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Abstract

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KINETICS OF THE TELOMERIZATION OF ETHYLENE WITH CARBON TETRACHLORIDE AND CHLOROFORM. THE $Q - e$ SCHEME

The kinetics of the telomerization of ethylene with carbon tetrachloride and chloroform has been little studied [1–4] because of the difficulties of determining the concentrations of reagents in gas-liquid systems and of analyzing a complex mixture of high-boiling reaction products. The mechanism of this reaction (using CCl_4 as an example) may be represented as follows:

$$R_i^{\bullet} + CCl_4 \xrightarrow{K_1} R_{iCl} + \dot{C}Cl_3 \qquad \text{chain initiation}$$

$$\left.\begin{aligned} &\dot{C}Cl_3 + CH_2{=}CH_2 \xrightarrow{K_2} CCl_3CH_2\dot{C}H_2 \\ &CCl_3(CH_2CH_2)_{n-1}CH_2\dot{C}H_2 + CH_2{=}CH_2 \xrightarrow{K_p} CCl_3(CH_2CH_2)_nCH_2\dot{C}H_2 \\ &\dot{C}Cl_3(CH_2CH_2)_{n-1}CH_2\dot{C}H_2 + CCl_4 \xrightarrow{K_{per}} \dot{C}Cl_3 + CCl_3(CH_2CH_2)_{nCl} \end{aligned}\right\} \quad \text{chain growth}$$

$$2R^{\bullet} \xrightarrow{K_{ob}} \text{products}; \qquad \text{chain termination},$$

where $R^{\bullet}$ denotes trichloropropyl or telomeric radicals.

The relative rates of telomer formation are characterized by the partial chain-transfer constants $C_n = K_{per}/K_p$. In the present work the effect of temperature on the transfer constants of trichloroalkyl radicals of different chain length has been studied.

The experiments were carried out in stainless-steel autoclaves (volume ~ 10 ml, weight ~ 500 g) in the presence of tert-butyl peroxide or azobisisobutyronitrile ($\sim 2 \cdot 10^{-3}$ mol/l). The ethylene/telogen ratio was varied from 3 to 12 times. The amount of charged products was determined by weighing* (± 0.02 g). The

initial pressure was 170–220 atm. To bring the reaction mixture more rapidly into a homogeneous state, periodic stirring was used**. The conversion*** and the final ratio of reagents were calculated from the amount and composition of the telomer mixture on the basis of chromatographic data. Analysis of the reaction products without distilling off the solvent was carried out by the gas-liquid chromatography method**** at several temperatures (from 120 to 210°).

To calculate the partial chain-transfer constants, the Mayo equation [5] was used:

$$C_n = \frac{[\mathrm{M}]}{[\mathrm{S}]} \cdot \frac{\mathrm{T}_n}{\sum_{n+1}^{\infty} \mathrm{T}}, \tag{1}$$

where [M], [S], and T_n are the concentrations of monomer, telogen, and telomer containing n monomer units. The data***** obtained by us are presented in Table 1.

* The oxygen content in ethylene did not exceed 0.003%. The amount of impurities in the telogens, according to gas-liquid chromatography data, was 0.1–0.2 wt.%.

** Special experiments established that carrying out the reaction under heterogeneous conditions leads to an overestimation of the chain-transfer constants.

*** In most experiments the conversion did not exceed 10–15%.

**** Column length 1.8 m, diameter 4 mm; stationary liquid phase—silicone elastomer (10%); carrier gas—helium (2–4 l/hour); analysis time from 10 to 30 min.

***** A detailed experimental section is given in work [6].

Table 1

Telogen	Temp., °C	$C_1 \cdot 10^2$	C_2	C_3	C_4	C_5	C_∞
CCl_4	70	10,3$±0,8	3,0±0,3	7,5±0,7	10,3±1,0	12,5±1,2	13,0±0,7

Notes. 1. C_n are the transfer constants for radicals of different chain length n. 2. Mean errors are from 7–14 experiments.

The partial transfer constants increase by a factor of 10–130 as the chain length n grows from 1 to 5 and thereafter remain constant. For $CHCl_3$ the transfer constants are 2–3 times lower than for CCl_4 (with the exception of the first constant), and for radicals with n and $n+1$ monomer units they differ much less. Thus, the ratio C_1/C_2 is 5,3 for $CHCl_3$ at 103° and 19,4 at 100° for CCl_4. In

both cases the first transfer constant (C_1) increases noticeably with temperature, the second is approximately constant, and all subsequent ones decrease.

Table 2

Telogen	ΔE; A_{per}/A_p $n=1$	$n=2$	$n=3$	$n=4$	$n \geqslant 5$
CCl_4	$\Delta E = E'_{per} - E_p$	+3,7	0,0	−1,6	−2,0	−2,0
CCl_4	A'_{per}/A_p	22,0	3,0	0,7	0,5	0,7
$CHCl_3$	$\Delta E = E_{per} - E_p$	+1,3	0,0	−0,6	−0,5	−0,6
$CHCl_3$	A_{per}/A_p	1,5	1,5	1,1	1,5	1,6
$CHCl_3$	$\Delta E' = E'_{per} - E^*_{per}$	+2,5**	0,0	−1,1	−1,6	−1,6
$CHCl_3$	A'_{per}/A^*_{per}	16,0	1,9	0,5	0,3	0,3

* See Table 4. Here and below, n is the number of monomer units.
** $\Delta E' = +2,5$ in work ([4]).

C_n as the ratio of the rate constants of two competing reactions can be expressed through the Arrhenius equation as follows:

$$C_n = \frac{A_{per}}{A_p} \cdot e^{-\Delta E/RT}, \tag{2}$$

where $\Delta E = E_{per} - E_p$ is the difference between the activation energies of the transfer reactions and the growth of radicals with n monomer units (kcal/mole); A_{per}/A_p is the ratio of the pre-exponential factors of the same reactions. The values of ΔE and A_{per}/A_p for radicals of different chain length n are presented in Table 2.

As can be seen from the data of Table 2, differences in the rates of the transfer and chain-growth reactions involving any radical (except the trichloromethyl radical) are explained mainly by differences in the activation energies of these processes, and not by steric effects. Telomerization of ethylene with $CHCl_3$, in contrast to CCl_4, is practically thermoneutral (ΔE decreases by only 1,9 kcal, $A_{per} \simeq A_p$ for all telomeric radicals). The temperature dependence of the constants is determined by the value of C_n. If $C_n < 1$, then $K_{per} < K_p$ ($\Delta E > 0$) and, with increasing temperature, the transfer constants increase; if $C_n > 1$, then $K_{per} > K_p$ ($\Delta E < 0$) and the reverse dependence is observed for such constants; $A_{per}/A_p \simeq 1$ for all radicals studied.

The transfer constants for radicals with long chain length (C_∞) in the telomerization of ethylene with polyhalomethanes have been determined only approximately, and the data obtained are highly contradictory (0,7 and 3,2 at 70° ([2]); 0,02 at 20° ([10]) and 32 at 65° ([1]) for CCl_4; 0,8 at 70° ([2]) for $CHCl_3$). To calculate C_∞ we used the Mayo method ([5]), which makes it possible to calculate C_∞ from the average degree of polymerization n and the partial chain-transfer constants.

$$\frac{d[M]}{d[S]} - 1 = \frac{1 + \frac{[M]}{C_\infty[S]} + \left(\frac{C_3[S]}{[M]} + 1\right)\left(\frac{C_2[S]}{[M]} + 2\right)}{\left(\frac{C_1[S]}{[M]} + 1\right)\left(\frac{C_2[S]}{[M]} + 1\right)\left(\frac{C_3[S]}{[M]} + 1\right)} \tag{3}$$

according to the data of experiments with $\bar{n} = 3$-4 (Table 1).

For estimating the inductive influence of the CCl_3 group (with which, apparently, the observed change in C_n with increasing radical chain length is connected ([2,4])), we used the Alfrey-Price scheme ([7]). The chain-transfer constants can be expressed in the $Q - e$ scheme as follows ([9]):

Table 3

Telogen	T, deg. °C	$C_n; e_n$	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n \geq 5$
CCl_4	60	C^*	0.087	3.0	7.4	11.4	14.6
CCl_4	60	e	+0.87	−0.03	−0.26	−0.37	−0.4
CCl_4	80	C^*	0.119	3.0	6.49	9.5	12.33
CCl_4	80	e	+0.75	−0.07	−0.27	−0.36	−0.43
$CHCl_3$	60	C^*	0.226	1.56	2.61	3.27	4.37
$CHCl_3$	60	e	+0.97	+0.06	−0.19	−0.29	−0.43
$CHCl_3$	80	C	0.247	1.55	2.49	3.12	4.13
$CHCl_3$	80	e	+0.81	0.0	−0.21	−0.31	−0.43

$$C_\infty = (Q_{tel}/Q_M) \cdot e^{-e_M(e_{tel} - e_M)}, \tag{4}$$

where Q_{tel} and Q_M are proportional to the resonance abilities of the telogen and monomer, while e_{tel} and e_M characterize their polar properties. Hence, knowing e_{tel} and e_M, as well as the particular and overall chain-transfer constants, one can determine e_n for all trichloroalkyl radicals from equation ([9]):

$$C_n/C_\infty = e^{(e_M - e_n)(e_{tel} - e_M)}, \tag{5}$$

* C_n and C_∞ were calculated from our data in Table 2.

e_{M} for ethylene has recently been determined experimentally ([11]). The values of e_{tel} (and also Q_{tel} from formula (4)) were calculated by us from equation ([10]):

$$C^1_\infty / C^2_\infty = (Q_{\mathrm{M2}}/Q_{\mathrm{M1}}) \cdot e^{(e_1 - e_2)(e_1 + e_2 - e_{\mathrm{tel}})}, \tag{6}$$

where C^1_∞ and C^2_∞ are the overall transfer constants of any two monomers with CCl_4 or $CHCl_3$*.

The following $Q-e$ values were obtained: for CCl_4, $Q_{\mathrm{tel}} = 3.9 \cdot 10^{-4}$, $e_{\mathrm{tel}} = +3.50$ (at 60 and 80°); for chloroform, $Q_{\mathrm{tel}} = 2.2 \cdot 10^{-4}$, $e_{\mathrm{tel}} = -1.68$ (at 60°) or $+1.84$ (at 80°). The large positive value of e_{tel} for CCl_4 (maximal for polyhaloalkanes) shows that it possesses considerable electron-acceptor properties and should exhibit increased reactivity with electron-donor radicals. For chloroform the $Q-e$ parameters are lower; however, e_{tel} is noticeably greater than zero. Table 3 and Fig. 1 present values of e_n for radicals of different chain length n, calculated by equation (5).

As is evident from the data in Table 3, the values of e_n for telomeric radicals with n monomer units coincide (within the error of e (± 0.2) and of our experiment), independently of the temperature and the nature of the telogen.

Fig. 1. Dependence of the chain-transfer constants C_n and e_n on the radical chain length (80°). 1 –e_n; 2 –C_n for chloroform; 3 –C_n for carbon tetrachloride; *a* –chloroform; *b* –carbon tetrachloride.

* All references to the literature used for the overall constants will be published in the journal *Izvestiya AN SSSR*, Chemical Series.

The electron-donating ability of telomeric radicals ($e < 0$) gradually decreases as the trichloromethyl group approaches the radical center, and the trichloropropyl radical already becomes a strong electron acceptor (reversal of the sign of e), close in its properties to such monomers as acrylonitrile ($e = +1.2$) or vinylidene chloride ($e = +0.6$). Consequently, as the chain length n decreases from 5 to 1 and the electrophilic properties of the telomeric radicals increase, the rate constant of the chain-transfer reaction with such electrophilic compounds as $CHCl_3$ and especially CCl_4 should decrease. For the first transfer constants at all temperatures an interesting dependence is observed: C_1 for CCl_4 is several times smaller than C_1 for $CHCl_3$ (possibly, this is associated with the more positive value of e_{tel} for CCl_4 and, consequently, with a lower probability of interaction of two electrophilic particles). The influence of the trichloromethyl group is still large for the radical with $n = 2$ (transmission of the inductive effect through four methylene groups) and is noticeable for the radical with $n = 3$.

Table 4

Temp., °C	P_1*	P_2	P_3	P_4	$P_5 = P_\infty$
60	0.385	1.92	2.84	3.49	3.69
80	0.482	1.94	2.61	3.05	3.26

Temp., °C	P_1*	P_2	P_3	P_4	$P_5 = P_\infty$
100	0.537**	1.95	2.31	2.75	3.08
140	0.804	1.91	2.11	2.21	2.33

* P_n of radicals of different chain length n.
** 0.68 at 100° in work (4).

Since the kinetic chain in the telomerization of ethylene by the telogens studied is carried by radicals of the same structure: $CCl_3(CH_2CH_2)_{n-1}CH_2\dot{C}H_2$, the transfer constants ($C'_n = K'_{tr}/K_p$ for CCl_4 and $C_n = K_{tr}/K_p$ for $CHCl_3$) will be composed of the ratio of the rate constants of the corresponding transfer reactions to the same rate constant of the propagation reaction. Hence it is easy to derive a new ratio

$$P_n = C'_n/C_n = K'_{tr}/K_{tr} = (A'_{tr}/A_{tr}) \cdot e^{-\Delta E'/RT}$$

(where $\Delta E' = E'_{tr} - E_{tr}$), which contains only the chain-transfer constants (Table 4).

P_n increase noticeably (consequently, K'_{tr} and K_{tr} change) with increasing n from 1 to 4 monomer units. For the trichloropropyl radical K_{tr} is significantly smaller than K'_{tr}. With increasing temperature, the differences in the transfer rate constants with CCl_4 and $CHCl_3$ decrease. The temperature course of P_n makes it possible to estimate to some extent the contribution of the change in K_{tr} to the change in C_n (Table 2 gives $\Delta E'$ and A'_{tr}/A_{tr}, calculated from the data of Table 4). As is seen from Table 2, the change in $\Delta E'$ and A'_{tr}/A_{tr} is close to the change in ΔE and A'_{tr}/A_p in the telomerization of ethylene and CCl_4. If K'_{tr} and K_{tr} depended little or not at all on the radical chain length, as was assumed earlier (1, 4), then $\Delta E'$ and A'_{tr}/A_{tr} should have been practically constant. Thus, it may be considered that the increase in the transfer constants C_n with growth of the radical chain length n from 1 to 5 monomer units is to a considerable extent associated with a change in the rate constants of the chain-transfer reactions due to the decrease in the inductive effect of the trichloromethyl group.

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Note: Figure translations are in progress. See original paper for figures.