COMPLEX INITIATORS OF RADICAL ADDITION

AND TELOMERIZATION BASED ON Mn2(CO)10

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Decacarbonyldimanganese is an initiator for the radical addition and telomerization reactions of olefins with polyhalomethanes [1]. At the same time, the use of systems, containing $Fe(CO)_5$ and cocatalysts [isopropanol, DMF, hexamethylphosphortriamide (HMPA)], for initiating such reactions makes it possible to greatly increase the conversion and change the distribution of the telomers in favor of the lower products [2, 3].

In the present paper we were the first to study catalytic systems, containing the binuclear carbonyl $Mn_2(CO)_{10}$ in combination with a cocatalyst, in order to ascertain the effect of the nature and concentration of the cocatalyst, and also of the $Mn_2(CO)_{10}$ concentration, on the course of the radical addition and telomerization of unsaturated compounds with polyhaloalkanes.

A study of the effect of the $Mn_2(CO)_{10}$ concentration on the course of adding CCl_4 to 1-hexene disclosed (Fig. 1, curve 1) that the yield of the adduct increase in the $Mn_2(CO)_{10}$ concentration and becomes quantitative when $[Mn_2(CO)_{10}] = 0.4$ mole % (to CCl_4). None of the employed cocatalysts had practically any effect on the course of adding $CHCl_3$ to 1hexene, a reaction that goes mainly via cleavage of the C-H bond; the yield of the reaction products was 37.7-64.7%, and their distribution also shows little change. In the case of 1,1,1,3-tetrachloropropane and 1-hexene the use of either isopropanol or HMPA inhibits the process and the main reaction product becomes compound (III) (Scheme 1), which is apparently formed by the cleavage of hydrogen from a molecule of the medium by the adduct radical.

The data on the telomerization of ethylene with CCl4 are summarized in Table 1.

In the absence of a cocatalyst the yield of the T_1-T_3 telomers reaches 50.3% (based on charged telogen), and here the amount of T_1 is 20.3 mole % when based on the sum of the identified products (see Table 1). Here the effect of the $Mn_2(CO)_{10}$ concentration differs from that incurred during the addition of CCL_4 to 1-hexene (see Fig. 1, curve 2). The total yield of the identified T_1-T_3 compounds (in % of charged telogen) passes through a maximum at $[Mn_2(CO)_{10}] = 0.1-0.2$ mole %, then it decreases somewhat, and further increase in the $Mn_2(CO)_{10}$ concentration has little effect on the yield of products. The amount of T_1 in the sum of the products is little dependent on the concentration of the taken carbonyl (see Fig. 1, curve 3). A further study of the reaction in the presence of complex initiators was run at $[Mn_2(CO)_{10}] = 0.4$ mole %, i.e., in the region where small changes in this value practically do not affect the reaction course. From the data in Table 1 it can be seen that the system $Mn_2(CO)_{10} + i-C_3H_7OH$ permits increasing the yield of the products substantially (up to 86.6% when based on charged telogen) only at high concentrations of the alcohol (1:50), but even in this case the yield of T_1 increases only from 20.3 to 30.6 mole % when based on the products.

A different picture was observed in the case of DMF. This cocatalyst has a noticeable effect on both the yield of the products (see Table 1) and the relative yield of T_1 , which increases from 20.3 to 50.7 mole % of the T_1-T_3 sum. The reaction is comparatively insensi-

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		Yield of reaction	n products	i in mole ⁰	% of sum c	of identifie	ed product				
$\mathbf{T}_{\boldsymbol{n}}$	Formula	$\operatorname{Mn}_2(\operatorname{CO})_{10}, \\ 0.4 \operatorname{mole} \sigma_0^{10}$	Mn ₂ ((20) 10 — 1-C3	Н,ОН	Mn ₂	(CO) 10 - D M	Æ	Mn	2(CO)10 H	MPA
		of CCI4	1:3	1:10	1:50	1:3	1:10	1:20	1:3	1:10	1:20
T,	ccl₃cH₂cH₂cl	20,3	19,8	21,9	30,6	37,4	57,3	50,7	38,0	49,4	61,8
$\mathbf{T}_{\mathbf{z}}$	CCl ₃ (CH ₂ CH ₂) 2Cl	51,0	52,9	49,9	48,0	46,7	32,5	32,1	47,8	28,8	24,2
T_1'	CH2ClCH2CCl2CH2CH2Cl	1	ļ	1	1,6	l	I	I	1	17,0	13,4
T_3	$CCl_3(CH_2CH_2)_3Cl$	18,2	20,0	17,6	12,1	15,9	10,2	13,6	14,2	4,7	3,7
	$CCl_2 = CH(CH_2)_{2i-1}Cl$	10,5	7,8	10,6	7,7	!	1	I	i .	1	I
lield of charge	identified products, in % of d telogen	50,3	59,3	58,2	86,6	66,8	91,2	125,2	35,8	122,8	117,3
Conversi	on of monomer K_m , %	25,9	28,9	24,0	32,4	30,5	35,8	55,2	17,2	47,6	43,0
Conversi	on of telogen $\mathrm{K}_{\mathbf{S}^{*}}$ $ au_{\mathbf{b}}$	36,3	42,6	44,2	68,2	49,4	70,3	93,8	26,6	95,6	93,1



Fig. 1. Yield of products in reaction of CCl₄ with 1hexene (1) and C₂H₄ (2, 3) as a function of $[Mn_2(CO)_{10}]$: 1) CCl₃CH₂CHClC₄H₉ (% of theory); 2) identified products (in % of charged telogen); 3) T₁ (in mole % of T₁-T₃ sum).

Fig. 2. Yield of products as a function of time in telomerization of C_2H_4 with CCl_4 (120°, $[Mn_2(CO)_{10}] = 0.4$ mole % of CCl_4): 1) mixture of T_1-T_3 telomers (in % of charged telogen); 2) T_1 , in % of T_1-T_3 sum; 3) 1,3,3,5-tetrachloropentane, in % of T_1-T_3 sum.

tive to low HMPA concentrations (1:3), but an increase in the HMPA concentration (1:10, 1:20) permits bringing the yield of the mixed telomers up to 117.3% (when based on charged telogen), with a relative T_1 content of 61.8 mole % (when based on T_1-T_3 sum). 1,3,3,5-Tetrachloropentane or T_3' was also identified among the reaction products, whose formation is apparently related to the involvement of 1,1,1,3-tetrachloropropane in a secondary reaction with ethylene [4].

In addition, we studied the course of the telomerization of ethylene with CC14 when initiated by the system $Mn_2(CO)_{10}$ + HMPA (1:10) with time (Fig. 2). The yield of mixed telomers reaches a maximum even within 60 min (99.5% when based on charged telogen; see Fig. 2, curve 1); the maximum amount of T_1 (62.2 mole % when based on the T_1-T_3 sum, curve 2); also corresponds to this point. In approximately 30-40 min the secondary process of forming 1,3,3,5-tetrachloropentane begins (curve 3), which subsequently leads (after 60 min) to a decrease in the T₁ concentration in the reaction mixture (curve 2). GLC analysis for the amount of $Mn_2(CO)_{10}$ in the reaction mixture shows that when the reaction time exceeds 90 min the consumption of the $Mn_2(CO)_{10}$ is practically complete. Consequently, from a preparative standpoint, a reaction time of 1.5 h is sufficient. In order to ascertain the possible formation of 1,3,3,5-tetrachloropentane via the secondary reaction shown in Scheme 2 we ran experiments on the telomerization of ethylene with 1,1,1,3-tetrachlor@propane, initiated by the system $Mn_2(CO)_{10}$ + HMPA (1:10; 1:20). Here it proved (see Table 2 and the Experimental section) that 1,1,1,3-tetrachloropropane in the presence of Mn₂(CO)₁₀ + HMPA (no reaction in its absence) is capable of reacting with ethylene to give the telomers $C1CH_2CH_2CC1_2(CH_2CH_2)_nC1$ (n = 1.2).

EXPERIMENTAL

The GLC analysis and identification of the reaction products were run on an LKhM-8MD chromatograph, using a 1000×3 mm column packed with 20% SKTFT-50 deposited on Chromosorb W (0.16-0.20 mm), with programming of the temperature, and a 2000×3 mm column packed with 15% Carbowax deposited on Chromaton N-Aw-DMCS (0.16-0.20 mm), at 160° , in a helium stream.

The products were identified using authentic specimens on two columns of different polarity. In the case of addition the chromatograms were calculated using the internal standards: 1,1,1,3-tetrachloropentane (in the experiments with CHCl₃), 1,1,1,9-tetra-chlorononane (CCl₃C₂H₄Cl), and 1,1,1,5-tetrachloropentane (CCl₄).

TABLE 2. Telomerization of Ethylene with (I) $(C_2H_4 \ 36.0 \pm 1.1 \ mmoles;$ (I) 12.0 \pm 0.02 mmole; 120°, 2 h. Monomer conversion 10-12%, telogen conversion 15-35%)

T _n	Formula	Yield of telomers when based on T_1 - T_2 sum, mole $\%$		
		Mn ₂ (CO) ₁₀ ,	Mn ₂ (CO) ₁₀ -HMPA	
		to telogen	1:10	1:20
${f T_1} {T_2}$	$\begin{array}{c} CH_2ClCH_2CCl_2CH_2CH_2Cl\\ CH_2ClCH_2CCl_2\left(CH_2CH_2\right)_2Cl \end{array}$	No reaction	49,1 50,9	63,0 37,0

<u>Addition of RCCl₃ to 1-Hexene.</u> The experiments were run in sealed 3-mm glass ampuls, previously evacuated and filled with argon. The reaction mixture was added to the ampul using a syringe. The ampuls were placed in metal holders. Mixing was accomplished by rotating the holders in a silicone bath at 120° for 2 h.

<u>Telomerization of Ethylene with CCl4</u>. The experiments were run in 10-ml steel test tube autoclaves as described in [5]. Into the autoclave were charged 15.7 \pm 0.3 mmole of CCl₄, 48.6 \pm 1.1 mmoles of C₂H₄, 0.4 mole % (of CCl₄) of Mn₂(CO)₁₀, and cocatalyst ([Mn₂(CO)₁₀]:[cocatalyst] = 1:3, 1:10, etc.). The volume of ethylene was metered from a buret, and the exact amount of charged ethylene was determined by weighing. The experiments were run at a mole ratio of C₂H₄:CCl₄ = 3:1. The obtained results and reaction conditions are given in Table 2 and plotted in Fig. 1 (curves 2 and 3) and Fig. 2.

<u>Telomerization of Ethylene with $CCl_3CH_2CL_2Cl$ (I).</u> The experiments were run as described above. The charges, reaction conditions, and obtained results are given in Table 2.

CONCLUSIONS

1. DMF, hexamethylphosphortriamide, and isopropanol can be used as cocatalysts for initiating radical addition and telomerization in complex systems based on $Mn_2(CO)_{10}$.

2. Based on the conversion data and yield of lower homologs, the efficiency of the studied cocatalysts in the telomerization of ethylene with CCl₄ decreases in the order: hexamethylphosphortriamide > DMF > isopropanol.

LITERATURE CITED

- A. B. Terent'ev, M. A. Moskalenko, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., <u>1980</u>, 1406.
- 2. E. Ts. Chukovskaya, R. G. Gasanov, I. I. Kandror, and R. Kh. Freidlina, Zh. Vses. Khim. Obshch., 24, 161 (1979).
- 3. R. Kh. Freidlina and F. K. Velichko, Synthesis, 1977, 145.
- 4. E. Ts. Chukovskaya, N. A. Kuz'mina, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1969, 1198.
- 5. N. S. Ikonnikov and A. B. Terent'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 1975, 371.