THE KINETIC STUDY OF THE ADDITION
OF TETRACHLOROMETHANE TO STYRENE IN THE PRESENCE
OF COPPER COMPLEXES

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Kinetics of the addition of tetrachloromethane to styrene catalyzed by copper–amine complexes was studied. The pseudo-first order kinetics in respect to styrene and the catalyst was observed at an excess of tetrachloromethane. The reaction mechanism involving a catalytic cycle compatible with the kinetic observations is proposed. The experimental activation energy, being about 104 kJ mol^{-1}, indicates a catalytic mechanism.

The addition of polyhalomethanes to alkenes yields 1 : 1 adducts in the presence of copper complexes[1-7]. These complexes formed from cuprous halides and amines or azaaromatic compounds are supposed to initiate the addition *via* a free radical, chain propagation[2,3,5-7].

Recently, we have studied the interaction between polyhalomethanes and complexes of various primary amines with CuCl[8]. These are oxidized reversibly to Cu(II) complexes in which radical species are assumed to be coordinated. Asahara *et al.*[4] studied the addition of tetrachloromethane to vinyl chloride catalyzed by this type of copper complexes. Contrary to the reaction initiated with azobisisobutyronitrile, in which higher telomers were formed *via* a free radical mechanism, the copper complexes yielded 1 : 1 adducts mainly, *e.g.* 85% with $CuCl_2$–1-butylamine or 68% with CuCl–1-butylamine complex in telomer mixture, respectively. The authors assumed that the trichloromethyl radicals are stabilised in a *cage complex* and the reaction does not proceed *via* a chain mechanism obvious with the classical initiators of chain radical reactions. A relevant kinetic model has been derived.

The reaction mechanism alternative to the chain propagation may involve an intermediate complex of Cu(I) halide, olefin, and addend, as proposed earlier by Schrautzer[9] and Zvedin *et al.*[10]. Also Bland *et al.*[11,12] examining in detail the kinetics of the addition of tetrachloroalkanes to olefins in presence of $RuCl_2(PPh_3)_3$

suggested that this reaction proceeds *via* a non-chain mechanism involving coordinated radical species. A detailed kinetic model has been also proposed.

The aim of the present work is to test experimentally the kinetic model of the non-chain catalytic mechanism of addition. The addition of tetrachloromethane to styrene catalyzed by amino complexes of cuprous chloride was used as the model reaction.

EXPERIMENTAL

Chemicals

Cuprous chloride was prepared *via* reduction of cupric sulphate with sulphur dioxide in presence of sodium chloride[8]. Anhydrous cupric chloride was obtained from cupric chloride dihydrate (BDH Chemicals Ltd., Poole, England) after drying at 150°C in a stream of dry nitrogen for 8 h. Tetrachloromethane, chloroform, and dichloromethane (Lachema, Brno) were dried with phosphorous pentoxide and rectified under nitrogen. Aliphatic primary amines (1-butylamine, tert. butylamine, and isobutylamine) were purchased from Fluka AG, Buchs, Switzerland and Lachema, Brno, Czechoslovakia, dried with sodium hydroxide and purified by distillation before use. Styrene of technical grade (Kaučuk, Kralupy) was rectified at reduced pressure of about 2 kPa under nitrogen atmosphere. Hexadecane (Fluka AG, Buchs, Switzerland), toluene, dioxane, and fluorene (Lachema, Brno) of analytical grade were used as obtained.

Kinetic Experiments

Tetrachloromethane (15 ml; 0·155 mol), 1·58 ml of styrene (0·013 mol), 82·5 µl of hexadecane (internal standard for GC), and the corresponding amount of cuprous chloride (0·25—1 mmol) were charged into dry glass reactor equipped with reflux condenser, nitrogen inlet, silicon rubber septum, and magnetic stirrer. The reactor was immersed in a water bath with controlled temperature ($\pm 0.2°C$). After the desired temperature of reaction mixture had been reached, the corresponding amount of amine (0·5—4 mmol) was added through the septum. A mixture of CCl_4--dioxane (2 : 1, v/v) had to be used in the study of the effect of amine structure (Table I) due to the limited solubility of tert. butylamine complexes in pure tetrachloromethane. The samples of reaction mixture (about 1 ml) withdrawn through the septum were purified from copper complexes by the adsorption on silica gel microcartridges (10 mm × 5 mm i.d.). The organic

TABLE I

Rate constants k_{exp} ($1 \text{ s}^{-1} \text{ mol}_{cat}$) for the reaction of styrene with CCl_4 in CCl_4–dioxane (2 : 1) at 70°C, molar ratio amine/CuCl = 8 and CuCl concentration $1.52 . 10^{-2} \text{ mol l}^{-1}$, for different amines; corresponding Taft substituent constants[17] for alkyls

Amine	k_{exp}	σ^*	E_s
1-Butylamine	0·25	−0·130	−0·39
Isobutylamine	0·19	−0·125	−0·39
Tert. butylamine	0·80	−0·300	−1·54

part obtained was used for GC analysis carried out on CHROM 5 gas chromatograph (Laboratorní přístroje, Praha) equipped with FID detector and glass column (120 cm × 3 mm i.d.) packed with Silicone OV 25 on Gas-Chrom Q, 80—100 mesh (Applied Science Europe BV, OUD-Beijerland, The Netherlands) operated at 160°C with nitrogen as a carrier gas. The conversions of styrene into the adduct were calculated from peak heights related to the internal standard.

RESULTS AND DISCUSSION

At an excess of tetrachloromethane and reaction temperatures below 75°C, the addition of tetrachloromethane to styrene yields practically the only reaction product — 1,1,1,3-tetrachloro-3-phenylpropane (Eq. (A)):

$$C_6H_5-CH=CH_2 \ + \ CCl_4 \ \xrightarrow{\text{Cu-complexes}} \ C_6H_5-CHCl-CH_2-CCl_3 \ . \quad (A)$$
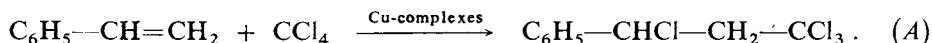
The high selectivity of the addition taking place in the presence of copper complexes has been also reported by Hájek et al.[6,7]. In our study, the molar ratio of tetrachloromethane to styrene was 12. As Fig. 1 shows, the rate of adduct formation obeys first-order kinetics in the presence of CuCl–primary amine complexes. Thus, the initial catalytic activity of the complexes could be expressed by the rate constant, k_{exp}, calculated from the linearized pseudo-first order kinetic curves (Fig. 1). At longer reaction times, $t_r > 1$ h, a precipitate was formed sometimes. In these cases, a deviation from the first-order plot observed at higher conversions can be explained by a stepwise destruction of the CuCl–amine complex, e.g. via side reactions with tetrachloromethane[4] or moisture[13], respectively.

As we have reported, the complexes formed from cuprous chloride, amines, and polyhalomethanes do not interact with hydrogen donors[8]. Free trichloromethyl radicals are known to abstract hydrogen from alkylaromatic hydrocarbons under formation of chloroform. Kooyman and Farenhorst[14] observed strong inhibition of radical addition of tetrachloromethane to 1-alkenes caused by alkylaromatic hydrocarbons. In our reaction system, the presence of fluorene at concentration of $1 . 10^{-3}$ mol l^{-1} had no influence upon the rate of addition and chloroform was absent in the reaction mixture. We therefore assume that the free trichloromethyl radicals are not formed accordingly to the chain mechanism proposed by Asscher and Vofsi[2,3].

The rate of the reaction increased with 1-butylamine : CuCl ratio, reaching a steady value at the ratio higher than 4. Similar dependence was found for the diethylamine –CuCl complex by Hájek and coworkers[6]. In Fig. 2 it is demonstrated that the reaction obeys first-order kinetics with respect to CuCl when the constant amine: : CuCl molar ratio of 8 is kept. The above experimental facts led us to the reaction scheme of a non-chain catalytic reaction. The scheme is analogical to the kinetic models proposed ealier by Ashara et al.[4] or Bland et al.[11,12], respectively.

We suppose that CuCl, which is practically insoluble in pure mixture of CCl_4 and styrene, is incorporated in a soluble complex with one or two amine ligands. Such complexes are described in literature[15]. The existence of catalytic complexes with two amine ligands has been also assumed by Hájek et al.[6,7]. The formation of "caged" trichloromethyl radicals is expected to be enhanced by the electron donating effect of amine ligands. Therefore, we suppose that the complex with two ligands is more active. As the complexation is an equilibrium process, an excess of amine must be used to convert CuCl completely into the active complex.

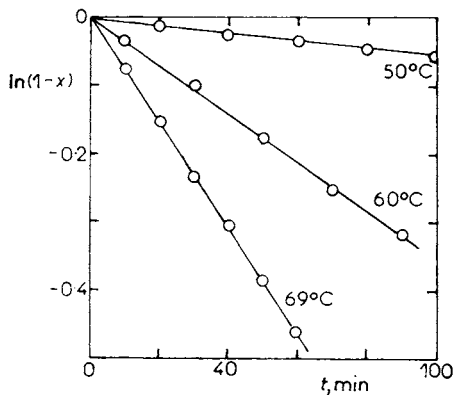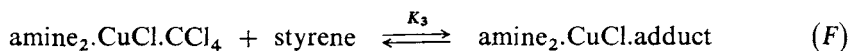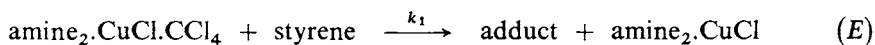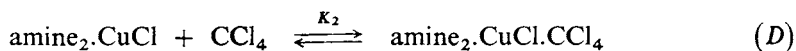Having in mind these possibilities we have proposed the following reaction scheme:

$$amine + CuCl \rightarrow amine.CuCl \qquad (B)$$

$$amine.CuCl + amine \xrightleftharpoons{K_1} amine_2.CuCl \qquad (C)$$

$$amine_2.CuCl + CCl_4 \xrightleftharpoons{K_2} amine_2.CuCl.CCl_4 \qquad (D)$$

$$amine_2.CuCl.CCl_4 + styrene \xrightarrow{k_1} adduct + amine_2.CuCl \qquad (E)$$

$$amine_2.CuCl.CCl_4 + styrene \xrightleftharpoons{K_3} amine_2.CuCl.adduct \qquad (F)$$
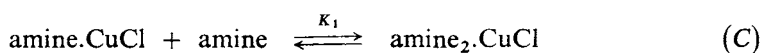

FIG. 1

The linearized dependence of conversion, x, in the reaction of styrene with CCl_4 on reaction time, t, measured at different temperatures. Concentration of CuCl $1·52 . . 10^{-2}$ mol l^{-1}, molar ratio 1-butylamine/ /Cu $= 8$
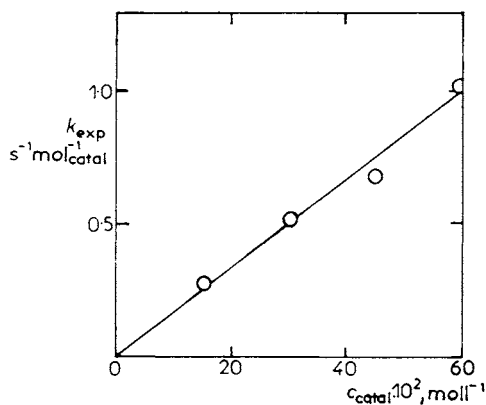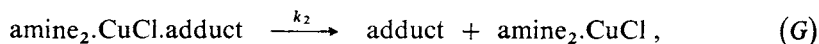
FIG. 2

The linear dependence of first-order rate constant, k_{exp}, on the concentration of catalyst at the reaction temperature 70°C and molar ratio amine/Cu $= 8$

$$\text{amine}_2.\text{CuCl.adduct} \xrightarrow{k_2} \text{adduct} + \text{amine}_2.\text{CuCl}, \tag{G}$$

where k_1 and k_2 are rate constants, K_1, K_2, and K_3 are equilibrium constants. Eq. (B) describes the dissolution of pure CuCl and is not therefore included in the model: all the active copper is supposed to be present in complexes. Taking into account steps $(C)-(E)$, we have obtained an expression for initial reaction rate:

$$r_0 = \frac{k_1 K_1 K_2 [\text{styrene}] [\text{CCl}_4] [\text{amine}] [\text{CuCl}]}{1 + K_1 [\text{amine}] + K_1 K_2 [\text{CCl}_4] [\text{amine}]}. \tag{1}$$

If steps (C), (D), (F), and (G) are considered, the following rate equation is obtained

$$r_0 = \frac{k_2 K_1 K_2 K_3 [\text{styrene}] [\text{CCl}_4] [\text{amine}] [\text{CuCl}]}{1 + K_1 [\text{amine}] + K_1 K_2 [\text{CCl}_4] [\text{amine}] + K_1 K_2 K_3 [\text{styrene}] [\text{CCl}_4] [\text{amine}]}. \tag{2}$$

In Eqs (1) and (2), the concentrations are initial. When r_0 is independent of the concentration of amine as shown in Fig. 2, the term $K_1 [\text{amine}] \gg 1$ and Eq. (1) is simplified

$$r_0 = \frac{k K_2 [\text{CuCl}] [\text{CCl}_4] [\text{styrene}]}{1 + K_2 [\text{CCl}_4]}. \tag{3}$$

Analogically, Eq. (2) yields

$$r_0 = \frac{k K_2 K_3 [\text{CuCl}] [\text{CCl}_4] [\text{styrene}]}{1 + K_2 [\text{CCl}_4] + K_2 K_3 [\text{CCl}_4] [\text{styrene}]}. \tag{4}$$

If the first-order kinetics with respect to styrene is to be kept, the term $(1 + K_2 K_3 \cdot [\text{CCl}_4] [\text{styrene}])$ in Eq. (4) must be much smaller than $K_2 [\text{CCl}_4]$.

As the next stage of this study, we have examined the influence of the structure of amine ligands upon the catalytic activity of CuCl complexes (Table I). We have found that k_{exp} can be correlated well (correlation coefficient 0·9660) with the Taft polar and steric constants (ref.[16])

$$\log k_{\text{exp}} = -1·010 - 3·99\sigma^* + 0·18 E_s. \tag{5}$$

The relative catalytic activity of complexes is therefore influenced by electronic effects mainly, and the steric effects play a minor role.

The activation energy, E_{exp}, calculated from temperature dependence of k_{exp} is 104 kJ mol^{-1} for the cuprous chloride–1-butylamine catalytic complex. This high

activation energy indicates that k_{exp} is probably composed of several rate and equilibrium constants (Eqs (3) or (4)). On the other hand, the possibility of free radical chain mechanism must be rejected again as the E_{exp} is too high in comparison with E_{act} of free radical additions[7]. Also Bland et al.[12] have found E_{exp} about 100 kJ . . mol^{-1} for the addition of tetrachloromethane to 1-octene in the presence of $RuCl_2(P(C_6H_5)_3)_3$.

In conclusion, the addition of tetrachloromethane to styrene taking place in the presence of copper–amine complexes does not proceed via a free radical chain mechanism. The catalytic system is complicated since it involves Cu(I) as well as Cu(II) complexes, and the trichloromethyl radicals are stabilized in "caged complexes". The catalytic activity is influenced markedly by the structure of amine ligands.

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