# RELATIVE KINETICS FOR THE TELOMERIZATION OF PROPYLENE BY THE METHYL ESTERS OF CHLOROACETIC AND TRICHLOROACETIC ACIDS AND $CCl_4$ INDUCED BY $Mn_2(CO)_{10}$ SYSTEMS

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A study of the reactions of unsaturated compounds with $CCl_4$ in the presence of complex initiators containing $Fe(CO)_5$ [1] and $Cr(CO)_6$ [2] showed marked differences in the telomer distribution related to the nature of the monomer and induction system. These effects may apparently be attributed both to change in the polarity of the growing radicals which react in the chain transfer step either with the electrophilic telogen or nucleophilic complex and the capacity of the individual monomers to enter the ligand sphere of the complex, thereby altering its chemical activity.

A study of the telomerization of ethylene by methyl chloroacetate and methyl trichloroacetate in the presence of coordination initiators (CI) $Mn_2(CO)_{10}$ and $Mn_2(CO)_{10}$ + DMF showed a significant difference in the nature of the effect of the CI on the course of the reactions which proceed due to breakage of either the C−Cl or C−H bonds [3]. Thus, in the case of $CCl_4$ and $CCl_3CO_2CH_3$, the use of a system containing DMF leads to a change in the distribution in the telomer homologs with enhancement of $T_1$. When $CH_2ClCO_2CH_3$ is used as the telogen, the individual chain transfer constants are similar in magnitude to those obtained in the presence of peroxide initiators. In this case, use of the $Mn_2(CO)_{10}$ + DMF system does not alter the telomer distribution and the relative extent of radical isomerization.

All the reactions with propylene, as in the case of ethylene [3], were carried out in a stainless-steel autoclave under comparable conditions. We do not exclude the possibility, in principle, of a reaction of the reaction mixture with the autoclave walls.

TABLE 1. Telomerization of Propylene (M) with $CH_2ClCO_2CH_3$ (S) Induced by $Mn_2(CO)_{10}$ at 140°C for 1 h with 0.3-0.4 mole % $Mn_2(CO)_{10}$ Relative to the Telogen

| Expt. No. | Amount, mmoles | | Conversion, % | | M/S (mean) | Yield of telomers, mole % divided by the sum of identified products | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | M | S | M | S | | $T_1$ | $T'_2$ | $T_2$ | $T^{t}_3$* | $T'_3$ | $T^{t}_4$ † | $T'_4$ | $\Sigma T_{m+n}$ and $T'_{m+n}$ |
| 1 | 6,9 | 52,4 | 35,5 | 1,7 | 0,11 | 60,8 | 10,8 | 7,1 | 4,4 | 10,8 | 1,7 | 2,6 | 1,8 |
| 2 | 12,1 | 53,6 | 33,1 | 3,7 | 0,19 | 43,9 | 13,2 | 10,3 | 7,0 | 16,0 | 2,6 | 4,2 | 2,9 |
| 3 | 17,4 | 53,0 | 17,0 | 2,5 | 0,30 | 37,7 | 12,7 | 9,9 | 9,5 | 17,2 | 3,7 | 5,0 | 4,3 |
| 4 | 21,0 | 52,5 | 20,5 | 3,7 | 0,36 | 35,3 | 11,9 | 12,8 | 9,2 | 18,1 | 3,4 | 5,3 | 4,0 |
| 5 | 26,0 | 52,0 | 17,2 | 3,3 | 0,46 | 25,6 | 11,1 | 10,7 | 9,3 | 18,5 | 4,7 | 8,4 | 11,6 |
| 6 | 34,3 | 53,0 | 5,2 | 1,2 | 0,63 | 19,2 | 10,9 | 9,1 | 9,8 | 18,5 | 4,6 | 10,5 | 17,4 |
| 7 | 45,0 | 53,7 | 17,4 | 5,9 | 0,76 | 20,2 | 8,5 | 12,2 | 10,1 | 16,9 | 6,6 | 8,0 | 17,3 |
| 8 | 26,2 | 26,3 | 10,1 | 3,2 | 0,95 | 18,5 | 8,4 | 9,3 | 9,3 | 14,2 | 5,2 | 9,6 | 25,4 |
| 9 | 30,0 | 27,7 | 6,6 | 2,4 | 1,05 | 18,5 | 10,2 | 11,1 | 10,2 | 18,0 | 5,3 | 9,7 | 17,0 |
| 10 | 34,5 | 23,3 | 4,7 | 2,3 | 1,45 | 19,9 | 8,3 | 11,6 | 9,0 | 14,7 | 5,5 | 8,8 | 22,2 |

* The unsaturated reaction products were identified in our previous work [4].

† Individual chain transfer constants for the total telomer series. The mean values are: $C_1 = 0.20 \pm 0.006$, $C_2 = 0.26 \pm 0.012$, and $C_3 = 0.66 \pm 0.019$.

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TABLE 2. Telomerization of Propylene (M) with $CCl_3CO_2CH_3$ (S) Initiated by $Mn_2(CO)_{10}$ at 140°C for 1 h, 0.3-0.4 mole % $Mn_2(CO)_{10}$ Relative to the Telogen

| Expt. No. | Amount, mmoles | | Conversion, % | | M/S (mean) | Yield of telomers, mole % divided by the sum of identified products | | | | $C_n^*$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | M | S | M | S | | $T_1$ | $T_2$ | $T_3$ | $\sum_{n\geqslant 3} T_n$ | $C_1$ | $C_2$ |
| | | | | | Initiator $Mn_2(CO)_{10}$ | | | | | | |
| 1 | 42,9 | 37,9 | 39,4 | 32,8 | 1,07 | 65,5 | 33,6 | 0,9 | – | 2,03 | 37,0 |
| 2 | 45,0 | 20,3 | 30,5 | 43,9 | 2,48 | 51,0 | 45,2 | 2,9 | 1,0 | 2,58 | 28,9 |
| 3 | 65,7 | 24,2 | 16,5 | 26,4 | 3,07 | 39,0 | 54,2 | 5,2 | 1,6 | 1,96 | 24,4 |
| 4 | 59,8 | 15,4 | 6,9 | 16,0 | 4,30 | 38,4 | 55,6 | 5,4 | 0,6 | 2,70 | 42,0 |
| 5 | 73,8 | 15,3 | 8,0 | 21,2 | 5,22 | 30,0 | 58,2 | 9,6 | 2,2 | 2,24 | 25,7 |
| | | | | | $Mn_2(CO)_{10}$ + DMF initiator system (3-4 mole % relative to the telogen) | | | | | | |
| 6 | 44,0 | 38,5 | 51,2 | 55,2 | 1,19 | 94,2 | 5,5 | 0,3 | – | – | – |
| 7 | 64,5 | 24,7 | 23,2 | 52,6 | 3,42 | 87,1 | 11,2 | 1,7 | – | – | – |
| 8 | 89,5 | 15,8 | 12,9 | 65,7 | 10,0 | 89,7 | 9,3 | 1,1 | – | – | – |

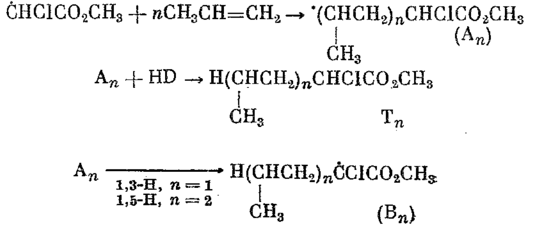
* Mean values of constants: $C_1 = 2.30$ and $C_2 = 31.6$. In the case of peroxide initiation, $C_1 = 2.1$ and $C_2 = 29.1$ [5].

TABLE 3. Telomerization of Propylene (M) with $CCl_4$ (S) Initiated by $Mn_2(CO)_{10}$ at 120°C for 20 min with 0.3-0.4 mole % $Mn_2(CO)_{10}$ Relative to the Telogen

| Expt. No. | Amount, mmoles | | Conversion, % | | M/S (mean) | Yield of telomers, mole % divided by the sum of identified products | | | | $C_n^*$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | M | S | M | S | | $T_1$ | $T_2$ | $T_3$ | $\sum_{n>3} T_n$ | $C_1$ | $C_2$ |
| | | | | | Initiator $Mn_2(CO)_{10}$ | | | | | | |
| 1 | 26,8 | 15,2 | 3,1 | 3,6 | 1,8 | 55,8 | 39,9 | 3,9 | 0,4 | 2,2 | 18,1 |
| 2 | 32,7 | 14,9 | 7,4 | 10,5 | 2,2 | 50,9 | 44,6 | 4,1 | 0,4 | 2,3 | 21,8 |
| 3 | 36,0 | 15,6 | 8,1 | 11,9 | 2,4 | 47,7 | 48,0 | 3,9 | 0,4 | 2,2 | 26,2 |
| 4 | 44,6 | 15,7 | 3,4 | 5,8 | 2,9 | 39,7 | 53,5 | 6,0 | 0,8 | 1,9 | 23,0 |
| 5 | 53,6 | 14,9 | 4,3 | 8,5 | 3,7 | 32,0 | 58,6 | 8,1 | 1,3 | 1,7 | 22,9 |
| 6 | 62,5 | 15,0 | 6,1 | 16,2 | 4,4 | 28,4 | 60.0 | 9,7 | 1,9 | 1,8 | 23,0 |
| | | | | | $Mn_2(CO)_{10}$ + DMF initiator system (3-4 mole % relative to the telogen) | | | | | | |
| 7 | 26,8 | 15,3 | 20,2 | 31,9 | 1,9 | 89,7 | 9,6 | 0,4 | 0,3 | 16,6 | 28,6 |
| 8 | 20,5 | 9,4 | 16,0 | 30,7 | 2,4 | 87,0 | 12,1 | 0,8 | 0,1 | 16,3 | 36,4 |
| 9 | 37,0 | 16,0 | 14,6 | 30,0 | 2,5 | 88,0 | 11,0 | 0,8 | 0,2 | 18,5 | 32,2 |
| 10 | 36,0 | 14,5 | 18,4 | 40,7 | 2,9 | 88,2 | 10,7 | 1,0 | 0,1 | 22,0 | 28,0 |
| 11 | 44,6 | 16,0 | 9,6 | 23,6 | 3.0 | 88,2 | 10,5 | 1,2 | 0,1 | 22,6 | 23,3 |
| 12 | 53,6 | 16,2 | 10,3 | 29,4 | 3,8 | 85,8 | 12,3 | 1,6 | 0,3 | 22,8 | 24,9 |
| 13 | 62,5 | 16,7 | 8,7 | 28,1 | 4,2 | 86,3 | 11,5 | 1,8 | 0,4 | 26,7 | 22,6 |

* Mean values of constants from Expts. 1-6: $C_1 = 2.0 \pm 0.04$ and $C_2 = 22.5 \pm 0.044$ and from Expts. 7-12: $C_1 = 20.8$ and $C_2 = 28.0$. In the case of peroxide initiation, $C_1 = 2.2$ [6].

In order to clarify the effect of the nature of the monomer and the growing radicals on the telomerization proceeding at C–H and C–Cl bonds, we studied the relative kinetics of the telomerization of propylene by the same telogens in the presence of $Mn_2(CO)_{10}$ and $Mn_2(CO)_{10}$ + DMF. The reaction of methyl chloroacetate with propylene yields the same series of telomers as in the case of peroxide initiation [4]:

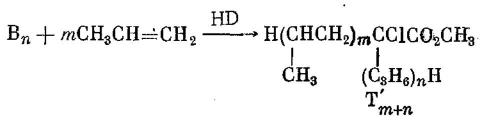


$$CH_2ClCO_2CH_3(HD) \xrightarrow{R^{\cdot}} \dot{C}HClCO_2CH_3$$

$$\dot{C}HClCO_2CH_3 + nCH_3CH{=}CH_2 \rightarrow {}^{\cdot}(\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_2)_nCHClCO_2CH_3 \quad (A_n)$$

$$A_n + HD \rightarrow H(\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_2)_nCHClCO_2CH_3 \quad T_n$$

$$A_n \xrightarrow[\substack{1,3\text{-H},\ n=1\\ 1,5\text{-H},\ n=2}]{} H(\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_2)_n\dot{C}ClCO_2CH_3 \quad (B_n)$$



$$B_n + m\mathrm{CH_3CH{=}CH_2} \xrightarrow{\mathrm{HD}} \mathrm{H(\underset{\displaystyle CH_3}{CH}CH_2)_m\underset{\displaystyle (C_3H_6)_nH}{C}ClCO_2CH_3}$$

$T'_{m+n}$

On the other hand, the telomer distribution and yield of rearranged products $T'_{m+n}$ are sensitive to the composition and nature of the CI. When using $Mn_2(CO)_{10}$ as the initiator in the M/S range from 0.11 to 1.45 (Table 1), the individual chain transfer constants $C_n^{tot}$ are similar in value to those obtained when running the reaction with TBP [4]. In this case, the relative amount of rearranged telomer $T_2'$ hardly changes with increasing M/S (see Table 1). While going from $Mn_2(CO)_{10}$ to $Mn_2(CO)_{10}$ + DMF in the initiation of this reaction with ethylene does not affect the course of the reaction and the values for $C_n$, a shift in the telomer homolog yields in favor of $T_1$ is found in the case of propylene. The increase in the yield of $T_1$ may be related to chain transfer directly at the allyl C−H bond of propylene. However, such a change was not observed at similar M/S values in experiments initiated by $Mn_2(CO)_{10}$ without additives. Thus, under our conditions, the presence of DMF creates a system with $Mn_2(CO)_{10}$ and propylene which is capable of increasing the efficiency of chain transfer at the C−H bond of a propylene molecule which may be located in the ligand sphere of the complex. Support for this hypothesis is the finding of 1,5-hexadiene in the reaction mixture.

The telomerization of propylene with methyl trichloroacetate yields a series of telomers $Cl(CH(CH_3)CH_2)_n$-$CCl_2CO_2CH_3$ ($T_n$) as in the case of peroxide initiation. In the presence of $Mn_2(CO)_{10}$, the individual chain transfer constants $C_n$ have the same values as under conditions of peroxide initiation [5] (Table 2). Use of the $Mn_2(CO)_{10}$ + DMF system for similar M/S values gives an increase in the yield of yield of $T_1$ from 39.0 to 87.1% (see Table 2, Expts. 3 and 7).

Similar behavior is found in the telomerization of propylene with $CCl_4$. This reaction is sensitive to change in the DMF/$Mn_2(CO)_{10}$ and M/S ratios. In the range of M/S from 1.8 to 4.4 in the presence of $Mn_2(CO)_{10}$ the telomer distribution is similar to that obtained upon peroxide initiation. The addition of DMF leads to an increase in the yield of $T_1$. Thus, the value for $C_1$ increases from 2.0 to 20.8 (Table 3). All the experiments in the presence of DMF were carried out with DMF/$Mn_2(CO)_{10}$ ratio equal to 20. In this case, the ratio cannot affect the telomer distribution. This was also taken into account in working with other telogens.

## EXPERIMENTAL

The gas−liquid chromatographic (GLC) analysis was carried out on an LKhM-8MD chromatograph on columns: 1) 1000 × 3 mm, packed with 20% SKTFT-50 on Chromosorb W (0.16-0.20 mm) with temperature programming, 2) 2000 × 3 and 3000 × 3 mm packed with 20% SKTFT-50 on Chromosorb W, and 3) 2000 × 3 and 3000 × 3 mm packed with 15% Carbowax on Chromatone N-AW-HMD (0.16-0.20 mm) at constant 150 or 170°C in a helium stream. The chromatograms were analyzed by internal normalization without correction. All the experiments were carried out in 10-$cm^3$ stainless-steel autoclaves.

Telomerization of Propylene with $CH_2ClCO_2CH_3$ (see Table 1). The experiments were carried out according to our previous procedure [4]. The monomer conversion was determined by the volume of released gas. GLC analysis using authentic samples showed that the reaction proceeds with the formation of the same products as in the case of peroxide initiation [4]. In control experiments carried out with $CH_2ClCO_2CH_3$ + $Mn_2(CO)_{10}$ + DMF and DMF + $Mn_2(CO)_{10}$ + propylene systems, there were no significant amounts of any products which hinder the quantitative analysis of the telomers.

The results obtained are given in Table 1. GLC analysis on columns 2 and 3 using an authentic sample showed the presence of 1,5-hexadiene.

Telomerization of Propylene with $CCl_3CO_2CH_3$ (see Table 2). This reaction was carried out similarly to that with methyl chloroacetate. The products were identified relative to authentic samples [5] on the indicated columns. In control experiments with the $CCl_3CO_2CH_3$ + $Mn_2(CO)_{10}$ + DMF system, there were no products which hinder the quantitative analysis of the reaction mixture. The results obtained are shown in Table 2.

Telomerization of Propylene with $CCl_4$ (see Table 3). The experiments were carried out according to our previous method [7]. The conversion of the telogen and the monomer was found by calculation. The $C_n$ constants were calculated using the Mayo equation [8]. In light of the relatively narrow range of M/S values, the method of individual chain transfer constants was used for a clear evaluation of the change in telomer distribution relative to the reaction conditions. The experimental results are given in Table 3. The nature of the effect of the reactor material may be analogous to that described by Karapet'yan et al. [9].

## CONCLUSIONS

Individual chain transfer constants found for the telomerization of propylene with methyl chloroacetate, methyl trichloroacetate, and $CCl_4$ initiated by $Mn_2(CO)_{10}$ are similar to the values obtained in the case of peroxide initiation.

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# NEW METHOD FOR THE STABILIZATION OF INTERMEDIATE RADICALS IN THE REACTION OF THIOUREA AND ITS N-SUBSTITUTED DERIVATIVES WITH PHENYL RADICALS

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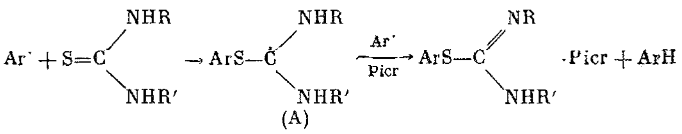
Aryl radicals react with thiourea and its N-substituted derivatives to form the corresponding isothiouronium bases which are isolated as picrates [1, 2]:



The radical-adducts (A) are stabilized by their "cross-disproportionation" with aryl radicals which abstract a β-hydrogen atom from the NH group in the (A) radicals.

In light of the ready addition of radicals to the thiocarbonyl group, we studied the possibility of growing radical-adducts such as (A) by their addition to the S = C group of a second molecule of a thione compound to form "telomeric" radical (B):

$$(A) + S{=}C(NHR)_2 \rightarrow \underset{(B)}{ArSC(NHR)_2S\dot{C}(NHR)_2}$$

Such reactions are unknown for organosulfur compounds.

The phenylation of thiourea by phenyldiazonium tetrafluoroboride in aqueous medium in the presence of a copper salt gives S-phenylisothiouronium (I) and bis(formamidine) sulfide (II) which are isolated as their picrates (see Table 1):

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