MECHANISM OF THE TELOMERIZATION OF ETHYLENE
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In general, the mechanism of the telomerization of ethylene with polyhalomethanes (for example, with CCl₄) can be represented in the following way:

\[
R_i + CCl_4 \xrightarrow{K_i} R_iCl + \cdot CCl_3
\]  
Chain initiation

\[
\cdot CCl_3 + C_2H_4 \xrightarrow{K_1} CCl_3CH_2CH_2
\]

\[
CCl_3(CH_2CH_2)_{n-1}CH_2CH_2 + CCl_4 \xrightarrow{K_{tr}} \cdot CCl_3 + \cdot CCl_3(CH_2CH_2)_{n}Cl
\]
Chain propagation

\[
CCl_3(CH_2CH_2)_{n}CH_2CH_2 \xrightarrow{K_g} CCl_3(CH_2CH_2)_{n}CH_2CH_2
\]
Chain termination

The ratios \(C_n = \frac{K_{tr}}{K_g} = (\frac{A_{tr}}{A_g}) e^{-\frac{(E_{tr} - E_g)}{RT}}\) for telomer radicals of various chain lengths \(n\) are called the particular constants of chain transfer.*

One of the basic problems in the study of the mechanism of the telomerization of ethylene with polyhalomethanes is the determination of the causes of the increase in \(C_n\) when \(n\) is increased from one to four or five monomer units. In most cases, such a change in \(C_n\) was explained by a decrease (as a result of polar or steric effects) in the rate constant of the reaction growth \(-K_g\). Thus, the authors of [2] investigating the telomerization of ethylene with CCl₄, proposed that the increase in \(C_n\) is associated with steric hindrances, arising in the reactions of growth of the trichloroalkyl radicals with increasing \(n\). In a study of the telomerization of ethylene with CHCl₃, the authors of [3] arrived at the conclusion that there is a decrease in \(K_g\), and explained this by the induction influence of the trichloromethyl group. In both cases, only the first and second transfer constants were determined with sufficient accuracy; moreover, in direct methods (influence of temperature and nature of the solvent) were used to demonstrate the change in \(K_g\).

As we demonstrated in an investigation of the kinetics of the telomerization of ethylene with CCl₄ [4], and CHCl₃ [5], the dependence of \(C_n\) on the length of the radical chain is explained basically not by steric effects, but by differences in the activation energies of the reactions of chain transfer and growth (Table 1). Consequently, the change in \(C_n\) may be related to the induction influence of the trichloromethyl group. This hypothesis is also supported by a comparison of the particular constants of transfer of trichloroalkyl radicals with \(n\) from 1 to \(\infty\), which we determined [4, 5] (the values of \(C_n\) are cited in Table 2).

\[
(I) \quad CCl_3(CH_2CH_2)_{n-1}CH_2CH_2 + CCl_4 \xrightarrow{K_{tr}} CCl_3(CH_2CH_2)_{n}Cl + \cdot CCl_3
\]

\[
(II) \quad CCl_3(CH_2CH_2)_{n-1}CH_2CH_2 + C_2H_4 \xrightarrow{K_g} CCl_3(CH_2CH_2)_{n}CH_2CH_2
\]

\[
C_n' = \frac{K_{tr}}{K_g}
\]

*\(K_{tr}\) and \(K_g\) are the rate constants of the reactions of chain transfer and growth. \(C_n\) is calculated according to the Mayo equation [1]: \(C_n = \frac{[M]}{[S]} \frac{T_n}{\sum T} \), where [M], [S], and \(T_n\) are the concentrations of the monomer, telogen, and tenomer with \(n\) monomer units.

Inasmuch as the kinetic chain in the telomerization of methylene with CHCl₃ and CCl₄ is carried on by radicals of the same structure, the rate constants $C_n$ for radicals of any given chain length $n$ with each of the telogens will be made up of the ratio of the rate constants of the corresponding reactions of chain transfer to the same rate constant of the reaction of growth. From this it is easy to derive a new ratio, $P_n = C_n' / C_n = K_{tr}' / K_{tr}$, which contains only the rate constants of the reactions of chain transfer. The values of $P_n$ of radicals of different lengths, calculated according to the data of Table 2, are presented in Table 3.

As can be seen from Table 3, the constant of transfer of the CCl₄CH₂CH₂ radical with CCl₄ ($K_{tr}'$) is substantially smaller than $K_{tr}$ with CHCl₃ ($P_n < 1$, especially at low temperature). For radicals with a longer chain, there is the opposite dependence ($K_{tr}' > K_{tr}$ and $P_n > 1$), although when the temperature is increased from 70 to 140°C, the $P_n / P_1$ ratios decrease several-fold ($P_n < 1$, increase, while $P_n > 1$ drop).

The observed inversion of the reactivity of telomer radicals with $n = 1$ and $n > 1$ to the telogens studied cannot be explained by a change in the rate constants of chain growth ($K_g$ for reactions II and IV do not enter into the values of $P_n$). At the same time, the increase in $P_n$ cannot be determined by the differences in the energies of dissociation of the C–Cl and C–H bonds broken and formed, which are constant for $n,$