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RELATIVE KINETICS OF THE TELOMERIZATION OF 1-HEXENE

BY DIETHYL PHOSPHITE

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Radical telomerization of 1-hexene (M) by diethylphosphite (DEP) leads to the formation of telomers of general formula $H(C_4H_9CHCH_2)_n \cdot P(0)(OC_2H_5)_2$ (n = 1-3) [1]. When the reaction is carried out in the presence of $Mn_2(CO)_{10}$ an induction period is observed together with a post-effect (progress of the reaction after heating is stopped). The formation of higher telomers of identical structure under different conditions of initiation (tert-butyl peroxide (TBP) or $Mn_2(CO)_{10}$) is evidence in favor of a radical mechanism for the $Mn_2(CO)_{10}$ process. It is known, for example, that the orientation of the addition of DEP to vinyl acetate is different depending on whether a radical [2] or an ionic [3] process is involved.

In the present work, we have studied the relative kinetics of the telomerization of 1hexene by DEP in the presence of different initiators. Initiation of this reaction by different peroxides - TBP, benzoyl peroxide (BPO), dicyclohexyl peroxydicarbonate (DCPDC) or UV light - leads to telomerization with identical distribution of telomers (Table 1, Nos. 1-17). Comparison of the results in Tables 1 and 2 of experiments which were carried out by different methods of initiation shows that in the case of $Mn_2(CO)_{10}$, with closely similar monomer-telogen ratios, the distribution of telomer homologs is significantly altered in favor of T_1 in comparison with peroxide initiation. From this, one can postulate that in the system $Mn_2(CO)_{10}$ -DEP chain transfer occurs through a manganese complex, whose structure has not been established, which for the sake of brevity we will denote by [K]. It has been shown that the presence of oxygen (air) significantly increases the overall reaction rate. This supposes its participation in the reaction process

$$(C_{2}H_{5}O)_{2}P(O)H \xrightarrow{\text{Initiator}} (C_{2}H_{5}O)_{2}\dot{P}(O)$$

$$(C_{2}H_{5}O)_{2}\dot{P}(O) + \kappa C_{4}H_{9}CH = CH_{2} \longrightarrow (C_{2}H_{5}O)_{2}P(O)(CH_{2}CHC_{4}H_{9})_{n}$$

$$A_{n}^{\circ} + C_{4}H_{9}CH = CH_{2} \xrightarrow{k_{growth}} A_{n+1}^{\circ}$$

$$A_{n}^{\circ} + DH \xrightarrow{k \text{ tr.}} (C_{2}H_{5}O)_{2}P(O)(CH_{2}CHC_{4}H_{9})_{n}H$$

$$DH = DEP \text{ and/or [K].}$$

Further support for this can be found from a consideration of the relative kinetics of the process. Since the reaction in the presence of $Mn_2(CO)_{10}$ takes place in fact at ~20°C and in the presence of TBP at 140°C, we started by carrying out the reaction under different conditions of initiation [4] and examining the effect of the reaction temperature on the distribution of the telomer homologs (Table 1). It can be seen from the results in Table 1 that

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Expt. No,	Conversion		<u>M</u>	Distrib T _n , m identifi	ution of te ple % on t ed	Partial chain transfer constants, C _n			
	м	DEP	DEP (average)	T 1	T2	T ≥ 3	<i>C</i> ₁	C2	
	· · · ·		TBP, mole	% on DE	P, 140°, 1	h		······	
1 2 3 4 5 6 7 8 9 10 11	46 23 6 7 5 2 1.5 1 1 1	37 31 12 13 10 6 7. 5 4 3 1	$\begin{array}{c} 0.95\\ 2.1\\ 3.1\\ 4.0\\ 5.0\\ 5.1\\ 6.1\\ 7.2\\ 8.1\\ 9.0\\ \end{array}$	79.5 60.4 55.9 54.0 52.8 48.3 44.0 43.3 40.6 37.4 29.1	16.3 33.1 35.8 35.5 37.9 38.3 40.0 39.1 40,1 39.2 44.6	4,2 6,5 8.3 10.5 9.2 13.4 16.0 17.6 19.3 23.4 26,3	$\begin{array}{c c} 3.7\\ 3.2\\ 3.9\\ 3.6\\ 4.6\\ 4.6\\ 4.6\\ 4.8\\ 4.7\\ 3.7\end{array}$	- 10,6 13,2 10,5 16,3 14,3 12,7 13,5 15,0 13,6 15,2	
					c	n (averag	e) = 4,1	13,5	
			BPO, 5 m	ole % on 2	DEP, 90°,	3 h			
12 13	82 15	65 39	1.1 3.2 DCPDC, 4	76.4 56.5	21.2 33.0	2.4 10,5	_	-	
14 15	52 13	42 24	0.94 3.2	78.8 52.5	19.6 38.0	1,6 9,5	-	-	
			UV-irrad	iation, 25	-30°, 26 h	L			
16 17 **	$\begin{bmatrix} 1\\7 \end{bmatrix}$	3 5	1.0 1.0	72,7 75,1	25.5 22.5	$\begin{array}{c} 1.8\\ 2.4\end{array}$	-		

TABLE 1. Radical Telomerization of 1-Hexene (M) by DE

*Arithmetic average of 11 experiments

**Experiment carried out without preliminary elimination of oxygen from air.

Expt. No.	Taken for reaction, mmole		τ, (from	Conversion.		M	M	Distribution of telomers T _n , mole % on total identified			C₁ ^{Mn}
	М	DEP.	opening ampul)	М	DEP	(ave- rage)	BER2(CO)10	T 1	T 2	T ≥ 3	
18 * 19	3.9 3,9	3.9 3.9	46 52 73 145 168	$1 \\ 1 \\ 2 \\ 16 \\ 17$	1 1 2 15	1	250 25	91 90 89 90 92	8 9 10 9 7	1 1 1 1	- 110 95 120 195
20 21 22 23 24	7.7 7.7 9,7 23.2 19.3	3.9 1.9 1.9 3.9 1,9	105	4 5 4 2 1	6 15 14 9 7	2 4 5 6 10	50 100 130 150 250	82 70 62 60 57	15 25 29 30 23	$ \begin{array}{c} 3 \\ 5 \\ 9 \\ 10 \\ 20 \\ \end{array} $	130 140 100 130 230

TABLE 2. Telomerization of 1-Hexene (M) by DEP $([Mn_2(CO)_{10}])$

**_{C1}^{Mn av}·≥140

*[Mn₂(CO)₁₀)] ~ 0.4 mole% on DEP. **Arithmetic average of experiments 19-24.

with similar [M]/[DEP] ratios the distribution of telomer homologs is practically unchanged over a wide range of temperatures (140-25°C). This is in agreement with the results of [5]. The relationship is expressed by the Mayo equation [6]; with allowance for the possibility in principle of chain transfer to both [K] and DEP this takes the form

$$(T_1 \sum_{n>1} T_n)^{Mn} = C_1^{P} [DEP] / [M] + C_1^{Mn} [K] / [M]$$

 T_1^{Mn} and T_n^{Mn} are the mole fractions of the primary and higher telomers; the superscripts P or Mn relate to reactions carried out in the presence of TBP or $Mn_2(CO)_{10}$ respectively.

Arising from the assumption that $k_{growth}^{Mn} = k_{growth}^{n}$ and taking into account that $[K] \leq [Mn_2(CO)_{10}]$, we can evaluate the difference in the chain transfer constants

$$C_1^{Mn}/C_1^{P} = k_{tr}^{Mn}/k_{tr}^{P} \ge 138.5/4.1 \ge 35$$

A similar calculation carried out without an allowance for chain transfer to DEP gives $k_{tr}^{Mn}/k_{tr}^{p} \gtrsim 60$, i.e., of the same order of magnitude. The difference in the values of C_1 for different methods of initiation shows that for the case of $Mn_2(CO)_{10}$ a change in mechanism occurs at the chain transfer stage which provides for more effective hydrogen transfer.

EXPERIMENTAL

Analyses by GLC were carried out on an LKhM-80 chromatograph using helium, a katharometer, and programmed temperature, 35-280°C at 6°C/min. Columns were 1) 3000 × 3 mm, 20% SKTFT-50 on Chromosorb W (60-80 mesh) and 2) 1000 × 3 mm, 15% SKTFT-50 on Chromaton N-AW-HMDS (0.16-0.20 mm). The structure of T_1 was confirmed from the results of proton and carbon-13 NMR spectroscopy on samples isolated from experiments with both TBP and $Mn_2(CO)_{10}$, of T_2 from experiments with TBP [1], of T_3 by observation of the linear relationship between log I and n; the amount of each in the reaction mixture was calculated by internal normalization and a weight correction coefficient (1.1). Determination of the quantitative composition of the reaction mixture using an internal standard (the methyl ester of pelargonic acid) gave similar results.

<u>Telomerization of 1-Hexene by DEP.</u> Initiator — peroxide. Experiments 1-15 (Table 1) were carried out in ampuls of around 3 ml capacity using the method of [1]. The experimental conditions, the results of GLC analysis, and C_n calculated from the Mayo equation are given in Table 1.

<u>UV Initiation</u>. Experiments 16 and 17 (Table 1) were carried out with irradiation for 28 h from a mercury-quartz DRSh-500 lamp at 25 cm distance from the lamp. Before starting, nitrogen was bubbled through the reaction mixture for 10-15 min. To hold the temperature at 25-30°C, the quartz "test-tubes" were cooled.

Initiation by $Mn_2(CO)_{10}$. Experiments 18-24 (Table 2) were carried out as described above for peroxides, at 140°C for 2 h. After heating had been discontinued, the ampuls were kept, still sealed off, for 4 days and then opened in air and the reaction mixture analyzed by GLC after 25-50 h, by which time 5-15% conversion on telogen had been attained. In addition to the telomers, an unidentified P-containing compound was formed in experiments 18-24 amounting to around 10% of the total T_n (n = 1-3). It was shown by mass-balance that no 1-hexene was lost by evaporation during working. On opening the ampuls under nitrogen the yield ΣT_1 - T_3 amounted to 1.5% and in air to 4.5% (after 25 h, on DEP taken).

CONCLUSIONS

According to relative kinetic data on the telomerization of 1-hexene by diethyl phosphite, a system based on $Mn_2(CO)_{10}$ effectively activates the transfer of hydrogen at the chain transfer stage.

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