

## RELATIVE REACTIVITIES OF 1,1,1-TRICHLOROETHANE AND 1,1,1-TRICHLOROTRIFLUOROETHANE IN COMPETITIVE ADDITION REACTIONS

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Relative reactivity of  $\text{CH}_3\text{CCl}_3$  and  $\text{CF}_3\text{CCl}_3$  measured in competitive addition reactions with 1-hexene in the presence of free radical initiators or Cu, Pd and Ru complexes was found to depend on the type of the catalyst. The unusual course of the reaction has been found in the additions catalyzed with copper(I)-amine complexes where  $\text{CH}_3\text{CCl}_3$  in competition with  $\text{CF}_3\text{CCl}_3$  was completely unreactive. The results have been explained in terms of the change of reaction mechanism and compared with classical free radical initiation.

The reactivity of halo compounds in radical addition reactions with alkenes has not yet been systematically studied. Halo compounds of the type  $\text{R}-\text{CCl}_3$  were examined in the reactions with styrene and their reactivity was expressed by the yields of the addition product<sup>1,2</sup>. The reactions were carried out in the presence of the redox system copper(I) chloride-triethylamine and were assumed to proceed via redox chain mechanism. It is known that in the presence of some transition metal complexes, the addition reactions of halo compounds with alkenes proceed via catalytic non-chain mechanism, i.e. the addition reaction takes place in the coordination sphere of the metal complex<sup>3-11</sup>.

In the course of our study of the reactivity of halo compounds in addition reactions catalyzed by copper complexes we have found recently that some pairs of halo compounds show different behaviour in competitive and separate reactions, which relates likely to mechanism of the addition reaction<sup>12</sup>. Preliminary results indicated that the reactivity of halo compounds in competitive reactions can be affected also by the type of the catalyst employed. To examine the effect of catalyst on the behaviour of halo compounds in competitive reactions in more detail, the pair 1,1,1-trichloroethane-1,1,1-trichlorotrifluoroethane has been chosen in the present study.

### EXPERIMENTAL

#### Chemicals

1-Hexene, 1,1,1-trichloroethane and dodecane (all Fluka A. G., Buchs) were used as obtained.

1,1,1-Trichlorotrifluoroethane (Fluka A. G.) was purified by rectification under atmospheric pressure (b.p. 46°C) before use. The amines — propylamine, dipropylamine, tripropylamine, *t*-butylamine, dibutylamine, tributylamine and morpholine (Fluka A. G.) were used as obtained, 2-propylamine and cyclohexylamine (Moravia Chemical Works, Ostrava) were distilled prior to using. Dibenzoyl peroxide (Lachema, Brno), di-*tert*-butyl peroxide (Koch-Light Ltd., Colnbrook) and azobis(isobutyronitrile) (Fluka A. G.) were used as obtained. Acetonitrile (Croft Laboratories Ltd.) was dried by phosphorus pentoxide and purified by rectification (b.p. 76 to 81°C) with exclusion of air moisture and stored in a flask over a molecular sieve. Copper(I) chloride was prepared by the reduction of copper sulfate by sulfur dioxide according to the reported procedure<sup>13</sup> and was stored under argon. Tris(triphenylphosphine)ruthenium(II) dichloride (Fluka A. G.) was used as obtained. Palladium acetate was prepared by boiling Pd fillings in a mixture of acetic acid and concentrated nitric acid, followed by filtration and recrystallization<sup>14</sup>. The copper complex  $\text{CuCl}(\text{PPh}_3)_3$  was obtained as white crystals by the reaction of triphenylphosphine with CuCl in chloroform<sup>15</sup>. The complexes  $\text{Cu}(2\text{-PrNH}_2)_2\text{Cl}$  and  $\text{Cu}(2\text{-PrNH}_2)_2\text{Cl}_2$  were prepared from CuCl or anhydrous  $\text{CuCl}_2$  in an evacuated flask by condensation of 2-propylamine vapours at  $-78^\circ\text{C}$  (dry ice-ethanol). The amine complexes formed,  $\text{Cu}(2\text{-PrNH}_2)_2\text{Cl}$  (blue-green) and  $\text{Cu}(2\text{-PrNH}_2)_2\text{Cl}_2$  (bright blue) were crystalline substances and were stored under argon. The amine/CuCl or amine/ $\text{CuCl}_2$  molar ratio was determined by weighing and equaled to 2.025 and 1.992, respectively. The immobilized copper complex was prepared by the reaction of CuCl with a styrene-divinylbenzene copolymer containing NH and  $\text{NH}_2$  groups.

#### Analytical Methods

GC analysis of the products was carried out on Hewlett-Packard, Model 5890 A chromatograph equipped with FID detector, using a glass column (1.8 m  $\times$  2 mm) filled with 3% Silicone elastomer OV-1 on Chromosorb W (100/120 mesh) and with a Hewlett-Packard, Model 3396 A integrator.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the products were measured on Varian 200 XL spectrometer.

#### Synthesis of 1 : 1 Adducts

A mixture of 1,1,1-trichlorotrifluoroethane *I* or 1,1,1-trichloroethane *II* (0.2 mol), 1-hexene (0.1 mol), CuCl (0.002 mol) and 2-propylamine (0.004 mol) was stirred and heated to reflux under nitrogen for 14 h (1-hexene conversion 90–95%). Then the reaction mixture was cooled, washed successively with 40 ml of 10% HCl and water and dried over calcium dichloride. Distillation under reduced pressure afforded 1,1,1-trifluoro-2,2,4-trichlorooctane *III* (b.p., 74–76°C/1.6 kPa) or 2,2,4-trichlorooctane *IV* (b.p. 87–88°C/1.5 kPa) in 82.4 and 74.9% yield, respectively.

**1,1,1-Trifluoro-2,2,4-trichlorooctane (III).** For  $\text{C}_8\text{H}_{12}\text{Cl}_3\text{F}_3$  (271.54) calculated: 35.35% C, 4.42% H; found: 35.49% C, 4.40% H.  $^{13}\text{C}$  NMR ( $\delta$ , ppm): 122.10 d (C-1)/ $J(^{19}\text{F}-^{13}\text{C})$  281.9 Hz; 83.47 d (C-2)/ $J(^{19}\text{F}-^{13}\text{C})$  35.0 Hz; 48.61 s (C-3); 56.40 s (C-4); 39.18 s; 28.16 s; 22.01 s (C-5, 6, 7); 13.86 s (C-8).

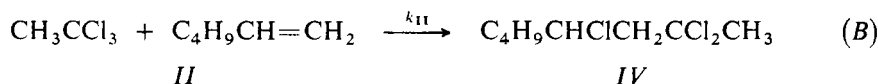
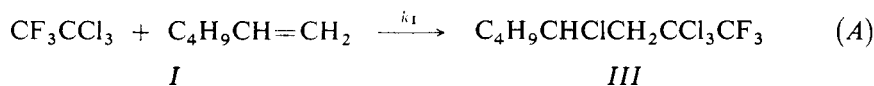
**2,2,4-Trichlorooctane (IV).** For  $\text{C}_8\text{H}_{15}\text{Cl}_3$  (217.57) calculated: 44.12% C, 6.89% H; found: 44.32% C, 6.75% H.  $^{13}\text{C}$  NMR ( $\delta$ , ppm): 37.56 s (C-1); 88.65 s (C-2); 57.69 s (C-3); 58.44 s (C-4); 39.22 s (C-5); 28.17 s (C-6); 22.06 s (C-7); 13.91 s (C-8).  $^1\text{H}$  NMR ( $\delta$ , ppm): 2.260 s (3 H,  $\text{CH}_3$ -1); 0.947, 0.933, 0.919 t (3 H,  $\text{CH}_3$ -8); 2.760, 2.751, 2.738 t (2 H,  $\text{CH}_2$ -3); 4.202 m (1 H,  $\text{CHCl}$ -4); 1.836, 1.834, 1.824 m (2 H,  $\text{CH}_2$ -5); 1.382, 1.364, 1.362 m (2 H,  $\text{CH}_2$ -6, 7).

## Competitive Kinetic Runs

A mixture of 1,1,1-trichlorotrifluoroethane *I*, 1,1,1-trichloroethane *II*, 1-hexene, dodecane (internal standard) and a catalyst or free radical initiator in a 2.5 : 2.5 : 1.0 : 0.01–0.05 molar ratio was placed into a 15 ml-glass ampoule filled with argon and provided with a silicone septum and stirred magnetically in a thermostatted bath (80–140°C). (In order to minimize the error caused by the weighing of small amounts of samples, the stock solution of the reaction mixture without catalyst was prepared and used for weighing the appropriate amount of the sample prior to the measurement proper). At fixed time intervals, samples of the reaction mixture were analysed by GC after removal of the catalyst. Kinetic runs were carried out in the conversion region up to 40 per cent. The relative rates of formation of 1 : 1 adducts *III* and *IV* were determined by calibration with authentic samples. The relative reactivities of polyhalogenated alkanes were determined as the ratios of the rate constants  $k_I$  and  $k_{II}$ , calculated according to the equation  $kt = -\ln(1 - x)$  where  $x$  is the conversion of 1-hexene to the adduct *III* and *IV*, respectively.

## RESULTS AND DISCUSSION

The pair of polyhalogenated ethanes, 1,1,1-trichlorotrifluoroethane *I* and 1,1,1-trichloroethane *II* reacts in general in the competitive addition reaction with 1-hexene to give 1 : 1 adducts *III* and *IV*, according to Eqs (A) and (B).



The rate of formation of these adducts, represented by the rate constants  $k_I$  and  $k_{II}$ , provides data on the reactivity of both polyhalogenated ethanes or their corresponding radicals ( $\text{CF}_3\text{CCl}_2^\cdot$ ,  $\text{CH}_3\text{CCl}_2^\cdot$ ). With respect to the fact that these addition reactions can be initiated either by classical methods or catalyzed by transition metal complexes, differing in mechanism, one could expect that the competitive additions of 1,1,1-trichloroethane and 1,1,1-trichlorotrifluoroethane may provide information on changes in reaction mechanism. For this purpose the relative reactivities of both polyhalogenated ethanes *I* and *II* were measured in dependence on the type of initiation or catalysis in the temperature range 0 to 140°C. The initiation of the competitive addition reaction was effected with organic peroxides, azo compounds, primary, secondary and tertiary amines (generation of radicals by means of amines was already used in our previous work<sup>16</sup>) by UV irradiation and by thermal initiation (Table I). Of the catalytic systems, copper, palladium and ruthenium complexes containing different ligands were selected to investigation (Table II).

The results presented in Table I show that under competitive conditions, 1,1,1-trichlorotrifluoroethane is more reactive than 1,1,1-trichloroethane. The values of the

relative reactivities  $k_I/k_{II}$  obtained had changed within the range 5.2 to 10.9. This scattering is caused obviously by the greater analytical error in the region of very low conversions  $x_{II}$  (0.04 to 0.4%) as some radical initiators had low efficiency (dibenzoyl peroxide, AIBN, tert-butylamine, dipropylamine, morpholine, tertiary amines, UV irradiation and thermal initiation). After the less reliable data had been excluded, the relative reactivities  $k_I/k_{II}$  changed in the more narrow region 7.8 to 8.8. The results demonstrated that under conditions of free radical chain addition,  $CF_3CCl_3$  and  $CH_3CCl_3$  react with 1-hexene in relation to their reactivities, irrespective of the way of generation of the radicals  $CF_3CCl_2$  and  $CH_3CCl_2$ . Temperature effect on the relative reactivity has not been observed.

As follows from the results presented in Table II, situation in the addition reactions catalyzed by transition metal complexes is much more complicated since the relative reactivities  $k_I/k_{II}$  determined in this case vary over two orders of magnitude. This marked difference between the values of the reactivities in the radical initiated and catalyzed reactions deserves more detailed analysis. First of all, the values of conversions  $k_{II}$  show that  $CH_3CCl_3$  in competitive reaction with  $CF_3CCl_3$  catalyzed by copper complexes is practically unreactive so that the relative reactivities  $k_I/k_{II}$  have no real meaning here. This finding is documented by the use of  $Cu(2-PrNH_2)_2Cl$

TABLE I

Relative reactivities ( $k_I/k_{II}$ ) of  $CF_3CCl_3$  and  $CH_3CCl_3$  in competitive addition to 1-hexene initiated by different radical initiators ( $x$  are conversions in % and  $k$  are rate constants in  $s^{-1}$ )

Initiator <sup>a</sup>	Reaction time, h	Temp. °C	$x_I$	$x_{II}$	$k_I \cdot 10^7$	$k_{II} \cdot 10^7$	$k_I/k_{II}$
Dibenzoyl peroxide	6	80	1.7	0.4	11	2.1	5.2
Di-tert-butyl peroxide	6	140	35.4	5.5	210	27.0	7.8
AIBN <sup>b</sup>	6	80	2.8	0.3	12	1.1	10.9
Propylamine	4	140	9.0	1.0	130	15.0	8.7
2-Propylamine	6	140	4.2	0.5	30	3.4	8.8
t-Butylamine	4	140	1.1	0.1	11	1.4	7.9
Cyclohexylamine	2	140	11.1	1.6	130	16.0	8.1
Dipropylamine	4	140	0.9	0.1	40	5.3	7.6
Dibutylamine	6	140	3.7	0.5	66	8.2	8.0
Morpholine	6	140	1.9	0.2	17	2.2	7.7
Tributylamine	6	140	1.0	0.1	5.4	0.61	8.9
Tripropylamine	6	140	0.4	0.05	5.3	0.65	8.2
UV	6	0	0.3	0.04	3.5	0.57	6.1
Thermal	13	140	0.4	0.05	3.9	0.60	6.5

<sup>a</sup> 5 mole % of the initiator with respect to 1-hexene; <sup>b</sup> azobis(isobutyronitrile), other conditions see Experimental.

where the adduct *IV* was not practically formed at 80°C ( $x_{II} = 0.02\%$ ). A detectable amount of the adduct *IV* ( $x_{II} = 0.10-0.28\%$ ) was observed only when the complex was prepared in situ or when the reaction was carried out at higher temperatures, i.e. at 140°C. However, the copper(I)-phosphine complex  $\text{Cu}(\text{PPh}_3)_3\text{Cl}$  showed very low activity even at 140°C, likely due to its low solubility. Its activity increased only in the presence of 2-propylamine, most likely as the result of ligand exchange. The same behaviour was exhibited also by the copper complex immobilized on a styrene-divinylbenzene copolymer. Nearly inactive was copper(I) chloride without and in presence of solvents (acetonitrile, 2-propanol). Also inactive was the copper(II) complex  $\text{Cu}(\text{2-PrNH}_2)_2\text{Cl}_2$ , as expected based on the mechanism of the reaction which predicts catalytic activity only for copper(I) complexes.

It is known that some palladium complexes or Pd salts activate carbon-halogen bond in addition reactions to alkenes<sup>17-19</sup>. Therefore, we have tested the efficiency of Pd(0)-phosphine complex of the type  $\text{Pd}(\text{PPh}_3)_n$  which was prepared in situ from  $\text{Pd}(\text{OAc})_2$  in the presence of a weak base ( $\text{K}_2\text{CO}_3$ , ref.<sup>19</sup>). It was found that in the presence of the phosphine and amine-palladium complex, both adducts *III* and *IV* were formed, relative reactivities  $k_I/k_{II}$  being 5.9 and 6.7 respectively. These values

TABLE II

Relative reactivities ( $k_I/k_{II}$ ) of  $\text{CF}_3\text{CCl}_3$  and  $\text{CH}_3\text{CCl}_3$  in competitive addition to 1-hexene catalyzed by transition metal complexes (for  $x$  and  $k$  see Table I)

Catalyst <sup>a</sup>	Reaction time, h	Temp. °C	$x_I$	$x_{II}$	$k_I \cdot 10^6$	$k_{II} \cdot 10^6$	$k_I/k_{II}$
$\text{Cu}(\text{2-PrNH}_2)_2\text{Cl}$	1	80	19.2	0.02	45.0	0.044	1 023.0
$\text{Cu}(\text{2-PrNH}_2)_2\text{Cl}^b$	3	80	54.7	0.10	336.0	0.43	780.0
$\text{Cu}(\text{2-PrNH}_2)_2\text{Cl}^b$	1	140	32.7	0.28	208.0	0.76	274.5
$\text{Cu}(\text{2-PrNH}_2)_2\text{CN}^b$	1	140	18.1	0.18	135.0	0.69	195.4
$\text{Cu}(\text{PPh}_3)_3\text{Cl}$	5	140	2.7	0.08	2.7	0.075	35.5
$\text{Cu}(\text{PPh}_3)_3\text{Cl} + \text{2-PrNH}_2$	1	140	13.9	0.27	160.0	2.67	59.9
Cu-komplex <sup>c</sup>	4	140	2.7	0.10	2.2	0.10	21.1
$\text{CuCl}$	7	140	0.3	0.0	—	—	—
$\text{Cu}(\text{2-PrNH}_2)_2\text{Cl}_2$	4	80	0.0	0.0	—	—	—
$\text{Pd}(\text{AcO})_2 + \text{PPh}_3 + \text{K}_2\text{CO}_3^d$	5	140	24.2	4.5	31.9	5.45	5.9
$\text{Pd}(\text{AcO})_2 + \text{2-PrNH}_2$	5	140	6.0	0.9	9.9	1.47	6.7
$\text{Ru}(\text{PPh}_3)_3\text{Cl}_2^e$	2	140	11.8	0.3	144.0	3.39	42.5
$\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$	3	140	65.9	3.5	253.0	32.5	7.8

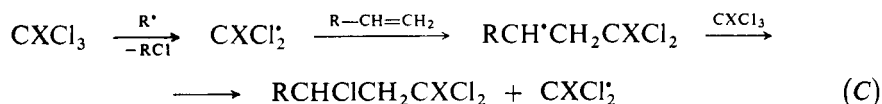
<sup>a</sup> 1 mole % of the catalyst with respect to 1-hexene, other conditions see Experimental; <sup>b</sup> the catalyst prepared in situ; <sup>c</sup> copper complex anchored to styrene-divinylbenzene copolymer;

<sup>d</sup>  $\text{Pd}(\text{OAc})_2 : \text{PPh}_3 : \text{K}_2\text{CO}_3$  mol. ratio = 1 : 2 : 95; <sup>e</sup> benzene as solvent.

are very close to those obtained for classical radical initiated reactions (Table I) and indicate the presence of free radicals in the course of the reaction.

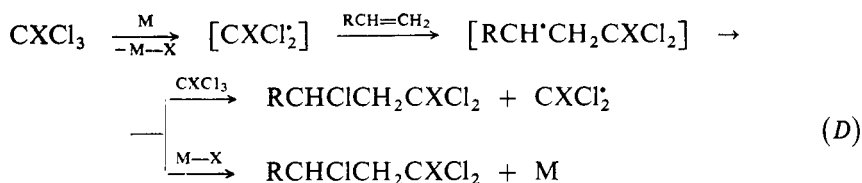
The ruthenium(II)-phosphine complex  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$  has proved to be suitable catalyst of the addition reactions of halogenated hydrocarbons to alkenes. This reaction is believed to proceed in the coordination sphere of the complex, even though the presence of free radicals has not been fully excluded<sup>6,7</sup>. However, the Ru complex is insoluble in the reaction mixture in the absence of solvents and the value of the relative reactivity  $k_I/k_{II}$  in this heterogeneously catalyzed addition reaction equaled to 7.8, which is similar to the Pd complexes and to classical free radical initiators. In the presence of benzene as the solvent, the homogeneous catalyzed reaction had  $k_I/k_{II} = 42.5$ . This value shows that in the competitive reaction catalyzed by the Ru complex and in contradistinction to the Cu complexes, both polyhalogenated ethanes *I* and *II* undergo reaction, their relative reactivity differing markedly from that of classical radical initiation. One can thus conclude that along with catalytic effect of the Ru complex, also free radical chain reactions are playing role in this case.

The results presented in this study can be summarized as follows. The different values of relative reactivities of  $\text{CF}_3\text{CCl}_3$  and  $\text{CH}_3\text{CCl}_3$  in competitive reaction with 1-hexene reflect to some degree differences in the mechanism of classical radical initiated and metal catalyzed addition reactions. In the radical initiated reactions proceeding via free radical chain mechanism, the relative reactivity of  $\text{CF}_3\text{CCl}_3$  and  $\text{CH}_3\text{CCl}_3$  is independent of the radical initiator, as expected, and its value  $k_I/k_{II}$  is 7.8 to 8.8, which corresponds to the relative reactivity of the radicals  $\text{CF}_3\text{CCl}_2^\cdot$  and  $\text{CH}_3\text{CCl}_2^\cdot$  under conditions of free radical reactions. The mechanism of such a reaction can be depicted by the simplified equation (C).



$\text{X} = \text{CF}_3, \text{CH}_3$

Metal complexes or metal salts can act in general both as initiators and as catalysts of the addition reactions (Eq. (D)).



In the case of catalysis, either chain-transfer catalysis (redox process) or coordination of radical intermediates to the central metal atom could be processes in action, the

addition reaction in the latter case taking place in the coordination sphere of the metal complex.

From the values of relative reactivities  $k_I/k_{II}$  one can conclude that the reaction had been initiated likely in the presence of palladium complexes and on the surface of the heterogeneous ruthenium complex. In general, one can further assume that in the other cases (including copper complexes at higher temperatures at which they can undergo decomposition), both possibilities of chain transfer mentioned above could operate, i.e. via  $CXCl_3$  or via  $M-X$ , one of the ways being predominant. In these cases the decision about the mechanism is very difficult and can lead to incorrect conclusions. The complexity of the situation can be also the reason why relative reactivities differ by one to two orders of magnitude.

Quite different situation is encountered in the case of copper(I)-amine complexes represented by  $Cu(2-PrNH_2)_2Cl$  which are very efficient catalysts even under mild reaction conditions. The basic finding is the confirmation of the fact that  $CH_3CCl_3$  in the competitive reaction with  $CF_3CCl_3$  is fully unreactive, in contrast to the separate reactions<sup>12</sup>. This exceptional case in catalytic reactions can be explained in terms of mutual competition between  $CH_3CCl_3$  and  $CF_3CCl_3$  in the one-electron transfer reaction for the Cu complex (Eqs (E) and (F)). The equilibrium of the reaction (E) is apparently markedly shifted in favour of intermediate V while in the case of reaction (F) it is to the contrary and intermediate VI is formed almost not at all.

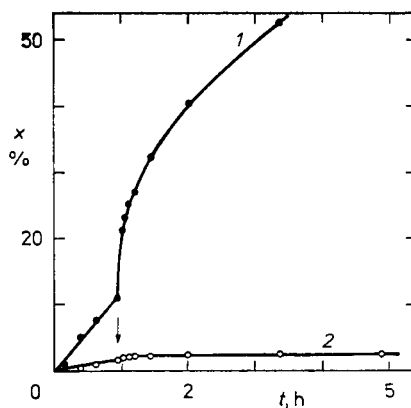
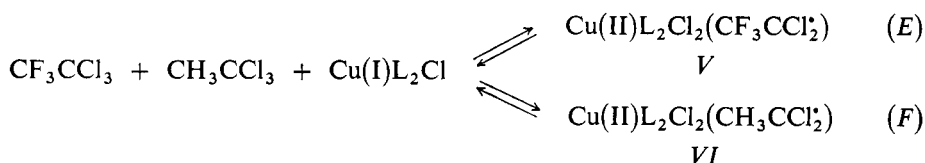


FIG. 1

The course of the addition reaction of  $CF_3CCl_3$  (1) and  $CH_3CCl_3$  (2) with 1-hexene at  $140^\circ C$  in the presence of cyclohexylamine as radical initiator ( $t < 1$  h) and  $Cu. (c-C_6H_{11}NH_2)_2Cl$  as catalyst ( $t > 1$  h);  $x$  is the conversion;  $[CF_3CCl_3]_0 : [CH_3CCl_3]_0 : [C_6H_{12}]_0 : [c-C_6H_{11}NH_2] : [CuCl] = 2.5 : 2.5 : 1 : 0.05 : 0.01$

In the course of the so catalyzed reaction, formation of free radicals  $\text{CH}_3\text{CCl}_2\cdot$  and  $\text{CF}_3\text{CCl}_2\cdot$  does not take place and the addition proceeds in the coordination sphere of the copper complex. This results in the exclusive formation of adduct *III*. Although the relative reactivities of  $\text{CH}_3\text{CCl}_3$  and  $\text{CF}_3\text{CCl}_3$  cannot be determined in such a case, the results of experiments provide nevertheless a valuable information about the mechanism of the reaction and participation of the copper complex in transition state of the reaction. It has been shown that competitive reactions carried out with different types of initiators and catalysts allow to find whether the addition proceeds via classical radical-chain or via catalytic non-chain mechanism.

It is worth illustrating a possible change of mechanism from the classical to catalytic one on example of cyclohexylamine which can act both as a radical initiator and as a ligand (Fig. 1). The competitive reaction of  $\text{CF}_3\text{CCl}_3$  and  $\text{CH}_3\text{CCl}_3$  with 1-hexene was started in the presence of cyclohexylamine as the radical initiator to form both adducts *III* and *IV* ( $k_I/k_{II} = 8:1$ ). After 1 hour, acetonitrile solution of copper(I) chloride was added as the catalyst, the rate of the adduct *III* formation steeply increased while formation of adduct *IV* stopped after several minutes and its concentration remained constant during further stage of the reaction.

The results concerning the reactivity of other halo compounds and their behaviour in separate and competitive reactions will be reported in a subsequent work<sup>12</sup>.

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