Chemistry

Corresponding Member of the USSR Academy of Sciences R. Kh. Freidlina, E. Ts. Chukovskaya,

1964

SovietRxiv

Abstract

Full Text

Chemistry

Corresponding Member of the USSR Academy of Sciences R. Kh. Freidlina, E. Ts. Chukovskaya,
B. A. Englin

A New Type of Chain Transfer in Radical Telomerization with the Aid of a "Mediator"

One of the authors of the present paper and A. B. Belyavskii found several new ways of using metal carbonyls as initiators of the telomerization of ethylene with polychloromethanes (1,2). It was shown that this reaction, initiated by carbonyls of iron (1), chromium, molybdenum, and tungsten (2), leads to the formation of products of the same structure as in the presence of benzoyl peroxide:

$$\mathrm{CCl_4 + C_2H_4 \xrightarrow{Fe(CO)_5} Cl(CH_2CH_2)_nCCl_3}, \tag{1}$$

$$\mathrm{CHCl_3 + C_2H_4 \xrightarrow{Fe(CO)_5} H(CH_2CH_2)_nCCl_3}. \tag{2}$$

Subsequently, the systems we had found, containing metal carbonyls and polyhalogen-substituted compounds, were used by Bamford (3,4) to initiate the polymerization of vinyl monomers.

The present work is devoted to the study of the mechanism of telomerization of olefins with carbon tetrachloride and chloroform, initiated by iron pentacarbonyl.* We assumed that these reactions are of a chain-radical character, and that the stages of chain growth and chain transfer are the same as in peroxide initiation. Reaction (1) can then be expressed as follows (scheme (3)):

$$\begin{array}{lll}
\text{a)} & \mathrm{Fe(CO)_5 + 2CCl_4 \rightarrow [Fe(CO)_4Cl_2] + CO + 2CCl_3^{\bullet}} & \text{initiation;} \\
\text{b)} & \mathrm{CCl_3^{\bullet} + CH_2{=}CH_2 \rightarrow CCl_3CH_2CH_2^{\bullet}} & \text{chain initiation;} \\
\text{c)} & \mathrm{CCl_3CH_2CH_2^{\bullet} + CCl_4 \xrightarrow{K_t} CCl_3CH_2CH_2Cl + CCl_3^{\bullet}} & \text{chain transfer;} \\
\text{d)} & \mathrm{CCl_3CH_2CH_2^{\bullet} + CH_2{=}CH_2 \xrightarrow{K_p} CCl_3(CH_2)_3CH_2^{\bullet}} & \text{radical growth.}
\end{array} \tag{3}$$

Since the transfer constants $C_\mathrm{p} = \frac{K_\mathrm{t}}{K_\mathrm{p}}$ for the telomerization of ethylene with $\mathrm{CCl_4}$ under peroxide initiation have been studied in detail (5,6), stages b), c), and d) can readily be proved by determining the transfer constants in reaction (1). The data obtained by us are summarized in Table 1. As can be seen from the data of this table (experiments 1-5), the transfer constants C_1, C_2, C_3, and C_4, within the limits of experimental error, coincide with the constants determined in initiation by azobisisobutyronitrile. This unambiguously proves the chain-radical mechanism of the reaction and the formation of CCl_3 radicals as the chain carriers of the reaction.

Assuming that iron pentacarbonyl in the course of the reaction exchanges one or more carbonyl groups for chlorine atoms (stage a) of scheme (3)), we decided, for comparison, to determine the transfer constants in the telomerization of ethylene with CCl_4 initiated by $FeCl_2 \cdot 4H_2O$. As can be seen from experiments 6-10 of Table 1, in this case also the values of the transfer constants, within the limits of experimental error, coincide with the known constants.

---

* One of the advantages of iron pentacarbonyl, in comparison with iron chlorides, is its solubility in CCl_4 and $CHCl_3$, which makes it possible to study the mechanism of the indicated reactions in the absence of solvents (alcohols, etc.) capable of participating in reactions with the radicals formed.

Table 1

Partial chain-transfer constants in the telomerization of C_2H_4 and CCl_4, initiated by iron compounds at 100°C*

No.	CCl_4, mmol	$\left(\frac{C_2H_4}{CCl_4}\right)_{av}$	FeX_n, mmol	CH_3OH, mmol	Conv. C_2H_4, mol. %	1	2	3	4	≥ 5	$C_1 \cdot 10^2$	C_2	C_3	C_4
Fe(CO)$_5$														
1	55,1	1,39	0,077	–	22,6	8,9	58,7	24,1	8,3	–	13,6	2,5	4,1	
2	35,0	2,41	0,079	–	21,0	6,3	50,9	28,3	10,7	3,8	16,2	2,9	4,7	6,8
3	28,9	2,80	0,077	–	12,5	6,3	50,6	28,9	10,8	3,4	18,7	3,3	5,7	8,9
4	22,8	3,62	0,077	–	0,5	5,8	41,6	28,8	13,4	10,4	22,3	2,9	4,4	
5	23,0	3,68	0,077	–	12,2	5,1	47,3	29,0	12,7	5,9	19,8	3,6	5,7	7,9
FeCl$_2$· $4H_2O$														
6	34,5	2,39	2,5	–	0,8	5,6	47,9	30,5	12,6	3,4	14,2	2,5	4,6	8,9
7	21,3	3,91	2,5	–	0,4	4,4	43,2	30,8	14,0	7,6	18,0	3,2	5,6	7,2
8	21,4	4,04	1,0	–	1,1	3,2	36,9	31,8	18,0	11,1	13,4	2,5	4,6	7,2
9	15,2	5,75	2,5	–	1,2	3,6	35,4	30,9	17,8	11,3	21,5	3,3	5,9	8,3
10	15,1	6,05	2,5	–	0,7	3,0	32,9	30,9	19,2	14,0	18,7	3,1	5,6	8,3
Fe(CO)$_5$ + CH$_3$OH														

No.	CCl_4, mmol	$\left(\frac{C_2H_4}{CCl_4}\right)_{\text{av}}$	FeX_n, mmol	CH_3OH, mmol	Conv. C_2H_4, mol. %	1	2	3	4	≥ 5	$C_1 \cdot 10^2$	C_2	C_3	C_4
11	27,9	2,86	0,077	2,3	31,2	6,5	48,0	29,7	11,6	4,2	19,9	3,0	5,4	7,9
12	27,9	2,96	0,077	5,4	4,2	7,4	49,3	29,2	10,9	3,2	23,6	3,4	6,1	10,1
13	27,3	3,03	0,077	10,0	3,5	9,2	53,8	26,2	8,4	2,4	30,7	4,4	7,4	10,6
14	27,9	3,03	0,077	10,0	3,5	10,5	50,8	26,9	9,1	2,7	35,6	4,0	6,9	10,2
15	27,9	3,20	0,077	20,6	9,1	40,5	32,0	17,7	7,1	2,7	218,0	3,7	5,8	8,4
16	27,9	3,06	0,077	32,8	17,4	66,7	23,7	7,8	1,8		613,0	7,6	13,3	
FeCl$_2$· $4H_2O$ + **CH$_3$OH**														
17	21,1	4,74	1,0	24,4	9,6	95,0	3,2	1,2	0,6		9480,0	8,4		
18	21,4	4,84	1,0	24,4	11,0	92,9	4,2	2,0	0,9		6330,0	7,0		
FeCl$_3$ + **iso-PrOH**														
19	16,2	5,70	1,16	16,2	8,3	74,9	24,2	0,9			1700,0			
20	16,2	5,48	0,75	22,3	3,8	76,9	21,9	1,2			1820,0	11,4	16,3	

Average C_n from experiments 1-5: $18,1 \pm 2,5$; $3,0 \pm 0,2$; $4,9 \pm 0,6$; $7,9 \pm 1,0$
Average C_n from experiments 6-10: $17,2 \pm 2,2$; $2,9 \pm 0,3$; $5,3 \pm 0,4$; $8,0 \pm 0,5$
Azobisisobutyric acid dinitrile (*): $15,5 \pm 2,0$; $3,0 \pm 0,2$; $5,5 \pm 0,4$; $8,2 \pm 0,8$

* The experiments were carried out in stainless-steel autoclaves. The reaction products were analyzed by the GLC method. For a more detailed experimental procedure, see work (*).

The results of the experiments with $FeCl_2 \cdot 4H_2O$ are unexpected, since in a series of interesting works Asher and Vofsi ($^{7-9}$) showed that initiation of reactions of olefins and CCl_4 by iron chlorides, even in the case of a large excess of an easily polymerizable olefin, leads to an increase in the content of the adduct, while the yield of telomer homologues decreases significantly. To explain this effect (effect A), Asher and Vofsi proposed a mechanism according to which the iron salt participates in chain transfer (stage c, scheme (4)):

$$\begin{aligned}
&\text{a) } Fe^{2+} + CCl_4 \rightarrow Fe^{2+}(Cl) + \dot{C}Cl_3;\\
&\text{b) } \dot{C}Cl_3 + CH_2{=}CH_2 \rightarrow CCl_3CH_2\dot{C}H_2;\\
&\text{c) } CCl_3CH_2\dot{C}H_2 + Fe^{2+}(Cl) \rightarrow CCl_3CH_2CH_2Cl + Fe^{2+};\\
&\text{d) } CCl_3CH_2\dot{C}H_2 + CH_2{=}CH_2 \rightarrow CCl_3(CH_2)_3\dot{C}H_2.
\end{aligned} \tag{4}$$

Fe^{2+} denotes the ion of divalent iron, and $Fe^{2+}(Cl)$ the ion of trivalent iron bound, at least, to one chlorine ion ([9]).

In the experiments of Asher and Vofsi, unlike ours, solutions of iron salts in CH_3OH, iso-C_3H_7OH, or CH_3CN were used, with the molar ratio of solvent to CCl_4 being $\sim 1:1$. In this connection we attempted to determine the transfer constants in the reaction of ethylene and CCl_4 in the presence of $Fe(CO)_5$ and CH_3OH. It turned out that at small amounts of alcohol (experiment 11) the constants are close to the ordinary ones; with an increase in the amount of alcohol (experiments 12-16), the yield of 1,1,1,3-tetrachloropropane sharply increases (i.e., effect A is observed), and the "constant" of transfer C_1 is not constant and is unusually large. An analogous incre-

an increase in the yield of tetrachloropropane also occurred in the presence of $FeCl_2 \cdot 4H_2O$ in methanol solution (experiment 17)*.

Consequently, effect A is possible only with the simultaneous presence in the reaction mixture of an iron compound and an alcohol, which cannot be explained by scheme (4). We believe that stage c) of scheme (4) is unlikely, since according to our data ([6]) (determination of the parameters $Q - e$ of trichloroalkyl radicals in the telomerization of ethylene with CCl_4 and $CHCl_3$), the radical $CCl_3CH_2\dot{C}H_2$ is highly electrophilic ($e = +0.8$) and therefore cannot react to any considerable extent with the electrophilic iron salt (at least, it is difficult to expect that this reaction would be responsible for the high yield of the adduct).

The participation of the alcohol in the reaction studied is also confirmed by the fact that among the products of the telomerization of ethylene and CCl_4 initiated by $FeCl_2 \cdot 4H_2O$ in the presence of *iso*-C_3H_7OH we found acetone and chloroform (cf. ([10])).

The telomerization of olefins with chloroform (reaction (2)) was studied by us using heptene-1 as an example in the presence of $Fe(CO)_5$** or $FeCl_2 \cdot 4H_2O$, both without solvent and in solutions of CH_3OH, *iso*-C_3H_7OH, and CH_3CN. The results obtained are summarized in Table 2. As can be seen from the data of Table 2, in the ab-

Table 2

Reaction of heptene-1 (74 mmoles) with chloroform (225 mmoles) at 130°[1]

No. of experiment	Catalyst, 1 mmole	Additive, 225 mmoles	Conversion of heptene-1, %	n_D^{20}	d_4^{20}	MR[2] found	Content in mixture: 1,1,1-trichlorooctane	Content in mixture: 1,1,3-trichlorooctane
1[3]	$(C_6H_{11}OC(=O)O)_2$	none	55	1.4590	1.0983	54.13	100	–
2	$Fe(CO)_5$	none	14	1.4620	1.0980	54.48	95	5
3	$FeCl_2 \cdot 4H_2O$	none	~ 1	–	–	–	87	13

No. of experiment	Catalyst, 1 mmole	Additive, 225 mmoles	Conversion of heptene-1, %	n_D^{20}	d_4^{20}	MR[2] found	Content in mixture: 1,1,1-trichlorooctane	Content in mixture: 1,1,3-trichlorooctane
4	$FeCl_3 \cdot 6H_2O$	*iso*-C_3H_7OH; $NH_2(CH_3)_2Cl$	40	1.4650	1.1222	54.00	–	100
5	$Fe(CO)_5$	*iso*-C_3H_7OH	35	1.4651	1.1237	53.51	20	80
6	$Fe(CO)_5$	CH_3OH	40	1.4642	1.1123	53.98	10	90
7	$Fe(CO)_5$	CH_3CN	33	1.4645	1.1113	54.07	10	90
8	$FeCl_2 \cdot 4H_2O$	*iso*-C_3H_7OH	15	1.4647	1.1154	53.77	–	100

[1] The chloroform was carefully washed with water to remove stabilizing additives. The reaction (except for experiment 1) was carried out in sealed ampoules for 18 h under an atmosphere of inert gas. Fractions containing a mixture of isomeric trichlorooctanes with b.p. 85–95°/6 mm were isolated and analyzed by gas-liquid chromatography (temperature 100°, column: 2 m, N -silicone-elastomer 0.3% on glass beads 0.25–0.5 mm, flame-ionization detector). Under the indicated conditions 1,1,1-trichlorooctane (found %: C 44.28, 44.00; H 7.07, 6.81) (experiment 1) has a retention time of 1 40 , and 1,1,3-trichlorooctane (experiment 4) (found %: C 44.31, 44.36; H 6.77, 6.78; Cl 49.07, 48.86) –3 30 . For $C_8H_{15}Cl_3$ calculated %: C 44.16; H 6.95; Cl 48.89.
[2] MR calculated 53.74.
[3] Experiment carried out at 55°.

sence of solvent (experiments 2, 3), the reaction initiated by $Fe(CO)_5$ or $FeCl_2 \cdot 4H_2O$ leads to the formation mainly of the same product as with dicyclohexyl peroxydicarbonate (experiment 1), namely 1,1,1-trichlorooctane (through cleavage of the C–H bond of chloroform). When alcohol or acetonitrile is introduced (experiments 5-8), the main reaction product formed is 1,1,3-trichlorooctane (through cleavage of the C–Cl bond of chloroform), along with some amount of 1,1,1-trichlorooctane.

The radical addition of chloroform to olefins through cleavage of the $Cl–CHCl_2$ bond was first observed by Asher and Vofsi ([9]), and this phenomenon

* We also studied the telomerization of pentene-1 with CCl_4 in the presence of dicyclohexyl peroxydicarbonate or the oxidation-reduction system benzoyl peroxide–sodium hydroxymethanesulfinate at 55°. From 38 experiments with variation of the C_5H_{10}/CCl_4 ratio from 1:1 to 6:1, values of $C_1 = 3.2 \pm 0.5$ were obtained. The composition of the telomers was determined by gas-liquid chromatography. Thus, in those cases where accelerating additives to the initiator do not interfere with chain transfer, C_1 remains unchanged.

** The reaction of olefins with chloroform initiated by $Fe(CO)_5$ proceeds considerably less readily than with carbon tetrachloride (higher temperature, longer time, lower conversion).

(effect B) the authors described by scheme (5):

$$\begin{array}{l}
\text{a) } Fe^{2+} + CHCl_3 \rightarrow Fe^{2+}(Cl) + \dot{C}HCl_2;\\
\text{b) } \dot{C}HCl_2 + CH_2{=}CHR \rightarrow CHCl_2CH_2\dot{C}HR;\\
\text{c) } CHCl_2CH_2\dot{C}HR + Fe^{2+}(Cl) \rightarrow CHCl_2CH_2CHClR + Fe^{2+}.
\end{array} \qquad (5)$$

According to this scheme, stages a) and c) (chlorine transfer with the aid of iron) determine the appearance of effect B. As can be seen from the data in Table 2, this effect appears chiefly when an iron compound and a solvent are jointly present in the reaction mixture. Consequently, the iron compounds themselves almost do not cause "activation of chlorine" (according to Asher and Vofsi)*.

Thus, it may be considered that reactions of olefins with CCl_4 and $CHCl_3$, initiated by $Fe(CO)_5$ or $FeCl_2 \cdot 4H_2O$ in the absence of solvents, proceed mainly according to scheme 3 (the chain-transfer and chain-growth stages are identical with the corresponding stages in peroxide initiation). We suppose that in the telomerization of olefins with CCl_4 or $CHCl_3$ in the presence of iron compounds and an alcohol (or another suitable solvent), a new type of chain transfer takes place with the participation of a "mediator," whose role is played, in particular, by the alcohol. Using the reaction of ethylene with CCl_4 in the presence of an iron compound and isopropyl alcohol as an example, this new type of transfer may be expressed by scheme (6):

$$\left.\begin{array}{ll}
\text{a) } Fe^{2+} + CCl_4 \rightarrow Fe^{2+}(Cl) + CCl_3^{\bullet} & \text{initiation;}\\
\text{b) } CCl_3^{\bullet} + CH_2{=}CH_2 \rightarrow CCl_3CH_2CH_2^{\bullet} & \text{chain initiation;}\\
\text{c) } CCl_3CH_2CH_2^{\bullet} + (C_3H_7O)Cl \rightarrow CCl_3CH_2CH_2Cl + (C_3H_7O)^{\bullet} & \\
\text{d) } (C_3H_7O)^{\bullet} + Fe^{2+}(Cl) \rightarrow (C_3H_7O)Cl + Fe^{2+} &
\end{array}\right\}\ \text{chain transfer.} \qquad (6)$$

Fe^{2+} may be either $Fe(CO)_5$ or $FeCl_2$; $(C_3H_7O)Cl$ is the product of chlorination —chlorocarbinol, hypochlorite.

The electrophilic radical $CCl_3CH_2CH_2^{\bullet}$ readily interacts with the nucleophilic chlorocarbinol (stage c)), in contrast to the reaction with the electrophilic iron salt. The nucleophilic radical thereby formed reacts with the iron compound (stage d)), which leads to propagation of the chain.

Thus, chain transfer between the electrophilic radical $CCl_3CH_2CH_2^{\bullet}$ and the electrophilic substrate (the iron compound) is accomplished with the aid of a nucleophilic "mediator." Apparently, the reverse combination is also possible:

chain transfer between a nucleophilic radical and a nucleophilic substrate with the aid of an electrophilic "mediator."

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
13 VIII 1964

CITED LITERATURE

1. R. Kh. Freidlina, A. B. Belyavskii, DAN, **127**, 1027 (1959).
2. R. Kh. Freidlina, A. B. Belyavskii, Izv. AN SSSR, OKhN, 1961, 177.
3. C. H. Bamford, C. A. Finch, J. Chem. Soc., 1962, 710.
4. C. H. Bamford, G. C. Eastmond, V. J. Robinson, Trans. Farad. Soc., **60**, 751 (1964).
5. C. David, P. A. Gossebain, Tetrahedron, **18**, 639 (1962).
6. B. A. Englin, R. Kh. Freidlina, DAN, **158**, 992 (1964).
7. M. Asscher, D. Vofsi, J. Chem. Soc., 1961, 2261.
8. M. Asscher, D. Vofsi, J. Chem. Soc., 1963, 1887.
9. M. Asscher, D. Vofsi, J. Chem. Soc., 1963, 3921.
10. V. A. Shushunov, G. A. Razuvaev et al., ZhFKh, **31**, 1203 (1957).

* It should be noted that even without alcohol, both effect A occur to a slight extent (C_1 is somewhat overestimated—experiments 1-10, Table 1) and effect B (from 5 to 13% 1,1,3-trichlorooctane—experiments 2 and 3, Table 2). A small impurity of the product formed through cleavage of the C—Cl bond of $CHCl_3$ was also obtained with peroxide initiation (9).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.