

CATALYTIC ACTIVITY OF COPPER OXIDES AND CHLORIDES IN THE REDOX CHAIN ADDITION OF TETRACHLOROMETHANE TO STYRENE*

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The catalytic activity of redox systems based on copper oxide or chloride and diethylamine (DEA) in the addition of tetrachloromethane to styrene at 76°C increases in the order $\text{CuO-DEA} < \text{Cu}_2\text{O-DEA} < \text{CuCl}_2\text{-DEA} \sim \text{CuCl-DEA} \approx \text{CuCl}_2 \cdot 2 \text{DEA}$. Reactions catalysed by systems $\text{Cu}_2\text{O-DEA}$ and CuO-DEA display significant induction periods which decrease with increasing DEA concentration. The dependence of reaction rates on the concentration of DEA indicates formation of the $\text{CuCl}_2 \cdot 2 \text{DEA}$ complex. Inhibition method was used to estimate the rate of the initiating step in the addition reaction catalysed by CuO-DEA .

Previous work revealed the capability of copper(I) and copper(II) oxides to induce the addition of tetrachloromethane to 1-alkenes forming 1 : 1 adducts in high yields¹. Reactions of tetrachloromethane with vinylic monomers and conjugated aliphatic dienes catalysed by copper(II) oxide gave, however, more or less telomeric and polymeric products¹ resulting also from reactions initiated by organic peroxides². The use of copper oxides in conjugation with amines or phosphines changed completely the reaction course and yielded the 1 : 1 adducts as major products¹. We supposed that the copper oxides were transformed into corresponding chlorides at the beginning of the addition reaction¹. As has earlier been suggested, reactions of this type follow a redox chain mechanism in which the metal ion functions as a chlorine-atom transfer agent (redox transfer)³. In this context, thorough studies were devoted to reactions of tetrachloromethane with metal chlorides alone, in particular with iron and copper chlorides⁴, as well as to reactions of tetrachloromethane with amines catalysed by copper ions⁵⁻⁷. In the absence of alkenes, the latter reaction was found to be a radical process yielding amine hydrochloride, chloroform⁵⁻⁷ and N-alkylimine as the major products^{6,7}; the ensuing secondary ionic reactions produced minor amounts of an aldehyde and a primary amine^{6,7}. It was of interest that formation of all these products was suppressed in the presence of unsaturated compounds

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such as isobutyl vinyl ether, styrene, octenes and cyclohexene⁵⁻⁷, in accordance with the expected predominating 1 : 1 addition of tetrachloromethane to a carbon-carbon double bond³.

In this communication we report the catalytic activity of redox systems such as copper(II) oxide-diethylamine (DEA), copper(I) oxide-DEA, copper(II) chloride-DEA, copper(I) chloride-DEA and the complex, CuCl₂·2 DEA. The redox chain addition of tetrachloromethane to styrene producing 1,1,1,3-tetrachloro-3-phenylpropane was chosen as the model reaction. Attention was centered in particular on the function of an amine base in the catalytic redox system.

EXPERIMENTAL

Chemicals. Styrene, tetrachloromethane, 2-propanol, benzene (all from Lachema, Brno) and diethylamine (Laborchemie, Apolda, GDR) were distilled under nitrogen prior to use. Galvinoxyl (Aldrich-Europe, Beerse, Belgium), hexadecane (internal standard) (Fluka AG., Buchs, Switzerland), copper(II) chloride dihydrate and copper(I) oxide (Lachema), all analytically pure chemicals, were used as obtained. Copper(I) chloride (Lachema) was purified according to a known procedure⁸. Copper(II) oxide was prepared by oxidation of copper powder in a stream of oxygen⁹. The complex CuCl₂·2 DEA was prepared as described by Clifton and Yoke¹⁰.

Analytical methods. Gas chromatographic analysis of reaction mixtures was carried out using a Chrom 31 instrument (Laboratory Instruments, Prague) equipped with a flame-ionisation detector and a stainless-steel column (1.7 m × 3 mm), which was packed with 7% Silicone OV-17 on Gas-Chrom Q (80—100 mesh).

Standard procedure for measuring the activity of catalysts. A mixture of tetrachloromethane (15.4 g, 0.1 mol), styrene (0.52 g, 0.005 mol), copper oxide or chloride (0.05 mmol), diethylamine (0.05—0.40 mmol) (molar ratio 20 : 1 : 0.01 : 0.01—0.08) and hexadecane (0.1 g) was magnetically stirred and heated to reflux (76°C) in an atmosphere of nitrogen. Samples of the reaction mixture were taken at fixed time intervals and the amount of 1,1,1,3-tetrachloro-3-phenylpropane formed was determined by gas chromatographic analysis. The same procedure was used for determining the activity of the CuCl₂·2 DEA complex (0.0123 g, 0.05 mmol) excluding strictly the contact with air oxygen. Identical procedure was accepted for determining the reaction time necessary to achieve maximum yield of the 1 : 1 adduct in the presence of various catalysts at 76°C (Table I). Experiments carried out at 120°C were performed under nitrogen using vibrationally stirred, sealed Pyrex glass ampoules.

Inhibition experiments. Inhibition of the addition reaction was investigated in three parallel experiments. A mixture of tetrachloromethane (15.4 g, 0.1 mol), styrene (0.52 g, 0.005 mol), copper(II) oxide (0.004 g, 0.05 mmol), diethylamine (0.015 g, 0.2 mmol) (molar ratio 20 : 1 : 0.01 : 0.04) and hexadecane (0.1 g) was magnetically stirred and heated to reflux (76°C) under nitrogen. After 90 min, when according to gas chromatography 17% of 1,1,1,3-tetrachloro-3-phenylpropane was formed, galvinoxyl was added to the reaction mixture in an amount of a) 0.0422 g (0.10 mmol), b) 0.0633 g (0.15 mmol) and c) 0.0844 g (0.20 mmol) and the product formation was followed further by gas chromatographic analysis.

RESULTS AND DISCUSSION

The redox chain addition of tetrachloromethane to styrene exhibits several extremes. In the presence of copper oxides or chlorides alone or in the absence of copper ion (thermal initiation), telomeric and polymeric products are formed at low as well as higher temperatures (Fig. 1, curves 1–4) (Table I). On the other hand, differences in the activity of copper oxides and chlorides disappear in the presence of DEA at elevated temperatures and the very fast reactions (≤ 0.5 h) produce 1,1,1,3-tetrachloro-3-phenylpropane in an almost identical yield (82–85%) (Table I). In an effort to gain deeper insight into the mechanism of this redox chain addition reaction, we measured the activity of the above catalytic systems (*cf.* introduction) in a reaction

TABLE I

Effect of the Copper Compound, Ligand, Solvent and Temperature on the Formation of 1,1,1,3-Tetrachloro-3-phenylpropane

Reaction on a 5 mmol styrene scale; $[\text{CCl}_4]_0 : [\text{C}_6\text{H}_5\text{CH}=\text{CH}_2]_0 : [\text{copper compound}] = 20 : 1 : 0.01$.

Copper compound	Ligand or solvent	X^a	Temperature °C	Time h	Conversion of styrene %	Yield ^b %
Cu_2O	DEA	0.02	76	5	>99	83
	DEA	0.02	120	<0.5	>99	85
CuO	DEA	0.02	76	8	>99	83
	DEA	0.04	76	4.5	>99	84
	DEA	0.02	120	0.5	>99	82
	—	—	160	1	37	0.2
	—	—	—	—	—	—
CuCl	DEA	0.02	76	4.5	>99	85
	DEA	0.02	120	<0.5	>99	85
	$(\text{CH}_3)_2\text{CHOH}$	— ^c	76	5	< 1	< 1
	$(\text{CH}_3)_2\text{CHOH}$	— ^c	120	9	>99	84 ^d
	C_6H_6	— ^c	120	4	7–12	1
	—	—	76	5	< 1	< 1
	—	—	120	5	18	< 1
CuCl_2	DEA	0.02	76	5	>99	85
	DEA	0.02	120	0.5	>99	85
	—	—	76	6	< 1	< 1

^a Moles of ligand or solvent per 1 mol of styrene; ^b yield of the 1 : 1 adduct determined by gas chromatographic analysis using hexadecane as the internal standard; ^c molar ratio of CCl_4 to styrene, 2-propanol or benzene and CuCl was 10 : 1 : 10 : 0.01; ^d using a molar ratio of CCl_4 to styrene, 2-propanol and CuCl equal to 2 : 1 : 2 : 0.01 (ref.³), the yield of the 1 : 1 adduct is 78%.

TABLE II

Dependence of the Induction Period (min) on the Molar Ratio (X) of the Copper Compound to Diethylamine in the Redox Chain Addition of Tetrachloromethane to Styrene at 76°C

Reactions on a 5 mmol styrene scale; $[\text{CCl}_4]_0 : [\text{C}_6\text{H}_5\text{CH}=\text{CH}_2]_0 : [\text{copper compound}] = 20 : 1 : 0.01$.

Copper compound	X				
	1 : 1	1 : 2	1 : 4	1 : 6	1 : 8
CuO	—	120	60	50	37
Cu ₂ O	210	90	50	40	—
CuCl ₂	15	9	6	4	2
CuCl	<1	<1	<1	<1	<1

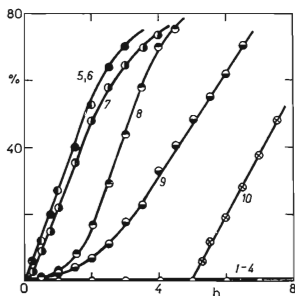


FIG. 1

Time Dependence of Formation of 1,1,1,3-Tetrachloro-3-phenylpropane in the Addition of Tetrachloromethane to Styrene Catalysed by 1 CuCl, 2 CuCl₂, 3 Cu₂O, 4 CuO, 5 CuCl-DEA (●), 6 CuCl. 2 DEA (○), 7 CuCl₂-DEA, 8 Cu₂O-DEA, 9 CuO-DEA and 10 CuCl in 2-Propanol, with DEA (0.02 mol) Being Added after 5 h

$[\text{CCl}_4]_0 : [\text{C}_6\text{H}_5\text{CH}=\text{CH}_2]_0 : [\text{Cu compound}] = 20 : 1 : 0.01$; 5-9 $[(\text{C}_2\text{H}_5)_2\text{NH}] : [\text{Cu compound}] = 0.02 : 0.0; 1$ 10 $[\text{CCl}_4]_0 : [(\text{CH}_3)_2\text{CHOH}] = 10 : 10$; temperature 76°C.

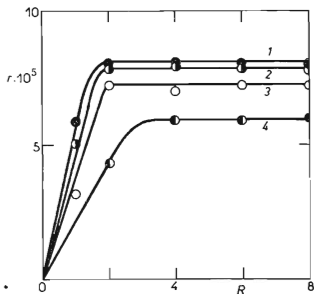


FIG. 2

Dependence of the Rate (r in s^{-1}) of Addition of Tetrachloromethane to Styrene upon the Molar Ratio (R) of DEA to the Copper Compound in a Reaction Catalysed by 1 CuCl-DEA, 2 Cu₂O-DEA, 3 CuCl₂-DEA and 4 CuO-DEA

$[\text{CCl}_4]_0 : [\text{C}_6\text{H}_5\text{CH}=\text{CH}_2]_0 : [\text{Cu compound}] = 20 : 1 : 0.01$; temperature 76°C.

conducted at 76°C (reflux temperature). The reaction time required to obtain the 1 : 1 adduct in 83 to 85% yield varied then between 4.5 and 8 h (Table I). As Fig. 1 shows, only the reactions catalysed by copper(I) chloride in conjugation with DEA (curve 5) and by the complex CuCl₂·2 DEA (curve 6) do not exhibit any induction period; for other catalytic systems (curves 7–9), the induction period increases in the order CuCl₂–DEA < Cu₂O–DEA < CuO–DEA (molar ratio of the copper compound to DEA is 1 : 2). This result is in harmony with our assumption that the copper oxides are transformed in the initial stage of the addition reaction into copper chlorides¹. The absence of an induction period in the reaction catalysed by copper(I) chloride–DEA corresponds well with the mechanism that has been suggested by Ascher and Vofsi³ considering the copper ion to act as the chlorine-atom transfer agent.

The results given in Table I show that in the reaction catalysed by copper(I) chloride, DEA can be replaced by 2-propanol³; this alcohol which functions presumably as a solvating agent⁵ is, however, less effective and the 1 : 1 adduct can be obtained in a comparable yield (84%) either at elevated temperatures (120°C) on prolonged heating or at lower temperature (76°C) by adding DEA to the 2-propanol solution

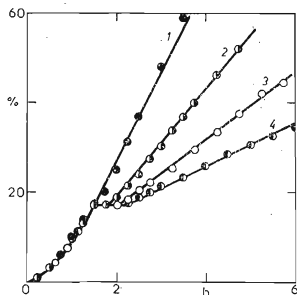


FIG. 3

Formation of 1,1,1,3-Tetrachloro-3-phenylpropane Catalysed by CuO–DEA (molar ratio 1 : 4) in the Absence 1 and Presence 2–4 of Galvinoxyl (*G*) as Inhibitor at 76°C

[CCl₄]₀ : [C₆H₅CH=CH₂]₀ : [CuO] : [(C₂H₅)₂NH] = 20 : 1 : 0.01 : 0.04; 2 [CuO] : [G]₀ = 0.01 : 0.02, 3 [CuO] : [G]₀ = 0.01 : 0.03, 4 [CuO] : [G]₀ = 0.01 : 0.04.

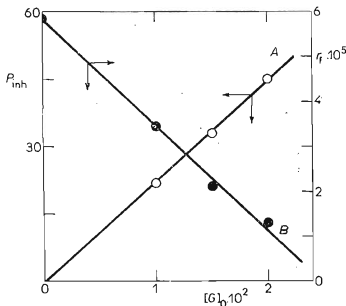


FIG. 4

Linear Dependence of the Inhibition Period (P_{inh} in min) (line A) and the Rate of Formation (r_f in s^{-1}) of 1,1,1,3-Tetrachloro-3-phenylpropane after Disappearance of the Induction Period (line B) upon the Galvinoxyl Concentration ($[G]_0$ in $mol\ l^{-1}$)

of copper(I) chloride (Fig. 1, curve 10). However, no 1 : 1 addition was observed by us in the homogeneous system tetrachloromethane–styrene–copper(I) chloride–benzene even at 120°C (Table I). This again is in good accordance with the finding of Smith and Malik⁶ that the rate of the tetrachloromethane reaction with a base slows down with decreasing dielectric constant of the solvent.

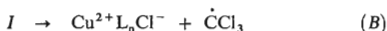
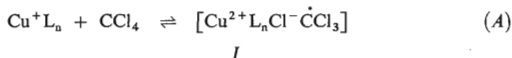
The comparison of rates of the addition reaction read from the linear sections of curves in Fig. 1 (for curves 7 to 9, after disappearance of the induction periods) gave the following order of activity: $\text{CuO-DEA} < \text{Cu}_2\text{O-DEA} < \text{CuCl}_2\text{-DEA} \sim \sim \text{CuCl-DEA} \approx \text{CuCl}_2\text{DEA}$. From the data in Table II it is evident that an increase in concentration of DEA is in close relation to the shortening of induction periods; at the same time, the effect caused by the presence of DEA increases in the order $\text{CuCl} < \text{CuCl}_2 < \text{Cu}_2\text{O} < \text{CuO}$. A plot of the reaction rates against the molar ratio of DEA to the copper compound (Fig. 2) clearly demonstrates that copper(I) chloride, copper(II) chloride and copper(I) oxide do attain optimum activity in the presence of two mol of DEA. This result strongly favours the view of direct participation of complexes CuCl_2DEA or $\text{CuCl}_2\text{DEA}^*$ in the redox chain addition of tetrachloromethane to a carbon–carbon double bond. Ensuing experiments confirmed this view; catalysis by the complex CuCl_2DEA and copper(I) chloride in conjugation with two mol of DEA as well gave an exactly identical dependence of formation of 1,1,1,3-tetrachloro-3-phenylpropane upon time (Fig. 1, curves 5 and 6). The absence of an induction period in the reaction catalysed by copper(I) chloride in conjugation with two mol of DEA or by the complex CuCl_2DEA is consistent with a very fast and exothermic complex formation observed earlier¹⁰ and evidenced also by our results. On the other hand, the use of systems such as copper(II) chloride–DEA, copper(I) oxide–DEA and copper(II) oxide–DEA necessitates first their transformation into the CuCl_2DEA complex; this again corresponds well to the induction periods increasing in the stated order during formation of the 1 : 1 adduct (Fig. 1).

As shown in Fig. 3, stable radicals such as galvinoxyl inhibit the formation of 1,1,1,3-tetrachloro-3-phenylpropane catalysed by copper(II) oxide in conjugation with DEA (molar ratio 1 : 4). Plotting the induction periods (P_{inh}) against the galvinoxyl concentration gave a linear dependence presented in Fig. 4. The rate of initiation (R_i) of the catalytic addition reaction at 76°C, which was estimated from the slope of the line A in Fig. 4 (refs^{12,13}), corresponds to a value of $7.4 \cdot 10^{-6} \text{ mol}^{-1} \text{ l}^{-1} \text{ s}^{-1}$ (correlation coefficient $r = 0.9998$). Determination of the induction period in a more broad range of galvinoxyl concentrations was hindered by occurrence of a retarding effect exerted by the products of inhibition on the rate of formation of the 1 : 1 adduct (Fig. 3). In this context, it is noteworthy that this retarding effect, which is expressed by the value of r_t read from the slopes of the lines 2 to 4 in Fig. 3, is pro-

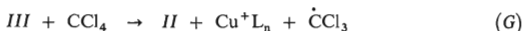
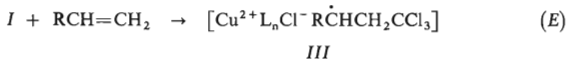
* Both complexes were already prepared in pure state by Clifton and Yoke^{10,11}.

portional to the galvinoxyl concentration (Fig. 4, line B). A more accurate determination of the initiation rates of these reactions by measuring directly the time decrease in the inhibitor concentrations^{14,15} is now in progress in our laboratory.

Taking into account all the above results, we come to the conclusion that the mechanism of the redox chain addition of tetrachloromethane to a carbon-carbon double bond catalysed by copper ions in the presence of an amine base can be described by equations (A) to (D) (L denotes a base).



The trichloromethyl radicals are formed evidently, in agreement with the view of other authors¹⁶⁻¹⁸, by interaction of tetrachloromethane with the Cu^+L_n complex arising from the reaction of copper(I) chloride with the amine base (Eqs (A) and (B)). Depending on the nature of the intermediate complex *I*, the trichloromethyl radical may react with an alkene either after escaping from the coordination sphere (Eq. (C)) or within the coordination sphere of the complex *III* (Eq. (E)).



The 1 : 1 adduct (*II*) can therefore be formed either according to Eq. (D), or by decomposition of the complex *III* (Eq. (F)) or by interaction of the latter with tetrachloromethane (Eq. (G)). A lack of the experimental material makes it difficult to decide ultimately between these pathways. A partial support for the mechanism described by Eqs (A)–(D) is given by the finding that the nature of the amine (DEA, diisopropylamine) or tertiary base such as pyridine or triphenylphosphine¹ as ligands does affect the activity and selectivity of the metal catalyst^{1,17,18}.

At present, the views of the intermediacy of the complex *III* are conflicting. The capability of unsaturated compounds to coordinate to the copper ions is well known¹⁹. Whereas some authors^{17,18} suggest that the redox chain addition reaction involves an alkene coordinated to the copper ion, other authors²⁰ do not find any evidence for the participation of the copper-alkene complex in this reaction.

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