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Telomerization of Ethylene with Chloroform Initiated by *N*-Chloroalkylamines

Teruzo Asahara, Manabu Senō, and Noritaka Ohtani
Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106

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N-Chloroalkylamines initiate the telomerization of ethylene with chloroform to give α,α,α-trichloroalkanes $CCl_3(C_2H_4)_nH$(I), which are the same products as those obtained by peroxide-initiated reactions. The *N*-chloroalkylamine-iron and *N*-chloroalkylamine–ferrous chloride systems also initiate the reaction of ethylene with chloroform to afford α,α,ω-trichloroalkanes $CHCl_2(C_2H_4)_nCl$ (II) as the main product, and a small amount of I along with other telomers. The rate of the reaction and the composition of the products vary widely with the kind of *N*-chloroalkylamine. The reaction mechanism was discussed, a "caged radical" mechanism being proposed for the *N*-chloroalkylamine–ferrous chloride system.

A number of reports have appeared on the radical telomerization of olefins with polyhaloalkanes. Various initiators have been examined in these reactions. Some redox systems such as copper chloride–amine[1] or iron chloride–triethyl phosphite[2] gave the 1 : 1 adduct as the main product. It was found that *N*-chloroalkylamine and *N*-chloroalkylamine–metallic salt also initiate the reactions of ethylene with carbon tetrachloride to afford the 1 : 1 adduct and telomers with low molecular weights. A coordinated radical or a caged radical reaction process was suggested in addition to the free radical reaction process.[3]

A "free" radical is considered to abstract the hydrogen atom of chloroform.[4] The reactions of ethylene with chloroform initiated by peroxides give α,α,α-trichloroalkanes instead of α,α,ω-trichloroalkanes. The results prompted us to examine the reaction of ethylene with chloroform using *N*-chloroalkylamines as initiators in order to clarify the reaction mechanism.

Experimental

Materials. Ethylene (purity 99.8%) was used without further purification. Commercial chloroform was purified through an activated alumina column, the purity being examined by gas chromatography. *N*-Chloroalkylamines were prepared and purified as described previously.[3]

Reactions of Ethylene with Chloroform. The reaction was carried out in a 200 ml stainless steel autoclave with a magnetic stirrer. Chloroform and initiators were placed in the autoclave and air was replaced several times by ethylene. After ethylene was charged to a definite pressure, the autoclave was heated up to a prescribed temperature. After the reaction, the autoclave was cooled to room temperature and the reaction mixture was washed by an aqueous potassium iodide solution and then an aqueous sodium thiosulfate solution.

Analyses of the Products. The reaction products were analysed by a temperature programmed gas chromatograph using a 2 m column of Silicone DC 550 at 40—200 °C. *n*-Hexane was used as an internal standard. The authentic samples were prepared by the following methods. α,α,α-Trichloroalkanes, $CCl_3(C_2H_4)_nH$ (I) ($n=1,2,3$), α,α,ω-trichloroalkanes, $CHCl_2(C_2H_4)_nCl$ (II) ($n=1,2$) and α,α,α,ω-tetrachloroalkanes, $CCl_3(C_2H_4)_nCl$ (IV) ($n=1,2$) were prepared by the telomerization of ethylene with chloroform initiated by di-*t*-butylperoxide (DTBP), by that of ethylene with chloroform initiated by the iron chloride-hexamethylphosphoric triamide (HMPA) system[5] and by that of ethylene with carbon tetrachloride initiated by DTBP, respectively. The products were fractionally distilled several times and the purity was confirmed by glc. α.α-Dichloroalkanes, $CHCl_2(C_2H_4)_nH$ (III) ($n=1,2$) and γ,γ-dichloroalkanes, $HC_2H_4CCl_2(C_2H_4)_nH$ (VII) ($n=1,2$) were prepared by the reaction of the corresponding aldehydes or ketones with phosphorus pentachloride and purified by distillation. For quantitative analyses of α,γ,γ-trichloroalkanes $ClC_2H_4CCl_2(C_2H_4)_nH$ (V) ($n=1,2$) and α,γ,γ,ω-tetrachloroalkanes $ClC_2H_4CCl_2(C_2H_4)_nCl$ (VI) ($n=1$), type I and IV telomers with the same molecular weight as that of V and VI, respectively, were used.

Results and Discussion

The reaction products can be classified according to their structures into the following seven telomers; $CCl_3(C_2H_4)_nH$ (I), $CHCl_2(C_2H_4)_nCl$ (II), $CHCl_2(C_2H_4)_nH$ (III), $CCl_3(C_2H_4)_nCl$ (IV), $ClC_2H_4CCl_2(C_2H_4)_nH$ (V), $ClC_2H_4CCl_2(C_2H_4)_nCl$ (VI), and $H(C_2H_4)_mCCl_2(C_2H_4)_nH$ (VII). Telomers I and IV, having a trichloromethyl group, can act again as a telogen, giving telomers V, VI, and VII.

In the telomerization of ethylene with chloroform, *N*-chloroalkylamines possibly play three roles:

(i) *N*-chloroalkylamines act as initiators, *viz.*, they decompose thermally[6] or under the action of metal[7] to yield amino radicals:

$$\mathrm{RNXCl} \xrightarrow{\Delta} \mathrm{R\dot{N}X} + \mathrm{Cl}\cdot \qquad (1)$$

$$2\mathrm{RNXCl} + \mathrm{Fe} \longrightarrow 2\mathrm{R\dot{N}X} + \mathrm{FeCl_2} \qquad (2)$$

$$\mathrm{X=H,\ Cl,\ or\ alkyl;\ R=alkyl}$$

(ii) *N*-chloroalkylamines have a large chain transfer constant and can act as chain transfer reagents.

$$\mathrm{R}\cdot + \mathrm{RNXCl} \longrightarrow \mathrm{RCl} + \mathrm{R\dot{N}X} \qquad (3)$$

(iii) Though the basicity of *N*-chloroalkylamines is not so large as that of amines, they can coordinate metal ions at nitrogen and/or chlorine atoms and affect the reactivity of metal ions with chloroform.

$$\mathrm{Fe^{2+}} + k\mathrm{RNXCl} \rightleftharpoons \mathrm{Fe(RNXCl)}_k{}^{2+} \qquad (4)$$

Iron–*N*-chloroalkylamine complex is likely a mixture of complexes with a different value of k, the value of k increasing with the concentration of *N*-chloroalkylamine.

In the absence of metal or metallic salt, the main products were telomers I (Table I), irrespective of the kind of *N*-chloroalkylamines. This suggests that *N*-chloroamine yields the free radical which initiates the reaction. The initiating radical is probably amino radical in Eq. 1 and/or aminium radical in the following reaction.[3]

$$\mathrm{RNXCl} \longrightarrow \mathrm{R'CH{=}NX} + \mathrm{HCl} \qquad (5)$$

$$\mathrm{RNXCl} + \mathrm{HCl} \longrightarrow \mathrm{R\overset{+}{N}HXCl\ Cl^-} \longrightarrow \mathrm{R\overset{+\cdot}{N}HX\ Cl^-} + \mathrm{Cl\cdot} \qquad (6)$$

The order of reactivity of *N*-chloroalkylamines is the same as that in the reaction with carbon tetrachloride;[3] *N*-chlorodibutylamine (CDBA) > *N*-chloromonobutylamine (CMBA) > *N,N*-dichlorobutylamine (DCBA). Among the products, a small amount of IV and a smaller amount of III were found. It is likely that α,α,α-trichloroalkyl radical abstracts chlorine atom not from chloroform but from *N*-chloroamine (Eq. 3), since the amount of IV is larger than that of III. The products of the reactions initiated by DTBP under the same conditions contain scarcely any IV and only 1% of III. Two explanations can be given for the formation of III. The amino radical abstracts chlorine atom from chloroform at 130 °C; *N*-chloroamine dissolves iron out of the surface of the autoclave and the stainless steel stirrer, especially in the case of DCBA leading to the formation of metallic salts which take part in the reaction.

In the presence of ferrous chloride (Table 1), the yield and composition of the products varied widely depending on the amount of ferrous chloride and the kind of *N*-chloroalkylamine. Addition of ferrous chloride to CDBA lowered the yield of telomers when the relative concentration of $\mathrm{FeCl_2}$ to CDBA was below 25%. Above 25%, however, the reactivity of this initiating system increases remarkably. A similar tendency was observed in the case of DCBA. This indicates that the decomposition of *N*-chloroalkylamines into free radicals (Eqs. 1 and 6) is suppressed by the addition of ferrous chloride and that another radical formation process exists. The suppression of free radical formation can be attributed to the consumption of the *N*-chloroamine to form the iron–*N*-chloroalkylamine complex (Eq. 4). The formation of the complex is confirmed by the following investigation. An equimolar mixture of CDBA and ferrous chloride in methanol has a new broad absorption band at 320 nm at room temperature. This band is different from that of CDBA (275 nm) and ferric chloride (360 nm) and resembles that of ferrous chloride–dibutylamine complex (about 315 nm). The intensity of absorption increases with an increase in the relative concentration of CDBA and decreases gradually with an increase in the absorption of ferric chloride. The complex reacts probably with chloroform to generate dichloromethyl radicals like the copper chloride–amine complexes.[1] If the dichloromethyl radicals thus formed are free radicals, the reaction products would not be II but I, as revealed in the system of ferrous chloride alone. Thus we might suppose that *N*-chloroalkylamine coordinates iron ion to form a cage around the ion and the dichloromethyl radical formed is trapped within the cage (Eq. 7). When dichloromethyl radicals leave the cage, they react with ethylene and then chloroform to yield III and free trichloromethyl radicals (Eq. 10), which afford I by a chain reaction (Eqs. 12 and 13). When dichloromethyl radicals react with ethylene in the cage, the chain transfer reaction with ferric chloride immediately occurs to afford $n=1$ telomers of II (Eq. 8).

$$\underset{\mathrm{X_0}}{\mathrm{Fe(RNXCl)}_k{}^{2+}} + \mathrm{CHCl_3} \rightleftharpoons \underset{\mathrm{X}}{[\mathrm{Fe(RNXCl)}_k\mathrm{Cl}^{2+}\cdot\mathrm{CHCl_2}]_{\mathrm{cage}}} \qquad (7)$$

Table 1. Telomerization of ethylene with chloroform using ferrous chloride–*N*-chloroalkylamine system[a]

Chloroamine $\times 10^{-2}$ mol		$\mathrm{FeCl_2\cdot 4H_2O}$ $\times 10^{-2}$ mol	Time min	ΔP of Ethylene kg/cm^2	Conv. of Chloroform %	Yield of Telomer g	Product mol%[b] I	II	III	IV	V	VI	VII
—		2.0	180	17	12	20	97	—	2	tr	—	—	1
$(n\text{-Bu})_2\mathrm{NCl}$	1.0	—	90	12	9	15	84	—	5	10	—	—	1
	2.0	0.5		1	1	2	8	59	15	18	—	—	—
		1.0		22	18	27	2	74	11	3	3	7	—
		1.5		25	18	27	5	60	16	5	6	8	tr
		2.0		22	16	24	4	61	16	5	5	9	tr
$n\text{-BuNHCl}$	1.0	—	120	12	6	10	74	1	9	14	—	—	2
	2.0	0.5	150	6	4	8	64	9	12	15	—	—	—
		1.0		6	5	10	37	19	19	20	5	—	—
		1.5		5	5	8	40	18	20	19	3	—	—
		2.0		1	1	2	38	20	22	18	—	—	2
$n\text{-BuNCl}_2$	1.0	—	120	1	3	4	34	19	18	26	3	—	—
		0.25		tr	2	3	31	23	21	25	tr	—	—
		0.5		2	3	4	45	13	19	22	1	—	1
		1.0		5	6	9	53	10	15	17	2	—	2
		2.0		6	6	9	65	9	10	12	1	—	1

a) Telomerization conditions: initial ethylene pressure, 20 Kg/cm^2 at 30 °C; chloroform, 1 mol; reaction temperature, 130 °C. b) The telomers except for those contained in Experimental were ignored since their amounts were very small in all runs.

$$[X+C_2H_4]_{cage} \longrightarrow X_0 + CHCl_2C_2H_4Cl \qquad (8)$$

$$X \longrightarrow \underset{X_1}{Fe(RNXCl)_kCl^{2+}} + \cdot CHCl_2 \qquad (9)$$

$$\cdot CHCl_2 \xrightarrow[CHCl_3]{nC_2H_4} III + \cdot CCl_3 \qquad (10)$$

$$\cdot CCl_3 \xrightarrow[CHCl_3]{nC_2H_4} I + \cdot CCl_3 \qquad (11)$$

$$CCl_3(C_2H_4)_n\cdot + X_1 \longrightarrow IV + X_0 \qquad (12)$$

$$CCl_3(C_2H_4)_n\cdot + RNXCl \longrightarrow IV + R\dot{N}X \qquad (13)$$

Figure 1 shows the telomer distribution of I and II. Although a considerable amount of $n \geq 2$ telomers was formed for type I, the $n=1$ telomer was selectively formed for type II. This indicates that the formation of II proceeds by a different mechanism from the free radical mechanism (Eqs. 14—16) and supports the above consideration.[8] The kind of *N*-chloroalkylamines would have some effect on the activation of ferrous ion in Eq. 7, on the stability of the cage (Eqs. 8 and 9), and on the reactivity of X_1 in Eq. 12.

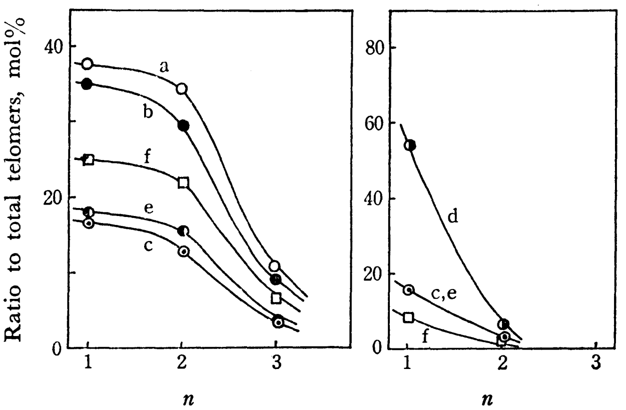
$$FeL_k^{2+} + CHCl_3 \longrightarrow FeL_kCl^{2+} + \cdot CHCl_2 \qquad (14)$$

$$\cdot CHCl_2 + nC_2H_4 \longrightarrow CHCl_2(C_2H_4)_n\cdot \qquad (15)$$

$$CHCl_2(C_2H_4)_n\cdot + FeL_kCl^{2+} \longrightarrow CHCl_2(C_2H_4)_nCl + FeL_k^{2+} \qquad (16)$$

L = ligand

Figures 2 and 3 show the dependence of the telomer composition on the concentration of CDBA, when the molar ratio of $[CDBA]/[FeCl_2 \cdot 4H_2O]$ is 1 and 2, respectively. In both cases, the telomer composition hardly changes at low concentrations but the ratio of II becomes high at high concentrations. The increase of II at higher concentrations seems to be due to the low solubility of the ferrous chloride–CDBA complex in chloroform. The reaction of Eq. 8 becomes dominant over the reaction of Eq. 9, since it appears on the solid complex.



I. $CCl_3(C_2H_4)_nH$ II. $CHCl_2(C_2H_4)_nCl$

Fig. 1. Molecular weight distribution of homologous telomers.
a; $(n\text{-}Bu)_2NCl$; b; $n\text{-}BuNHCl$; c; $n\text{-}BuNCl_2$; d; $(n\text{-}Bu)_2NCl/FeCl_2 \cdot 4H_2O$; e; $n\text{-}BuNHCl/FeCl_2 \cdot 4H_2O$; f; $n\text{-}BuNCl_2/FeCl_2 \cdot 4H_2O$.

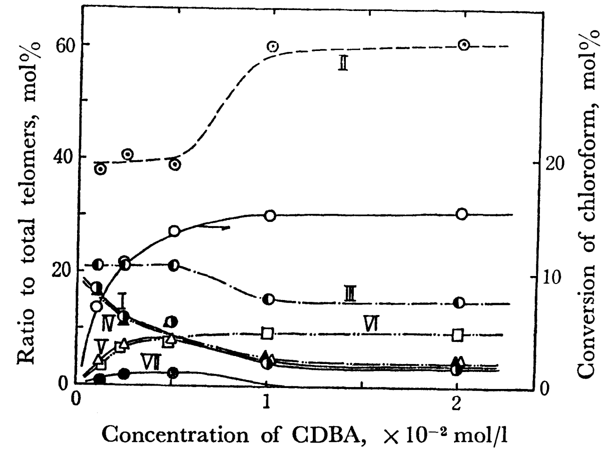


Fig. 2. Effect of the concentration of CDBA–$FeCl_2$ complex.
$[CDBA]_0/[EeCl_2 \cdot 4H_2O]_0 = 1$; Chloroform, 1 mol; Reaction temperature, 130 °C; Reaction time, 90 min.

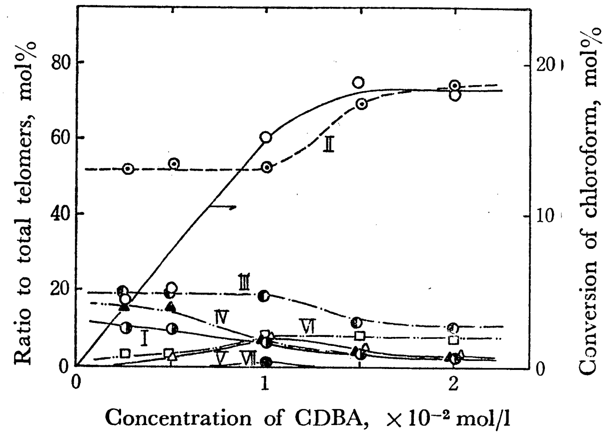


Fig. 3. Effect of the concentration of CDBA–$FeCl_2$ complex.
$[CDBA]_0/[FeCl_2 \cdot 4H_2O]_0 = 2$; Chloroform, 1 mol; Reaction temperature, 130 °C; Reaction time, 90 min.

The results of telomerization using the *N*-chloroalkylamine–iron system are given in Table 2. As the amounts of iron increase, the rate of telomerization reaction and the product ratio of II increase, irrespective of *N*-chloroalkylamines used. In these systems, it is expected that the reaction of *N*-chloroamine with iron takes place first (Eq. 2). The amino radical then initiates the telomerization according to Eqs. 17 and 11. The ferrous chloride produced by Eq. 2 forms the complex (X_0) with *N*-chloroamine and also induces the telomerization (Eqs. 7—13). In the case of CDBA, the ratio of II

$$R\dot{N}X \xrightarrow[CHCl_3]{nC_2H_4} RNX(C_2H_4)_nH + \cdot CCl_3 \qquad (17)$$

was not so large as that in the binary system of CDBA and ferrous chloride. This suggests that the free radical processes are not so feasible and supports the above explanation. However, in the cases of CMBA and CDBA, the ratio of II was larger than that in the binary system of *N*-chloroamine and ferrous chloride. The results can not be explained on the assumption that amino radicals abstract chlorine atom from chloroform. Since these reaction systems are heterogeneous,

Table 2. Telomerization of ethylene with chloroform using iron-N-chloroalkylamine system[a)]

Chloroamine $\times 10^{-2}$ mol	Fe $\times 10^{-2}$ mol	Time min	ΔP of Ethylene kg/cm^2	Conv. of Chloroform %	Yield of Telomer g	Product mol%[b)]						
						I	II	III	IV	V	VI	VII
	2.0	120	7	5	8	98	—	2	—	—	—	—
(n-Bu)$_2$NCl 1.0	—	90	12	9	15	84	—	5	10	—	—	1
	0.25		13	11	18	72	3	7	13	3	—	3
	0.5		17	11	17	47	15	10	13	8	2	5
	1.0		27	21	34	24	35	11	8	12	7	3
	1.5		24	18	29	23	39	12	7	12	6	1
	2.0		25	20	32	23	40	12	6	11	7	1
n-BuNHCl 1.0	—	120	12	6	10	75	1	9	13	—	—	2
	0.25		13	9	15	57	8	11	14	5	—	5
	0.5		11	7	11	46	13	15	15	6	—	5
	1.0		10	9	14	23	32	18	13	7	4	3
	1.5		16	9	13	17	38	18	12	7	5	3
	2.0		12	10	14	16	39	17	12	7	6	3
n-BuNCl$_2$ 1.0	—	120	1	3	4	34	19	18	26	3	—	—
	0.25		4	5	9	20	34	19	20	3	3	tr
	0.5		8	9	14	9	48	18	13	5	6	1
	0.75		11	12	18	7	51	17	11	5	8	tr
	1.0		13	13	21	6	54	17	10	5	8	tr
	1.5		14	14	22	5	56	16	9	5	9	tr
	2.0		11	12	19	6	55	16	10	4	8	tr

a) Telomerization conditions: initial ethylene pressure, 20 kg/cm^2 at 30 °C; chloroform, 1 mol; reaction temperature, 130 °C. b) The telomers except for those contained in Experimental were ignored since their amounts were very small in all runs.

we can presume that the reaction proceeds mainly on the surface of solid complexes or the iron particles making the chlorine abstraction by generated radicals easier. The surface of iron particles activated by N-chloroamines reacts presumably with chloroform to generate dichloromethyl radicals.[9)]

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References

1) D. J. Burton and L. J. Kehoe, *J. Org. Chem.*, **35**, 1339 (1970); T. Asahara, M. Senō, and C. C. Wu, This Bulletin, **43**, 1127 (1970); T. Asahara, M. Seno, and C. C. Wu, *Kogyo Kagaku Zasshi*, **72**, 1822 (1969).

2) T. Asahara and T. Sato, *ibid.*, **74**, 703 (1971): T. Asahara, A. Kurita, and T. Sato, *ibid.*, **74**, 1847 (1971).

3) T. Asahara, M. Seno, and N. Ohtani, This Bulletin, **46**, 3193 (1973).

4) D. F. Detar and D. V. Wells, *J. Amer. Chem. Soc.*, **82**, 5839 (1960).

5) T. Asahara and T. Sato, *Seisan Kenkyu* **23**, 138 (1971).

6) H. Okamoto, S. Hagiwara, and T. Kagiya, *Kogyo Kagaku Zasshi*, **74**, 1466 (1971).

7) T. Otsu, S. Aoki, M. Nishimura, M. Yamaguchi, and Y. Kusuki, *Polymer Lett.*, **5**, 835 (1967).

8) M. Assher and D. Vofsi, *J. Chem. Soc.*, **1963**, 3921.

9) F. Minisci and R. Galli, *Tetrahedron Lett.*, **1962**, 533.