SELECTIVE INHIBITION OF SOME RADICAL REACTIONS BY IRON CARBONYLS

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The ability of iron carbonyls to inhibit homolytic processes was first observed in the radical addition reactions of thiols to certain unsaturated hydrocarbons [1] and in the cis–trans isomerization of vinyl sulfides [2]. The authors explained the inhibition by the coordination of the RS radicals, which propagate the kinetic chain, on the iron atom with the formation of the stable complex $[FeRS(CO)_3]_2$. Starting with this explanation, it may be assumed that iron carbonyls will also prove to be effective inhibitors of the reactions of other radicals that are capable of giving stable coordination compounds with the transition metals. The first example of this type of highly selective inhibition is described in the present communication, in which a study was made of the effect of $Fe(CO)_5$ and $Fe_2(CO)_9$ in two parallel homolytic processes: in the peroxide-initiated telomerization of either the α-trans-β-d_2- or the cis-β-d_1-vinyl chlorides with bromotrichloromethane, and in the accompanying isomerization of the starting deuterated vinyl chlorides under the influence of the bromine atom.

EXPERIMENTAL METHOD

The NMR spectra were taken on a Hitachi–Perkin–Elmer R-20 spectrometer, 34°C, TMS, 40-50 vol.% in CCl_4, while the accuracy of determining the intervals within each multiplet was ± 0.03 Hz.

The deuterovinyl chloride was obtained in two steps by a modification of the method given in [3].

Into a flask containing ground CaC_2 was added in drops, in 6 h, 12 ml of D_2O with an isotope purity of 97-99%, after which the mixture was heated at 170° for 4 h. The formed dideuteroacetylene was collected in a gas meter which was filled with saturated NaCl solution. The addition of HCl to the C_2D_2 was run in a glass reactor containing $HgCl_2$ catalyst, which was deposited in an amount of 15% on active carbon. The maximum C_2D_2 conversion was reached at 170° and a feed rate of the reactants of ~ 2 liters/h (the yield of deuterovinyl chlorides was 92% when based on D_2O).

Based on the NMR data (Fig. 1), the main reaction products proved to be α,β-d_2-vinyl chloride (72%), d_0-vinyl chloride (15%), and β-d_1-vinyl chloride (9%). In addition, 4% of α-d_1-vinyl chloride and less than 1% of β,β-d_2-vinyl chloride were detected. The composition of the products was practically independent of the ratio of the reactants (Expts. 1 and 2, Table 1). The amount of the cis–trans isomers in the β-d_1- and α,β-d_2-vinyl chlorides corresponded to the predominant trans-addition of HCl (from 70 to 80%, see Table 1) to the dideuteroacetylene.*

The obtained deutero-substituted vinyl chloride was washed free of HCl, dried over $CaCl_2$, separated from the C_2D_2 by recondensation and entered into the telomerization reaction with $CBrCl_3$ (see Table 1 for the conditions). The experimental procedure, the estimate of the distribution of the telomer homologs by GLC, and a calculation of the partial chain transfer constants were described previously [6].

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* This result proved to be contrary to that obtained by the authors of [5] under close conditions (180°, $HgCl_2$). Since the experimental procedure is not described in detail in [5] and the NMR spectrum of the synthesized α,β-d_2- and β-d_1-vinyl chlorides is not given, the reasons for the divergence remain unexplained.

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TABLE 1. Ratio of Deuterium-Substituted Isomers of Vinyl Chloride in Some Reactions*

Expt. No.	Reaction	Conditions	Relative amount, %				Ratio of isomers	
			XB	α-d_1	β-d_1	α,β-d_2	$\frac{\text{cis}}{\text{trans}}$ β-d_1	$\frac{\text{trans}}{\text{cis}}$ α,β-d_2
1	Synthesis of monomer	$[HCl]/[C_2D_2]$ = 0.7, 170°	15	4	9	72	2.6	2.5
2	The same	$[HCl]/[C_2D_2]$ =2.0, 170°	15	4	10	71	3.3	3.1
3†	Telomerization with $CBrCl_3$	DP, 45°, 2 h	15	5	9	71	1.8	1.0
4	The same	BP, 85°, 10 min or 3 h	17	5	13	65	1.3	0.9
5	Polymerization	BP, or thermally, 85°, 4 h	13	5	11	71	2.9	3.3
6	Telomerization with CCl_4	$FeCl_3$, 145°, 3 h	15	3	11	71	2.2	3.3
7	Telomerization with $BrClHCCCl_2Br$	BP, 85° 10 min or 4 h	15	6	11	68	1.0	0.9
8	Telomerization with $CBrCl_3$	DP, 45° 3 h $Fe_3(CO)_9$	13	5	12	70	2.8	2.6
9	The same	DP, 45°, 3 h $Fe(CO)_5$	7	5	17	71	3.3	2.2

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*See the subscript to Fig. 1 for the designations of the isomers. BP is benzoyl peroxide (~0.01 M), and DP is dicyclohexyl peroxydicarbonate (~ 0.01 M). Experiment 6 was run in the presence of ~ 0.015 M $FeCl_3$. The composition of the vinyl chloride isomers was determined with an accuracy of ± 10% based on the relative intensities of the signals of either the CH_2 or CH groups in the NMR spectrum.

†In this and subsequent experiments the monomer composition is given after reaction. As a rule, the amount of isomers in the starting monomer varied within the limits indicated for the first two experiments.

The composition of the mixture was determined by NMR before and after reaction; this method makes it possible to identify five of the six deuterated derivatives of the vinyl chloride isomers (see Fig. 1). In assigning the lines we took into account the data given by the authors of [4], who calculated the spectrum of vinyl chloride as an ABC approximation. As can be seen from Fig. 1, the isotopic substitution led to ABX systems for the α-d_1- and β-d_1-vinyl chlorides or an AX system for α,β-d_2-vinyl chloride that could be integrated with relative ease. The spin–spin coupling constants of the protons J_{HH}, determined from the splitting on the deuteron ($J_{HH} = J_{HD} \cdot 6.55$), coincided completely with those calculated for vinyl chloride [4]. However, the position of the signals in the proton spectrum of the D-isomers changed somewhat, in which connection, in contrast to aliphatic compounds [7], the shift for the CH_2 and CH groups proved to be opposite in sign. Thus, for example, in the case of the CHCl group, replacing the adjacent protons by deuterons led to a shift of the H_C signals downfield, which reached 2.7 Hz in the case of the cis-orientation of the D atom and H_C (trans-β-d_1-vinyl chloride). The reverse, but less expressed effect was observed for the methylene protons. The course of the isomerization was followed by the change in the relative intensities of the signals in the region of the absorption of the protons of the CH_2 (α,β-d_2-vinyl chloride) or CH (β-d_1-vinyl chloride) groups.

DISCUSSION

The telomerization of vinyl chloride with $CBrCl_3$ proceeds either thermally or in the presence of peroxides by the following scheme [6]

$$CBrCl_3 \xrightarrow{t^\circ} \dot{C}Cl_3 + Br \text{ or}$$

$$\text{Peroxide} \xrightarrow{t^\circ} \dot{R}_i \xrightarrow{CBrCl_3} \dot{C}Cl_3 + R_iBr,$$

$$\dot{C}Cl_3 + CH_2{=}CHCl \rightarrow CCl_3CH_2\dot{C}HCl \xrightarrow{CBrCl_3} CCl_3CH_2CHClBr + \dot{C}Cl_3,$$

$$CCl_3CH_2\dot{C}HCl + CH_2{=}CHCl \xrightarrow{CBrCl_3} CCl_3CH_2CHClCH_2CHClBr + \dot{C}Cl_3 \text{ etc.}$$

When this reaction was run with deuterium-substituted vinyl chlorides it was found that cis–trans isomerization of the α-trans-β-d_2- or cis-β-d_1-deuterovinyl chlorides, which predominate in the starting mixture, occurs during the telomerization process (see Expt. 3 in Table 1 and the change in the intensities of

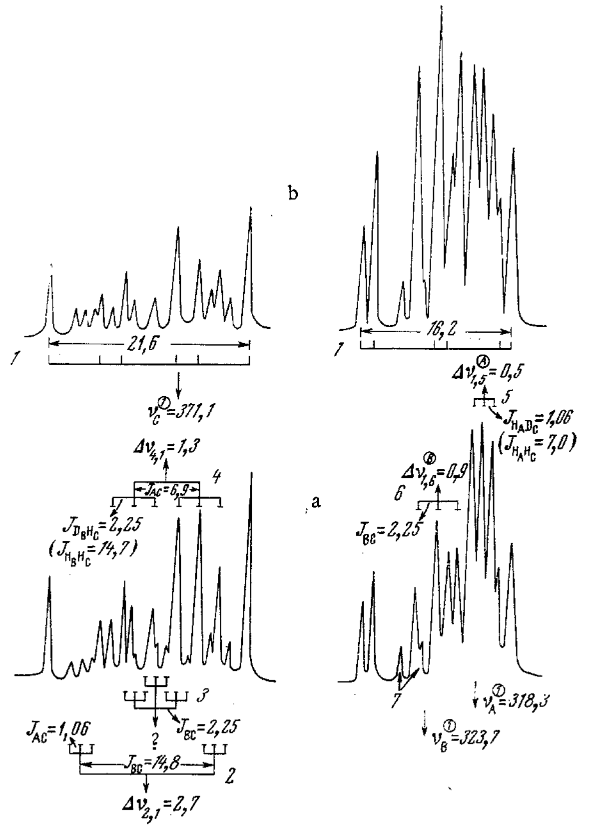
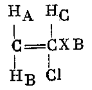
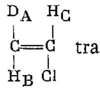
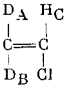
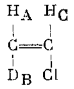
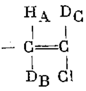
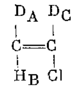
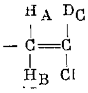


Fig. 1. NMR spectrum: a) starting deuterovinyl chloride or isolated after reaction in Expts. 5, 6, 8-10 (see Table 1); b) unreacted deuterovinyl chloride, isolated after reaction in Expts. 3, 4, and 7:

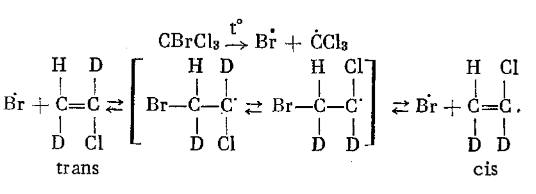
1 — 
$\overset{H_A}{\underset{H_B}{C}}=\overset{H_C}{\underset{Cl}{C}}XB$ —based on the data given in [4] in CS_2 soln. at 37°, $J_{AB}=1{,}5$, $J_{AC}=6{,}3$, $J_{BC}=14{,}8$ Hz;

2 — 
$\overset{D_A}{\underset{H_B}{C}}=\overset{H_C}{\underset{Cl}{C}}$ trans-β-d_1-XB; 3 — 
$\overset{D_A}{\underset{D_B}{C}}=\overset{H_C}{\underset{Cl}{C}}$ β, β-d_2-XB; 4 — 
$\overset{H_A}{\underset{D_B}{C}}=\overset{H_C}{\underset{Cl}{C}}$ cis-β-d_1-XB;

5 — 
$\overset{H_A}{\underset{D_B}{C}}=\overset{D_C}{\underset{Cl}{C}}$ trans-α,β-d_2-XB; 6 — 
$\overset{D_A}{\underset{H_B}{C}}=\overset{D_C}{\underset{Cl}{C}}$ cis-α,β-d_2-XB; 7 — 
$\overset{H_A}{\underset{H_B}{C}}=\overset{D_C}{\underset{Cl}{C}}$ α-d_1-XB.

the signals in Fig. 1). The ratio of the cis/trans isomers depended somewhat on the temperature. At 85° a constant composition was reached within 10 min (Expt. 4) and was 53 and 47% for the cis/trans-α, β-d_2-vinyl chloride, or 57 and 43% for the cis/trans-β-d_1-vinyl chloride.

Since $CBrCl_3$ is capable of homolytic decomposition at elevated temperatures [6, 8], we postulated that isomerization initiated by bromine atoms also proceeds by the well-known [9] addition–cleavage mechanism:



$$CBrCl_3 \xrightarrow{t^\circ} \dot{Br} + \dot{C}Cl_3$$

$$\dot{Br} + \overset{H}{\underset{D}{C}}=\overset{D}{\underset{Cl}{C}} \rightleftarrows \left[Br-\overset{H}{\underset{D}{C}}-\overset{D}{\underset{Cl}{C}}\cdot \rightleftarrows Br-\overset{H}{\underset{D}{C}}-\overset{Cl}{\underset{D}{C}}\cdot \right] \rightleftarrows \dot{Br} + \overset{H}{\underset{D}{C}}=\overset{Cl}{\underset{D}{C}}.$$

trans cis

This postulation was supported by the absence of isomerization during the thermal and peroxide-initiated polymerization of the deuterium-substituted vinyl chlorides (Expt. 5), or in the $FeCl_3$ catalyzed telomerization of the deuterovinyl chlorides with CCl_4 (Expt. 6). At the same time the telomerization with $BrCCl_2CHClBr$, the kinetic chain in which propagates the bromine atom [10], was accompanied by isomerization of the starting deuterated vinyl chlorides (Expt. 7)

TABLE 2. Composition of Telomerization Products of Deuterium-Substituted Vinyl Chlorides (M) with $CBrCl_3$ (S) in the Presence of Dicyclohexyl Peroxydicarbonate (DP) and Some Iron Compounds (45°C, 3 h, starting concentrations, M/liter)*

Expt. No.	[S]	[M]	$DP\cdot 10^3$	$Feh_x\cdot 10^3$	K_S, %	K_M, %	Amount of telomers T_n with n monomeric units, mole%			$\frac{[M]}{[S]}$ average	C_1†
							T_1	T_2	$T_{n\geqslant 3}$		
1	1,40	6,50	12,4	None	85,3	41,9	17,3	54,2	28,5	11,3	2,37
2	1,39	5,50	11,3	2,47	78,0	38,8	24,0	57,7	18,3	7,5	2,37
3	1,29	5,76	9,4	7,76	23,3	8,5	41,2	54,0	4,8	4,9	3,46

*$Fe_2(CO)_9$ was added in Expt. 2; $Fe(CO)_5$ was added in Expt. 3; K_S and K_M are the conversions of the reactants, calculated from the chromatographic data; T_n is the amount of each telomer homolog, which was determined for the sum of all of the possible deuterium-substituted vinyl chloride isomers.

†The partial chain transfer constant C_1 for the CCl_3 M radical was calculated using the Mayo equation (see [6] for more details).

$$\text{Peroxide} \xrightarrow{t^\circ} \dot{R}_i \xrightarrow{BrCCl_2CHClBr} R_iBr + \dot{C}Cl_2{-}CHClBr \rightarrow \dot{B}r + CCl_2{=}CHCl,$$
$$\dot{B}r + CH_2{=}CHCl \rightarrow BrCH_2\dot{C}HCl \xrightarrow{BrCCl_2CHClBr} BrCH_2CHClBr + \dot{C}Cl_2{-}CHClBr,$$
$$\dot{C}Cl_2CHClBr \rightarrow \dot{B}r + CCl_2 = CHCl, \text{ etc.}$$

The addition of catalytic amounts of $Fe_2(CO)_9$ (Expt. 2, Table 2) does not affect the yield and distribution of the homologs in the telomerization of the deuterovinyl chlorides with $CBrCl_3$ (when compared with peroxide initiation, Expt. 1, see Table 2), but completely inhibits the cis–trans isomerization (Expt. 8, see Table 1). Suppression of the isomerization was also observed with $Fe(CO)_5$, although the conversion of the reactants decreased by a matter of 4-5 times and the partial chain transfer constant C_1 increased somewhat (Expt. 9, see Table 1, and Expt. 3, see Table 2). As a result, the inhibiting action of iron carbonyls in the studied system is characterized by a high selectivity in that the inhibitor, apparently trapping the bromine atoms, does not rupture the kinetic chain involving the polychloroalkyl radicals.

It is possible to assume that this selectivity is associated with the well-known ability of metal carbonyls to undergo exchange replacement [11]. Thus, for example, for the bromine atom and $Fe(CO)_5$ the reaction should lead to the formation of the stable coordination compound $Fe(CO)_4Br_2$ [12], and consequently to the effective removal of $\dot{B}r$ from the reaction sphere.

$$Fe(CO)_5 + 2\dot{B}r \rightarrow Fe(CO)_4Br_2 + CO.$$

In the case of trichloroalkyl radicals the low stability of the σ-complexes of the transition metals with aliphatic hydrocarbons [13] makes chain rupture unlikely.

CONCLUSIONS

1. In the radical telomerization of deuterium-substituted vinyl chlorides with $CBrCl_3$, accompanied by cis–trans isomerization of the starting deuterovinyl chlorides, it was found that the isomerization is selectively inhibited by $Fe(CO)_5$ and $Fe_2(CO)_9$.

2. α,β-d_2-Vinyl chloride (ratio of trans/cis isomers = 2.5-3.3/1) was synthesized by the addition of HCl to dideuteroacetylene in the presence of $HgCl_2$.

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