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Immobilized Complexes of Copper(II) Chloride with Triethylenetetramine as Catalysts for the Reaction of C–Cl Bond Metathesis

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Abstract—The structure and activity of C–Cl bond metathesis catalysts containing $CuCl_2$ and triethylenetetramine (TETA) supported on silica were studied. The catalysts were found to contain ~40% Cu(II) as paramagnetic complexes of the composition $Cu(TETA)_2Cl_2$ and diamagnetic binuclear or polynuclear copper complexes, which are undetectable by EPR spectroscopy. The catalytic activity of the test systems in the radical reaction of C–Cl bond metathesis in the CCl_4–$C_{10}H_{22}$ system was maximum at a Cu(II) concentration of ~0.5 wt % on the support. A kinetic scheme was proposed, which suggests that only mononuclear copper complexes participate at the stage of radical generation, whereas termination can also occur on binuclear or polynuclear complexes.

INTRODUCTION

The reaction of C–Cl bond metathesis is the exchange of a chlorine atom in a polychlorinated organic compound for hydrogen from an aliphatic hydrocarbon (RH):

$$CCl_4 + RH \longrightarrow CHCl_3 + RCl.$$

Copper(II) chloride complexes with dimethylformamide (DMF) supported on silica are successfully used as catalysts of this reaction [1–4]. It is well known [5–7] that alkyl halides can oxidize the copper(I) complexes formed under the reaction conditions to give free trichloromethyl radicals:

$$[Cu(I)Cl_2]^- + CCl_4 \longrightarrow [Cu(II)Cl_3]^- + CCl_3^{\bullet}. \qquad (I)$$

Next, the reaction occurs by a chain-radical mechanism [8] as follows:

$$CCl_3^{\bullet} + RH \longrightarrow CHCl_3 + R^{\bullet}, \qquad (II)$$

$$R^{\bullet} + CCl_4 \longrightarrow RCl + CCl_3^{\bullet}. \qquad (III)$$

Copper(II) complexes can react with radicals to regenerate active centers [9]:

$$[Cu(II)Cl_3]^- + R^{\bullet} \longrightarrow [Cu(I)Cl_2]^- + RCl. \qquad (IV)$$

We found that under conditions of catalytic metathesis DMF decomposes to form dimethylamine and CO. In this case, the kinetic curves of the buildup of metathesis products exhibit a portion of self-acceleration. An induction period disappears if a small amount of an amine (for example, dimethylamine) is added to the initial solution [10]. This fact may indicate that the copper complexes with amines formed in the system are active catalysts of the metathesis reaction. Systems based on copper(II) chloride and amines are also of interest because they allow an alternative path of radical formation. According to Weiss *et al.* [11], amines reduce copper with the formation of radical ion species. The deprotonation of these species by the interaction with, for example, another amine molecule can result in the formation of free radicals. These latter can initiate a chain process by the reaction with CCl_4.

The subject matter of this work is a study of the structure and catalytic properties of copper(II) chloride complexes with triethylenetetramine (TETA) supported on Silochrome in the reaction of C–Cl bond metathesis using the CCl_4–$C_{10}H_{22}$ system as an example.

EXPERIMENTAL

Carbon tetrachloride, decane, and ethanol were purified according to well-known procedures [12] and additionally dried with molecular sieves 4 Å. Anhydrous copper(II) chloride was prepared from the crystal hydrate by the procedure in [13]; TETA of reagent grade was used without additional purification.

Silochrome—mesoporous silica with a uniform pore distribution and a specific surface area of 100 m^2/g (pore diameter of ~10 nm; particle size of 0.2–0.4 mm)—was used as a support. Adsorbed water was removed from Silochrome by long-term evacuation at 10^{-3} torr and 140°C.

Supported catalysts were prepared as follows: 0.5 ml of TETA and a specified amount of copper(II) chloride were dissolved in 10 ml of ethanol; after adding 0.5 g of Silochrome to the solution, the solvent was

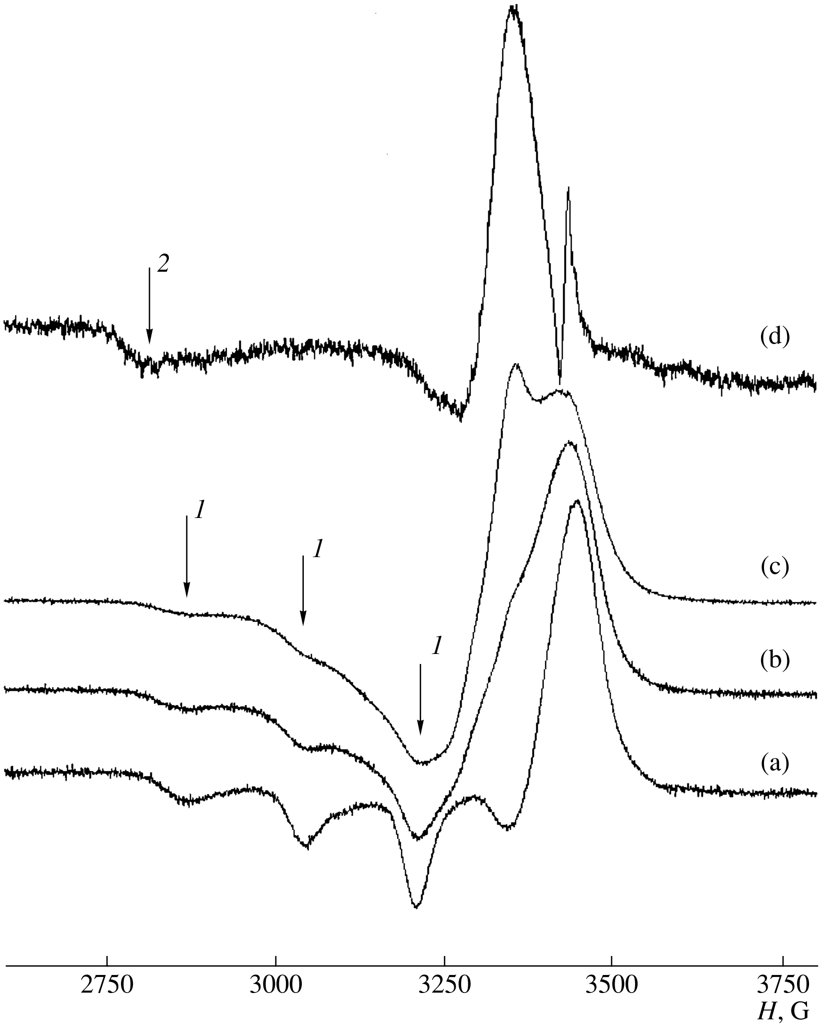

Fig. 1. EPR spectra (77 K) of catalysts with copper concentrations (wt %) of (a) 0.2 (catalyst IV), (b) 1.0 (catalyst VI), and (c) 2.0 (catalyst VII) before reaction and (d) of catalyst VI after reaction. (*1*, *2*) HFS components with parameters specified in Table 2.

evaporated on a rotary evaporator; the catalysts were stored in an inert atmosphere in tightly stoppered vessels. A reference sample containing no copper chloride was prepared in a similar manner. In all catalysts, the TETA content was 6.7×10^{-3} mol per one gram of support; Table 1 summarizes the copper content.

Table 1. Copper content of test catalysts

Catalyst	Copper added	
	wt %	mol/g Silochrome
I	0	0
II	0.025	2.7×10^{-6}
III	0.1	1.5×10^{-5}
IV	0.2	2.3×10^{-5}
V	0.5	7.8×10^{-5}
VI	1.0	1.6×10^{-4}
VII	2.0	3.1×10^{-4}

The metathesis reaction in the CCl_4–$C_{10}H_{22}$ system was performed at 150°C and the ratio $[CCl_4] : [C_{10}H_{22}] = 4 : 1$ as described previously [3]. The products were analyzed on a Model 3700 chromatograph with a flame-ionization detector and a 1.5-m column packed with 5% SE-30 on Chromaton. The products were separated under conditions of linear temperature programming. The product identification was performed by a comparison with reference substances. To perform quantitative measurements, the detector was calibrated using mixtures with known ratios between components.

The solutions of $CuCl_2$ and TETA for EPR studies were prepared as follows: 0.0034 g of $CuCl_2$ and 0.0037, 0.0073, or 0.0146 g of TETA were dissolved in 5 ml of ethanol (96%) to obtain a TETA : Cu(II) ratio of 1 : 1, 2 : 1, or 4 : 1, respectively (copper concentration in solution was 5×10^{-3} mol/l).

The EPR spectra of supported catalysts and frozen solutions were measured on a Varian E-3 EPR spectrometer at 77 K. To accurately calibrate the *g*-factor scale, the following reference substances were used: Mn^{2+} ions in an MgO matrix and a 5×10^{-3} M $Cu(NO_3)_2$ solution in a mixture of CD_3OD and D_2O (1 : 1). The number of paramagnetic centers in a sample (N_x) was determined by the double integration of spectra in comparison with the standard sample of a $CuCl_2 \cdot 2H_2O$ single crystal with a known number of spins.

RESULTS AND DISCUSSION

The EPR spectrum of the initial catalyst at a Cu(II) content lower than 0.2 wt % (catalyst IV) corresponds to the spin Hamiltonian with axially symmetrical *g*-tensor and HFS constant (Fig. 1a). At a Cu(II) content higher than 1 wt % (catalyst VI), HFS components exhibit a considerable broadening because of magnetic dipole–dipole interactions between complexes (Fig. 1b). At a 2 wt % concentration of Cu(II) on the support (catalyst VII), along with a significant broadening of HFS lines, a singlet component appeared in the EPR spectrum (Fig. 1c), probably because of spin exchange between copper complexes. It is believed that these changes are associated with differences in the local concentrations of Cu(II) ions on the surface of Silochrome.

To determine the composition of copper complexes formed on the surface of the support, we analyzed the EPR spectra of $CuCl_2$ and TETA solutions in ethanol over a wide range of TETA : Cu(II) ratios, and a water–ethanol solution of $Cu(NO_3)_2$ (Fig. 2). This allowed us to obtain the spin Hamiltonian parameters $g_{||}$, $g_{\perp}$, and $A_{||}$ for the spectra of copper complexes containing different ligands in the coordination sphere, in particular, TETA and chloride ions simultaneously, and to compare them with analogous values for supported complexes. Table 2 summarizes the found values.

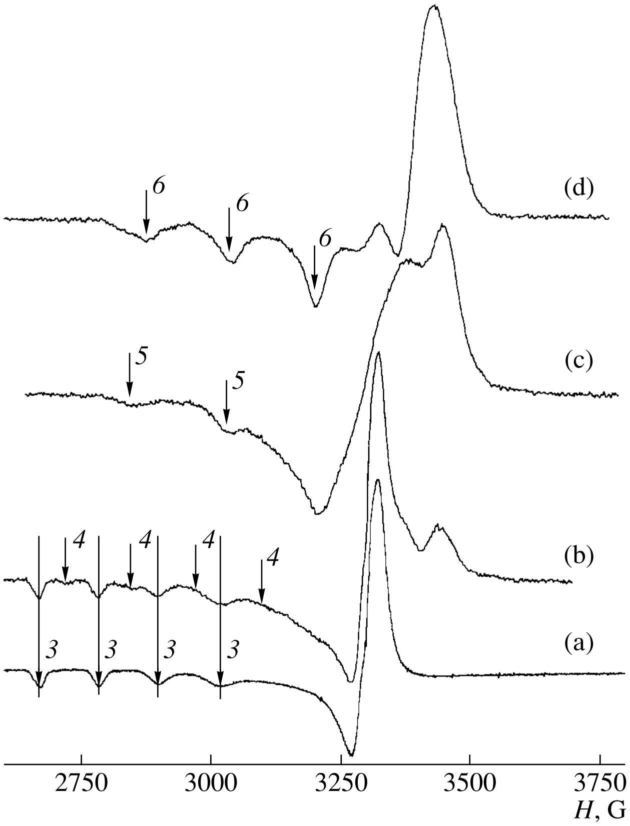

Fig. 2. EPR spectra (77 K) of solutions of (a) $Cu(NO_3)_2$ in 50% aqueous ethanol and of $CuCl_2$ and TETA in ethanol at [TETA] : [Cu(II)] = (b) 1, (c) 2, or (d) 4; [Cu(II)] = 5×10^{-3} mol/l. (*3*–*6*) HFS components with parameters specified in Table 2.

An analysis of the EPR spectra shown in Fig. 2 demonstrated the presence of four types of signals *3*–*6*, which are clearly defined in the region of components that correspond to a parallel orientation with respect to the external magnetic field (Fig. 2). The parameters of HFS lines *3* correspond to an aqua complex of copper

Table 2. Parameters of the EPR spectra of $CuCl_2$ complexes with TETA adsorbed on a Silochrome surface or in a water–ethanol medium at 77 K

No.	Sample	EPR parameters			Assumed composition of the complex
		$A_{\|\|} \pm 3$, G	$g_{\|\|} \pm 0.005$	$g_{\perp} \pm 0.005$	
1	Initial catalyst VI	167	2.202	2.045	$Cu(TETA)_2Cl_2$
2	Catalyst VI after reaction	–	2.44*	2.08*	–
3	Solution of $Cu(NO_3)_2$ in an ethanol–water mixture (1 : 1)	117	2.420	2.091	$Cu(H_2O)_6^{2+}$
4	Solution of TETA and $CuCl_2$ (1 : 1) in ethanol	130	2.356	–	$CuCl_2(EtOH)_4$
5	Solution of TETA and $CuCl_2$ (2 : 1) in ethanol	184	2.200	2.072	$Cu(TETA)Cl_2$
6	Solution of TETA and $CuCl_2$ (4 : 1) in ethanol	164	2.201	2.070	$Cu(TETA)_2Cl_2$

* Measurement error in the *g*-factor is ±0.01.

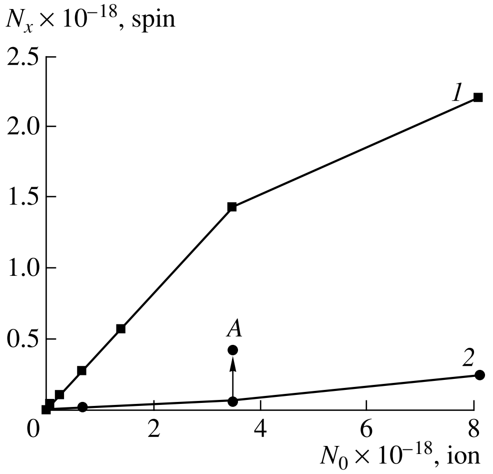

Fig. 3. Number of paramagnetic centers on the catalyst (N_x) as a function of the amount of copper on the support (N_0) (*1*) before reaction and (*2*) after reaction performed for 30 min. Point *A* corresponds to the value of N_x after storage of the sample in air for 5 days.

and are consistent with the published data [14]. EPR signals *4* are typical of neutral chloride–alcohol complexes [14] and correspond to a complex of the composition $CuCl_2(EtOH)_4$. HFS lines *5* and *6* were obtained with an excess of TETA. Signals *6* were observed in a more than twofold excess of ligand molecules; hence, it follows that nitrogen atoms, which, in our opinion, belong to two TETA molecules, enter the coordination sphere of the Cu(II) ion. Copper(II) complexes of the same composition were observed in water–alcohol solutions of TETA and $Cu(NO_3)_2$ [15].

The EPR spectrum of complexes at a molar ratio between TETA and Cu equal to two (Fig. 2c) is a superposition of signal *5* and a broad singlet line, which is inconvenient for accurately measuring the values of $A_{||}$ and $g_{||}$. The estimated values (Table 2) and a comparison with published data [15] allowed us to suggest that HFS lines *5* correspond to a complex of the composition $Cu(TETA)Cl_2$. The appearance of a singlet signal in the EPR spectra of solutions of copper complexes measured at 77 K is possible only with the strong spin–spin interaction of Cu(II) ions at the average distance between them no longer than 7–9 Å [16]. This situation can take place if a portion of TETA oligomers coordinates two copper ions to each form small-sized polynuclear structures. It is easy to see that HFS parameters *1* of the spectrum shown in Fig. 1a, which correspond to $CuCl_2$ complexes with TETA supported on Silochrome, are close to HFS parameters *6* of the spectrum in Fig. 2d. Consequently, we may believe that complexes of the composition $Cu(TETA)_2Cl_2$ are predominant on the surface of the support.

The EPR spectrum of a catalyst after performing the reaction (Fig. 1d) is dramatically different from the initial spectrum. Along with a sharp decrease in the integral intensity, the shape of the spectrum and the spin Hamiltonian parameters changed considerably. The shape of the spectrum is indicative of the presence of several types of complexes in the sample. It is likely that these complexes are different in the structure and composition of the coordination sphere of Cu(II) ions. Therefore, Table 2 summarizes the apparent values of $A_{||}$ and $g_{||}$. Based on the estimated value of $g_{||}$, the paramagnetic Cu(II) complexes detected after the reaction do not contain TETA molecules as ligands. Note that all catalyst samples after the reaction exhibited a narrow symmetrical signal with $g = 2.005 \pm 0.001$ and the line width $\Delta H = 11–12$ G. We failed to identify the nature of paramagnetic species responsible for this signal; it is believed that this is the $CCl_3^{\bullet}$ radical stabilized on the Silochrome surface.

Figure 3 demonstrates the number of paramagnetic centers detected by EPR as a function of the total number of copper ions in the catalyst adsorbed on the support. It can be seen that the number of paramagnetic Cu(II) ions in initial catalysts is lower than the total number of copper ions on the support by a factor of ~2.5. We believe that this is due to the aggregation of bivalent copper compounds to form polynuclear (two or more atoms) diamagnetic clusters, as is a well-known fact for many oxide supports (see, for example, [17, 18]).

Figure 3 also demonstrates a decrease in the number of paramagnetic centers in the course of reaction: the number of the centers decreased by a factor of ~10 in 30 min. This is likely due to the reduction of Cu(II) to Cu(I) because the signal intensity increased again after exposure to air because of a partial oxidation of Cu(I) by atmospheric oxygen.

The catalytic activity of the prepared catalysts in the reaction of C–Cl bond metathesis was found to be comparable to the activity of previously studied supported complexes of copper chloride with DMF. Chlorodecane, chloroform, and C_2Cl_6 (the product of recombination of trichloromethyl radicals) in minor amounts (no more than 1%) were detected as the products of the reaction of CCl_4 with $C_{10}H_{22}$. Figure 4 demonstrates the kinetic curves of chlorodecane buildup. Note that TETA supported on silica initiates the metathesis reaction only slightly. Figure 5 shows the initial rates of the metathesis reaction as functions of copper concentration on the support for two catalysts containing DMF and TETA. In both cases, the functions exhibit extremums. One possible explanation for this phenomenon is that only mononuclear copper-containing centers take part in chain initiation, whereas the decay of radicals by reaction (IV) can take place on any, including polynuclear, copper complexes.

The mechanism of the overall reaction involves a great number of steps with unknown rate constants; therefore, the kinetics is difficult to simulate. At the same time, from the above reasoning, we can qualitatively describe the dependence of the reaction rate on the metal concentration. For simplicity, we take that the efficiency of initiation with the participation of Cu(I) and Cu(II) is equal. Next, we assume that radical chains are also terminated on Cu(I) and Cu(II) complexes with similar rate constants. Note that, according to Navon *et al.* [19], chloride complexes of copper(I) can bind active radicals to form inactive complexes and hence participate in the chain termination

$$\{\mathrm{Cu(I)}\} + \mathrm{R}^{\bullet} \rightleftarrows \{\mathrm{Cu(II)–R}\}.$$

Neglecting the reactions of copper-containing complexes with alkyl radicals for simplicity, a simplified reaction scheme can be written as follows:

$$\mathrm{CCl_4} \xrightarrow{\{\mathrm{Cu}\},\, k_1} \dot{\mathrm{C}}\mathrm{Cl_3},$$

$$\dot{\mathrm{C}}\mathrm{Cl_3} + \mathrm{RH} \xrightarrow{k_2} \mathrm{CHCl_3} + \dot{\mathrm{R}},$$

$$\dot{\mathrm{R}} + \mathrm{CCl_4} \xrightarrow{k_3} \mathrm{RCl} + \dot{\mathrm{C}}\mathrm{Cl_3},$$

$$\mathrm{C\dot{C}l_3} + \{\mathrm{Cu}\} \xrightarrow{k_4} \text{termination},$$

$$\mathrm{C\dot{C}l_3} + \{\mathrm{Cu_2}\} \xrightarrow{k_5} \text{termination},$$

$$2\mathrm{C\dot{C}l_3} \xrightarrow{k_6} \text{termination},$$

$$2\{\mathrm{Cu}\} \overset{K}{\rightleftarrows} \{\mathrm{Cu_2}\},$$

where {Cu} denotes all types of species containing a single copper ion; $\{\mathrm{Cu_2}\}$ denotes dimeric complexes; and {Cu(I)} and {Cu(II} denote all types of species containing copper(I) and copper(II), respectively.

On the assumption of steady-state concentrations of $\dot{\mathrm{C}}\mathrm{Cl_3}$ and $\mathrm{R}^{\bullet}$ radicals, the reaction rate w can be expressed in terms of this scheme as

$$w = k_3[\mathrm{R}^{\bullet}][\mathrm{CCl_4}] = k_2[\mathrm{RH}][\dot{\mathrm{C}}\mathrm{Cl_3}]. \qquad (1)$$

At low copper concentrations, when quadratic termination is predominant, we have

$$w = k_2[\mathrm{RH}](k_1/2k_6)^{0.5}[\mathrm{CCl_4}]^{0.5}[\{\mathrm{Cu}\}]^{0.5}, \qquad (2)$$

and the reaction rate increases with the concentration of {Cu}. At higher concentrations of {Cu}, when termination with the participation of copper becomes a determining factor, we obtain

$$w = k_1k_2[\mathrm{RH}][\mathrm{CCl_4}][\{\mathrm{Cu}\}]/(k_4[\{\mathrm{Cu}\}] + k_5K[\{\mathrm{Cu}\}]^2). \qquad (3)$$

Thus, in this case, the reaction rate decreases with [{Cu}]. Taking into account that the concentration of mononuclear copper complexes {Cu} is related to the concentration of total copper $\{\mathrm{Cu}\}_0$ by the equation

$$[\{\mathrm{Cu}\}] = \frac{-1 + \sqrt{1 + 8K[\{\mathrm{Cu}\}_0]}}{4K}, \qquad (4)$$

the dependence of the reaction rate on the total copper concentration exhibits a maximum.

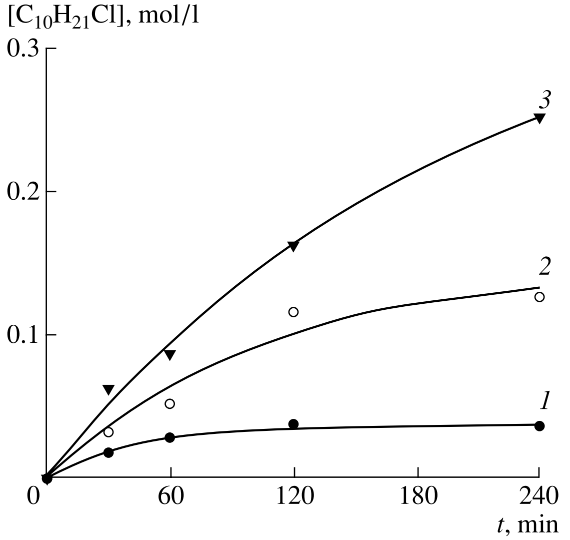

Fig. 4. Kinetic curves of the buildup of chlorodecane in the presence of catalysts with copper concentrations (wt %) of (*1*) 0, (*2*) 0.025, and (*3*) 0.1.

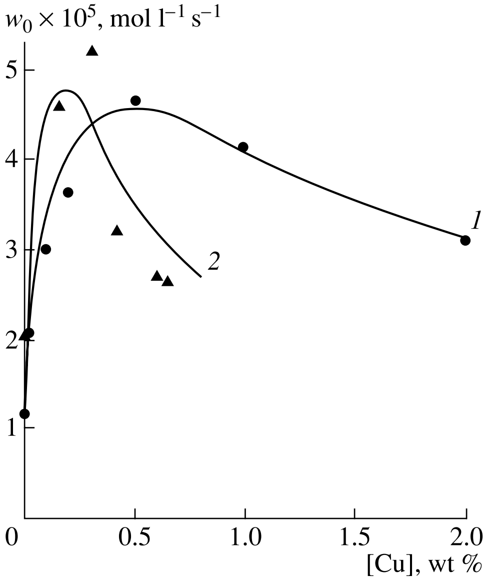

Fig. 5. Initial rate of the metathesis reaction as a function of copper concentration in catalysts for $\mathrm{CuCl_2}$ complexes with (*1*) TETA and (*2*) DMF. Points depict experimental data, and curves demonstrate data calculated by Eqs. (1)–(4) at the following rate constants of the steps: (*1*) $K = 0.1$ l/mol; $k_1 = 4.0 \times 10^7$; $k_2 = 0.16$; $k_4 = 5.0 \times 10^3$; $k_5 = 2.0 \times 10^6$; $k_6 = 1.0 \times 10^3$; (*2*) $K = 5.0 \times 10^{-3}$ l/mol; $k_1 = 6.0 \times 10^7$; $k_2 = 0.23$; $k_4 = 1.0 \times 10^3$; $k_5 = 2.0 \times 10^8$; $k_6 = 1.0 \times 10^3$ (k_i in l mol^{-1} s^{-1}).

Figure 5 demonstrates approximating curves plotted with the use of Eqs. (1)–(4) with a conceivable set of constants.

Although a number of assumptions were made in deriving Eqs. (2) and (3), the qualitative conclusion is beyond question: ideas of the participation of dimeric copper complexes in termination (rather than initiation) allow us to adequately describe the shape of the rate of reaction of CCl_4 with alkanes plotted as a function of the total concentration of copper complexes.

Thus, in this work, we found the composition of copper(II) chloride complexes with TETA supported on silica. In these complexes, ~30% copper exists as diamagnetic species; we suggested that this is due to the formation of binuclear or polynuclear copper complexes. We found that the initial rate of metathesis is an extremal function of copper concentration on the support. This function could be a consequence of the fact that structurally different copper-containing complexes take part at the stages of the initiation and decay of radicals.

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