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RELATIVE TELOMERIZATION RATE OF ETHYLENE WITH CCl_4, INITIATED BY $Cr(CO)_6$ AND $Cr(CO)_5PPh_3$

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In the telomerization of ethylene with CCl_4 the partial chain-transfer constants [1] and the distribution of the telomer homologs [2] coincide when initiation is with peroxides and $Fe(CO)_5$, whereas when this reaction is initiated with $Mn_2(CO)_{10}$ [3] the chain-transfer constants are 2-3 times greater. This is apparently related to the fact that $Mn_2(CO)_{10}$, in contrast to $Fe(CO)_5$, facilitates an increase in the transfer rate of chlorine atom to the growing telomeric radicals.

In the present paper we studied the effect of $Cr(CO)_6$ and $Cr(CO)_5PPh_3$ on the course of the telomerization of ethylene with CCl_4 and its relative rate.

TABLE 1. Telomerization of 47.7 ± 2.3 mmoles of C_2H_4 with 47.9 ± 0.8 mmoles of CCl_4 in Presence of Benzoyl Peroxide (BP), $Cr(CO)_6$, and $Cr(CO)_5PPh_3$ (120°, C_2H_4/CCl_4 = 1.0± 0.1)

Expt. No.*	Initiator,* mmole · 10^2	Time, min	Conversion, %		Amount of $CCl_3(CH_2CH_2)_n \cdot Cl(T_n)$ telomers with n = 1, 2, 3, 4, and 5, mole %				
			C_2H_4	CCl_4	T_1	T_2	T_3	T_4	T_5
1	2,4	25	48,8	21,6	18,9	59,1	18,7	2,9	0,4
2	4,5	18	14,8	6,6	15,6	57,6	20,2	5,6	1,0
3	4,5	20	25,6	11,8	15,5	60,4	18,1	5,1	0,9
4	4,5	40	57,0	28,5	17,6	59,7	17,5	4,5	0,7
5	4,5	60	92,9	40,5	14,0	56,8	23,3	5,2	0,7
6	2,2	60	64,6	30,9	15,0	63,1	16,8	4,3	0,8
7	0,5	60	10,0	4,7	13,6	62,2	19,8	3,7	0,7
8	0,3	60	11,7	5,2	15,0	60,9	20,0	3,5	0,6
9	0,1	60	24,7	11,8	15,3	63,0	17,7	3,3	0,7
10	0,3	60	32,3	15,6	15,3	62,7	18,1	3,3	0,6
11	1,1	60	53,7	26,9	20,8	59,3	16,7	2,7	0,5
12	1,1	25	34,8	15,9	19,5	57,2	19,3	3,6	0,4
13	1,1	15	18,2	8,9	17,4	60,0	18,9	3,2	0,5
14	1,1	10	8,8	4,1	13,4	59,6	21,5	4,7	0,8

*Expt. 1 was run in the presence of PB, expts. 2-8 in the presence of $Cr(CO)_6$, and expts. 9-14 in the presence of $Cr(CO)_5PPh_3$.

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TABLE 2. Telomerization of C_2H_4 with CCl_4 in Presence of 0.023 mmole of $Cr(CO)_6$ (120°, 30 min)

C_2H_4	CCl_4	Conversion, %		$\left(\frac{C_2H_4}{CCl_4}\right)_{av}$	Amount of $CCl_3(CH_2CH_2)Cl(T_n)$ telomers with n = 1, 2, 3, 4, 5, mole %						Partial chain-transfer constants C_t^*				
mmoles		C_2H_4	CCl_4		T_1	T_2	T_3	T_4	T_5	$\Sigma T_n \geqslant 6$	C_1	C_2	C_3	C_4	C_5
19,64	62,66	32,2	5,9	0,26	37,9	54,5	7,2	0,4	–	–	0,162	1,90	4,77	–	–
40,71	55,45	20,4	7,8	0,68	24,2	61,6	12,6	1,3	0,3	–	0,217	2,95	4,51	–	–
42,86	47,86	19,9	8,8	0,84	20,0	60,9	16,2	2,5	0,4	–	0,210	2,68	4,70	5,25	–
58,57	42,21	11,6	7,1	1,36	13,4	54,7	24,7	5,8	1,2	0,2	0,210	2,33	4,67	5,63	8,16
66,07	37,40	11,6	8,3	1,74	9,9	50,9	26,4	9,8	2,4	0,6	0,191	2,26	3,59	5,68	6,96
72,86	37,74	9,5	8,0	2,08	7,9	52,0	28,0	8,7	2,7	0,7	0,178	2,70	4,81	5,32	8,02
73,93	32,73	11,4	10,3	2,24	8,9	50,7	26,9	9,7	3,0	0,8	0,219	2,81	4,46	5,72	8,40
81,79	30,84	15,3	15,0	2,64	6,7	44,1	29,4	13,4	4,8	1,6	0,190	2,37	3,93	5,54	7,94
82,86	28,70	14,7	14,7	2,89	4,7	41,7	28,4	17,4	6,2	1,6	0,143	2,26	3,27	6,47	11,24
90,71	26,17	10,7	12,9	3,51	5,4	40,3	28,8	16,3	6,5	2,7	0,200	2,60	3,96	6,22	8,45
										Average	0,192	2,49	4,27	5,73	8,45
										σ †	0,006	0,05	0,08	0,20	0,38

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* Calculated by the Mayo equation.

† Standard arithmetical mean error.

TABLE 3. Telomerization of C_2H_4 with CCl_4 in Presence of 0.011 mmole of $Cr(CO)_5PPh_3$ (120°, 25 min)

C_2H_4	CCl_4	Conversion, %		$\left(\frac{C_2H_4}{CCl_4}\right)_{av}$	Amount of $CCl_3(CH_2CH_2)_nCl(T_n)$ telomers with n = 1, 2, 3, 4, 5 mole%						Partial chain-transfer constants C_t^*				
mmoles		C_2H_4	CCl_4		T_1	T_2	T_3	T_4	T_5	$\Sigma T_n \geqslant 6$	C_1	C_2	C_3	C_4	C_5
20,36 †	63,38	31,3	6,1	0,28	41,5	52,2	5,8	0,5	–	–	0,199	2,32	3,25	–	–
33,57 †	55,71	30,9	9,8	0,53	26,1	59,3	13,0	1,5	0,1	–	0,187	2,15	4,31	7,95	–
45,71	48,12	34,8	15,9	0,84	19,5	57,2	19,3	3,6	0,4	–	0,203	2,06	4,05	7,56	–
60,71	42,47	21,5	13,6	1,37	12,6	57,6	23,0	5,1	1,4	1,7	0,198	2,57	4,11	5,14	9,59
70,36	37,60	14,2	11,3	1,84	11,1	55,2	23,9	7,7	1,7	0,4	0,230	3,01	4,49	6,75	7,82
76,43	34,94	5,6	4,8	2,18	9,0	48,2	29,2	10,0	2,9	0,7	0,216	2,46	4,68	6,00	9,03
82,14	33,38	10,1	9,5	2,46	7,6	44,3	31,4	12,1	3,5	1,1	0,202	2,26	4,61	6,44	7,80
78,57	28,18	15,8	16,2	2,79	7,2	42,5	30,3	13,2	5,1	1,7	0,216	2,36	4,23	5,42	8,37
88,57	29,42	5,9	6,6	3,02	6,8	43,8	30,4	12,3	4,8	1,9	0,220	2,68	4,83	5,54	7,63
92,85	26,23	7,0	8,5	3,57	5,2	38,7	29,9	15,7	7,1	3,4	0,196	2,46	4,07	5,34	7,46
										Average	0,207	2,43	4,26	6,23	8,25
										σ ‡	0,006	0,05	0,13	0,16	0,14

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* Calculated by the Mayo equation.

† The experiment was run for 15 min.

‡ Standard arithmetical mean error.

EXPERIMENTAL

The GLC analysis was run on an LKhM-8MD instrument in a helium stream (6 liters/h) and using a katharometer, a 2000 × 3 mm steel column packed with 15% SKTPT deposited on Chromaton N-AW, and programming of the temperature from 40 to 150° and from 170 to 210°C (8 deg/min). The reactions were run in 10-ml stainless-steel test tube autoclaves. The experimental procedure was the same as described in [3]. The amount of starting reactants, the experimental conditions, and the GLC analysis results of the reaction mixture are given in Tables 1-3.

DISCUSSION OF RESULTS

The telomerization of ethylene with CCl_4 in the presence of $Cr(CO)_6$ and $Cr(CO)_5PPh_3$ goes at 120°C with high conversions (see Table 1, Expts. 2-14) and without the formation of by-products. In contrast to the telomerization initiated by $Mn_2(CO)_{10}$ [3], the distribution of the telomer homologs in this reaction was independent of both the reaction time and the initiator concentration, and coincided with the distribution when initiation was with benzoyl peroxide (BP) (see Table 1, Expts. 1 and 2-14). The mechanism of the initiation and the transfer of Cl in the telomerization, initiated by metal carbonyls, postulates the formation of complexes in which the carbonyl groups are replaced by the monomer molecules and halogen atoms. The absence of differences in the distribution of the telomer homologs when the telomerization is initiated by BP, $Cr(CO)_6$ or $Cr(CO)_5PPh_3$ indicates that similar complexes are formed from $Cr(CO)_6$ and $Cr(CO)_5PPh_3$, which do not take part in transfer of the chlorine atom.

Replacing the carbonyl groups by such ligands as PPh_3 leads to an increase in the activity of the metal carbonyl$-CCl_4$ initiating systems [4]. And actually, the overall telomerization rate proved to be higher when initiation was with $Cr(CO)_5PPh_3$ as compared to $Cr(CO)_6$. Thus, with the same reaction time and the same $Cr(CO)_6$ and $Cr(CO)_5PPh_3$ concentrations the conversion of the reactants was three times greater in the case of $Cr(CO)_5PPh_3$ (see Table 1, Expts. 8 and 10). In Expt. 8 the $Cr(CO)_6$ concentration is three times that of $Cr(CO)_5PPh_3$; in Expt. 9 for $Cr(CO)_6$ the ethylene and CCl_4 conversions proved to be twice lower. In addition, an induction period of ≈15 min [no reaction for 15 min in the presence of $4.5 \cdot 10^{-2}$ mmole of $Cr(CO)_6$] is observed when the telomerization is initiated with $Cr(CO)_6$, whereas when initiation is with $1.1 \cdot 10^{-2}$ mmole of $Cr(CO)_5PPh_3$ the ethylene and CCl_4 conversions in 10 min were respectively 8.8 and 4.1% (see Table 1, Expt. 14).

Since the distribution of the telomer homologs was independent of the reaction time and the $Cr(CO)_6$ and $Cr(CO)_5PPh_3$ concentration we ran a series of experiments to determine the partial chain-transfer constants C_t (see Tables 2 and 3). The partial chain-transfer constants for the telomerization of ethylene with CCl_4, initiated by $Cr(CO)_6$, and also by $Cr(CO)_5PPh_3$, proved to be close to the C_t when using peroxide initiation (C_1-C_5 = 0.157; 3.0; 5.5; 8.2; 11.3 at 100° and 0.282; 3.0; 4.7; 6.5; 8.2 at 140° [5]). This coinciding in the C_t values is convincing proof that when the telomerization of ethylene with CCl_4 is initiated by $Cr(CO)_6$ or $Cr(CO)_5PPh_3$ both chain growth and transfer proceed by the free radical chain mechanism.

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CONCLUSIONS

1. We determined the constants for the chain transfer of the $CCl_3(CH_2CH_2)_n\cdot$ radicals (n = 1-5) to CCl_4 in the telomerization of ethylene with CCl_4, initiated by $Cr(CO)_6$ or $Cr(CO)_5PPh_3$ at 120°.

2. A coinciding of the partial chain-transfer constants when the telomerization is initiated by peroxide as compared to initiation by $Cr(CO)_6$ or $Cr(CO)_5PPh_3$ indicates that the reaction proceeds by the free radical mechanism in the presence of the last two initiators.

3. $Cr(CO)_5PPh_3$ is a more active initiator of radical telomerization than $Cr(CO)_6$.

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