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ORGANIC SYNTHESES BY MEANS OF METAL COMPLEXES–XI[1]

COPPER COMPLEX CATALYZED ADDITION REACTIONS OF ORGANIC POLYHALIDES TO ACRYLIC MONOMERS

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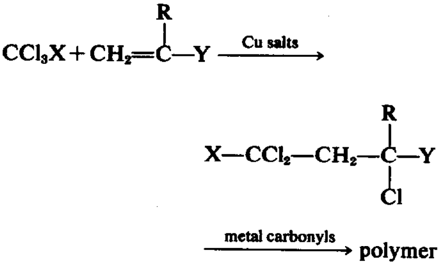
Abstract—Telomerization, especially 1:2 adduct formation from organic polyhalides and acrylic monomers catalyzed by a copper complex has been studied. Reaction of carbon tetrachloride with acrylic monomers catalyzed by a copper salt gave a 1:2 adduct. Methyl trichloroacetate afforded a 1:2 adduct with acrylic monomers, addition of LiCl increased the yield. No 1:2 adduct was obtained from $CHCl_3$ even in the presence of LiCl. The 1:2 adduct formation mechanism is discussed.

Organic polyhalides such as carbon tetrachloride, trichloroacetate, or chloroform are known to generate radical species on reaction with metal complexes which add to olefins. The nature of these radicals seems to vary depending on the nature of metal complexes. Thus the reported reactions of organic polyhalides with vinyl monomers can be classified in two ways. First is selective formation of a 1:1 adduct catalyzed by copper salts.[2–4] Secondly polymerization catalyzed by various metal carbonyls and their derivatives.[5,6]



$$\mathrm{CCl_3X + CH_2{=}\overset{R}{C}{-}Y \xrightarrow{\text{Cu salts}} X{-}CCl_2{-}CH_2{-}\underset{Cl}{\overset{R}{C}}{-}Y}$$

$$\xrightarrow{\text{metal carbonyls}} \text{polymer}$$

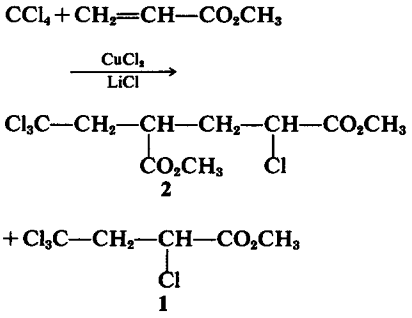
$$\left(\begin{array}{l}\mathrm{X{:}\ H, Cl, or\ {-}CO_2R'}\\ \mathrm{Y{:}\ {-}CO_2R''\ or\ {-}CN}\\ \mathrm{R{:}\ H\ or\ {-}Me}\end{array}\right.$$

The termination step is predominant with the former catalyst and the propagation step predominates with the latter catalysts. Thus it is expected that modification of the catalyst might change the mode of reaction. Investigation of the copper complex's has led us to discover a new reaction of organic polyhalides with acrylic monomers. Preliminary accounts have been given[7] and the details are presented here.

RESULTS AND DISCUSSION

Reaction of carbon tetrachloride with acrylic monomers

Carbon tetrachloride with methyl acrylate was first investigated. The reaction catalyzed by $CuCl_2$ in MeCN gave a 1:1 adduct, methyl 2,4,4,4-tetrachlorbutyrate (**1**), as shown by Asscher and Vofsi.[2] Addition of LiCl to this system markedly changed the reaction and a 1:2 adduct, dimethyl 2-chloro-4-(2,2,2-trichloroethyl)glutarate (**2**), was obtained as main product along with **1**.



$$\mathrm{CCl_4 + CH_2{=}CH{-}CO_2CH_3 \xrightarrow[LiCl]{CuCl_2}}$$

$$\mathrm{Cl_3C{-}CH_2{-}\underset{CO_2CH_3}{CH}{-}CH_2{-}\underset{Cl}{CH}{-}CO_2CH_3}\quad \mathbf{2}$$

$$\mathrm{+\,Cl_3C{-}CH_2{-}\underset{Cl}{CH}{-}CO_2CH_3}\quad \mathbf{1}$$

The ratio of **2** to **1** was affected by several factors such as molar ratio of methyl acrylate to carbon tetrachloride and catalyst system.

Table 1 shows the effect of the molar ratio of methyl acrylate to carbon tetrachloride in MeCN. The weight ratio of **2** to **1** increased with increasing molar ratio of methyl acrylate to carbon tetrachloride and a linear relationship was observed between these two ratios as shown in Fig 1. Total yields of the 1:1 adduct and the 1:2 adduct decreased when the molar ratio (methyl acrylate/carbon tetrachloride) was greater than 4·4. The

Table 1. Effect of molar ratio of methyl acrylate (MA) to carbon tetrachloride (CT)[a]

Run	MA/CT molar ratio	Products (g) 1 : 1 adduct (1)	1 : 2 adduct (2)	2/1
1	3·6	10·69	9·49	0·89
2	3·8	8·32	10·84	1·30
3	4·0	6·56	11·84	1·80
4	4·2	4·92	13·16	2·67
5	4·4	3·05	10·06	3·30

[a] Reaction carried out with CCl_4 (13·00 g), methyl acrylate, $CuCl_2 2H_2O$ (0·80 g) and LiCl (1·00 g) in MeCN (15 ml) at 170° for 16 h.

result might be due to the formation of higher telomers.

Results of the reactions catalyzed by various copper salts are shown in Table 2. It is clear that the weight ratio of **2** to **1** is greatly influenced by the catalyst system. The highest ratio was obtained by the Cu_2O–LiCl system and the highest yield of the 1 : 2 adduct was obtained by the cuprous or cupric chloride–LiCl system under these conditions. Higher telomers might be formed by cuprous oxide or cupric acetate under similar conditions.

As seen from Table 2, an increased amount of added LiCl also results in an increased yield of the 1 : 2 adduct.

The KCl–copper salt catalyst system can also be used for 1 : 2 adduct formation.

Next the reaction of carbon tetrachloride with acrylonitrile was investigated. The 1 : 2 adduct, 2-chloro-4-(2,2,2-trichloroethyl)glutaronitrile (**3**) was obtained along with the 1 : 1 adduct, 2,4,4,4-tetrachlorobutyronitrile (**4**).

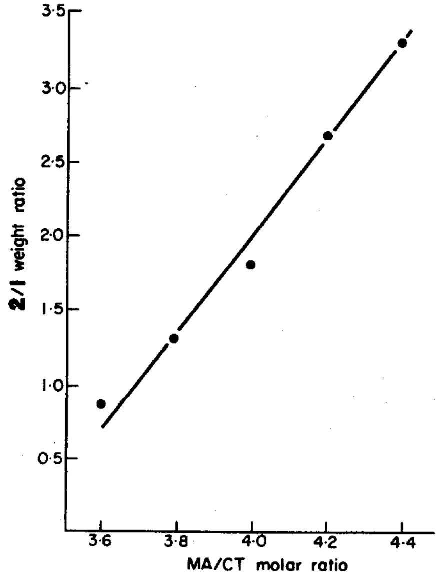


Fig 1. Reaction of carbon tetrachloride (CT) with methyl acrylate (MA).

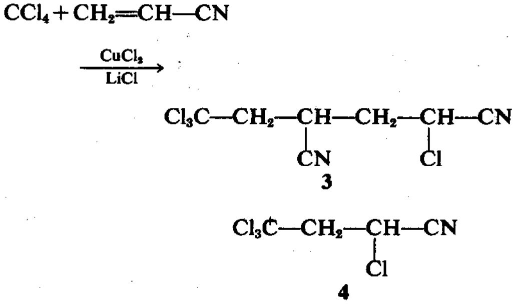
Table 2. Reaction of carbon tetrachloride with methyl acrylate by various copper salts[a]

Run	Copper salt	Products 1	2	2/1
3	$CuCl_2 2H_2O$	6·56	11·84	1·80
6	Cu_2Cl_2	6·62	11·95	1·81
7	Cu_2O	2·30	9·81	4·27
8	$Cu(OAc)_2$	3·62	9·01	2·49
9	$CuCl_2 2H_2O$[b]	5·37	12·53	2·33
10	$CuCl_2 2H_2O$[c]	10·19	8·10	0·79

[a] Reaction carried out with CCl_4 (13·00 g), methyl acrylate (29·04 g) (MA/CT molar ratio: 4·0), copper salt (4·7 mmol), LiCl (1·00 g) in MeCN (15 ml) at 170° for 16 hr.

[b] 2·00 g LiCl added.

[c] 1·00 g KCl added.



$$CCl_4 + CH_2{=}CH{-}CN \xrightarrow[LiCl]{CuCl_2} Cl_3C{-}CH_2{-}\underset{CN}{CH}{-}CH_2{-}\underset{Cl}{CH}{-}CN \quad (3)$$

$$Cl_3C{-}CH_2{-}\underset{Cl}{CH}{-}CN \quad (4)$$

A linear relationship was also observed between the weight ratio of **3** to **4** and the molar ratio of acrylonitrile to carbon tetrachloride as shown in Table 3.

Table 4 shows the results obtained using various catalysts. Unlike the reaction of carbon tetrachloride with methyl acrylate, $CuCl_2$, $Cu(OAc)_2$ and Cu_2O showed almost the same selectivity.

Solvents and reaction temperature were found to effect 1 : 2 adduct formation and the results are

Table 3. Effect of molar ratio of acrylonitrile (AN) to carbon tetrachloride (CT)[a]

Run	AN/CT molar ratio	Products (g) 1 : 1 adduct (4)	1 : 2 adduct (3)	3/4
11	3·2	15·21	6·34	0·42
12	3·4	15·14	8·89	0·59
13	3·6	12·60	11·87	0·94
14	3·8	10·46	12·86	1·23
15	4·0	8·39	12·83	1·53

[a] Reaction carried out with CCl_4 (18·00 g) acrylonitrile, $CuCl_2{\cdot}2H_2O$ (0·80 g) and LiCl (1·00 g) in MeCN (15 ml) at 150° for 16 h.

Table 4. Reaction of carbon tetrachloride with acrylonitrile by various copper salts[a]

Run	copper salt	Products (g) 1:1 adduct 4	 1:2 adduct 3	3/4
14	$CuCl_22H_2O$	10·46	12·86	1·23
16	Cu_2Cl_2	13·96	8·24	0·59
17	Cu_2O	7·91	11·14	1·41
18	$Cu(OAc)_2$	9·46	12·50	1·32
19	$Cu(NO_3)_23H_2O$	17·33	trace	

[a] Reaction carried out with CCl_4 (18·00 g), acrylonitrile (23·56 g) (AN/CT molar ratio: 3·8), copper salt (4·7 mmol), LiCl (1·00 g) in MeCN (15 ml) at 150° for 16 h.

Table 5. Effect of solvent and reaction temperature in the reaction of carbon tetrachloride with acrylonitrile

Run	Solvent	Reaction temp. (C)	Products (g) 1:1 adduct (4)	 1:2 adduct (3)	3/4
13[a]	MeCN	150	12·60	11·87	0·94
20[a]	MeCN	170	8·03	13·64	1·70
11[b]	MeCN	150	15·21	6·34	0·42
21[b]	MeOH	150	6·20	10·67	1·72

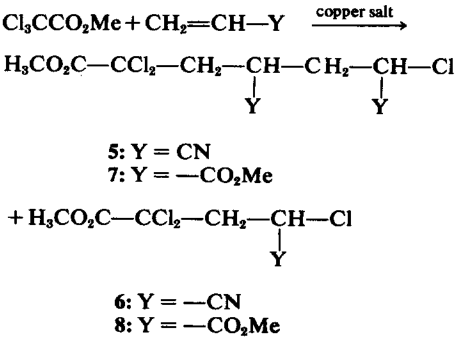
[a] Reaction carried out with CCl_4 (18·00 g), acrylonitrile (22·32 g)(AN/CT molar ratio: 3·6), $CuCl_2·2H_2O$ (0·80 g) LiCl (1·00 g) in 15 ml of solvent for 16 h.

[b] CCl_4 (18·00 g) and acrylonitrile (19·84 g) (AN/CT molar ratio: 3·2) were used.

in Table 5. In MeOH a higher weight ratio (3/4) was obtained than in MeCN. Higher reaction temperature tends to increase the yield of the 1:2 adduct.

Reaction of methyl trichloroacetate with acrylic monomers

Unlike carbon tetrachloride, methyl trichloroacetate gave 1:2 adducts with acrylic monomers in the presence of copper salts without addition of LiCl.



$$Cl_3CCO_2Me + CH_2{=}CH{-}Y \xrightarrow{\text{copper salt}}$$

$$H_3CO_2C{-}CCl_2{-}CH_2{-}\underset{Y}{\underset{|}{C}}H{-}CH_2{-}\underset{Y}{\underset{|}{C}}H{-}Cl$$

5: Y = CN
7: Y = —CO_2Me

$$+\ H_3CO_2C{-}CCl_2{-}CH_2{-}\underset{Y}{\underset{|}{C}}H{-}Cl$$

6: Y = —CN
8: Y = —CO_2Me

In these reactions, the weight ratio of the 1:2 adduct to the 1:1 adduct was also found to be proportional to the molar ratio of acrylic monomer to methyl trichloroacetate. Results obtained with acrylonitrile are in Table 6. It should be noticed that the higher ratio of the 1:2 adduct (**5**) to the 1:1 adduct (**6**) can be obtainable at a lower ratio of reactants as compared with the reaction of carbon tetrachloride with acrylonitrile. Table 7 shows the effect of various copper catalysts in the reaction of methyl trichloroacetate with acrylonitrile. High selectivity of 1:2 adduct formation was observed with Cu_2O or $Cu(NO_3)_2$.

Effect of the reaction temperature is shown in Table 8. It is obvious that a higher temperature favors 1:2 adduct formation. The difference between these results and that of Tsutsumi *et al.*[4] in which only a 1:1 adduct was obtained, might be attributed to reaction temperature.

Table 9 shows the effect of solvent and an amount of catalyst in this reaction. The highest ratio of 1:2 adduct to 1:1 adduct was obtained in MeOH, the lowest ratio in a nonpolar solvent. It is noteworthy that the amount of catalyst has no effect on the ratio (runs 36 and 37).

Table 6. Reaction of methyl trichloroacetate (MTA) with acrylonitrile (AN)[a]

Run	AN/MTA molar ratio	Products (g) 1:1 adduct (6)	 1:2 adduct (5)	5/6
22	2·0	13·02	12·66	0·97
23	2·2	7·95	15·69	1·98
24	2·4	7·06	17·45	2·48
25	2·6	4·11	17·26	4·21
26	2·8	3·17	16·97	5·35

[a] Reaction carried out with methyl trichloroacetate (20·0 g), acrylonitrile, $CuCl_2·2H_2O$ (0·80 g) in MeCN (25 ml) at 150° for 16 h.

Table 7. Reaction of methyl trichloroacetate with acrylonitrile catalyzed by various copper salts[a]

Run	copper salt	Products (g) 1:1 adduct (6)	 1:2 adduct (5)	5/6
23	$CuCl_22H_2O$	7·95	15·69	1·98
27	Cu_2Cl_2	9·35	15·67	1·68
28	$Cu(OAc)_2$	10·10	13·56	1·34
29	Cu_2O	2·85	12·39	4·34
30	CuO	12·51	11·69	0·93
31	$CuSO_4$	13·77	5·60	0·41
32	$Cu(NO_3)_23H_2O$	3·45	20·67	5·99

[a] Reaction carried out with methyl trichloroacetate (20·0 g), acrylonitrile (13·20 g) (AN/MTA molar ratio: 2·2), copper salt (4·7 mmol) in MeCN (25 ml) at 150° for 16 h.

Table 8. Effect of reaction temperature in the reaction of methyl trichloroacetate with acrylonitrile[a]

Run	Reaction temp. (°C)	Products (g) 1 : 1 adduct (6)	1 : 2 adduct (5)	5/6	Recovered MTA (g)
33	170	8·23	17·73	2·16	0·12
34	150	8·55	15·87	1·86	0·53
35	130	2·50	trace	0	16·75

[a] Reaction carried out with methyl trichloroacetate (20·0 g), acrylonitrile (13·20 g), $CuCl_2 \cdot 2H_2O$ (0·80 g) in MeCN (20 ml) for 6 h.

Table 9. Effect of solvent and an amount of catalyst in the reaction of methyl trichloroacetate with acrylonitrile[a]

Run	Solvent	Products (g) 1 : 1 adduct (6)	1 : 2 adduct (5)	5/6
36		8·45	17·46	2·07
37[b]		8·16	16·84	2·06
23	MeCN	7·95	15·69	1·98
38	MeOH	2·01	10·92	5·42
39	Ether	18·76	5·78	0·31
40	C_6H_6	19·90	trace	0
41	CH_2Cl_2	19·34	6·35	0·33
42	EtOAc	10·50	13·05	1·24

[a] Reaction carried out with methyl trichloroacetate (20·0 g), acrylonitrile (13·20 g), $CuCl_2 \cdot 2H_2O$ (0·80 g), solvent (25 ml) at 150° for 16 h.

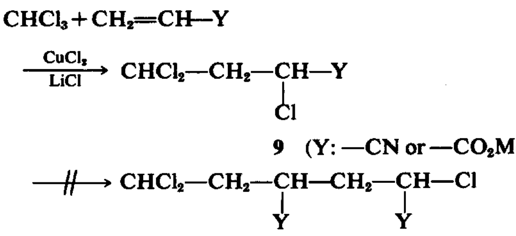
[b] 0·10 g of $CuCl_2 2H_2O$ was used.

Addition of LiCl to this system increased the 1 : 2 adduct yield and the results are shown in Table 10.

Results of the reaction of methyl trichloroacetate with methyl acrylate catalyzed by $CuCl_2$ in MeOH are shown in Table 11.

Reaction of chloroform with acrylic monomer

Reaction of $CHCl_3$ with acrylic monomers was different from that of CCl_4 or methyl trichloroacetate. No 1 : 2 adduct was obtained even with a large excess of acrylic monomer in the presence of LiCl, and only 1 : 1 adduct (9) was formed.



$$CHCl_3 + CH_2{=}CH{-}Y \xrightarrow[LiCl]{CuCl_2} CHCl_2{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{C}}H{-}Y$$

$$\mathbf{9}\ (Y: {-}CN \text{ or } {-}CO_2Me)$$

$$\xrightarrow{/\!/} CHCl_2{-}CH_2{-}\underset{\displaystyle Y}{\underset{|}{C}}H{-}CH_2{-}\underset{\displaystyle Y}{\underset{|}{C}}H{-}Cl$$

MECHANISM

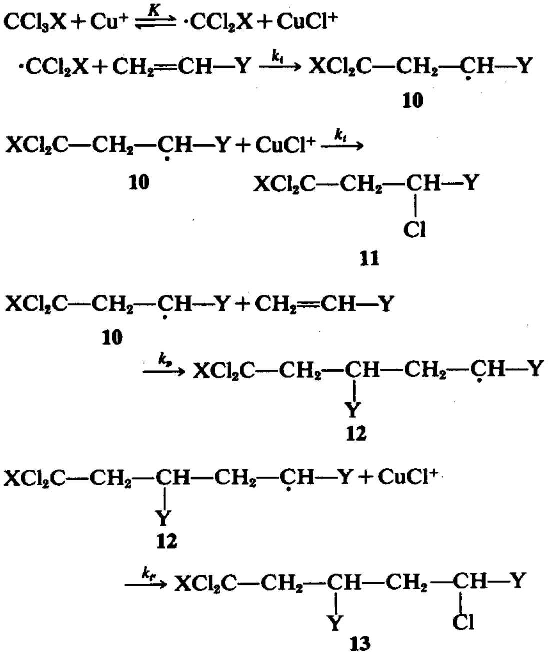
Asscher and Vofsi proposed a redox-transfer mechanism for the 1 : 1 addition reaction of CCl_4 and $CHCl_3$ to olefins catalyzed by copper salts.[2,3]

Table 10. Effect of LiCl in the reaction of methyl trichloroacetate with acrylonitrile[a]

Run	LiCl (g) added	Products (g) 1 : 1 adduct (6)	1 : 2 adduct (5)	5/6
36	0	8·45	17·46	2·07
43	0·5	7·15	18·71	2·62
44	1·0	6·33	19·58	3·09
45	2·0	6·02	20·40	3·39
46	3·0	4·84	20·36	4·21

[a] Reaction carried out with methyl trichloroacetate (20·0 g), acrylonitrile (13·20 g), $CuCl_2 \cdot 2H_2O$ (0·80 g) at 150° for 16 h.

Assuming the same mechanism, the following reaction scheme would be applicable to 1 : 2 adduct formation.



$$CCl_3X + Cu^+ \overset{K}{\rightleftharpoons} \cdot CCl_2X + CuCl^+$$

$$\cdot CCl_2X + CH_2{=}CH{-}Y \xrightarrow{k_i} \underset{\mathbf{10}}{XCl_2C{-}CH_2{-}\underset{\cdot}{C}H{-}Y}$$

$$\underset{\mathbf{10}}{XCl_2C{-}CH_2{-}\underset{\cdot}{C}H{-}Y} + CuCl^+ \xrightarrow{k_t} \underset{\mathbf{11}}{XCl_2C{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{C}}H{-}Y}$$

$$\underset{\mathbf{10}}{XCl_2C{-}CH_2{-}\underset{\cdot}{C}H{-}Y} + CH_2{=}CH{-}Y \xrightarrow{k_p} \underset{\mathbf{12}}{XCl_2C{-}CH_2{-}\underset{\displaystyle Y}{\underset{|}{C}}H{-}CH_2{-}\underset{\cdot}{C}H{-}Y}$$

$$\underset{\mathbf{12}}{XCl_2C{-}CH_2{-}\underset{\displaystyle Y}{\underset{|}{C}}H{-}CH_2{-}\underset{\cdot}{C}H{-}Y} + CuCl^+ \xrightarrow{k_t} \underset{\mathbf{13}}{XCl_2C{-}CH_2{-}\underset{\displaystyle Y}{\underset{|}{C}}H{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{C}}H{-}Y}$$

(X: Cl or $-CO_2Me$
Y: $-CO_2Me$ or $-CN$)

Table 11. Reaction of methyl trichloroacetate with methyl acrylate[a]

	MA/MTA			
	molar	Products (g)		
Run	ratio	1 : 1 adduct (8)	1 : 2 adduct (7)	7/8
47	1·8	3·55	14·85	4·18
48	2·2	3·16	15·86	5·02
49	2·6	2·88	16·49	5·73
50[b]	1·8	trace	11·27	

[a]Reaction carried out with methyl trichloroacetate (14·0 g), methyl acrylate, $CuCl_2{\cdot}2H_2O$ (0·80 g), MeOH (20 ml) at 150° for 16 h.

[b]1·00 g LiCl added.

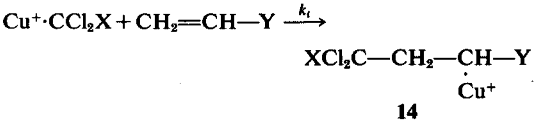
By applying the steady-state approximation, namely assuming that the reaction intermediates (**10**) and (**12**) are in a stationary state, and assuming that k_t is equal to $k_{t'}$, following equation is obtained for the rate ratio of 1 : 2 adduct (**13**) formation and 1 : 1 adduct (**11**) formation.

$$\frac{d(1:2\ \text{adduct})}{dt}\bigg/\frac{d(1:1\ \text{adduct})}{dt} = \frac{k_p}{k_t}\frac{(CH_2{=}CH{-}Y)}{(CuCl^+)}.$$

According to the above scheme k_p would change depending on the nature of monomer, reaction temperature and solvent and k_t would change depending on the nature of monomer and copper salt, reaction temperature and solvent. Thus the ratio of 1 : 2 adduct to 1 : 1 adduct should change depending on the nature of monomer and copper salt, concentration of monomer and copper salt, reaction temperature, and solvent. The ratio should be independent of the nature of organic polyhalide. This inference conflicts with our results. Methyl trichloroacetate afforded a 1 : 2 adduct using copper salt at low ratio of acrylic monomer to methyl trichloroacetate, whereas CCl_4 afforded a 1 : 2 adduct only in the presence of LiCl and with a large excess of acrylic monomer. On the other hand, $CHCl_3$ did not give a 1 : 2 adduct even in the presence of LiCl and with large excess of acrylic monomer and only a 1 : 1 adduct was obtained. Therefore it seems probable that organic polyhalides take part in the termination step. Furthermore, changing the amount of copper salt did not alter the ratio of 1 : 2 to 1 : 1 adduct.

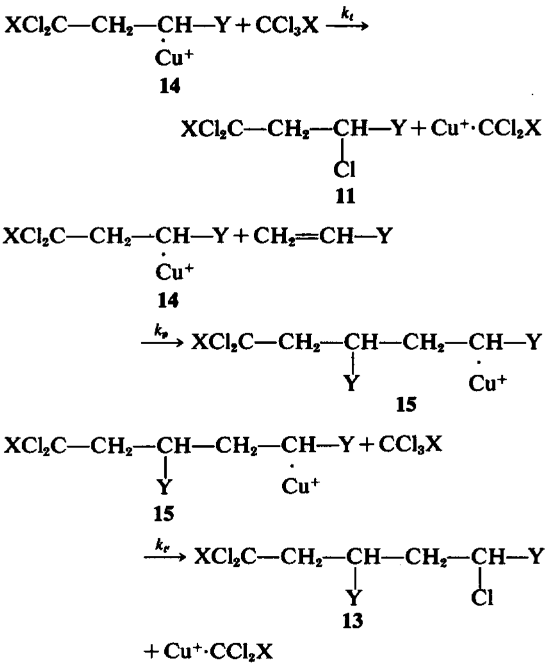
Thus, we propose the following radical complex mechanism.

$$CCl_3X + 2Cu^+ \overset{K}{\rightleftharpoons} Cu^+{\cdot}CCl_2X + CuCl^+$$



$$Cu^+{\cdot}CCl_2X + CH_2{=}CH{-}Y \xrightarrow{k_i} XCl_2C{-}CH_2{-}\underset{\substack{\cdot\\ Cu^+}}{CH}{-}Y$$

14



$$XCl_2C{-}CH_2{-}\underset{\substack{\cdot\\ Cu^+}}{CH}{-}Y + CCl_3X \xrightarrow{k_t}$$

14

$$XCl_2C{-}CH_2{-}\underset{\substack{|\\ Cl}}{CH}{-}Y + Cu^+{\cdot}CCl_2X$$

11

$$XCl_2C{-}CH_2{-}\underset{\substack{\cdot\\ Cu^+}}{CH}{-}Y + CH_2{=}CH{-}Y$$

14

$$\xrightarrow{k_p} XCl_2C{-}CH_2{-}\underset{\substack{|\\ Y}}{CH}{-}CH_2{-}\underset{\substack{\cdot\\ Cu^+}}{CH}{-}Y$$

15

$$XCl_2C{-}CH_2{-}\underset{\substack{|\\ Y}}{CH}{-}CH_2{-}\underset{\substack{\cdot\\ Cu^+}}{CH}{-}Y + CCl_3X$$

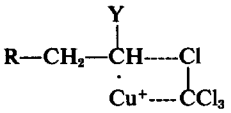
15

$$\xrightarrow{k_{t'}} XCl_2C{-}CH_2{-}\underset{\substack{|\\ Y}}{CH}{-}CH_2{-}\underset{\substack{|\\ Cl}}{CH}{-}Y$$

13

$$+ Cu^+{\cdot}CCl_2X$$

The termination step can be described as a four center process as shown below.

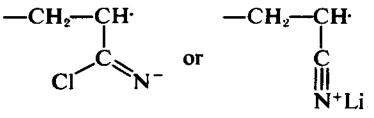


According to this mechanism, k_t would change depending on the copper salt and organic polyhalide, reaction temperature and solvent and k_p would change depending on the copper salt and monomer, reaction temperature and solvent. The following equation can be derived.

$$\frac{d(1:2\ \text{adduct})}{dt}\bigg/\frac{d(1:1\ \text{adduct})}{dt} = \frac{k_p}{k_t}\frac{(CH_2{=}CH{-}Y)}{(CCl_3X)}$$

This is consistent with our results.

There seems to be two possible roles for LiCl. First one is complex formation with the intermediate radical as postulated in the polymerization of acrylonitrile by Bamford *et al.*[8] They showed that the propagation coefficient (k_p) is substantially increased by the addition of LiCl, while the termination coefficient (k_t) is little affected and postulated the complex formation between LiCl and the terminal nitrile group of a radical as shown below.



The second one is complex formation with copper salt like Li_2CuCl_4 which would change both k_p and k_t.

EXPERIMENTAL

NMR spectra were determined on a Varian A-60 in CCl_4 (τ values). All experiments were carried out using a glass vessel with a gas inlet capillary. The vessel was placed in an autoclave and the reaction carried out by shaking. Only typical examples are shown.

Reaction of CCl_4 with methyl acrylate. Methyl acrylate (30·49 g), CCl_4 (13·00 g), MeCN (15 ml), $CuCl_2 \cdot 2H_2O$ (0·80 g) and LiCl (1·00 g) were mixed in a glass vessel and the vessel was placed in an autoclave. The autoclave was shaken at 170° for 16 h. Distillation of the product gave 4·92 g of methyl 2,4,4,4-tetrachlorobutyrate b.p. 90–98°/15 mm and 13·16 g of dimethyl 2-chloro-4-(2,2,2-trichloroethyl)glutarate b.p. 150–158°/3 mm.

Dimethyl 2-chloro-4(2,2,2-trichloroethyl)glutarate (Found: C, 33·33; H, 3·69; Cl, 43·75; MW 338 (acetone). $C_9H_{12}O_4Cl_4$ requires: C, 33·15; H, 3·72; Cl, 43·50; MW 326). IR (cm^{-1}): 1750, 1195, 1168. NMR: 5·30 (1 H), 6·15 (6 H), 6·20–7·90 (5 H).

Similarly, 2-chloro-4-(2,2,2-trichloroethyl)glutaronitrile (12·86 g, b.p. 138–146°/1 mm) and 2,4,4,4-tetrachlorobutyronitrile (10·46 g, b.p. 102–108°/23 m m) were obtained by reaction of CCl_4 (18·00 g) with acrylonitrile (23·56 g) in the presence of $CuCl_2 \cdot 2H_2O$ (0·80 g) and LiCl (1·00 g) in MeCN (15 ml) at 150° for 16 h. 2-chloro-4-(2,2,2-trichloroethyl)glutaronitrile (Found: C, 32·53; H, 2·45; N, 10·55; Cl, 54·80; MW 254 (acetone). $C_7H_6N_2Cl_4$ requires: C, 32·34; H, 2·33; N, 10·78; Cl, 54·55; MW 260). IR (cm^{-1}): 2250. NMR: 5·09 (1 H), 6·20–7·80 (5 H).

Reaction of methyl trichloroacetate with acrylonitrile. Methyl trichloroacetate (20·00 g), acrylonitrile (16·80 g), $CuCl_2 \cdot 2H_2O$ (0·80 g) were reacted at 150 for 16 h in an autoclave. Distillation of the product gave 20·84 g of methyl 2,2,6-trichloro-4,6-dicyanocaproate b.p. 140–154/0·6 mm which on standing crystallized and 3·61 g of methyl 2,2,4-trichloro-4-cyanobutyrate at 86–90/0·6 mm.

Methyl 2,2,6-trichloro-4,6-dicyanocaproate m.p. 77–79 (recrystallized from acetone–ether) (Found: C, 38·25; H, 3·29; N, 9·62; Cl, 37·33; MW 283 ($CHCl_3$). $C_9H_9N_2O_2Cl_3$ requires: C, 38·16; H, 3·18; N, 9·89; Cl, 37·45; MW 283). IR (cm^{-1}): 2250, 1758, 1222. NMR: 5·19 (1 H), 6·13 (3 H), 6·75–7·55 (5 H).

Similarly, trimethyl 1,1,5-trichloro-1,3,5-pentanetricarboxyrate (16·49 g, b.p. 152–157/1 mm) and dimethyl 2,2,4-trichloroglutarate (2·88 g, b.p. 88–93°/1 mm) were obtained from methyl trichloroacetate (14·00 g) and methyl acrylate (17·70 g). Trimethyl 1,1,5-trichloro-1,3,5-pentanetricarboxyrate (Found: C, 37·98; H, 4·41; Cl, 30·15; MW 347 ($CHCl_3$). $C_{11}H_{15}O_6Cl_3$ requires: C, 37·82; H, 4·30; Cl, 30·37; MW 349). IR(cm^{-1}): 1750, 1275, 1170. NMR: 5·40 (1 H), 6·22 (9 H), 6·7–7·9 (5 H).

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