

# Catalysts Based on the Immobilized Complexes of Copper with Quaternary Ammonium Bases for Chlorination of Alkanes with Carbon Tetrachloride

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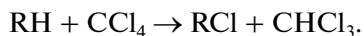
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**Abstract**—The complexes of copper chloride with quaternary ammonium bases supported on silica are highly active in the reaction of carbon tetrachloride with decane in the presence of an electron donor (ethanol). The effectiveness of the catalysts depends on the method of their deposition onto the support. The catalysts obtained as a result of covalent binding with the surface through the formation of siloxane bonds (immobilization) exhibit high stability and higher activity than the analogues prepared by the impregnation of the support with the catalytic complex. The introduction of ethanol into the reaction system substantially increases the activity and stability of all of the catalysts.

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## INTRODUCTION

Chlorinated alkanes are widely used as organic synthesis intermediates and plasticizers for commercial polymers. A promising method for their production is the reaction of saturated hydrocarbons with carbon tetrachloride, which is an abundant by-product of a number of chemical processes and needs to be utilized. This reaction is of considerable current interest because it makes it possible to completely use the initial chlorine as  $\text{CCl}_4$  in the manufacture of valuable products:



Compositions based on copper chlorides and quaternary ammonium bases (QABs) are known as effective catalysts for radical chain processes [1, 2].

In a previous study of the similar exchange reaction between  $\text{CCl}_4$  and methylene chloride, it was found that the productivity of the catalyst depends directly on the structure of the QAB: as a rule, the higher the oxidation resistance of the QAB, the higher the efficiency of the catalyst [1]. Among the alkyl-substituted QABs, derivatives containing ethyl or methyl groups meet this requirement. There are published data on the effectiveness of the catalytic complexes of copper with quaternary derivatives of imidazole (also known as thermally stable ionic liquids), both free and covalently fixed (immobilized on silica gel), in the Kharasch reaction [3, 4].

In this work, we studied the catalytic activity of these systems and complexes containing ammonium ions with short alkyl substituents in the reaction of decane with carbon tetrachloride, which is performed under more severe conditions than the Kharasch reaction. For the purpose of process optimization, we

studied the covalent immobilization of the above complexes on an inert heterogeneous support. We compared the effectiveness of the immobilized complexes and the catalysts prepared by impregnation.

## EXPERIMENTAL

### Chemicals

Organic substances were purified via standard procedures. Carbon tetrachloride and 1,2-dichloroethane of chemically pure grade were dried and distilled from  $\text{P}_2\text{O}_5$ . Decane (98%, Merck), and chemically pure toluene was dried and distilled from sodium. Tetraethylammonium chloride (98%, Merck), tetramethylammonium chloride (97%, Merck), triethylamine (99.5%, Merck), ethanol (distilled, 96%), absolute ethanol (99.9%, Merck), ethylimidazole (EI) (99%, Aldrich) and 3-chloropropyltrimethoxysiloxane (CPMS) (98%, Acros) were used without further purification.

KSK-2 silica gel ( $S_{\text{sp}} = 300 \text{ m}^2/\text{g}$ ) was washed with 0.1 N HCl and then with distilled water until the washings were neutral to a universal indicator. For removal of chemically unbound water, the powder was kept at  $150^\circ\text{C}$  for 2 h. The silica gel used in the synthesis of the immobilized catalysts was additionally dried in toluene by azeotropic distillation with the use of a Dean–Stark receiver; if necessary, it was stored under a layer of dried toluene.

### Synthesis of Quaternary Ammonium Chlorides

To prepare triethylchloroethylammonium chloride  $\text{Et}_3(\text{ClCH}_2\text{CH}_2)\text{NCl}$ , 2 mL ( $1.43 \times 10^{-3} \text{ mol}$ ) of triethylamine, 1.15 mL ( $1.46 \times 10^{-3} \text{ mol}$ ) of 1,2-dichloroethane,

and 1.5 mL of absolute ethanol were placed in a tube with a ground-glass joint and a constricted neck. The tube was connected to a vacuum system, frozen with liquid nitrogen, and pumped; thereafter, it was sealed and kept at 120°C for 5 h. After cooling the tube to room temperature, the released white crystals were washed with absolute ethanol and dried in a vacuum. The yield of the product was 78%.

*N*-Chloroethyl-*N'*-ethylimidazolium chloride  $\text{Et}(\text{ClCH}_2\text{CH}_2)\text{ImCl}$  was prepared in a similar way: 1 mL of ethylimidazole ( $1.03 \times 10^{-2}$  mol) and 1.5 mL ( $1.90 \times 10^{-2}$  mol) of dichloroethane were thermostated in an evacuated glass tube at 100°C for 1 h. As a result of the reaction, viscous liquid was obtained, which hardened at room temperature in a few days without the formation of a well-defined crystal structure. The yield of the product was 96%.

#### *Preparation of Supported Metal Complexes with Quaternary Ammonium Bases by the Impregnation Method*

The solid reactants—1.25 g of copper(II) chloride crystal hydrate ( $7.3 \times 10^{-3}$  mol) and 2.5 g ( $1.51 \times 10^{-2}$  mol)  $\text{Et}_4\text{NCl}$ —were gradually introduced into a glass vessel containing 180 mL of 96% ethanol under vigorous stirring. The solution was stirred at room temperature with weak heating ( $\sim 50^\circ\text{C}$ ) until the complete dissolution of the solid components; thereafter, silica gel (50 g) was added and stirring was continued for another 2 h. Next, the liquid was decanted, and the residual ethanol was removed from the sediment on a rotary evaporator. The copper content of the  $\text{CuCl}_2\text{—Et}_4\text{NCl/SiO}_2$  catalyst was determined by chelatometric titration to be 1.45%.

The  $\text{CuCl}_2\text{—Et}_3(\text{ClCH}_2\text{CH}_2)\text{NCl/SiO}_2$ ,  $\text{CuCl}_2\text{—Et}(\text{ClCH}_2\text{CH}_2)\text{ImCl/SiO}_2$ , and  $\text{CuCl}_2\text{—Me}_4\text{NCl/SiO}_2$  copper-containing catalysts were obtained in a similar way. The amounts of quaternary salts and copper chloride were chosen so that the salt : copper(II) molar ratio was 2 : 1 and the amount of supported copper(II) was 2% of the catalyst weight.

#### *Synthesis of the Complex of Copper(II) Chloride with Immobilized *N*-Propyl-*N'*-Ethylimidazolium Chloride<sup>1</sup>*

The synthesis was performed via a modified procedure [4] (Fig. 1a). The main difference was that quaternization was carried out in glass tubes. For this purpose, an tube containing a mixture of 5 mL ( $5 \times 10^{-2}$  mol) of EI and 9.4 mL ( $5 \times 10^{-2}$  mol) of CPMS

was connected to a vacuum system, cooled to the temperature of liquid nitrogen, pumped, and sealed. The sample was kept at 185°C under stirring for 8 h. The resulting *N*-3-trimethoxysilanopropyl-*N'*-ethylimidazolium chloride was a yellowish brown, thick, homogeneous mass. The mass was stored in the initial tube, which was opened immediately before use.

For the purpose of immobilization, the synthesized quaternary salt was introduced into a flask with pre-dried silica gel under a layer of toluene. The weight ratio between the quaternary salt and the support was 1 : 1. A Dean–Stark receiver and a reflux condenser were fitted into the neck of the flask and the contents were boiled under stirring for 12 h. Next, the solid phase was filtered and washed with 10 mL of dry toluene per gram of silica gel. The dried precipitate was placed in a Soxhlet apparatus and the unreacted salt was extracted with dry methylene chloride for 6 h. As a result, white powder was obtained, which contained 7.85 wt % C, 1.95 wt % H, and 2.16 wt % N according to elemental analysis data.

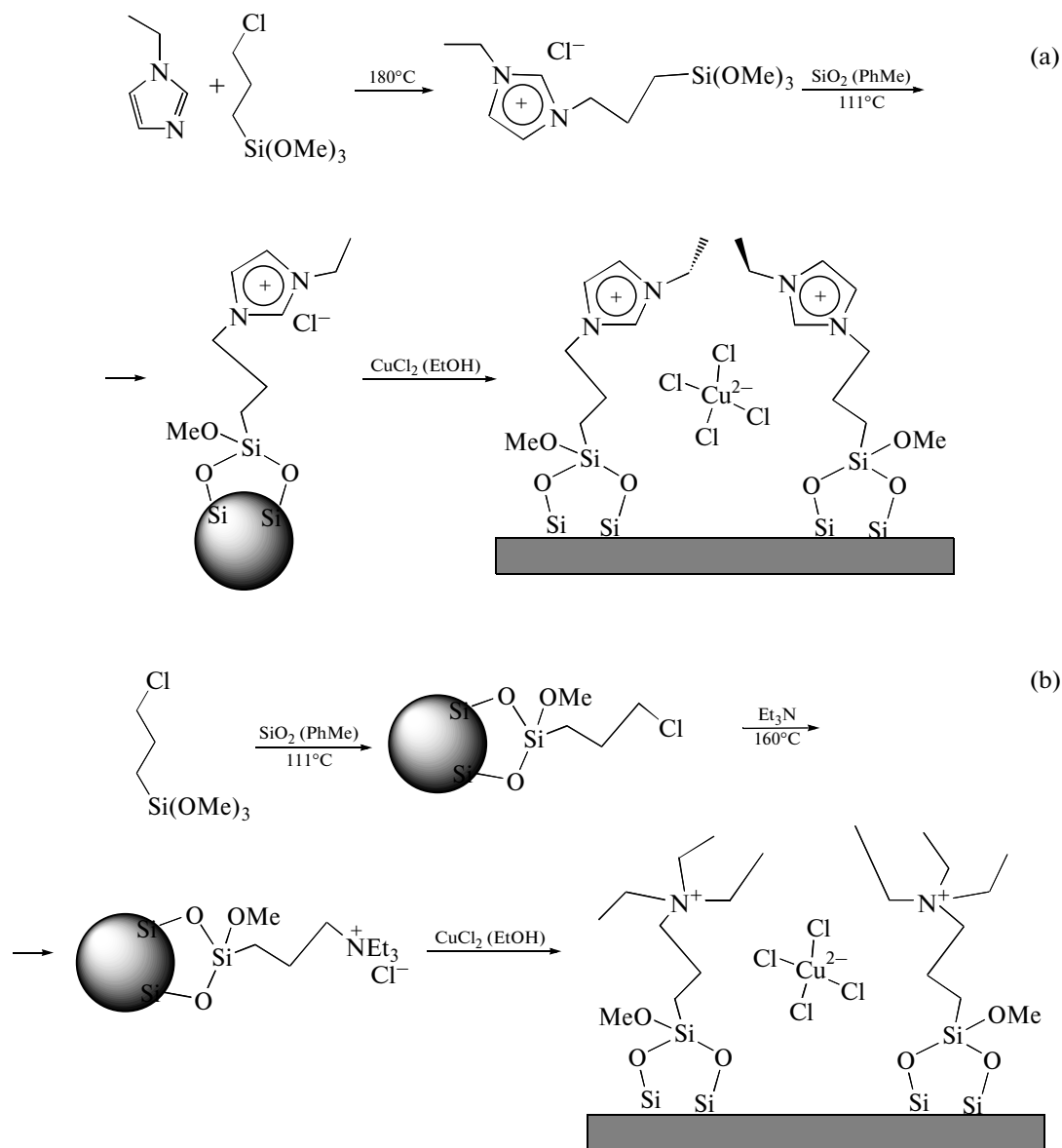
The copper-containing chloride complex was obtained by deposition of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  from an ethanolic solution (the calculated amount of Cu(II) was 2% of the silica gel weight). For this purpose, an appropriate amount of the crystal hydrate was dissolved in 95% ethanol, a weighed portion of the modified silica gel was introduced into the resulting solution, and the contents were stirred for 30 min. Excess solvent was removed on a rotary evaporator. The resulting bright yellow powder was placed in a Soxhlet apparatus, and the residual free copper chloride was extracted with dry acetonitrile for 4 h. The copper content of the catalyst was determined by chelatometric titration; it was 1.97% of the total sample weight.

#### *Synthesis of the Complex of Copper(II) Chloride with Immobilized Propyltriethylammonium Chloride*

Figure 1b schematically shows the preparation of the chloride complex of copper(II) and propyltriethylammonium. At the first stage, CPMS was added to dehydrated silica gel, which was under a layer of toluene, in a weight ratio of 2 : 1 in a flask equipped with a Dean–Stark receiver and a reflux condenser. The reaction mixture was boiled for 6 h; then, the solid phase was filtered, washed with 10 mL of dry toluene per gram of silica gel, and dried. The elemental analysis of the product showed the following results (wt %): C, 4.92; H, 1.31.

The reaction between triethylamine (2.8 mL) and modified silica gel (2.0 g) was carried out in an evacuated glass tube under stirring for 6 h at 160°C. At the end of the synthesis, unreacted triethylamine was washed with ethanol (25 mL) for 20 min with stirring. After filtration and drying (50–70°C), copper chloride was supported according to the procedure described above. As a result, yellow powder with a cop-

<sup>1</sup> Hereafter, the term *propyl* is used to designate the hydrocarbon constituent of the immobilized QAB; this moiety consists of three methylene groups ( $-\text{CH}_2-$ )<sub>3</sub> and is bound to silica gel through siloxane bridges. We assume that the nature of this moiety is not fundamentally different from the nature of the true propyl radical and the use of this term by no means falsifies the consideration and the interpretation of experimental results.



**Fig. 1.** Reaction schemes for the preparation of the immobilized (a)  $\text{CuCl}_2\text{--EtPrImCl--SiO}_2$  and (b)  $\text{CuCl}_2\text{--Et}_3\text{NPrCl--SiO}_2$  complexes.

per content of 1.9 wt % was obtained. According to elemental analysis data, it contained 6.32 wt % C, 2.03 wt % H, and 0.51 wt % N.

#### *Physicochemical Analysis of the Samples*

EPR spectra were recorded on an E-3 X-band radiospectrometer from Varian (high-frequency modulation at 100 kHz) in thin-walled tubes of quartz glass with a diameter of 4 mm at  $-196^\circ\text{C}$ . The  $g$ -factor scale was graduated by the simultaneous recording of the spectra of a diamagnetically diluted solid solution of  $\text{Mn}^{2+}$  ions in  $\text{MgO}$ . The constant conditions in the resonator of the EPR spectrometer were controlled by recording the spectrum components of an intermedi-

ate standard—a single crystal of ruby ( $\text{Al}_2\text{O}_3$  containing  $\text{Cr}^{3+}$ )—simultaneously with the spectrum of the sample.

The silica gel after its preparation for the modification and the immobilized  $\text{CuCl}_2\text{--EtPrImCl--SiO}_2$  complex thermally treated in a vacuum at  $180^\circ\text{C}$  for 5 h were studied by IR spectroscopy. The samples were pressed into pellets with KBr. The spectra were measured on an Infracum FT-801 Fourier transform IR spectrophotometer (Simeks, Russia) in the range of  $4000\text{--}400\text{ cm}^{-1}$ .

Diffuse reflectance electronic spectra were recorded on an HR4000CG-UV-NIK spectrometer (Ocean Optics) with an integrating sphere in the range of  $300\text{--}1200\text{ nm}$ .

Thermogravimetric studies were carried out in the laboratory of microanalysis at the Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, on a Derivatograph-C instrument (MOM, Hungary) in an atmosphere of air and argon at a heating rate of 10 K/min with the use of ~15-mg samples.

To perform electrospray ionization (ESI) analysis, a Bruker micrOTOF II instrument was used (department of structural studies, Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences).

### Catalytic Experiments

The experiments were carried out in sealed evacuated glass tubes. The samples were kept at a specified temperature in an air thermostat equipped with a device for rotating the tubes at variable speed and for changing the direction of rotation. The experimental conditions ensured that the results were independent of the rotational speed.

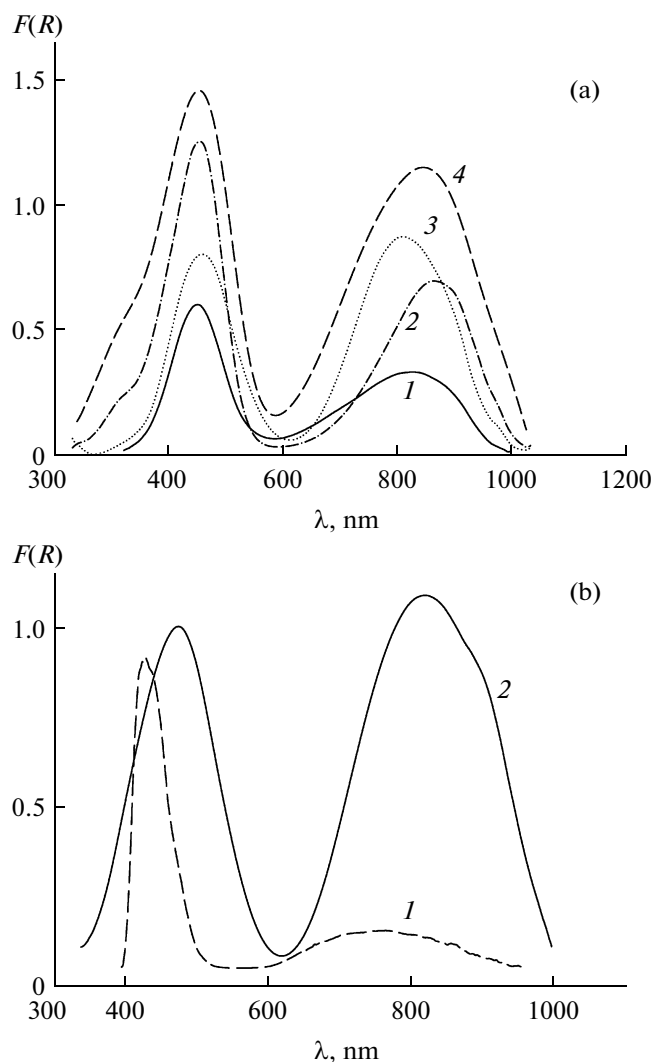
The activity of the supported catalysts was evaluated from the total yield of the chlorination products – monochlorodecanes and dichlorodecanes – in 5 h at 175°C and constant initial concentrations of the reactants: 0.05 g of the heterogeneous catalyst, 0.4 mL of  $\text{CCl}_4$  ( $4.1 \times 10^{-3}$  mol), and 0.2 mL of decane ( $1.0 \times 10^{-3}$  mol), and also the necessary amount of the donor. The orders of the reaction were determined from the initial rates by varying the amounts of the catalyst from 0.01 to 0.05 g and decane from  $0.2 \times 10^{-3}$  to  $1.0 \times 10^{-3}$  mol at a constant sample volume. The activation energy of the reaction was measured in the temperature range of 165–195°C.

The procedures used to perform the catalytic experiments in solution and the GLC analysis of the products were described in detail elsewhere [5]. The products were identified by gas chromatography–mass spectrometry (GC–MS) using a THERMO TRACE DSQ II instrument (Thermo Fisher Sci.). The quantitative analysis of the products was performed by GLC on a Kristall-2000 chromatograph (Khromatek, Russia) equipped with a flame-ionization detector and a 3-m column with the nonpolar phase SE-30.

## RESULTS AND DISCUSSION

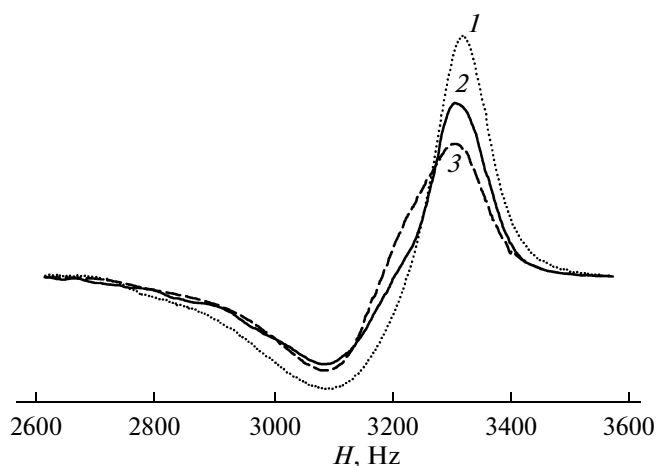
### Spectroscopic and Thermogravimetric Data

The catalysts prepared by the impregnation of silica gel with the chloride complexes of copper and QABs or immobilization on the silica gel framework were yellow or orange powders stable in air; they contained 5–10 wt % organic matter and 1.5–2 wt % copper. Figure 2 shows the electronic diffuse reflectance spectra of the samples obtained. In all of the spectra, two absorption bands characteristic of the chloride complexes of  $\text{Cu}^{2+}$  are observed: a charge-transfer band in



**Fig. 2.** Electronic diffuse reflectance spectra of catalysts prepared by (a) impregnation and (b) immobilization in the Kubelka–Munk coordinates: (a) (1)  $\text{CuCl}_2\text{--Et}_3(\text{ClCH}_2\text{CH}_2)\text{NCl/SiO}_2$ , (2)  $\text{CuCl}_2\text{--Me}_4\text{NCl/SiO}_2$ , (3)  $\text{CuCl}_2\text{--Et}_4\text{NCl/SiO}_2$ , and (4)  $\text{CuCl}_2\text{--Et}(\text{ClCH}_2\text{CH}_2)\text{ImCl/SiO}_2$ ; (b) (1)  $\text{CuCl}_2\text{--Et}_3\text{NPrCl--SiO}_2$  and (2)  $\text{CuCl}_2\text{--EtPrImCl--SiO}_2$ .

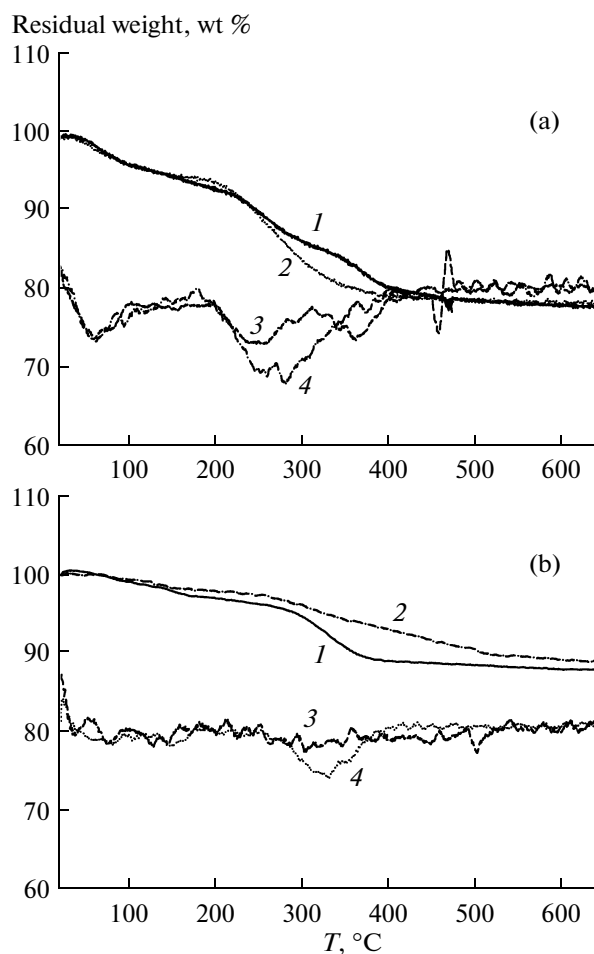
the region of 420–480 nm and a band at 750–820 nm, which is due to the  $d\text{--}d$  transitions in the  $\text{Cu}^{2+}$  ions in a tetragonal octahedral complex [5]. Such complexes with axial chloride bridges can result from the interaction of closely spaced  $\text{CuCl}_4^{2-}$  ions, as is suggested by EPR data. The typical spectrum (Fig. 3) is characterized by axial  $g$ -factor anisotropy and by the absence of hyperfine structure in the region of  $g_{\parallel}$ , which is a consequence of the strong dipole–dipole interaction that occurs upon the association of the above complexes [2]. For the same reason, the fraction of  $\text{Cu}^{2+}$  ions detected by EPR spectroscopy was no higher than 15% of the total copper content of the sample.



**Fig. 3.** EPR spectra of the  $\text{CuCl}_2\text{--EtPrImCl--SiO}_2$  sample: (1) the initial complex, (2) upon the addition of ethanol, and (3) after reaction.

An analysis of the IR spectra of the immobilized  $\text{CuCl}_2\text{--EtPrImCl--SiO}_2$  metal complex allowed us to conclude that the ionic liquid is bonded to the terminal silanol groups of the support (Table 1). This is evident from the irreversible disappearance of the band at  $3745\text{ cm}^{-1}$  (stretching vibrations of isolated hydroxyl groups on the surface) and the appearance of bands in the region of  $2800\text{--}2900\text{ cm}^{-1}$ , which are due to the stretching vibrations of C–H bonds in the methylene and methyl moieties.

The thermal stability of the samples depends on the method of their synthesis. Figure 4 illustrates the results of the thermogravimetric analysis of the  $\text{CuCl}_2$  complex with  $\text{Et}_3(\text{ClCH}_2\text{CH}_2)\text{NCl}$  supported by impregnation and immobilized  $\text{CuCl}_2\text{--Et}_3\text{PrNCl--SiO}_2$ . A comparison shows that the weight loss of the immobilized complex in air occurs in the range of  $250\text{--}350^\circ\text{C}$ , whereas the analogous thermolysis of the former sample comes into play below  $200^\circ\text{C}$ . Thus, in both cases, the catalysts are suitable for use in the reaction considered, which occurs at  $160\text{--}190^\circ\text{C}$ ; however, the catalyst prepared by impregnation is unlikely to be very stable for a long time.



**Fig. 4.** (1, 2) Integral and (3, 4) differential TGA curves of (a) the  $\text{CuCl}_2\text{--Et}_3(\text{ClCH}_2\text{CH}_2)\text{NCl/SiO}_2$  catalyst prepared by impregnation and (b) the immobilized  $\text{CuCl}_2\text{--Et}_3\text{PrNCl--SiO}_2$  catalyst: (1, 3) in air and (2, 4) under argon.

The metal complex deposition method is also responsible for the activity and stability of the samples during the reaction. The highest yield was attained with the use of the immobilized  $\text{CuCl}_2\text{--Et}_3\text{PrNCl--SiO}_2$  complex as the catalyst. The other systems were also sufficiently effective, but only in the presence of ethanol as the donor in an amount of 8–10% of the sample volume (Tables 2–4). Under the conditions

**Table 1.** Characteristic bands in the IR spectra of silica gel prepared for modification and a sample containing an immobilized complex after thermal treatment at  $180^\circ\text{C}$  for 5 h

Sample	Wavenumber, $\text{cm}^{-1}$	
	isolated OH groups	$\text{CH}_2$ and $\text{CH}_3$ groups
$\text{SiO}_2$	3745	—
$\text{CuCl}_2\text{--EtPrImCl--SiO}_2$	—	2850, 2920

**Table 2.** Yield of chlorodecanes on catalysts prepared by different methods

Sample	Yield of chlorodecanes, %	
	without a donor	in the presence of EtOH (1.1 mol/L)
$\text{CuCl}_2\text{--Me}_4\text{NCl/SiO}_2$	9	37
$\text{CuCl}_2\text{--Et}_4\text{NCl/SiO}_2$	12	42
$\text{CuCl}_2\text{--Et}_3(\text{ClCH}_2\text{CH}_2)\text{NCl/SiO}_2$	14	52
$\text{CuCl}_2\text{--Et}(\text{ClCH}_2\text{CH}_2)\text{ImCl/SiO}_2$	15	44
$\text{CuCl}_2\text{--Et}_3\text{PrNCl--SiO}_2$	43	59
$\text{CuCl}_2\text{--EtPrImCl--SiO}_2$	34	52

Note: Initial conditions: catalyst weight, 0.05 g; reaction mixture volume, 0.7 mL;  $[\text{CCl}_4] = 6 \text{ mol/L}$ ;  $[\text{C}_{10}\text{H}_{22}] = 1.5 \text{ mol/L}$ ; temperature,  $175^\circ\text{C}$ ; and reaction time, 5 h.

**Table 3.** Effect of the concentration of ethanol on the yield of chlorodecanes on the  $\text{CuCl}_2\text{--Et}_3(\text{ClCH}_2\text{CH}_2)\text{NCl/SiO}_2$  catalyst prepared by impregnation

Concentration of EtOH, mol/L	0	0.4	0.65	0.8	1.1	1.5	1.9
Yield of chlorodecanes, %	14	23	28	42	52	40	35

Note: The reaction conditions are specified in Table 2.

**Table 4.** Yield of chlorodecanes on catalysts prepared by different methods in the course of sequential reaction cycles

Catalyst	Yield of chlorodecanes, %				
	cycle number				
	1	2	3	4	5
$\text{CuCl}_2\text{--Et}_3(\text{ClCH}_2\text{CH}_2)\text{NCl/SiO}_2$	52	38	34	31	23
$\text{CuCl}_2\text{--Et}_3\text{PrNCl--SiO}_2$	59	55	58	57	—
$\text{CuCl}_2\text{--EtPrImCl--SiO}_2$	52	51	53	52	—

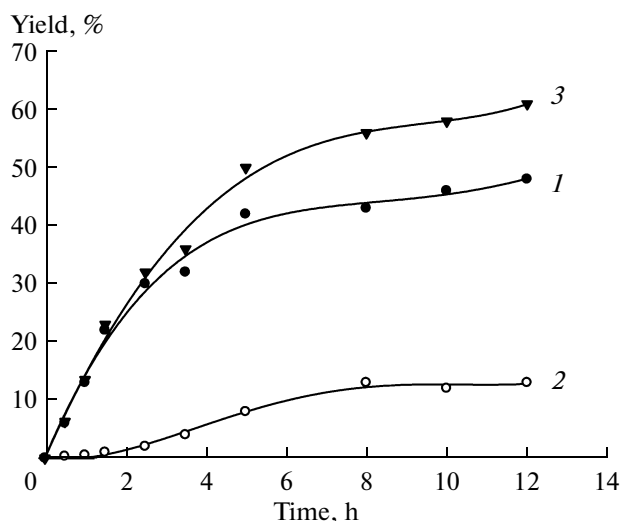
Note: The reaction conditions are specified in Table 2. The EtOH concentration is 1.1 mol/L.

examined, the main products of the interaction of decane and  $\text{CCl}_4$  were monochlorodecane isomers and also a mixture of dichlorodecane isomers, whose total yield did not exceed 15% on the converted decane basis (Fig. 5). The formation of hexachloroethane as a result of the recombination of trichloromethyl radicals, which is characteristic of similar reactions, was not observed.

#### *Properties of the Catalysts Prepared by the Impregnation Method*

In the presence of the catalyst obtained by the impregnation of silica gel with the complex of copper chloride with  $\text{Et}_3(\text{ClCH}_2\text{CH}_2)\text{NCl}$ , the total yield of chlorodecanes in the reaction of decane with  $\text{CCl}_4$  was 14%. The introduction of ethanol into the system led to an increase in the efficiency of the process (Table 2).

A similar effect of alcohols was noted earlier in the reactions of  $\text{CCl}_4$  with olefins,  $\text{CH}_2\text{Cl}_2$ , adamantane, and a number of heterocycles [1, 6–9]. It was found [1, 6, 7] that ethanol acted as the donor of hydrogen in the course of reactions with the participation of  $\text{CCl}_4$ , and it was oxidized to yield acetaldehyde and vinyl chloride. We detected the same products by GC–MS in the course of the process. We assume that ethanol, which competes with the alkyl substituents of the quaternary salts of the supported complex in the oxidation reaction, increases the catalyst lifetime and, as result, the yield of chlorodecanes. However, as can be seen in Table 3, the dependence of the yield of decane chlorination products on the amount of ethanol introduced into the system exhibits an extremum: the yield of the target product decreases if the alcohol concentration becomes somewhat higher than the concentration of decane. The causes of this phenomenon will be considered below.



**Fig. 5.** Kinetics of the buildup of chlorodecanes on the  $\text{CuCl}_2\text{-Et}_3\text{PrNCl-SiO}_2$  catalyst: (1) monochlorodecanes, (2) dichlorodecanes, and (3) the total yield of chlorodecanes. Initial conditions: reaction mixture volume, 0.7 mL;  $[\text{EtOH}]_0 = 1.2$  mol/L;  $[\text{CCl}_4]_0 = 6$  mol/L;  $[\text{C}_{10}\text{H}_{22}]_0 = 1.5$  mol/L; reaction time, 5 h; temperature,  $175^\circ\text{C}$ ; and catalyst weight, 0.05 g.

We studied the kinetics of the model reaction using the catalyst containing the complex of copper chloride with  $\text{Et}_3(\text{ClCH}_2\text{CH}_2)\text{NCl}$  as an example. In the decane and catalyst concentration ranges of 0.3–1.5 mol/L and 15–80 mg/mL, respectively, at  $[\text{C}_2\text{H}_5\text{OH}]_0 : [\text{C}_{10}\text{H}_{22}]_0 = 0.7 : 1$ , which is the optimum ratio, as follows from Table 3, and with an excess of  $\text{CCl}_4$ , the process is adequately described by the equation  $w = k[\text{RH}]^{1.0 \pm 0.1}[\text{Cat}]^{0.8 \pm 0.1}$ . Note that an analogous equation with a fractional order with respect to the catalyst is valid for this reaction on polymetalorganosiloxanes supported on silica in the absence of additives [10]; moreover, it was shown that this equation corresponded to the occurrence of a chain process. Thus, it is possible to assume that, in the presence of ethanol, the reaction is also develops by a radical chain mechanism.

Ethanol exerts a similar effect on all of the catalytic systems containing QAB chlorides. In all cases, the introduction of the alcohol several times increases the yield of chlorodecanes (Table 2). The catalysts exhibit high stability in several sequential reaction cycles. Table 4 indicates that the activity of the system consisting of  $\text{Et}_3(\text{ClCH}_2\text{CH}_2)\text{NCl}$  and  $\text{CuCl}_2$  noticeably decreases after the first cycle; this is likely due to the removal of weakly immobilized copper complexes from the surface of the support under severe reaction conditions. In the subsequent cycles, the number of metal-containing sites changes insignificantly. An analysis of the catalyst composition after five cycles showed that the metal content decreased by approximately 20%.

### *Properties of the Catalysts Prepared by the Immobilization of Chloride Complexes*

The complexes of copper chloride with covalently immobilized propylethylimidazolium and propyltriethylammonium exhibited much higher efficiency in the reaction in the presence of ethanol. In Tables 2 and 4, it can be seen that these catalysts are not only more active (the yield of products is almost 60%) but also, more importantly, more stable than the systems obtained by the impregnation method: their productivity remained almost unchanged within the limits of the error of analysis ( $\pm 5\%$ ) in the course of several sequential cycles.

Among the immobilized catalysts, the  $\text{CuCl}_2\text{-Et}_3\text{PrNCl-SiO}_2$  complex possesses somewhat higher productivity. It also exhibits high activity in the absence of ethanol. Thus, the yields of chlorodecanes in the first cycle on  $\text{CuCl}_2\text{-EtPrImCl-SiO}_2$  and  $\text{CuCl}_2\text{-Et}_3\text{PrNCl-SiO}_2$  were 34 and 43%, respectively. In this case, both of the catalysts also retained sufficiently high activity after conducting several reaction cycles. On the imidazole catalyst, the yields of chlorodecanes in the last three sequential cycles were 34, 26, and 21%, respectively (Table 4).

The effective activation energy determined from the linear dependence of  $\ln w_0$  on  $1/T$  ( $w_0$  is the initial rate of the reaction) for the  $\text{CuCl}_2\text{-Et}_3\text{PrNCl-SiO}_2$  catalyst in the presence of ethanol in the temperature range of  $165\text{--}195^\circ\text{C}$  was  $86 \pm 8$  kJ/mol. This is approximately 10 kJ/mol lower than the value reported in [10].

The influence of the donor on the effectiveness of catalysis by the immobilized complexes is not as strong as in the presence of the systems prepared by impregnation: the addition of ethanol in an amount of 1–1.3 mol/L to the immobilized  $\text{CuCl}_2\text{-Et}_3\text{PrNCl-SiO}_2$  complex increases the yield of chlorodecanes from 43 to 59%, whereas the yield on the impregnated catalysts increases by a factor of 3–4 (Table 2). Furthermore, the addition of a donor somewhat increases the productivity of the catalyst, which was already used in the first cycle without the participation of ethanol, in the second cycle. For example, in the case of  $\text{CuCl}_2\text{-Et}_3\text{PrNCl-SiO}_2$ , it increases from 43 to 48%.

### *Role of the Donor*

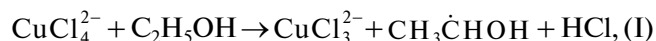
The reaction systems containing transition metal compounds, polyhalogenated alkanes, and alcohols have long been used in organic synthesis [1, 6, 7]. However, the mechanism of the action of alcohols and other donors in the reactions involving  $\text{CCl}_4$  remains unclear.

The presence of an alcohol in the systems examined here can lead to a change in the dielectric constant of the medium, which is especially important in view of the high polarity of ionic liquids. We studied the influence of a number of additives with different dielectric constants on the effectiveness of catalysis.

The data listed in Table 5 indicate that, upon the introduction of high-polarity agents (water and acetonitrile) and even methanol, the yield of the target product is lower than in the presence of ethanol.

Khusnutdinov et al. [7–9] obtained data that indicate the participation of alkyl hypochlorites (ROCl) in reactions of this kind. We verified the possibility of the formation of compounds of this type using the ESI technique for analysis. In the high-resolution mass spectra of the samples of a reaction solution containing immobilized  $\text{CuCl}_2\text{--Et}_3\text{NPrCl--SiO}_2$ , we did not detect even trace amounts of expected ethyl hypochlorite; this fact argues against the mechanism proposed by Khusnutdinov et al. [8].

Freidlina et al. [6] demonstrated that the interaction of  $\text{CCl}_4$  with alcohols (based on the example of isopropanol) in the presence of transition metal compounds is accompanied by the detachment of a hydrogen atom from the  $\alpha$ -carbon atom of the alcohol with the formation of trichloromethyl radicals and alcohol oxidation products. In our opinion, this mechanism of the participation of ethanol in the reaction is most probable. In this case, the detachment of hydrogen from the  $\alpha$ -C atom can occur as a result of both the reduction of the chloride complex of Cu(II)



and the interaction of trichloromethyl radicals with the ethanol molecule:



The conclusion that ethanol is involved in steps (I) and (II) is in good agreement with published data [6, 12]. Thus, ethanol participates in chain initiation and propagation. The above reaction scheme explains the extremal dependence (Table 3): at a high concentration of ethanol, reaction (III) competes with an analogous reaction of  $\dot{\text{C}}\text{Cl}_3$  with decane; as a result, the yield of chlorodecanes decreases. The further transformation of the  $\text{CH}_3\dot{\text{C}}\text{HOH}$ -radical into alcohol oxidation products (aldehyde and vinyl chloride) can occur by its interaction with a complex of Cu(II) or with  $\text{CCl}_4$ .

For the analysis of catalyst evolution in the presence of ethanol, we recorded the EPR spectra of the immobilized complex at different stages of the process (Fig. 3). As shown above, the initial spectrum is a singlet with unresolved hyperfine structure characteristic of the chloride complexes of copper in the presence of the spin-exchange interaction of spatially ordered closely spaced paramagnetic centers. The spectrum changes upon the addition of the alcohol: against the background of a singlet, signals from three complexes appear. For two of these complexes, it was possible to determine the following parameters:  $g_{\parallel} = 2.46$ ,  $g_{\perp} =$

**Table 5.** Effect of the polarity of an additive on the yield of chlorodecanes on the  $\text{CuCl}_2\text{--EtPrImCl--SiO}_2$  catalyst

Additive	Permittivity [11]	Yield of chlorodecanes, %
No additive	—	34
Triethylamine	2.4	15
Ethanol	24.3	52
Methanol	32.6	36
Acetonitrile	37.5	25
Water	81	23

Note: The reaction conditions are specified in Table 2. The amount of additive is 0.05 mL.

2.15, and  $A = 100\text{--}110$  G (I) and  $g_{\parallel} = 2.39$ ,  $g_{\perp} = 2.15$ , and  $A = 120$  G (II). This spectrum is typical of mixed-ligand complexes of copper with different numbers of chloride ions and alcohol molecules in the coordination sphere [13]. In the course of the reaction, the spectrum disappears because of the reduction of Cu(II) ions to Cu(I). After the completion of the reaction, the initial singlet with the unresolved hyperfine structure was restored in the spectrum and, according to the results of GC–MS analysis, ethanol was completely oxidized to acetaldehyde, vinyl chloride, and chloroethane. As a result, at a certain stage of the process, the initial complex is regenerated; thus, it can be considered as a valuable catalytic system. This argument is consistent with kinetic data.

The results obtained in this work demonstrate that the strong immobilization of the catalytic complex on a support along with the use of a donor additive makes it possible to obtain active and stable heterogeneous catalysts for the chlorination of alkanes with carbon tetrachloride.

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## REFERENCES

1. Tarkhanova, I.G., Smirnov, V.V., Krotova, I.N., Zelikman, V.M., Shabalin, D.A., Novikova, M.D., and Spiridonov, V.S., *Khim. Prom—st. Segodnya*, 2010, no. 7, p. 23.
2. Golubeva, E.N., Kharitonov, D.N., Kochubey, D.I., Ikorskii, V.N., Kriventsov, V.V., Kokorin, A.I., Stoetsner J., and Bahnmann, D.W., *J. Phys. Chem. A*, 2009, vol. 113, p. 10219.
3. Sasaki, T., Zhong, C., Tada, M., and Iwasawa, Y., *Chem. Commun.*, 2005, p. 2506.
4. Sasaki, T., Tada, M., Zhong, C., Kume, T., and Iwasawa, Y., *J. Mol. Catal. A: Chem.*, 2008, vol. 279, p. 200.
5. Smith, D.W., *Coord. Chem. Rev.*, 1976, vol. 21, p. 93.
6. Freidlina, R.Kh., Gasanov, R.G., Kuz'mina, N.A., and Chukovskaya, E.Ts., *Usp. Khim.*, 1985, vol. 54, p. 1127.
7. Khusnutdinov, R.I., Shchadneva, N.A., Oshnyakova, T.M., and Dzhemilev, U.M., *Pet. Chem.*, 2009, vol. 49, p. 331.
8. Khusnutdinov, R.I., Shchadneva, N.A., Baiguzina, A.R., and Lavrent'eva, Yu.Yu., *Pet. Chem.*, 2004, vol. 44, p. 126.
9. Khusnutdinov, R.I., Shchadneva, N.A., Baiguzina, A.R., Mukminov, R.R., Mayakova, Yu.Yu., Smirnov, A.A., and Dzhemilev, U.M., *Pet. Chem.*, 2008, vol. 48, p. 471.
10. Smirnov, V.V., Levitskii, M.M., Tarkhanova, I.G., Nevskaya, S.M., and Golubeva, E.N., *Kinet. Catal.*, 2001, vol. 42, no. 4, p. 506.
11. Reichardt, C., *Solvents and Solvent Effects in Organic Chemistry*, Weinheim: VCH, 1988.
12. Gritsan, N.P., Plyusnin, V.F., and Bazhin, N.M., *Teor. Eksp. Khim.*, 1986, vol. 22, p. 39.
13. Larin, G.M., Minin, V.V., Levin, B.V., and Buslaev, Yu.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, no. 12, p. 2725.