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Abstract

Full Text

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EFFECT OF ETHYLENE OXIDE OR AMINES ON CHAIN TRANSFER WITH PARTICIPATION OF A MEDIATOR IN THE TELOMERIZATION OF ETHYLENE WITH CARBON TETRACHLORIDE

It was shown by two of the authors of the present article and by B. A. Englin (^{1}) that the partial transfer constants ($C_\mathrm{p} = K_\mathrm{p}/K_\mathrm{r}$) for the telomerization of ethylene with carbon tetrachloride, initiated by $Fe(CO)_5$ or $FeCl_2 \cdot 4H_2O$ at 100° in the absence of any solvents, are close to the constants obtained when the same reaction is initiated by azobisisobutyronitrile under the same conditions. This indicates the identity of the chain-transfer mechanism in both cases, with chain transfer being effected through carbon tetrachloride according to the usual scheme of radical telomerization:

$$\left.\begin{aligned}
&\mathrm{CCl_3^{\bullet} + CH_2{=}CH_2 \rightarrow CCl_3CH_2CH_2^{\bullet}}\\
&\mathrm{CCl_3CH_2CH_2^{\bullet} + CCl_4 \xrightarrow{K_p} CCl_3CH_2CH_2Cl + CCl_3^{\bullet}} \quad \text{chain transfer}\\
&\mathrm{CCl_3CH_2CH_2^{\bullet} + n\text{-}CH_2{=}CH_2 \xrightarrow{K_r} CCl_3(CH_2CH_2)_nCH_2CH_2^{\bullet}} \quad \text{growth of the radical chain}\\
&\mathrm{CCl_3(CH_2CH_2)_nCH_2CH_2^{\bullet} + CCl_4 \rightarrow CCl_3(CH_2CH_2)_nCH_2CH_2Cl + CCl_3^{\bullet}.}
\end{aligned}\right\} \tag{1}$$

Carrying out the reaction in the presence of an iron compound and such a solvent as isopropyl alcohol, at a molar ratio iso-$C_3H_7OH : CCl_4 = 1 : 2$, leads to almost complete suppression of telomerization; at any ratio $CH_2{=}CH_2 : CCl_4$ the main reaction product is 1,1,1,3-tetrachloropropane.

An increase in the yield of the first member of the series of telomer homologs in the reaction of olefins with carbon tetrachloride, initiated by iron or copper halides in the presence of alcohol, was first observed by Asher and Vofsi (^{2}); the authors, however, considered the alcohol as a solvent for the indicated salts.

To explain this phenomenon we assumed that, in the presence of an iron compound and alcohol, a new type of chain transfer occurs in radical telomerization, with participation of a mediator (^{1}). Thus, in the presence of isopropyl alcohol, which acts as mediator, the reaction of ethylene with carbon tetrachloride initiated by an iron compound can be described by scheme 2:

$$\left.\begin{array}{l}
Fe^{2+} + CCl_4 \xrightarrow{a} Fe^{2+}Cl + CCl_3^{\bullet} \quad \text{initiation} \\
CCl_3^{\bullet} + CH_2{=}CH_2 \xrightarrow{b} CCl_3CH_2CH_2^{\bullet} \\
CCl_3CH_2CH_2^{\bullet} + (CH_3)_2CClOH \xrightarrow{c} CCl_3CH_2CH_2Cl + (CH_3)_2\dot{C}OH \quad \text{chain} \\
(CH_3)_2\dot{C}OH + Fe^{2+}Cl \xrightarrow{g} Fe^{2+} + (CH_3)_2CClOH \quad \text{transfer} \\
2R^{\bullet} \xrightarrow{d} \text{products} \quad \text{chain} \\
(CH_3)_2CClOH \xrightarrow{e} HCl + (CH_3)_2CO \quad \text{termination}
\end{array}\right\} \qquad (2)$$

where $R^{\bullet}$ are radicals formed in this system.

The role of the mediator (for example, iso-C_3H_7OH) apparently consists in the formation of chlorocarbinol "A" (or hypochlorite), which readily gives up a chlorine atom to the trichloropropyl radical. Chlorocarbinol "A" is initially formed in the course of the chain reaction of carbon tetrachloride with isopropyl alcohol (^{3}):

$$CCl_3^{\bullet} + (CH_3)_2CHOH \rightarrow CCl_3H + (CH_3)_2\dot{C}OH,$$

$$(CH_3)_2\dot{C}OH + CCl_4 \rightarrow (CH_3)_2CClOH + CCl_3^{\bullet},$$

and then also at stage "g" of Scheme 2.

It may be expected that, when compounds capable of reacting with the intermediate products of stages "v" or "g" of Scheme 2 with abstraction of chlorine are introduced into the reaction mixture, ordinary telomerization according to Scheme 1 will occur instead of the predominant formation of 1,1,1,3-tetrachloropropane, with formation of a mixture of telomer homologs.

To test this assumption, we studied the reaction of ethylene with carbon tetrachloride under the same conditions; only the initiating system was varied. As follows from the data in Table 1 (experiment 3), this reaction in the presence of $Fe(CO)_5$ + iso-C_3H_7OH leads to the predominant formation of 1,1,1,3-tetrachloropropane according to Scheme 2. Carrying out the reaction in the presence of iron pentacarbonyl alone leads to ordinary telomerization according to Scheme 1, giving approximately the same ratio of telomers as upon initiation with azobisisobutyronitrile (experiments 1 and 2).

Table 1

Reaction of ethylene (1.4 mol) with CCl_4 (0.5 mol)*

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6**
Initiator, mmol	DINIZ***3.4			$Fe(CO)_5$3.6		
iso-C_3H_7OH, mmol	no	no	0.34	0.34	0.34	0.34
Additives, mol	no	no	no	C_2H_4O0.06	C_2H_4O0.12	$(C_2H_5)_3N$0.034
Conversion of CCl_4, %	50	20	50	66	50	2
Relative content of C_3****, %	23	23	73	46	20	23
Relative content of C_5****, %	77	77	27	54	80	77

* The experiments were carried out in a rocking enamel-lined autoclave at 100° for 1 hour at a pressure of 45 atm. Carrying out the experiments in stainless-steel autoclaves leads to the same conditions and to the same ratios of reaction products. The reaction mixture was analyzed by gas-liquid chromatography (temperature 140°, glass column 2 m, N. F. silicone elastomer 12% on brick 0.25-0.5 mm, flame ionization detector). A preliminary calibration of ternary mixtures was carried out: CCl_4, 1,1,3-tetrachloropropane (C_3), 1,1,5-tetrachloropentane (C_5).

** Carrying out the experiment for 4 hours led to an increase in conversion to 50%. However, because triethylamine was removed from the reaction sphere in the form of the amine hydrochloride, the ratio of yields $C_3 : C_5$ was unchanged.

*** DINIZ —azobisisobutyronitrile.

**** The sum of C_3 and C_5 was taken as 100%.

The reaction in the presence of iron pentacarbonyl, isopropyl alcohol, and ethylene oxide leads to the formation of substantial amounts of 1,1,1,5-tetrachloropentane, i.e., as was assumed, shifts the process toward telomerization (experiment 4). Comparison of experiments 4 and 5 shows that varying, within a small range, the amount of ethylene oxide added makes it possible to vary widely the ratio of the telomers formed with $n = 1$ and 2.

The role of ethylene oxide in changing the mechanism of the reaction under consideration can be explained by abstraction of chlorine from the intermediate products of stages "v" or of scheme "d" of 2, for example, according to one of the following equations:

$$(CH_3)_2CClOH + C_2H_4O \rightarrow (CH_3)_2CO + ClCH_2CH_2OH$$

or

$$Fe^{2+}Cl + C_2H_4O \rightarrow Fe^{2+}(OCH_2CH_2Cl).$$

Obviously, other compounds capable of binding HCl, for example amines, may exert the same influence on the mechanism.

Asscher and Vofsi ([4]) described the reaction of octene-1 or ethylene with carbon tetrachloride, initiated by copper halides in a methanol solution in the presence of triethanolamine. In this case telomerization occurred, rather than the preferential formation of 1,1,1,3-tetrachloropropane (as should have been expected when the reaction is initiated by a metal salt in an alcohol solution). This fact was not explained in the cited work, and this explanation is difficult to give from the standpoint of the mechanism proposed by the authors, which includes specific chlorine transfer through an iron (or copper) compound, without taking into account the role of a mediator (alcohol).

It seems highly probable to us that, in the present case, triethanolamine plays the same role as ethylene oxide.

To confirm this explanation of the role of the amine, we studied the effect of adding an even more basic amine—triethylamine—on the mechanism of the reaction of ethylene with carbon tetrachloride, initiated by iron pentacarbonyl in the presence of isopropyl alcohol.

As expected, in this case too triethylamine exerted the same influence on the reaction mechanism as ethylene oxide (experiments 4–6), i.e., the process shifted toward telomerization. It should be noted that appreciable amounts of triethylamine hydrochloride were present among the reaction products, as well as the fact that in the presence of triethylamine the reaction proceeds very slowly (experiment 6).

The above-described effect of additives of compounds capable of shifting the reaction to the path of ordinary telomerization is further evidence for the new type of chain transfer with the participation of a mediator in radical telomerization that we have proposed.

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