# CHAIN TERMINATION IN THE TELOMERIZATION OF PROPYLENE WITH $CCl_4$ INITIATED BY TERT-BUTYL PEROXIDE AND THE $W(CO)_6$—$PPh_3$ SYSTEM

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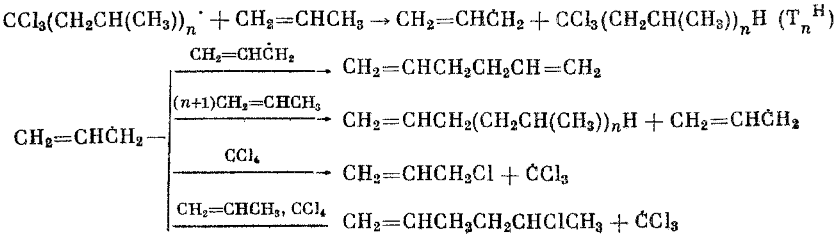
In the radical telomerization of unsaturated compounds with $CCl_4$, the recombination of trichloromethyl radicals is usually taken as the chain termination step [1]. On the other hand, Takehisa et al. [2], in a gas-liquid chromatographic analysis of the products of the telomerization of propylene with $CCl_4$ initiated by $\gamma$-radiation, identified compounds obtained due to hydrogen abstraction from the monomer by the telomer radicals (allylic termination) and products of the transformation of the allyl radicals formed. The overall yield of such compounds did not exceed 10%. These authors showed that allylic termination has only a slight effect on the rate of formation of the major reaction products. In the present work, we studied the chain termination for different initiation modes of the telomerization of propylene with $CCl_4$ (using peroxide and the $W(CO)_6$—$PPh_3$ system) by analyzing the side products by chromato-mass spectrometry. Since the content of the higher telomers $CCl_3[CH_2CH(CH_3)]_nCl(T_n^{Cl})$ with $n \geq 3$ is about 20% with the selected concentrations for $C_3H_6$ (12.8 moles/liter) and $CCl_4$ (1.2 moles/liter) [3], the identification of the reaction products was carried out only to $T_2^{Cl}$.

A chromato-mass spectrometric study of the fraction boiling above $CCl_4$ showed that both upon initiation with tert-butyl peroxide (TBP) and with the $W(CO)_6$—$PPh_3$ system, the side products of the telomerization (four compounds) have identical structure. Two of these are products formed as a result of the abstraction not of chlorine but rather hydrogen by the growing telomer radicals $CCl_3[CH_2CH(CH_3)]_n$: $CCl_3[CH_2CH(CH_3)]_nH$ ($T_n^H$, n = 1 and 2).† Propylene is the most likely hydrogen donor for the formation of $T_n^H$. In this case, allyl radicals are formed and, thus, the products of their subsequent transformations should be found in the reaction mixture (see scheme below). Indeed, the two remaining side products were identified as $CH_2{=}CHCH_2CH_2CHClCH_3$ (I) and $C_9H_{18}$ (II) (Table 1).

Products of the transformation of the allyl radicals were also found in the fraction boiling below $CCl_4$. These are diallyl (III) and 1-hexene (IV) for the telomerization initiated by TBP, while these are diallyl and allyl chloride (V) in the case of initiation by the $W(CO)_6$—$PPh_3$ system. The mass spectra of $T_1^H$, $T_2^H$, and (III)-(V) were identical to the mass spectra of samples prepared independently ($T_1^H$ and $T_2^H$ were synthesized according to Englin et al. [4]).

Thus, the finding of a series of products of the transformation of the allyl radicals proves that the $T_n^H$ telomers may be formed due allylic termination. The pathways for the transformation of the allyl radicals are given by the following scheme:



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*Deceased.

†The mass spectra of all the identified compounds are given in the Experimental.

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TABLE 1. Telomerization of 12.8 mole/liter $C_3H_6$ with 1.2 moles/liter $CCl_4$ at 140°C over 1 h

| Experiment No. | Initiator (moles/liter) | Yield, % | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | i-PrCl | n-PrCl | $CHCl_3$ | $\Sigma T_{1,2}^{Cl}$ | $\Sigma T_{1,2}^{H}$ | (I) | (II) | (III) | (IV) | (V) |
| 1 | TPB (0,07) | – | – | – | 25,8 | 1,6 | <1 | <1 | <1 | <1 | – |
| 2 | $W(CO)_6$ (0,03) | – | – | – | 10,5 | 0,8 | <1 | <1 | <1 | <1 | <1 |
| 3 | $W(CO)_6$ (0,035)+ +$PPh_3$ (0,24) | 3,6 | <0,1 | 9,2 | 26,0 | 7,1 | <1 | <1 | <1 | – | <1 |
| 4 | TPB (0,07)+ +$PPh_3$ (0,24) | 4,0 | <0,1 | 7,9 | 15,5 | 5,8 | <1 | <1 | <1 | – | – |
| 5 ** | $PPh_3$ (0,26) | 5,2 | <0,1 | 10,2 | – | – | — | — | — | – | – |

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*Calculated using gas-liquid chromatographic data.

†Experiment carried out without the addition of initiator.

The yield of $T_n^H$ upon the initiation of telomerization by the $W(CO)_6$–$PPh_3$ system is several times greater than that upon initiation by TBP or $W(CO)_6$ and may reach 30% of the major products, $T_n^{Cl}$ (see experiments 1-3 in Table 1). The effect of the various initiation modes is also seen in the finding of i-PrCl, n-PrCl, and $CHCl_3$ in the telomerization products upon initiation by the $W(CO)_6$–$PPh_3$ system, while these products are lacking in the reaction mixture obtained upon initiation by TBP or $W(CO)_6$ (Table 1). However, the addition of $PPh_3$ to TBP led to the appearance of i-PrCl and $CHCl_3$ in the reaction products and an increase in the yield of $T_n^H$ (experiments nos. 1 and 4). Thus, the difference in the reactions is independent of the nature of the initiator and is a function of the presence of $PPh_3$.

Triphenylphosphine may react with $CCl_4$ in the presence of nucleophilic hydrogen donors such as alcohols or amines to give $CHCl_3$ and HCl [5]. Propylene may presumably act as such a hydrogen donor in the reaction study. Then, the HCl formed should add at the double bond of propylene to give i-PrCl and n-PrCl. In order to check this hypothesis, we carried out the reaction of $PPh_3$ with $CCl_4$ and propylene without the addition of an initiator (Table 1, experiment 5). The only reaction products are $CHCl_3$, i-PrCl, and n-PrCl (experiment 5). These results indicate that $PPh_3$ reacts with $CCl_4$ and propylene upon initiation by a system containing $PPh_3$ in addition to telomerization.

The enhanced yield of $T_n^H$ in the reactions initiated by systems containing $PPh_3$ may be related to reaction of $CHCl_3$ formed with the growing telomar radicals to give $T_n^H$. However, the kinetic data of Englin et al. [6] indicate that the rate constants for hydrogen transfer from $CHCl_3$ to the telomer radicals are 15-20 times less than the corresponding constants for the transfer of chlorine from $CCl_4$. Indeed, carrying out the telomerization of a mixture of 0.3 mole/liter $CHCl_3$ and 1.2 moles/liter $CCl_4$ under the conditions of experiment 1 did not lead to an increase in the $T_n^H$ content, which remained the same as in experiment 1. Thus, the increase in the yield of products formed due to allylic termination is not related to a side reaction leading to $CHCl_3$ and is a specific feature of initiating systems containing $PPh_3$.

## EXPERIMENTAL

The telomerization was carried out in sealed 4-ml galss ampuls by a procedure analogous to that described in our previous work [3]. The quantitative gas-liquid chromatographic analysis was carried out on an LKhM-80 chromatography with a katharometer detector using a 3000 × 3 mm steel column packed with 5- SE-30 on Chromaton N-AW with temperature programming from 50 to 180°C at 12 deg/min. The helium gas carrier flow rate was 2.7 liter/h. The chromato-mass spectrometric identification was carried out on a Nermag R-10-10C chromatograph with a Spectral 500–Sidar 2/2 data treatment system. The scanning rate was $0.728\ sec^{-1}$ in the mass range from 34 to 284. The analysis was carried out on a 60 m × 0.32 mm J&W DB-5 capillary column with 0.25 μ stationary phase layer thickness, 0.5 helium gauge pressure, and temperature programming from 50 to 135°C at 2.4 deg/min. The temperature of the ionization chamber was 220°C. The ionizing energy was 70 eV. The mass spectrum of $T_1^H$ $CCl_3CH_2CH_2CH_3$ (here and subsequently, the ion mass (m/z) is given for the $^{35}Cl$ isotope and the relative intensity is given in parentheses, %):

[M—Me] 145(0,1), [M—Et] 131(0,1), [M—Pr] 117(1), [M—Cl] 125(18), [M—HCl—Me] 109(5), [M—Cl—Et] 96(10), [M—Cl—HCl] 89(58), [M—Cl—2HCl] 53(10), $Pr^+$ 43 (100). Mass spectrum of $T_2^H$ $CCl_3CH_2CH(CH_3)CH_2CH_2CH_3$: [M—HCl—Me] 151(0,1), [M—HCl—Et] 137(0,2), [M—HCl—Pr] 123(2), $CCl_3^+$ 117(0,5), $CCl_2{=}CH^+$ 95(4), $C_4H_6Cl^+$ 89(7), $C_6H_{13}^+$ 85(7), $C_5H_{11}^+$ 71(29), $C_5H_{10}^+$ 70(100), $Pr^+$ 43(39). Mass spectrum of $CH_2{=}CHCH_2CH_2CHClCH_3$: M 118(2), [M—HCl] 83(33), $C_5H_7^+$ 67(100), $C_2H_4Cl^+$ 63(4), $C_4H_7^+$ 55(43), $C_3H_5^+$ 41(47). Mass spectrum of $C_9H_{18}$: M 126(10), [M—Me] 111(1), [M—Et] 97(0,7), [M—Pr] 83(26), $C_5H_{11}^+$ 71(25), $C_5H_{10}^{+\cdot}$ 70(100), $C_5H_9^+$ 69(20), $C_4H_8^{+\cdot}$ 56(34), $C_4H_7^+$ 55(47). Mass spectrum of diallyl: [M—H] 81(2), [M—3H] 79(1), [M—5H] 77(0,5), [M—Me] 67(50), $C_4H_6^{+\cdot}$ 54(40), $C_3H_5^+$41(100), $C_3H_3^+$ 39(50). Mass spectrum of 1-hexene: M 84(16), [M—Me] 69(17), $C_4H_8^{+\cdot}$ 56(100), $C_4H_6^{+\cdot}$ 54(45), $Pr^+$ 43(17), $C_3H_5$ (70). Mass spectrum of allyl chloride: M 76(8), $CH_2Cl^+$ 49(2), $C_3H_5^+$ 41(100), $C_3H_3^+$ 39(45). Mass spectrum of *i*-PrCl: M 78(80), [M—Me] 63(95), M—Cl 43(100), $C_3H_6^{+\cdot}$ 42(30), $C_3H_5^+$ 41(99), $C_3H_3^+$ 39(75). Mass spectrum of *n*-PrCl: M 78(4), [M—Me] 63(4), $ClCH_2^+$ 49(3), [M—Cl] 43(30), $C_3H_6^{+\cdot}$ 42(100), $C_3H_5^+$ 41(30), $C_3H_3^+$ 39(12). Mass spectrum of $CHCl_3$: M 118(20), [M—H] 117(10), [M—Cl] 83(100), [M—2Cl] 48(30), [M—2Cl—H] 47(60), $Cl^+$ 35(20).

## CONCLUSIONS

1. The use of $PPh_3$ as a coinitiator in the telomerization of propylene with $CCl_4$ leads to a significant increase in the yield of allylic termination products relative to initiation with TBP or $W(CO)_6$.

2. Independently of the course of the telomerization, $PPh_3$ reacts with propylene and $CCl_4$ with the formation of $CHCl_3$, i-PrCl, and n-PrCl.

## LITERATURE CITED

1. C. M. Starks, Free Radical Telomerization, Academic Press, New York—London (1974).
2. M. Takehisa, J. Urano, and M. Yasumoto, J. Chem. Soc. Japan, 69, 426 (1966).
3. N. A. Grigor'ev, A. L. Tumanskaya, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 2583 (1982).
4. B. A. Englin, V. A. Valovoi, L. G. Zelenskaya, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2700 (1970).
5. R. Appel, Angew. Chem. Int. Ed. Engl., 14, 801 (1975).
6. B. A. Englin, N. A. Grigor'ev, and R. Kh. Friedlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1568 (1972).