medium and on Taft's induction constants have been investigated.

3. A proposed mechanism has been given of the transformation of N-nitroso(nitroalkyl)amines into N-nitro(nitroalkyl)amines under the action of HNO₃.

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RELATIVE KINETICS IN THE TELOMERIZATION OF PROPYLENE WITH CC14

INITIATED BY COORDINATION INITIATORS BASED ON Cr(CO)₆

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In the telomerization of propylene with CCl₄ initiated by systems based on $Fe(CO)_5$ [1] nucleophilic additives (DMFA, i-CH₃H₇OH, CH₃OH) accelerate the transfer of a chlorine atom from CCl₄ to the growing telomer radicals and substantially increase the content of adduct in the reaction mixture. Acetonitrile, for which the donor properties are low, had no effect on the distribution of telomer homologs.

In a continuation of the study into the effect of the nature of metal carbonyls on the course of telomerization we have investigated the telomerization of propylene with CCl₄ initiated by $Cr(CO)_6$ in conjunction with HMPA, DMFA, CH₃OH, and CH₃CN in order to estimate by the method of relative kinetics the effect of nucleophilic additives on chlorine atom transfer in this reaction.

EXPERIMENTAL

GLC analysis was conducted with an LKhM-8MD instrument in a stream of He (6 liters/h) with a Katharometer, a steel column 2000 \times 3 mm containing 15% SKTFT-50 on Chromaton N-AW. The analysis temperature for the experiments in which HMPA, CH₃CN, and CH₃OH were present was 150°C; in the presence of DMFA the temperature programming was from 100 to 160°C (8 deg/min). The reactions were conducted with sealed glass 4-ml ampuls. The experimental procedure was

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1515-1518, July, 1981. Original article submitted November 5, 1980. TABLE 1. Telomerization of 16.4 ± 1.2 mmoles C_3H_6 with 4.9 ± 0.1 mmoles CCl₄ ($C_3H_6/CCl_4 = 3.6 \pm 0.2$) Initiated by 3 ± 10^{-2} mmoles Cr(CO)₆ in Combination with Various Nucleo-philic Additives ($120^{\circ}C$, 30 min)

Expt. No.*	Nucleophilic additive, mmole • 10 ²	Conversion, %		Content of $CCl_3[CH_2CH(CH_2)]_nCl$ telomers (T_n) having $n = 1, 2$, and 3, mole $\%$		
		C ₃ H ₆	CC14		T2	T ₃
$\begin{array}{c} 1 [2]^{\frac{1}{2}} \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \end{array}$	$ \begin{array}{c} - \\ 5 \\ 10 \\ 50 \\ 183 \\ 5 \\ 9 \\ 50 \\ 175 \\ 5 \\ 11 \\ 48 \\ 183 \\ 7 \\ 13 \\ 52 \\ \end{array} $	7,0 9,64 8,9 14,9 8,9 4,9 8,9 7,9 8,9 4,7 5,8 9,3 6,2 8,9 8,6 2	$\begin{array}{c} 13.7\\ 18.2\\ 11.7\\ 20,4\\ 30,9\\ 12.2\\ 9.2\\ 12.4\\ 17.2\\ 9,0\\ 15.6\\ 11.6\\ 9,6\\ 17.2\\ 16.5\\ 12.7\end{array}$	$\begin{array}{c} 32,5\\ 30,1\\ 30,3\\ 27,2\\ 30,7\\ 28,1\\ 31,9\\ 25,3\\ 29,6\\ 34,0\\ 31,2\\ 31,0\\ 31,7\\ 29,4\\ 27,4\\ 27,4\\ 34,9\end{array}$	$\begin{array}{c} 59.9\\ 61.0\\ 62.9\\ 65.0\\ 64.6\\ 63.8\\ 59.8\\ 67.1\\ 63.2\\ 59.3\\ 57.0\\ 58.4\\ 56.9\\ 59.8\\ 63.9\\ 58.4\\ 56.9\\ 59.8\\ 63.9\\ 58.4\\ \end{array}$	7,6 8,9 6,8 7,8 4,7 8,1 8,3 7,6 7,2 6,7 11,8 10,6 11,4 10,8 8,7 7,0
17	186	7,5	14,5	26,1	63,8	10,1

*In experiments 2-5 the nucleophilic additive was HMPA, in 6-9 it was DMFA, in 10-13 it was $CH_{3}CN$, and in 14-17 it was $CH_{3}OH$.

†Experiment conducted for 60 min.

TABLE 2. Partial Chain-Transfer Constants (C_n) in the Telomerization of $C_{3}H_{6}$ (M) with CCl₄ (S) in the Presence of 0.025 mmole Cr(CO)₆ and 0.089 mmole of Nucleophilic Additive (120°C, 20 min)*

Nucleophilic additive	Range of varia- tion (M/S) _{av}	C_1	_{σi} †	C2	σ ₂ †.
- [2] ГМФА ДМФА СН₃СN СН₃ОН	$\begin{array}{c} 1,35-15,39\\ 1,36-14,67\\ 1,46-16,54\\ 1,38-16,52\\ 1,28-15,90\end{array}$	1,53 1,51 1,60 1,59 1,51	0,02 0,01 0,03 0,03 0,03 0,02	34,9 26,7 28,2 22,3 23,2	0,6 0,9 0,5 0,8 0,6

 $*C_n$ is the arithmetic mean of 10 values of C_n determined over the range of $(M/S)_{av}$ indicated; C_n was calculated from the Mayo equation [3].

 $\dagger \sigma_n$ is the mean-square error of the arithmetic mean.

the same as that described in [2]. The amount of the initial reactants, the experimental conditions, and the results of the GLC analysis of the reaction mixture are presented in Table 1. To determine the partial chain-transfer constants C_n series of 10 experiments were conducted for each nucleophilic additive. The propylene/CCl₄ (M/S) ratio within a series was varied by a factor of more than 10 (Table 2) at approximately the same intervals. The conversion of propylene and CCl₄ did not exceed 16%.

DISCUSSION

Over the concentration range studied, none of the nucleophilic additives effect the distribution of telomer homologs in the reaction mixture (see Table 1), whereas when this reaction was initiated by $Fe(CO)_5$ in combination with DMFA, i-C₃H₇OH, and CH₃OH an appreciable increase was observed in the yield of adduct compared with peroxide initiation [1]. The special features in the initiation of telomerization by metal carbonyls and the transfer of chlorine are represented by the scheme* [1]

$$M (CO)_n + C_3 H_6 \simeq C_3 H_6 \dots M (CO)_{n-1} + CO$$

$$C_{3}H_{6}...M(CO)_{n-1} \rightarrow \text{Inactive products}(\bar{P})$$
 (2)

$$C_{3}H_{6}...M(CO)_{n-1} + CCI_{4} \rightarrow C_{3}H_{6}...M(CO)_{n-2}...CCI_{4} (I) + CO$$
⁽³⁾

$$(I) \rightarrow (II) + CCI_{3} \tag{4}$$

(I)
$$+ CO(P) \rightarrow$$
 Inactive products (5)

$$CCl_3 + C_3H_6 \rightarrow CCl_3CH_2CHCH_3$$
(6)

$$CCl_{3}CH_{2}CHCH_{3} + (II) \rightarrow CCl_{3}CH_{2}CHClCH_{3}(T_{1}) +$$

$$+ \text{ Reduced form \% (II)}$$
(7)

Reduced form
$$\%$$
 (II) $+$ CCl₄ \rightarrow CCl₃ $+$ (II) . (8)

According to the scheme the stages of initiation (4) and (8) and of Cl transfer (7) require the preliminary penetration of the monomer and the telogen into the ligand shell of the metal carbonyl [stages (1) and (3)].

Nucleophilic additives possessing high coordinating properties may replace the carbonyl groups in metal carbonyls, thereby facilitating a higher activation of the initiator. It is known that the activity of metal carbonyl—CCl₄ initiating systems increases with the successive replacement of the carbonyl groups by such ligands as CNAr or $P(C_6H_5)_3$ [4]. In the telomerization of: propylene with CCl₄ initiated by $Fe(CO)_5$ in combination with nucleophilic additives [1] the formation of such complexes is confirmed by the adduct content in the reaction mixture, increasing in parallel with an increase in the coordinating properties of the nucleo-philic additives (CH₃OH < i-C₃H₇OH < DMFA). The distribution of the telomer homologs also varies with the reaction period, which is due to the necessity for a sufficient amount of the complexes responsible for the transfer of Cl to the growing telomer radicals to accumulate in the reaction mixture.

For the initiation of this telomerization by $Cr(CO)_6$ in combination with DMFA the distribution of telomer homologs was independent of the reaction period; in an experiment leading to 3 h for $K_S = 74.2\%$ and $K_M = 37.7\%$ the contents T_1 , T_2 , and T_3 were 24.5, 67.0, and 8.5\%, respectively, and did not differ from the telomer content for experiments lasting 30 min (experiments 6-9, Table 1). In addition, nucleophilic additives increase the overall rate of telomerization (cf. K_S and K_M in experiments 1 and 2-17, Table 1) and this may be evidence in favor of the nucleophilic additive penetrating into the ligand sphere of $Cr(CO)_6$. Furthermore, using spin traps it has been shown by EPR that the radical $ClCr[ONC(CH_3)_3](OP[N(CH_3)_2]_3)$ is formed in the reaction of $Cr(CO)_6$ with CCl₄ and HMPA [5]. In this radical three carbonyl groups are replaced by Cl, a trap molecule, and an HMPA molecule. These facts indicate that in the telomerization of propylene with CCl₄ a complex similar to (II) (see scheme) is formed but still containing the nucleophilic additive. Since the distribution of the telomer homologs in telomerization initiated by $Cr(CO)_6$ without nucleophilic additives and is independent of the reaction period the complex (II) would not seem to participate in the transfer of Cl at stage (7) in the case of $Cr(CO)_6$.

It can be supposed that the initiation of telomerization by $Fe(CO)_5$ and $Cr(CO)_6$ takes place by an analogous mechanism and for both carbonyls the complex (II) has a similar structure. As one of the arguments favoring such an assumption we may cite the proof that the $ClFe(CO)_4$ radical is formed in the reaction of $Fe(CO)_5$ with CCl_4 [6] and $ClCr(CrO)_5$ in the reaction of $Cr(CO)_6$ with CCl_5 [5]. With the transfer of Cl to the telomer radicals [stage (7)] reduction of the complex (II) takes place. If the ligand environment in complex (II) is similar in composition for Fe and Cr, then the absence of acceleration of Cl transfer

(1)

(0)

101

^{*}The scheme principally coincides (except for the last three stages) with the scheme representing the mechanism for the initiation of the polymerization of vinyl monomers by the system metal carbonyls-CC14 and although it is "idealized," in the opinion of the authors of [4], it can explain many experimental observations.

in the case of initiation by $Cr(CO)_6$ would seem to be associated with the oxidation potential of Cr^{3+} (-0.41 V) being considerably lower than that of Fe³⁺ (+0.77 V) and the complex (II) containing Cr in the oxidized form may not be reduced by the telomer radicals. For this reason the reduction of the radicals by means of Cr^{2+} salts [7] or the system $Cr(CO)_6$ -i- C_3H_7OH [8] is nonchain in nature.

The partial chain-transfer constants C_n in the telomerization of propylene with CCl₄ initiated by $Cr(CO)_6$ in combination with HMPA, DMFA, CH₃CN, and CH₃OH (see Table 2) were found to be close in value to C_n for telomerization initiated by $Cr(CO)_6$ without nucleophilic additives and to C_n for peroxide initiation [2]. The agreement between C_n for all three methods of initiation shows once more that chain growth and transfer in telomerization initiated by the $Cr(CO)_6$ -nucleophilic additive system take place by a free-radical mechanism and the nucleophilic additives do not participate in these stages.

CONCLUSIONS

1. The first and second chain-transfer constants have been determined in the telomerization of propylene with CCl₄ initiated by $Cr(CO)_6$ in the presence of HMPA, DMFA, CH₃CN, and CH₃OH at 120°C.

2. The partial chain-transfer constants for telomerization initiated by benzoyl peroxide, $Cr(CO)_6$, and $Cr(CO)_6$ in combination with nucleophilic additives coincide, from which it follows that the additives studied do not affect chain growth and transfer stages.

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