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STUDIES ON THE TELOMERIZATION OF ETHYLENE WITH
CARBON TETRACHLORIDE

I. Kinetics of the Telomerization Initiated by Azo-bis-isobutyronitrile

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The telomerization of ethylene with carbon tetrachloride initiated by AIBN (azo-bis-isobutyronitrile) has been investigated kinetically. Reactions were carried out continuously in a tubular coil reactor at temperatures between 85° and 100°C at constant pressure of 150 kg/cm².

It has been shown that the reaction rate of ethylene follows the rate equation: $-d[C_2H_4]/dt = k[C_2H_4][AIBN]^{\frac{1}{2}}$. Chain transfer constants of the telomer radicals to carbon tetrachloride were calculated as follows: $C_1=0.1$, $C_2=2.1$, $C_3=3.8$ and $C_4=5.2$.

Introduction

The telomerization of ethylene with carbon tetrachloride gives rise to a homologous series of tetrachloro-alkanes of general formula $Cl(CH_2CH_2)_nCCl_3$, where n is an integer which can be varied between wide limits by varying reaction conditions: the reaction under atmospheric pressure gives solely the 1:1 adduct $ClCH_2CH_2CCl_3$ ¹⁾ and telomers with higher molecular weights are obtained by reactions at higher pressures²⁾. Being a free radical chain reaction, the telomerization of ethylene with carbon tetrachloride is initiated by free radical sources like benzoyl-peroxide¹⁾²⁾³⁾, azo-bis-isobutyronitrile⁴⁾⁵⁾, di-tert-butylperoxide⁶⁾ and so on.

Several substances of industrial importance, such as polyamide, may be derived from the telomers, and a number of investigations on the synthesis of the tetrachloro-alkane telomers have been reported⁶⁾. The batchwise reactions in autoclaves under pressures below 100 atm have been studied most extensively, but a continuous flow reaction system of pilot-scale has been also reported by investigators of USSR⁶⁾. It has been found that phase behaviors of the reaction mixtures under conditions suitable for batchwise operations are very much complicated⁷⁾. Moreover, the telomerization is highly exothermic and is considered to be very dangerous for batch operations. In fact, explosions have been reported for batches of more than 100 m³. Consequently, detailed kinetic analysis of the

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telomerization has been very few, hitherto.

In the present paper, the telomerization of ethylene with carbon tetrachloride has been investigated kinetically. Reactions were carried out by means of a continuous flow reaction system with a tubular coil reactor. AIBN was used for the initiation. All the experiments were carried out at a pressure of 150 kg/cm^2 to avoid complications due to the change in phase state; it is assured that the reaction mixture is in homogeneous solution states at the pressure⁶⁾.

Experimentals

Substances

Ethylene was of "polyethylene grade" (with purity over 99.9% and contained oxygen below 1ppm), supplied by Nippon Petrochemicals Co., Ltd. (Kawasaki Factory). Carbon tetrachloride and AIBN were of commercial C.P. grade, which were used without further purifications. The effects of the purifications on the reaction were checked in the preliminary batch experiments. Redistilled carbon tetrachloride and twice recrystallized AIBN from benzene were compared with the reagents without purifications, respectively. However differences were not detected.

Equipment and operation procedures

A schematic diagram of the equipment for continuous flow reactions is shown in Fig. 1. The figure is made to illustrate the work principles of the system, so that, several accessory parts such as stop-valves, check-valves, by-path flow lines and systems for temperature controls and for measurements are omitted.

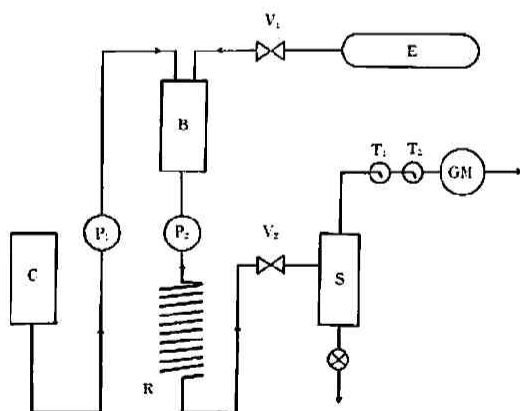


Fig. 1 The schematic lay-out of the apparatus for continuous flow reactions

The feed mixture was prepared in a 2 l high pressure vessel B, which served both as the premixer and as the reservoir of the feed. It was made of stainless-steel (SUS-27) and was fitted with a magnetic stirrer and a level gauge. The temperature in the premixer was controlled by the circulation of thermostatted water through an external jacket around the vessel. Ethylene from a commercial 50 l bomb E was introduced into the premixer through a control-valve V_1 , by which the pressure of the premixer was regulated. Carbon tetrachloride in which a given amounts of AIBN was previously

dissolved, was fed to the premixer continuously, at a controlled rate by means of a plunger pump P_1 .

The feed mixture in the premixer was injected into a reactor R at a controlled feed rate by another plunger pump P_2 . The reactor was of tubular coil type, fabricated with stainless-steel tubing (SUS-32) of 5 mm inner diameter and 10 mm outer diameter. The reactor coil was immersed in a thermostatted oil-bath. The heated volume of the reactor space was about 240 ml. The reactor was made so as to withstand operations at pressures up to 350 kg/cm².

The reaction pressures were controlled by an automatic-valve V_2 at the discharge end of the reactor, from which the reaction mixture was throttled into a ethylene separator S. The separator was a glass cylinder of about 1 l capacity. The separator pressure was maintained slightly higher than atmospheric pressure and the temperature was maintained between -10° and -25°C to reduce the amount of carbon tetrachloride in separated ethylene gas.

At usual experimental conditions, the temperatures of the separator were kept at the favorable point without external cooling by the expansion of separated ethylene from reaction mixture.

Ethylene gas from the separator was passed through two dry-ice methanol traps T_1 and T_2 , measured by a gas meter GM and released. The liquid part condensed at the bottom of the separator was taken out intermittently from the valve at the bottom and submitted to analysis.

Measurements and analysis

The feed rate of ethylene was measured by weighing the bomb E. The feed rate of carbon tetrachloride was measured volumetrically at the vessel C. The mole feed ratio of ethylene to carbon tetrachloride was also checked by sampling the feed mixture in the premixer. The volumetric feed rate of the mixture to the reactor was measured by means of the level gauge. (Feeds of the ingredients were stopped during the measurement.)

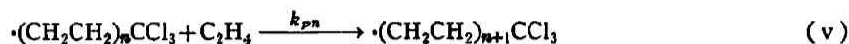
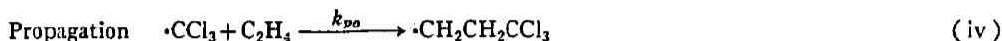
The hold up time in the reactor was calculated from the reactor volume divided by the volumetric feed rate of the pump P_2 .

The mixture from the bottom of the separator was submitted to a series of fractional distillations using a column with about 50 theoretical stages, divided into six parts and weighed respectively: CCl_4 which distills at $77^\circ\text{C}/760\text{mmHg}$, $\text{ClCH}_2\text{CH}_2\text{CCl}_3$ at $54^\circ\text{C}/20\text{mmHg}$, $\text{Cl}(\text{CH}_2\text{CH}_2)_2\text{CCl}_3$ at $69\sim71^\circ\text{C}/2\text{mmHg}$, $\text{Cl}(\text{CH}_2\text{CH}_2)_3\text{CCl}_3$ at $91\sim93^\circ\text{C}/2\text{mmHg}$, $\text{Cl}(\text{CH}_2\text{CH}_2)_4\text{CCl}_3$ at $110\sim119^\circ\text{C}/2\text{mmHg}$ and the distillation residue which remained as non-volatile at $120^\circ\text{C}/2\text{mmHg}$ ⁹. The residue is a mixture of higher telomers and non-volatile by-products.

Constituents in the reaction mixture was also analyzed by gas chromatography; for the purpose Hitachi EPU-2A Gas-chromatograph with 1m polyethylene succinate column was operated at 150°C using helium carrier. The compositions were determined by the peak-area-method. The results of distillation and gas-chromatography agreed each other within experimental errors (within 5%).

Results and Discussions

The kinetic scheme of the telomerization of ethylene with carbon tetrachloride initiated by AIBN has been assumed⁹ as follows:



where $\text{X}\cdot$ is dimethylcyano radical from the decomposition of AIBN, and $\text{R}\cdot$ represents whole radical species.

Steps (iii) and (iv) are represented in a single chemical equation using $\text{R}\cdot$ as



where k_p is the average value of k_{pn} .

The rate of ethylene consumption (addition) r_p is expressed from (viii) as

$$r_p = -d[\text{C}_2\text{H}_4]/dt = k_p[\text{C}_2\text{H}_4][\text{R}\cdot] \quad (1)$$

The stationary state of $\text{R}\cdot$ is expressed from (1) and (2) as

$$[\text{R}\cdot] = (k_i/k_r)^{1/2} [\text{AIBN}]^{1/2} \quad (2)$$

From (1) and (2), we obtain the rate equation of ethylene addition:

$$r_p = -d \ln [\text{C}_2\text{H}_4]/dt = k' [\text{AIBN}]^{1/2} \quad (3)$$

where

$$k' = k_p(k_i f/k_r)^{1/2}$$

Thus, the rate of ethylene addition should be first order with respect to ethylene concentration and proportional to the square root of the initiator concentration.

In an isothermal condition, the rate equation (3) is rewritten as

$$-d \ln [\text{C}_2\text{H}_4]/dt = k' [\text{AIBN}]_0^{1/2} \exp[-k_i t/2] \quad (4)$$

hence, the first order decomposition of AIBN is expressed as

$$[\text{AIBN}] = [\text{AIBN}]_0 \exp[-k_i t],$$

and the integration of equation (4) gives

$$-\ln [\text{C}_2\text{H}_4]/[\text{C}_2\text{H}_4]_0 = k' [\text{AIBN}]_0^{1/2} (1 - \exp[-k_i t/2]) \quad (5)$$

$$k'' = 2k'/k_i = 2k_p(f/k_i k_r)^{1/2}$$

where $[\text{C}_2\text{H}_4]_0$ and $[\text{AIBN}]_0$ are the initial concentrations of ethylene and AIBN, respectively.

The limiting ethylene conversion x at sufficiently long reaction time is determined by the relation:

$$-\ln[C_2H_4]/[C_2H_4]_0 = -\ln(1-x) = k''[AIBN]_0^{\frac{1}{2}} \quad (6)$$

On the other hand, the molar compositions of the telomer-products can be also expressed from the reaction scheme. Considering the stationary state of the growing radical $\cdot(CH_2CH_2)_nCCl_3$, and neglecting products by radical recombination steps (vii),

$$v_n = -d[Cl(CH_2CH_2)_nCCl_3]/dt = k_{tn}[\cdot(CH_2CH_2)_nCCl_3][CCl_4] \quad (6)$$

and
$$\sum_{i=n+1}^{\infty} v_i = -\sum_{i=n+1}^{\infty} d[Cl(CH_2CH_2)_iCCl_3]/dt = k_{pn}[\cdot(CH_2CH_2)_nCCl_3][C_2H_4], \quad (7)$$

hence,

$$v_n / \sum_{i=n+1}^{\infty} v_i = k_{tn}[CCl_4] / k_{pn}[C_2H_4]. \quad (8)$$

If the mole ratio of ethylene to carbon tetrachloride is not changed during the course of the reaction, we may write

$$T_n / \sum_{i=n+1}^{\infty} T_i = C_n / N, \quad (9)$$

where T_n is the mole fraction of the telomer $Cl(CH_2CH_2)_nCCl_3$, $N = [C_2H_4]/[CCl_4]$ the mole ratio of ethylene to carbon tetrachloride, and $C_n = k_{tn}/k_{pn}$ the chain transfer constant of radical $\cdot(CH_2CH_2)_nCCl_3$ to carbon tetrachloride⁸⁾.

Thus, the parameters C_n can be calculated from the measurement of the telomer compositions obtained at a known mole ratio.

The values of C_n may be also obtained graphically. Equation (9) can be transformed into

$$T_n / T_{n+1} = (N + C_{n+1}) / C_n, \quad (10)$$

so that the parameter C_n can be obtained from a plot of T_n / T_{n+1} versus N , as the reverse of its slope, and C_{n+1} as the intersection of ordinate divided by C_n .

Provided the values N , C_1 , C_2 , $C_3 \dots$ are known, the composition of products can be predicted by

$$\left. \begin{aligned} T_1 &= C_1 / (N + C_1) \\ T_2 &= C_2 N / (N + C_1)(N + C_2) \\ &\dots\dots\dots \\ T_n &= C_n N^{n-1} / \prod_{i=1}^n (N + C_i) \end{aligned} \right\} \quad (11)$$

Effect of AIBN concentration

The effect of AIBN concentration in the feed mixture (mole ratio to carbon tetrachloride) was examined at a condition of 95°C, 1.7 mole ratio of ethylene to carbon tetrachloride, and of 12.5 minutes apparent retention time. The result is shown in Fig. 2. The ethylene conversion increases with an increase in AIBN concentration, but the efficiency of the initiator (ethylene consumed/initiator consumed) diminished with increasing AIBN concentration. As are shown in Fig. 3, the value of

8) C. Walling, "Free Radicals in Solution", p. 257, J. Wiley (1957)

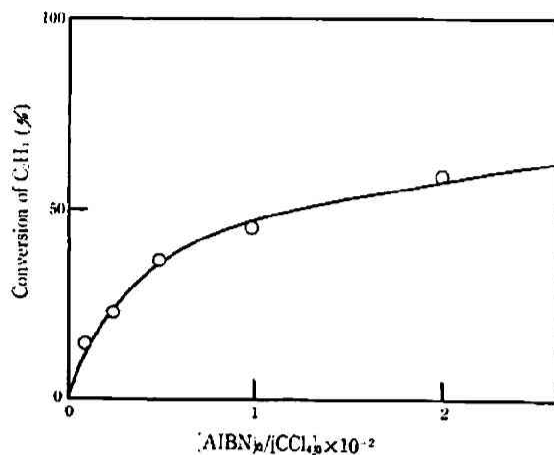


Fig. 2 Effect of the initiator concentration

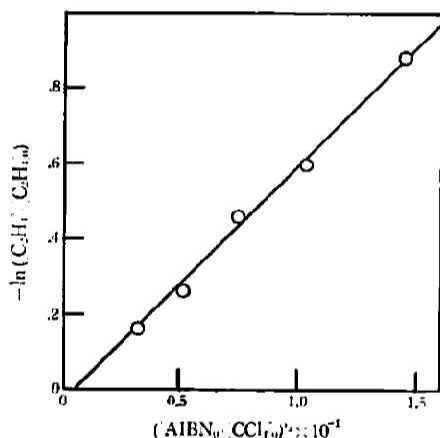


Fig. 3 The relation between square root of AIBN concentration and logarithm of ethylene retention (same data with Fig. 2)

$-\ln([C_2H_4]/[C_2H_4]_0)$ is nearly proportional to the square root of the initial AIBN concentration, so that equation (6) agree well with the experimental results.

Effect of reaction temperature and reaction time

Fig. 4 shows the time courses of the ethylene consumption at several temperatures. At each temperature there appears an apparent induction time of about 5 minutes, probably showing the warming-up time. After the induction, the reaction rate is larger at the earlier stage and decreases with the reaction time as the reactants and the initiator are consumed. The rate of the reaction is initially larger at a higher temperature. However, the higher the temperature, the more rapidly the initiator is consumed, and the reaction ceases within the shorter period, so that there appears a maximum of ethylene conversion at certain temperatures in a definite reaction time.

These effects can be explained quantitatively from the reaction mechanism by equations (4), (5) and (6). In fact, each line in the figure was obtained from the parameters k_t , k'' and t , by equation (5). The reaction time t was assumed as the retention time minus the warming-up time. k_t for the

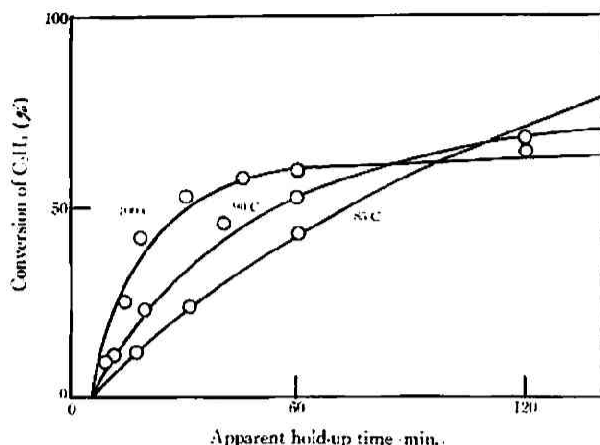


Fig. 4 Effect of reaction temperature on the time course of the telomerization

decomposition of AIBN was those reported by Talât et al.⁹⁾, and the composite parameter k'' was estimated by way of trial and error so as to accord the experimental results. The parameters k' and k'' estimated are shown in Table 1. The Arrhenius' parameters defined as $E' = RT^2 d \ln k' / dT$ and $E'' = RT^2 d \ln k'' / dT$ are calculated to be 21 kcal/mole and -11 kcal/mole respectively.

Table 1 Parameters k' and k''

$T, ^\circ\text{C}$	$k_t \times 10^4 \text{ sec.}^*$	$k' \times 10^4 (M/l)^{\frac{1}{2}} \text{ sec.}^{**}$	$k'' \times (M/l)^{\frac{1}{2}}$
85	1.9	5.5	5.8
90	3.9	7.4	3.8
100	15.4	24	3.1

* calculated by the equation $k_t (\text{sec.}^{-1}) = 2.67 \times 10^{15} \exp(-31.1 \text{ kcal}/RT)$, presented by Talât-Erben and Bywater

** calculated from k_t and k'' by the relation: $k' = k_t k'' / 2$

From the definitions of k' and k''

$$E' = E_p + \frac{1}{2}E_t - \frac{1}{2}E_r + \frac{1}{2}E_f \quad (12)$$

and

$$E'' = E_p - \frac{1}{2}E_t - \frac{1}{2}E_r + \frac{1}{2}E_f \quad (13)$$

where $E_p = RT^2 d \ln k_p / dT$, $E_t = RT^2 d \ln k_t / dT$, $E_r = RT^2 d \ln k_r / dT$ and $E_f = RT^2 d \ln f / dT$; the activation energies of ethylene addition, of AIBN decomposition, of radical recombination and of the factor f , respectively. Therefore, $E_p - E_r / 2 + E_f / 2$ is calculated to be about 6 kcal/mole. Since E_r and E_f are assumed to be small compared with E_p , the value of 6 kcal/mole may be substantially of E_p . In fact, this value is coincident with radical polymerizations of olefines¹⁰⁾.

9) M. Talât-Erben and S. Bywater, *J. Am. Chem. Soc.*, **77**, 3710 (1955)

10) M. G. Evans, *Disc. Faraday Soc.*, **2**, 271 (1947); E. W. R. Steacie, *ibid.*, **2**, 80 (1947)

Effect of mole feed ratio

As are inferred already, the mole feed ratio of ethylene to carbon tetrachloride affects greatly the composition of the telomer products. As are shown in Fig. 5, an increase in the mole ratio increases

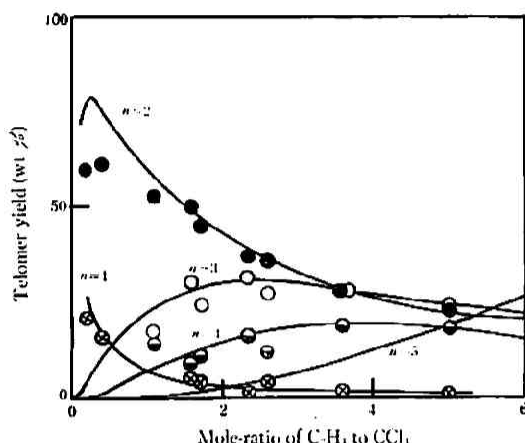


Fig. 5 Influence of mole ratio of ethylene to carbon tetrachloride on the telomer compositions

higher telomer products. The 1:1 adduct decreases sharply with the increasing mole ratio, and the yield of ethylene dimer may take a maximum value at $N < 0.5$, decreases gradually with further increase in N . There are a maximum of the yield of the trimer at about $N=3$, and that of the tetramer at about $N=4$. The fraction of the higher telomer increases with an increase in N .

The chain transfer constants C_1 , C_2 , C_3 and C_4 are calculated from the above results from equations (9) and (10). In each calculation by equation (9) the distillation residue was assumed as the telomer with one additional ethylene unit than the final distillates. The C_n values were also calculated graphically by equation (10), both from the slopes and from the intersections. The values obtained are as listed in Table 2. The unusual small value of C_1 may probably be due to the stabilization of the trichloro-propyl radical by the near-by trichloro-methyl group.

Table 2 Chain transfer constants

N	Telomer Composition, wt %					Chain Transfer Constant $C_n = \frac{k_{tn}}{k_{tm}}$			
	$n=1$	2	3	4	>5	$n=1$	2	3	4
1.22	2.2	58.0	26.8	6.0	6.5	0.062	2.14	3.07	—
1.58	5.3	50.2	29.8	7.7	8.4	0.109	2.09	3.34	—
2.34	1.5	35.7	32.5	15.8	15.2	0.067	2.23	4.07	3.8
2.6	4.1	36.3	27.0	11.7	9.3	0.16	2.36	3.94	5.05
3.55	1.6	27.7	28.0	18.8	10.8	0.088	2.10	3.95	7.0
5.0	1.7	23.9	24.3	18.1	18.9	0.133	2.43	3.85	5.4
mean.						0.099	2.08	3.77	5.23
Graphically (From slope)						—	2.1	3.8	—
Graphically (From intersection)						—	—	3.8	—

Examples with lower ethylene conversion than 20% were selected here.

Reactions were carried out at temperatures between 92° and 98°C.

The transfer constants obtained here are similar to those of Karapetyan et al.¹¹⁾, Freidlina et al.¹²⁾, David et al.¹³⁾, and of Mayo⁹⁾.

The effect of the mole feed ratio shown in Fig. 5 is well explained by the C_n values obtained above; each line in the figure is a calculated one using the mean C_n values.

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12) B. A. Englin and R. Kh. Freidlina, *Doklady Akad. Nauk. S.S.S.R.*, **158**, 922 (1964)

13) C. David and P. A. Gossain, *Tetrahedron*, **18**, 639 (1962)