiation and the subsequent chain transfer to alcohol molecules and then to decane molecules. At an *n*-PrOH:CB₄ ratio of 5 to 6, the curve flattens out, presumably, as a result of direct competition between the *n*-propanol and decane bromination reactions.

A similar interpretation may apply to the behavior of curve **a** in Fig. 10 (resembling the curve obtained previously for decane chlorination with tetrachloromethane [22,23]). In this case, catalytic initiation is possible, resulting in a considerably steeper rise of the initial portion of the curve. At an alcohol to CBr₄ ratio greater than 4, the yield of bromodecanes decreases because of the parallel bromination of *n*-propanol and decane. Furthermore, an increase in the amount of alcohol, which is capable of solvating the catalytic sites and CBr₄, gradually hampers the catalytic initiation, thereby decreasing the decane bromination rate.

In addition, it was found that the nature of the alcohol (ethanol or *n*-propanol) does not have a significantly effect on the rate of product formation in the non-catalyzed reaction. At 150°C, the yields of bromodecanes after 2 h are nearly equal (43% and 44%, respectively).

4. Conclusions

It has been shown that the catalytic bromination and chlorination of decane with polyhalomethanes follow similar mechanisms. Product compositions in both reactions and high activity of the catalysts, previously used in the chlorination, in the bromination reaction are the signs of that. There are also significant differences between these two processes: the milder conditions needed for bromination and the substantially greater influence of the donor additives (alcohols) on the decane interaction with CBr₄ compared to CCl₄, even initiation of the radical process in the absence of catalyst.

The results of the study lead to the conclusion that under the selected optimal conditions, immobilized bromide (as well as chloride) catalytic complexes in the presence of donor additives can be effectively applied in the selective synthesis of secondary bromo-substituted linear aliphatic compounds with tetrabromomethane being used as a brominating agent.

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