REDOX CHAIN ADDITION OF CHLOROFORM TO 1-ALKENES CATALYSED BY COPPER COMPLEXES

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The addition of chloroform to alkenes to give 1 : 1 adducts has been studied at 60–160°C. In the addition to styrene taken as a model reaction, copper complexes formed from metallic copper or cuprous oxide and 1,10-phenanthroline showed highest catalytic activity and selectivity even under mild conditions and gave 1,1,3-trichloro-3-phenylpropane in up to 95% yields. Aliphatic alkenes and vinyl monomers were less reactive than styrene. The mechanism proposed for redox chain additions of chloroform involves chain transfer *via* copper complexes.

In recent years, much attention has been paid to radical additions of polyhalomethanes to C—C double bond, using salts or complexes of some transition metals as catalysts (redox process). While the addition of highly reactive tetrachloromethane to alkenes proceeds easily in the presence of various catalytic systems[1], the addition reaction of chloroform, that is much less reactive[2–4], requires the most efficient catalysts. In connection with the study of additions of chloroform to various unsaturated compounds, the effectiveness of iron chlorides[2,5,6], copper chlorides[2,5,7], metal carbonyls[4,8] and ruthenium complexes[3] has been examined. High yields of 1 : 1 adducts (≦84%) were obtained in the addition of chloroform to 1-octene catalysed by an iron(III) chloride–diethylamine system; however, the reaction of chloroform with styrene catalysed by the same catalyst gave the 1 : 1 adduct in only 38% yield. Dichlorotris(triphenylphosphine)ruthenium(II) gave less satisfactory results; the reaction of chloroform with 1-octene catalysed by this complex yielded the 1 : 1 adduct in only 67% yield[3]. Low yields of products were found also for systems based on pentacarbonyl iron and amine[8] (≦43%); other metal carbonyls[4] showed very low activity, similarly as copper chlorides–diethylamine complexes[2]. The increased yield of 1 : 1 adducts has been achieved by combination of cuprous chloride catalysis with UV irradiation at high dilution[7].

1,1,3-Trichloroalkanes are products of redox chain addition reactions of chloroform with 1-alkenes catalysed by transition metal compounds; this contrasts with reactions initiated by organic peroxides affording 1,1,1-trichloroalkanes as main products[2,9]. In the presence of transition metal compounds, homolysis of the C—Cl bond is by far the predominating process, whereas in the case of peroxides, the C—H bond is cleaved preferentially. Compared to the chain addition initiated by organic peroxides, the important advantage of redox chain additions of polyhalomethanes to 1-alkenes is a substantial decrease in or even elimination of telomer and polymer formation, especially in reactions of electron-deficient 1-alkenes, *e.g.* vinyl monomers that easily undergo polymerization[1,2].

In the preceding work we reported on addition reactions of tetrachloromethane to 1-alkenes in the presence of redox systems based on copper. The results indicate that the catalysts responsible for initiation of the reaction and chain transfer are

obviously copper complexes formed, *e.g.*, by interaction of copper chlorides or copper oxides with amines. This idea was supported by finding that the addition of tetrachloromethane to styrene did not proceed under mild conditions by using cuprous chloride even in the presence of 2-propanol, but it started immediately after adding diethylamine in catalytic amounts[10].

In the present work we summarize the results of our study of redox chain addition of chloroform to terminal C=C bond. Special attention has been paid to the choice and catalytic activity of coordinated redox copper systems in dependence on the type of ligands.

EXPERIMENTAL

Chemicals. Chloroform, allyl alcohol (both Lachema, Brno), styrene (Kaučuk, Kralupy n/Vlt.), acrylonitrile, methyl acrylate, methyl methacrylate, 1-octene (all Fluka AG), were distilled prior to use. 1,10-Phenanthroline monohydrate and copper powder (both Lachema, Brno) were used as obtained. Cuprous chloride was purified as reported[10]. Cuprous oxide was prepared by the modified Fehling's procedure[11]: a solution of 35 g of cupric sulphate-pentahydrate in 500 ml of water was mixed with a solution of 36 g of sodium-potassium tartrate and 12·5 g of sodium hydroxide in 500 ml of water. Then, 30 g of glucose dissolved in 100 ml of water were added to the above solution and the reaction mixture was brought to boil. The red precipitate was filtered off, washed with water and acetone, and then dried in air to give 9·4 g of cuprous oxide (94% yield). Cu(I)(phen)Cl complex was obtained by modifying the procedure reported by Munakata[12]: cuprous chloride (0·396 g, 4 mmol) and 1,10-phenanthroline monohydrate (0·7928 g, 4 mmol) were dissolved in 10 ml of dry ethanol and the reaction mixture was stirred for 3 h. The brown precipitate was filtered off, washed with 1 ml of dry ethanol and dried under vacuum to give 0·916 g (82%) of the dark violet complex. All operations were carried out in an atmosphere of nitrogen. The complex was sensitive to air oxygen and was therefore stored under nitrogen. For $C_{12}H_8CuClN_2$ (279·2) calculated: 51·62% C, 2·89% H, 22·76% Cu, 12·70% Cl; 10·0% N; found: 50·14% C, 2·98% H, 22·88% Cu, 12·40% Cl, 9·45% N.

Analytical methods. The course of addition reactions was followed by gas chromatographic analysis of reaction mixtures, using Chrom 41 instrument (Laboratorní přístroje, Prague) that was equipped with a flame ionisation detector and a stainless steel column (1·2 m × 3 mm) filled with 3% Silicone OV-17 on Gas-Chrom Q (80—100 mesh). ^{1}H-NMR spectra of products were measured with the use of BS 467 Tesla 60 spectrometer; ^{13}C-NMR spectra were recorded with BS 497-BP 4970 Tesla 100 instrument, using $CDCl_3$ solutions.

General procedure for preparing 1 : 1 *adducts. a*) Reactions in sealed ampoules. Chloroform, 1-alkene, copper or its compounds (Cu_2O, CuCl, Cu(I)(phen)Cl complex), and 1,10-phenanthroline monohydrate were introduced into 20 ml ampoules in corresponding molar ratios, the ampoules were sealed under nitrogen and stirred vibrationally on an oil bath at 140 or 160°C. After completion of the reaction, the reaction mixture was cooled, washed with water and the organic layer was freed of chloroform or eventually also of the unreacted alkene by evaporation; the product was isolated by distillation under reduced pressure. *b*) Reaction under normal pressure. A mixture of chloroform (143 g, 1·2 mol), styrene (25 g, 0·24 mol), copper powder (0·305 g, 4·8 mmol), and 1,10-phenanthroline monohydrate (1·903 g, 9·6 mmol) was heated to reflux (66°C) with magnetic stirring in an atmosphere of nitrogen, using a glass flask provided with a reflux condenser and a thermometer. After 15 h (when the conversion of styrene in the reaction

mixture was 95%), the reaction mixture was cooled, washed with 40 ml of water and the excess chloroform and the unreacted styrene were removed by distillation. Vacuum distillation gave 39·8 g of 1,1,3-trichloro-3-phenylpropane (74% yield with respect to the styrene charged).

Determination of catalyst activity. *a*) At 140°C. A series of sealed ampoules (10 ml) containing chloroform, styrene, copper or its compounds (1/2 Cu_2O, CuCl, Cu(I)(phen)Cl complex), and 1,10-phenanthroline monohydrate in molar ratio 5 : 1 : 0·003 : 0·006 were stirred vibrationally in an atmosphere of nitrogen in an oil bath at 140°C. The ampoules were taken from the oil bath at fixed time intervals, cooled, and the amount of 1,1,3-trichloro-3-phenylpropane in the reaction mixture was determined by using pentadecane as the internal standard.

b) At 66°C. The reaction mixture containing chloroform, styrene, copper or its compounds (1/2 Cu_2O, CuCl, Cu(I)(phen)Cl complex), and 1,10-phenanthroline monohydrate in molar ratio 5 : 1 : 0·02 : 0·04 was heated to reflux (66°C) and the samples removed at fixed time intervals were analysed by gas chromatography, using pentadecane as the internal standard.

1,1,3-*Trichloro-3-phenylpropane*, b.p. 91°C/93 Pa (ref.[2] 62°C/13 Pa). For $C_9H_9Cl_3$ (223·5) calculated: 48·36% C, 4·06% ; found: 48·57% C, 4·06% H.

α,γ,γ-*Trichlorobutyronitrile*, b.p. 81°C/1·6 kPa (ref.[13] 90·5°C/2·67 kPa). For $C_4H_4Cl_3N$ (172·4) calculated: 27·86% C, 2·34% H; found 28·05% C, 2·34% H. ^{1}H-NMR δ: 5·88 (t, $CHCl_2$, J = 6·7 Hz), 4·68 (t, CHCl, J = 7·5 Hz), 2·90 (t, CH_2) (ref.[7]: δ 5·88 (t, 1 H,) 4·68 (t, 1 H), 2·95 (t, 2 H).

Methyl α,γ,γ-*trichlorobutyrate*, b.p. 87°C/1·6 kPa (ref.[13] 98°C/2·27 kPa). For $C_5H_7Cl_3O_2$ (205·5) calculated: 29·23% C, 3·43% H; found: 29·38% C, 3·40% H. ^{1}H-NMR δ: 3·83 (s, CH_3), 5·93 (d, d, $CHCl_2$, J = 5·0, J = 7·5), 4·53 (d, d, CHCl, J = 6·0, J = 8·0), 2·8 (m, CH—H).

Methyl α,γ,γ-*trichloro-α-methylbutyrate*, b.p. 93°C/1·6 kPa (ref.[6] 45—46°C/0·34 kPa). For $C_6H_9Cl_3O_2$ (219·5) calculated: 32·83% C, 4·13% H; found: 33·19% C, 4·06% H. ^{1}H-NMR δ: 6·0 (t, $CHCl_2$, J = 6·3), 3·77 (s, OCH_3), 3·03 (q, CH—H), 3·01 (q, CH—H), 1·85 (s, CH_3).

2,4,4-*Trichlorobutanol*, b.p. 103°C/1·6 kPa. For $C_4H_7Cl_3O$ (177·5) calculated: 27·07% C, 3·98% H; found: 27·58% C, 3·75% H. ^{13}C-NMR δ: 70·18 ($CHCl_2$), 66·00 (CH_2OH), 59·73 (CHCl), 47·49 (CH_2).

1,1,3-*Trichlorononane*, b.p. 108—109°C/1·6 kPa (ref.[2] 90°C/66 Pa). For $C_9H_{17}Cl_3$ (231·6) calculated: 46·67% C, 7·40% H; found: 47·06% C, 7·37% H.

RESULTS AND DISCUSSION

Preliminary experiments on the redox chain addition of chloroform to 1-alkene confirmed that chloroform is much less reactive than tetrachloromethane, in accordance with reported results[2–4]. In this case, copper complexes that were efficient catalysts for addition reactions of tetrachloromethane[1,10] showed low activity and selectivity, and 1 : 1 adducts were formed in yields not exceeding 40%. For that reason, we have sought first for a suitable copper complex with satisfactory activity and selectivity. The addition of chloroform to styrene was chosen as the model reaction.

As copper complexes based on cupric chloride or cupric oxide were almost inactive, the determination of catalytic activity was limited to cuprous complexes; cuprous oxide was used as the source of copper(I) ions. It was found that the activity of cop-

per(I) complexes depended strongly on the type of ligands; some of them are presented in Table I. The activity of these complexes decreased in the order: Cu(I)-1,10-phenanthroline > Cu(I)-2,2'-bipyridine > Cu(I)-pyrazole > Cu(I)-pyrrolidine > Cu(I)-diethylamine. Other types of ligands investigated (diisopropylamine, triethylamine triethanolamine, ethylenediamine, phthalocyanine, triphenylphosphine) gave copper(I) complexes showing very low or no catalytic activity. Similarly to the addition of tetrachloromethane, the effectiveness of catalytic systems depended on the type of copper compound[10]. The study of the effect of copper compound on the catalytic activity of the complex containing 1,10-phenanthroline (phen) as the ligand in addition reaction of chloroform was made both under normal pressure at 66°C (Fig. 1) and under increased pressure at 140°C (Fig. 2). The catalytic activity of complexes was measured by the method of initial reaction rates at 66°C and was found to decrease in the order: Cu(0)-2 phen : 1/2 Cu_2O-2 phen : CuCl-2 phen : Cu(I)(phen)Cl-phen = 1·7 : 1·4 : 1 : 1. The optimum molar ratio of Cu(I) ions to 1,10-phenanthroline was 1 : 2; at 1 : 1 molar ratio a decrease in catalytic activity was observed during the reaction. Surprisingly, the highest catalytic activity showed the Cu(0)-2 phen complex and the lowest one CuCl-2 phen and Cu(I)(phen)Cl-phen (Fig. 1). The high effectiveness of Cu-2 phen or Cu_2O-2 phen complexes was not influenced by hetero-

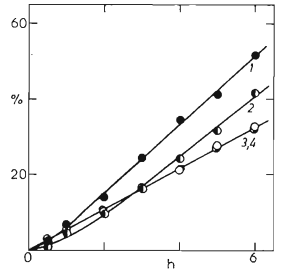

FIG. 1

Dependence of formation of 1,1,3-trichloro-3-phenylpropane (in %) on the type of copper complex used in the addition of chloroform to styrene at 66°C. *1* Cu(O)-2 phen, *2* 1/2 Cu_2O-2 phen, *3* CuCl-2 phen, *4* Cu(I)(phen)Cl-phen; $[CHCl_3]_0$: [PhCH=CH_2]$_0$: [Cu] : [phen] = 5 : 1 : 0·02 : 0·04

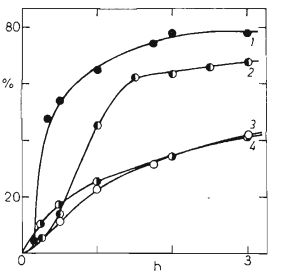

FIG. 2

Dependence of formation of 1,1,3-trichloro-3-phenylpropane (in %) on the type of copper complex used in the addition of chloroform to styrene at 140°C. *1* Cu(O)-2 phen, *2* 1/2 Cu_2O-2 phen, *3* CuCl-2 phen, *4* Cu(I)(phen)Cl-phen; $[CHCl_3]_0$: [PhCH=CH_2]$_0$: [Cu] : [phen] = 5 : 1 : 0·003 : 0·06

TABLE I

Redox chain addition of chloroform to unsaturated compounds catalysed by copper complexes. Reaction was carried out on a 5—20 mmol alkene scale; temperature 140°C

Substrate	Copper(0) or copper(I) compd.	Ligand[a]	Mol. ratio[b]	Reaction time h	Conversion %	Yield[c] %	Product
Styrene	Cu_2O	DEA	10 : 1 : 0·005 : 0·02	6	56	21	$C_6H_5CHClCH_2CHCl_2$
		Pyrro	10 : 1 : 0·005 : 0·02	6	63	32	
		Pyra	10 : 1 : 0·005 : 0·02	6	81	50	
		Bipy	10 : 1 : 0·005 : 0·02	6	100	82	
		Phen	10 : 1 : 0·005 : 0·02	6	100	87	
		Phen	5 : 1 : 0·005 : 0·02	8	100	78 (76)	
		Phen	7 : 1 : 0·005 : 0·02	8	100	80	
		Phen	20 : 1 : 0·005 : 0·02	5	100	95	
	Cu	Phen	5 : 1 : 0·002 : 0·002	9	99	75	
		Phen	5 : 1 : 0·005 : 0·01	2	100	78	
		Phen	5 : 1 : 0·02 : 0·04	15	95	— (74)[d,e]	
		Phen	10 : 1 : 0·002 : 0·002	9	98	84	
		Phen	10 : 1 : 0·002 : 0·002	10	100	87[f]	
		Phen	20 : 1 : 0·005 : 0·01	6	100	95	
	CuCl	Phen	5 : 1 : 0·02 : 0·04	13	99	77	
		Phen	10 : 1 : 0·02 : 0·04	8	95	81	
		Bipy	5 : 1 : 0·02 : 0·04	7	—	38	
	Cu(I)(phen)Cl	Phen	5 : 1 : 0·02 : 0·02	2	100	78	

Acrylonitrile	Cu_2O	Phen	10 : 1 : 0·02 : 0·04	20	90	55	$CHCl_2CH_2CHClCN$
	Cu	Phen	10 : 1 : 0·02 : 0·04	12	95	56	
Methyl acrylate	Cu_2O	Phen	5 : 1 : 0·02 : 0·04	19	100	— (60)	$CHCl_2CH_2CHClCO_2CH_3$
		Phen	10 : 1 : 0·02 : 0·04	6	100	70	
		Phen	20 : 1 : 0·02 : 0·04	8	100	73	
	Cu	Phen	10 : 1 : 0·02 : 0·04	8	—	56	
		Phen	20 : 1 : 0·04 : 0·08	8	—	67	
Methyl methacrylate	Cu_2O	Phen	5 : 1 : 0·02 : 0·04	5	—	39 (37)	$CHCl_2CH_2C(CH_3)ClCO_2.CH_3$
Allyl alcohol	Cu_2O	Phen	10 : 1 : 0·01 : 0·04	12	—	29[f]	$CHCl_2CH_2CHClCH_2OH$
	Cu	Phen	10 : 1 : 0·02 : 0·04	12	—	29[f]	
1-Octene	Cu_2O	Phen	5 : 1 : 0·01 : 0·02	10	66	— (55)	$CHCl_2CH_2CHCl(CH_2)_5CH_3$
		Phen	10 : 1 : 0·02 : 0·04	16	78	69	

[a] DEA = diethylamine, Pyrro = pyrrolidine, Pyra = pyrazole, Bipy = 2,2'-bipyridine, Phen = 1,10-phenanthroline; [b] Chloroform: substrate: Cu or Cu compound: ligand; [c] chromatographic yield, isolated yield is given in parentheses; [d] temperature 66°C; [e] 0·24 mol of styrene; [f] temperature 160°C.

geneous nature of the catalyst system in the initial stage of reaction that was characterized by only short induction period. An increase in the reaction temperature to 140°C led to a greater differentiation in the catalytic effectiveness of copper complexes, *i.e.* Cu(0)-2 phen : 1/2 Cu_2O- phen : CuCl- 2 phen : Cu(I)(phen)Cl-phen = 10 : 2·4 : 1·3 : : 1 (Fig. 2). The above results demonstrate that 1,10-phenanthroline complex formed from copper or cuprous oxide and 1,10-phenanthroline is the highly active redox catalyst for the addition of chloroform to styrene, allowing to obtain high yields of 1,1,3-trichloro-3-phenylpropane (*I*) (up to 95%, Table I) even at low catalyst concentrations. The results also show that the most efficient ligand is 1,10-phenanthroline. This aromatic base forms easily complexes with copper salts, stabilizes the lower oxidation state of the metal by acting both as electron acceptor and electron donor[14,15]. Several types of complexes differing in copper valency and containing different number of phenanthroline molecules are known: $Cu(II)(phen)_n (n = 1-3)$, $Cu(I)(phen)_n (n = 1, 2)$ (ref.[12,14-16]).

Cuprous chloride forms Cu(I)(phen)Cl complexes ($n = 1, 2$) that are known to exist only in solution[12,16]. We suceeded in preparing and isolating the Cu(I)(phen)Cl complex; the $Cu(I)(phen)_2Cl$ complex is highly soluble and for that reason we were not able to isolate it in the pure state. The fact that catalytic systems CuCl–2 phen and Cu(I)(phen)Cl–phen show nearly the same catalytic activity can be easily understood (Figs 1 and 2). The distinctly higher catalytic effectiveness of Cu(0)–2 phen system deserves explanation. Concerning the mechanism of radical redox addition reactions, the redox system $Cu(I) \rightleftharpoons Cu(II)$ is known to play an important role. One can therefore assume that in the presence of Cu(0), the above equilibrium is shifted to the left, which results in an increased rate of initiation and thus also in an increase in the total reaction rate. Contrary to this, the increased concentration of Cu(II) complexes, *e.g.* due to radical termination (dimerisation, disproportionation) leads to the loss of catalytic activity and thus to a decrease in the reaction rate or even to a complete cease of the reaction. This redox process of the complex is accompanied by colour change from brown to bright green.

We have further examined the effect of the chloroform to styrene molar ratio on the yield of adduct *I*. In contradistinction to tetrachloromethane addition[1], we have observed a significant dependence of the yield of adduct I on the molar ratio. By increasing the ratio from 5 : 1 to 20 : 1, the yield of adduct *I* increased from 78% to 95% (Table I), irrespective of the type of catalyst and its concentration. The dependence of the yield of 1 : 1 adduct on the molar ratios of reaction components was observed also in additions of chloroform to other 1-alkenes (Table I).

The yields of 1 : 1 adduct (29–70%) obtained in additions of chloroform to 1-octene, acrylonitrile, methyl methacrylate, and allyl alcohol depended on the reactivity of C=C bond of 1-alkenes. Styrene was more reactive than aliphatic alkenes and vinyl monomers. No marked difference between the activity of Cu(0)–2 phen and Cu_2O–2 phen complexes was found in these cases.

Despite of some doubts about the catalytically active form of the complex formed from Cu(0)–2 phen or similar systems, one can pressume that the mechanism of redox chain addition of chloroform to 1-alkenes is similar to the mechanism of addition of tetrachloromethane[10] and can be described by the following simplified equations (*A*)–(*C*) (L = 1,10-phenanthroline).

$$Cu^{I}L_n + CHCl_3 \rightarrow Cu^{II}L_nCl + \dot{C}HCl_2 \qquad (A)$$

$$\dot{C}HCl_2 + RCH{=}CH_2 \rightarrow R\dot{C}HCH_2CHCl_2 \qquad (B)$$

$$R\dot{C}HCH_2CHCl_2 + Cu^{II}L_nCl \rightarrow RCHClCH_2CHCl_2 + Cu^{I}L_n \qquad (C)$$

In the initiation stage of reaction (*A*), the complex $Cu(I)_n$ plays a decisive role in formation of dichloromethyl radical that then adds to the C=C double bond (equation (*B*)). Catalytic process can be described in terms of redox chain mechanism in which copper passes through oxidation states Cu(I) and Cu(II) (equations (*A*) and (*C*)). The question whether organic radicals that are intermediates of the addition reaction are present as free radicals or as species coordinated to metal cannot be answered at present.

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