ISSN 0023-1584, Kinetics and Catalysis, 2007, Vol. 48, No. 5, pp. 711–715. © MAIK "Nauka/Interperiodica" (Russia), 2007.
Original Russian Text © I.G. Tarkhanova, M.G. Gantman, V.M. Zelikman, V.V. Smirnov, 2007, published in Kinetika i Kataliz, 2007, Vol. 48, No. 5, pp. 761–765.

Reactions of Polyhalomethanes with Olefins Catalyzed by Copper Complexes with Aromatic Amino Alcohols

I. G. Tarkhanova, M. G. Gantman, V. M. Zelikman, and V. V. Smirnov
Faculty of Chemistry, Moscow State University, Moscow, 119991 Russia
e-mail: ITAR_msu@mail.ru

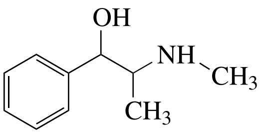
Received March 23, 2006

Abstract—Copper complexes with amino alcohols structurally similar to ephedrin (1-phenyl-3-(*N*-methylamino)propan-1-ol and 1-phenyl-2-(*N*-methylamino)ethanol) are catalytically very active in the free-radical addition of CCl_4 and CBr_4 to linear alk-1-enes. These amino alcohols themselves are initiators of radical addition reactions, and, in the reaction with CBr_4, they are more active than the metal complexes. In the presence of the amino alcohols, as distinct from classical radical initiators, the reaction is highly selective and affords an addition product. An analysis of kinetic equations and the data obtained for the reaction involving $CHCl_3$ suggest that the amino alcohols and the corresponding metal complexes are involved in different ways in the addition of CCl_4 and CBr_4 to linear alk-1-enes.

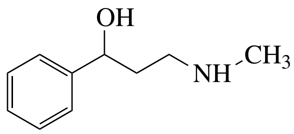
DOI: 10.1134/S0023158407050163

INTRODUCTION

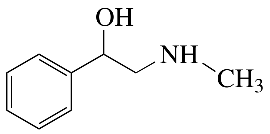
The copper complex with the natural amino alcohol ephedrin reacts with CCl_4 at room temperature to form the trichloromethyl radical [1]. Therefore, it seems promising to use similar complexes as catalysts of radical reactions of polyhaloalkanes. In the present work, the catalytic properties of copper complexes with amino alcohols structurally similar to ephedrin, namely, 1-phenyl-3-(*N*-methylamino)propan-1-ol (**I**) and 1-phenyl-2-(*N*-methylamino)ethanol (**II**), were studied in the free-radical addition of CCl_4 and CBr_4 to linear alk-1-enes.



Ephedrin



I



II

EXPERIMENTAL

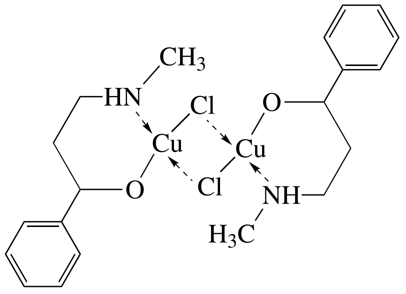
The copper complexes were synthesized as follows. An equimolar amount of an amino alcohol was added to a solution of CuCl (0.11 g, 0.001 mol) in acetonitrile (25 ml). A dark green precipitate that resulted from the addition of amino alcohol **I** was filtered and dried in air. No precipitate was formed when compound **II** was used, and acetonitrile was distilled off in vacuo. The copper content of the complexes was determined by chelatometric titration with EDTA in the presence of the 1-(2-pyridineazo)-2-naphthol indicator [2].

The reaction of oct-1-ene with CCl_4 was carried out in the temperature range of 80 to 130°C using a procedure described in [3]. The concentration of the complexes in CCl_4 was varied between 0.015 and 0.04 mol/l, and the olefin concentration ranged between 0.6 and 1.3 mol/l. Chloroform was added using the same procedure at 130°C for 15–20 h. The concentrations of the reactants were the following: 0.015 mol/l of the initiator (benzoyl peroxide, 1-phenyl-2-(*N*-methylamino)ethanol, or its complex with copper) and 0.64 mol/l of octene. Chloroform was the solvent. The addition of CBr_4 to hex-1-ene was carried out at 100–130°C. Standard samples contained 0.015 mol/l amino alcohol **I** or its complex with copper, 0.064 mol/l olefin, and 0.64 mol/l tetrabromomethane in a nonane solution. The products were identified chromatographically on a Kristall-4000 instrument with a flame-ionization detector. The products of the reaction with CCl_4 were analyzed using a 3-m-long packed column (nonpolar silicone SE-30 as the stationary phase) in the temperature-programmed mode. The bromine-containing products were analyzed on a 30-m-long capillary column (nonpolar silicone SE-50 as the stationary phase) in the temperature-programmed mode. The products were identified by comparing their retention indices with reference data [4]. Selectivity was determined as the ratio of the addition product yield to the total olefin conversion.

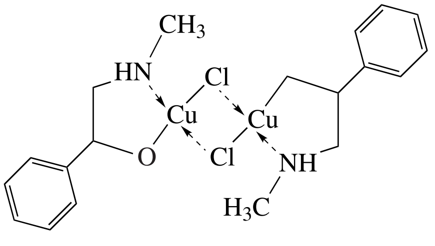
In the reactions involving CCl_4, the kinetic parameters were determined from the initial rates. The reaction orders were determined only with respect to the catalyst and olefin because CCl_4 was in a more than tenfold excess over olefin and a decrease in its concentration would inevitably greatly change the selectivity of the reaction [5].

RESULTS AND DISCUSSION

The results of chelatometric titration show that the metal, ligand, and chlorine in the copper complexes with **I** and **II** are in the 1 : 1 : 1 molar ratio. Based on this and published data on the geometry of the copper complex with the structural analog of the used amines (ephedrin) [1], we can assume that the compounds synthesized have the following structures:



Ia



IIa

Both complexes exhibit high activity in the reactions of olefins with CCl_4 throughout the temperature range examined. The main products of both reactions are equimolar adducts: 1,1,1,3-tetrachloroalkanes and 1,1,1,3-tetrabromoalkanes, respectively. Together with the addition products, the products of allyl substitution (mainly the corresponding 3-haloalk-1-enes) were found in insignificant amounts. The telomerization product content did not exceed 1%.

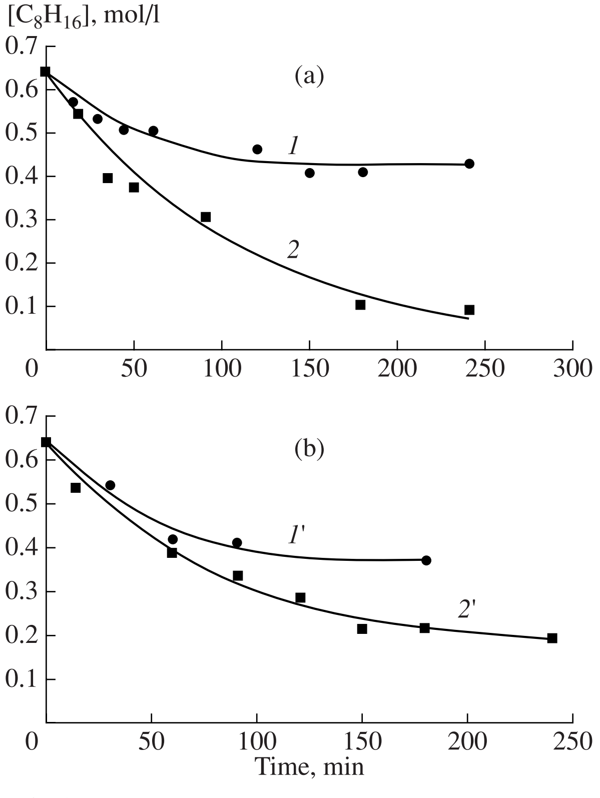


Fig. 1. Kinetics of the consumption of (a) octene in the presence of (*1*) **I** and (*2*) its copper-containing complex **Ia** and (b) oct-1-ene in the presence of (*1*') **II** and (*2*') its copper-containing complex **IIa**. Reaction conditions: temperature 130°C, $[CCl_4] = 9.6$ mol/l, $[C_8H_{16}] = 0.63$ mol/l, and [initiator] = 0.015 mol/l.

It turned out that both the metal-containing complexes and individual aromatic amino alcohols exhibit high activity and selectivity in the reactions studied, although the activity of the complexes is somewhat higher in the reaction with CCl_4 [6]. In the absence of the metal, the pure amino alcohol is rapidly consumed and the reaction ceases (Fig. 1a). This behavior is characteristic of radical initiators being irreversibly consumed, for instance, organic peroxides. However, unlike the amino alcohols, classical radical initiators, for example, benzoyl peroxide, perform the reaction nonselectively: under similar conditions, the yield of the addition product does not exceed 40% and the telomerization and substitution products are mainly formed. The activity and high selectivity of the pure amino alcohols in the reaction examined can be due to the intermediate formation of stable benzyl radicals and the participation of the corresponding amines in chain transfer (this problem was discussed in detail earlier [6]).

The effect is more pronounced in the reaction involving CBr_4: the initial step of the reaction proceeds much more rapidly in the presence of the amino alcohol than in the presence of the corresponding complex. Data characterizing the activity of the catalytic systems in the addition of CBr_4 to hex-1-ene are given in the table (the use of an olefin lighter than that in the reaction with CCl_4 is explained by the difficulties in the chromatographic analysis of heavy polybromosubstituted compounds; in this case, the rate of addition is virtually independent of the substrate used, namely, hex-

1,1,1,3-Tetrabromoheptane yield in the reactions of hex-1-ene with CBr_4 in the presence of different initiators (reaction time of 1 h)

Initiator	Yield, %	
	100°C	130°C
Copper complex with 1-phenyl-2-(*N*-methylamino)propan-1-ol (**IIa**)	11	42
1-Phenyl-2-(*N*-methylamino)propan-1-ol	41	68

1-ene or oct-1-ene). As can be seen from the data in the table, both at 100 and 130°C, in the initial step the yield of the addition product in the presence of the pure amino alcohol is much higher than that in the presence of the complex.

It was found that the kinetics of the processes initiated by the complexes and individual amino alcohols differ. The octene consumption curves for the reaction with CCl_4 in the presence of both complexes and amino alcohols are shown in Fig. 1. As can be seen, in the presence of the amino alcohols, the reaction ceases in approximately 1.5–2 h, whereas no similar retardation is observed in the presence of the metal complexes. The plots of the logarithm of the initial rate of product formation versus the logarithms of the initial concentration of the olefin and initiator are shown in Figs. 2 and 3, respectively. The kinetic equation derived from the initial rates in the presence of the metal complexes has the form

$$-\frac{d[C_8H_{16}]}{dt} = k_{app}[CuLCl][C_8H_{16}], \qquad (1)$$

where [CuLCl] is the concentration of complex **Ia**.

For the initiation of this reaction by the pure amino alcohols, another kinetic equation was obtained

$$-\frac{d[C_8H_{16}]}{dt} = k'_{app}[L], \qquad (2)$$

where [L] is the concentration of amino alcohol **I**.

The difference between Eqs. (1) and (2) led us to conclude that the reaction mechanism in the presence of the individual amino alcohols differs from that in the presence of their copper complexes. Kinetic equation (1) corresponds to the scheme describing the so-called coordination mechanism [7, 8]:

$$Cu^{2+}LCl \xrightarrow{k_1} Cu^{+}L^{+*}Cl,$$

$$Cu^{+}L^{+*}Cl + CCl_4 \xleftrightarrow{k_2,\, k_{-2}} Cl_3C{-}Cl{\cdots}Cu^{+}L^{+*}Cl,$$

$$Cl_3C{-}Cl{\cdots}Cu^{+}L^{+*}Cl + C_8H_{16}$$

$$\xrightarrow{k_3} L^{+*}ClCu^{2+}Cl^{-}{\cdots}Cl_3C{-}CH_2{-}\dot{C}H{-}(CH_2)_5CH_3,$$

$$L^{+*}ClCu^{2+}Cl^{-}{\cdots}Cl_3C{-}CH_2{-}\dot{C}H{-}(CH_2)_5CH_3$$

$$\xrightarrow{k_4} Cu^{+}L^{+*}Cl + Cl_3C{-}CH_2{-}C(Cl)H{-}(CH_2)_5CH_3,$$

where L^{+*} is the oxidized form of the ligand. This mechanism obeys the kinetic reaction

$$-\frac{d[C_8H_{16}]}{dt} = \frac{k_2k_3[Cu^{+}L^{+*}Cl][C_8H_{16}][CCl_4]}{k_{-2} + k_3[C_8H_{16}]},$$

which is transformed into (1) under the condition $k_{-2} \gg k_3[C_8H_{16}]$.

In this mechanism, the key step is the oxidation of the Cu(I) ion in the complex by the corresponding halogen derivative [8]. However, the reaction of the Cu^+ complex with chloroalkane is reversible. This fact is in good agreement with the first order of the kinetic equation with respect to olefin [9].

As follows from the analysis of kinetic equation (2) (the zeroth order with respect to olefin and the first order with respect to L), the amino alcohol itself acts as the initiator, like peroxides, and the reaction in its presence proceeds via a free-radical mechanism [10]. In the first step, the amino alcohol is oxidized by carbon tetrachloride to form trichloromethyl radicals and the oxidized forms of the amino alcohol (*N*-chloroamine, α-chloroamine), probably through the formation of a radical-cation iminium salt. Similar reactions involving amines were described earlier [9, 11]. The trichloromethyl radical adds to the olefin to form the 1-(1',1',1'-trichloromethyl)octyl radical, which abstracts a chlo-

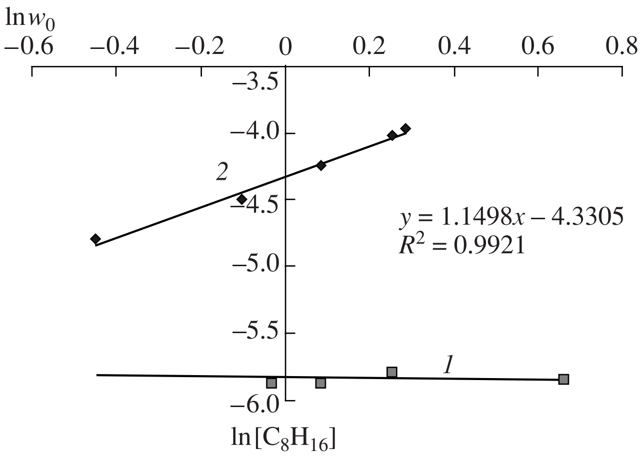


Fig. 2. Determination of the reaction order with respect to olefin in the presence of (*1*) amino alcohol **I** and (*2*) complex **Ia** (130°C).

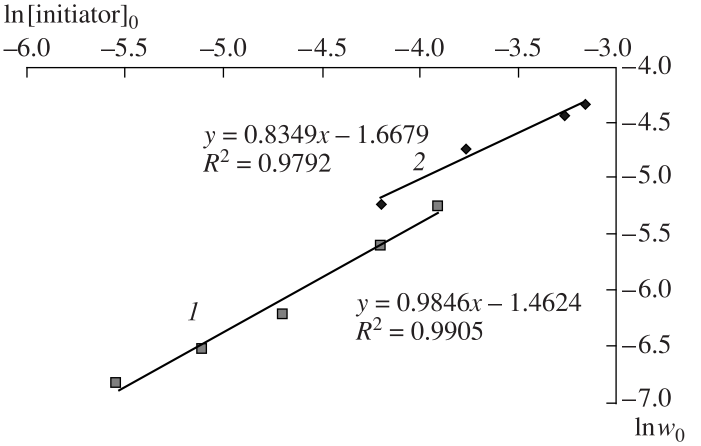


Fig. 3. Determination of the reaction order with respect to the initiator in the presence of (*1*) amino alcohol **I** and (*2*) complex **Ia** (130°C).

rine atom from the oxidized amino alcohol molecule or a carbon tetrachloride molecule

$$\mathrm{L + CCl_4 \xrightarrow{k_1} L^{Ox}{-}Cl + \dot{C}Cl_3}, \tag{I}$$

$$\mathrm{\dot{C}Cl_3 + C_8H_{16} \xrightarrow{k_2} CCl_3{-}CH_3{-}\dot{C}H{-}(CH_2)_5{-}CH_3}, \tag{II}$$

$$\begin{gathered}\mathrm{CCl_3{-}C\dot{H}_2{-}CH{-}(CH_2)_5{-}CH_3 + L^{Ox}{-}Cl}\\ \mathrm{\xrightarrow{k_3} CCl_3{-}CH_2{-}C(Cl)H{-}(CH_2)_5{-}CH_3 + \dot{L}^{Ox}},\end{gathered} \tag{III}$$

$$\mathrm{\dot{L}^{Ox} + CCl_4 \xrightarrow{k_4} L^{Ox}{-}Cl + \dot{C}Cl_3}, \tag{IV}$$

$$\mathrm{\dot{L}^{Ox} \longrightarrow decay.} \tag{V}$$

In this scheme, $\dot{\mathrm{L}}^{\mathrm{Ox}}$ is the radical formed by the oxidation of the amino alcohol and $\mathrm{L^{Ox}{-}Cl}$ is *N*-chloroamine or α-chloroamine. Under the condition that the concentration of the $\dot{\mathrm{L}}^{\mathrm{Ox}}$ radical is low [6] and, as a consequence, the rate of step (IV) is much lower than the chain transfer rate, the following kinetic equation corresponds to the above mechanism:

$$-\frac{\mathrm{d}[\mathrm{C_8H_{16}}]}{\mathrm{d}t} = k_1[\mathrm{L}][\mathrm{CCl_4}]. \tag{3}$$

For excess $\mathrm{CCl_4}$, Eq. (3) reduces to Eq. (2). It can be assumed that the addition of $\mathrm{CBr_4}$ proceeds similarly. However, as already mentioned, in this case the metal complex is less active than the individual amino alcohol. The comparatively low activity of the metal complex can be attributed to the steric hindrance that appears in the complex formation and subsequent transformations of the $\mathrm{CBr_4}$ molecule and $\mathrm{Br^-}$ ion, which are bulkier than their chlorine counterparts. In turn, the formation of a metal complex decreases the ability of the amino alcohol to participate in the free-radical addition of $\mathrm{CBr_4}$ to olefin.

The conclusion about the different mechanisms for the amino alcohols and corresponding metal complexes is confirmed by the data obtained for the reaction involving $\mathrm{CHCl_3}$. According to [9], if a peroxide is the initiator, the C–H bond of chloroform participates in the reaction with alk-1-ene, and 1,1,1-trichlorononane should be the addition product in this case:

$$\mathrm{(PhCOO)_2 = 2PhCOO^{\bullet}},$$

$$\mathrm{PhCOO^{\bullet} = Ph^{\bullet} + CO_2\uparrow},$$

$$\mathrm{Ph^{\bullet} + CHCl_3 = PhH + {}^{\bullet}CCl_3},$$

$$\mathrm{{}^{\bullet}CCl_3 + C_8H_{16} = CCl_3{-}CH_2{-}\dot{C}H{-}(CH_2)_5{-}CH_3},$$

$$\begin{gathered}\mathrm{CCl_3{-}CH_2{-}\dot{C}H{-}(CH_2)_5{-}CH_3 + CHCl_3}\\ \mathrm{= C_9H_{17}Cl_3 + {}^{\bullet}CCl_3}.\end{gathered}$$

The C–Cl bond in chloroform is activated by the action of the metal complexes, and 1,1,3-trichloroalkanes are the addition products [9]:

$$\mathrm{Cu^{2+}LCl \xrightarrow{k_1} Cu^{+}L^{+*}Cl},$$

$$\mathrm{Cu^{+}L^{+*}Cl + CHCl_3 \xleftrightarrow{k_2,\,k_{-2}} Cl_2HC{-}Cl\cdots Cu^{+}L^{+*}Cl},$$

$$\begin{gathered}\mathrm{Cl_2HC{-}Cl\cdots Cu^{+}L^{+*}Cl + C_8H_{16}}\\ \mathrm{\xrightarrow{k_3} L^{+*}ClCu^{2+}Cl^{-}\cdots Cl_2HC{-}CH_2{-}\dot{C}H{-}(CH_2)_5CH_3},\end{gathered}$$

$$\begin{gathered}\mathrm{L^{+*}ClCu^{2+}Cl^{-}\cdots Cl_2HC{-}CH_2{-}\dot{C}H{-}(CH_2)_5CH_3}\\ \mathrm{\xrightarrow{k_4} Cu^{+}L^{+*}Cl + Cl_2HC{-}CH_2{-}C(Cl)H{-}(CH_2)_5CH_3}.\end{gathered}$$

We carried out the reactions of aromatic amino alcohol **I** and its copper complex **Ia** with chloroform under identical conditions in the presence of a classical radical initiator (benzoyl peroxide). The process involving chloroform is much slower than the reaction with carbon tetrachloride (in all cases, the extent of the reaction for 15 h did not exceed 10%). This result is in agreement with the literature and can be explained by the low stability of the resulting dichloromethyl radical [9]. The use of peroxide and aromatic amino alcohol results in the formation of only 1,1,1-trichlorononane (the extent of the reaction is 11 and 8%, respectively). In the system containing the metal complex, the olefin conversion is 6%. The main product is 1,1,3-trichlorononane (the 1,1,1-trichlorononane content of the products did not exceed 2–3%). Thus, in the presence of the aromatic amino alcohols and peroxide, the reaction proceeds via a free-radical mechanism, whereas in the presence of the copper complexes with the amino alcohols, the coordination–radical mechanism is observed.

The coordination mechanism is described in the literature. In particular, we earlier observed this mechanism when studying the reaction of oct-1ene with CCl_4 on immobilized copper complexes with simple amino alcohols and amino acids. The metal complexes with aromatic amino alcohols obtained in the present work make it possible to carry out the reaction under milder conditions (the reaction temperature is lowered from 130 to 80°C). The results of studying the reaction involving CBr_4 show that this mechanism is valid for the polybromosubstituted derivatives as well. The high activity and selectivity of the aromatic amino alcohols in the reaction with CBr_4 allow one to use them as initiators of the reactions involving polybromolalkanes.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, grant no. 06-03-32394.

REFERENCES

1. Amano, Y. and Uno, T., *J. Chem. Soc. Jpn.*, 1965, vol. 86, no. 11, p. 1087.
2. *Osnovy analiticheskoi khimii: Prakticheskoe rukovodstvo* (Fundamentals of Analytical Chemistry: Practical Course) Zolotov, Yu.A., Ed., Moscow: Vysshaya Shkola, 2001, p. 244.
3. Smirnov, V.V., Tarkhanova, I.G., Kokorin, A.I., Pergushov, V.I., and Tsvetkov, D.S., *Kinet. Katal.*, 2005, vol. 46, no. 1, p. 73 [*Kinet. Catal.* (Engl. Transl.), vol. 46, no. 1, p. 65].
4. Kovats, E., *Helv. Chim. Acta*, 1958, vol. 41, p. 1915.
5. Freidlina, R.Kh., Vasil'eva, E.I., Chukovskaya, E.Ts., and Englin, B.A., in *Uspekhi khimii polimerov* (Advances in Polymer Chemistry), Rogovin, Z.A., Berlin, A.A., and Korshak, V.V., Eds., Moscow: Khimiya, 1966, p. 138.
6. Tarkhanova, I.G., Gantman, M.G., Chizhov, A.O., and Smirnov, V.V., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2006, no. 9, p. 1565.
7. Bland, W.J., Davis, R., and Durrant, J.L.A., *J. Organomet. Chem.*, 1985, vol. 280, p. 397.
8. Tarkhanova, I.G., Smirnov, V.V., and Rostovshchikova, T.N., *Kinet. Katal.*, 2001, vol. 42, no. 2, p. 216 [*Kinet. Catal.* (Engl. Transl.), vol. 42, no. 2, p. 193].
9. Freidlina, R.Kh., Chukovskaya, E.Ts., and Englin, B.A., *Dokl. Akad. Nauk SSSR*, 1964, vol. 159, no. 6, p. 1346.
10. Emmanuel', N.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Chemical Kinetics), Moscow: Vysshaya Shkola, 1962, p. 269.
11. Asscher, M. and Vofsi, D., *J. Chem. Soc.*, 1961, p. 2261.