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Telomerization of Ethylene with Carbon Tetrachloride Initiated by *N*-Chloroalkylamines

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By using various *N*-chloroalkylamines, the telomerization of ethylene with carbon tetrachloride was carried out in a stainless steel autoclave at 130 °C. It was found that the yields and the compositions of telomers varied widely according to the kinds and the structures of *N*-chloroalkylamines. When *N*-chloromonoalkylamines or *N*-chlorodialkylamines were used, the total yield of telomers was high compared with the case using *N*,*N*-dichloroalkylamines. In the presence of both *N*-chloromonoalkylamines and *N*-chlorodialkylamines, the total yield of telomers became higher and the greater part of the telomers was 1:1 adduct ($n=1$ telomer $CCl_3CH_2CH_2Cl$) of ethylene with carbon tetrachloride.

The telomerization of ethylene with carbon tetrachloride by using various initiators, has been examined by many investigators. *N*-Chloroamine, which is known to have a small value of bond energy and a large value of chain transfer constant, adds easily to olefins by a free radical mechanism.[1] As an initiator of polymerization or telomerization, however, *N*-chloroalkylamine was not noticed except for some studies.[2-3] The previous report from our laboratory illustrated that telomerization of ethylene with carbon tetrachloride occurred by use of systems of *N*,*N*-dichloro-*n*-butylamine and amines to give the $n=1$ telomer, $CCl_3CH_2CH_2Cl$, as a main product.[4]

On the other hand, we found that *N*,*N*-dichloroalkylamines reacted with primary or secondary amines to produce *N*-chloromonoalkylamines and *N*-chlorodialkylamines as shown by the following equation.[5]

$$RNCl_2 + R'R''NH \longrightarrow RNHCl + R'R''NCl$$
$$R, R' = \text{alkyl}, R'' = \text{alkyl or H}$$

These findings lead us to the attempt of telomerizations initiated by various *N*-chloroalkylamines. Furthermore, the systems of *N*,*N*-dichloroalkylamines and

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[1] R. S. Neale and N. L. Marcus, *J. Org. Chem.*, **33**, 3457 (1968); R. S. Neale and N. L. Marcus, *ibid.*, **32**, 3273 (1967) and references cited therein; F. Minisci, R. Galli, and M. Cecere, *Tetrahedron Lett.*, **1966**, 3163; F. Minisci and R. Galli, *ibid.*, **1964**, 167.

[2] T. Otsu, S. Aoki, and K. Itakura, *J. Polym. Sci., Part A-1*, **8**, 445 (1970).

[3] T. Otsu, S. Aoki, M. Nishimura, M. Yamagucni, and Y. Kusuki, *Polym. Lett.*, **5**, 835 (1967).

[4] T. Asahara and T. Sato, *Kogyo Kagaku Zasshi*, **74**, 1845 (1971).

[5] This result was presented at the 26th Annual Meeting of Chemical Society of Japan, Tokyo (1972).

amines were studied in detail and the result was compared with that for the cases of *N*-chloromonoalkylamines and *N*-chlorodialkylamines.

Experimental

Materials. Ethylene (purity 99.8%), carbon tetrachloride, and amines of commercial special grade were used without purification. *N,N*-Dichloroalkylamines6) and *N*-chlorodialkylamines were prepared by bubbling chlorine gas into the aqueous solution of amines and sodium bicarbonate and were purified by distillation. *N,N*-Dichloro-*n*-butylamine, bp 55°C/28 mmHg, *N,N*-dichloro-*t*-butylamine, bp 42 °C/19.5 mmHg, *N,N*-dichloro-*s*-butylamine, bp 45.5 °C/20 mmHg, *N,N*-dichloroisobutylamine, bp 39 °C/25 mmHg, *N*-chlorodi-*n*-butylamine, bp 33 °C/2.5 mmHg, *N*-chloropiperidine, bp 29 °C/10 mmHg.

N-Chloromonoalkylamines7) were prepared by mixing slowly the solution of corresponding amine hydrochloride with the aqueous solution of sodium hypochlorite in the presence of carbon tetrachloride. The resulting carbon tetrachloride solution was dried over sodium sulfate and the concentration was determined by the iodometric analysis.

Apparatus and Method. Telomerization was carried out in a 200 ml stainless steel (SUS 7) autoclave with a magnetic stirrer. In the autoclave, 1 mol of carbon tetrachloride and prescribed amounts of *N*-chloroamines were placed. After the autoclave was sealed, the air inside was replaced several times by ethylene. Ethylene was then charged to show a definite pressure. The autoclave was heated up to 130 °C and kept for a desired time. After the reaction, the autoclave was chilled to room temperature and the reaction mixture was washed by an aqueous potassium iodide solution and then an aqueous sodium thiosulfate solution. The product was fractionated by distillation into $n=1$ and $n=2$ telomers, which were identified by boiling point and NMR spectra.

Results and Discussion

Reactions of N,N-*Dichloroalkylamines with Primary or Secondary Amines.* It was made clear from the observations described later that primary and secondary amines react with *N,N*-dichloroalkylamines to form *N*-chloromonoalkylamine and *N*-chlorodialkylamine, respectively.

The reaction of *N,N*-dichloro-*n*-butylamine with *n*-butylamine in isooctane at 40 °C was examined by means of UV spectrometer. The absorption at 309 nm by *N,N*-dichloro-*n*-butylamine diminished in strength instead of the increase in strength of the absorption at 264 nm, which was identified to be owing to *N*-chloromono-*n*-butylamine. The ^{1}H NMR measurement of this reaction in carbon tetrachloride showed that the triplet absorption at δ 3.60 diminished and at the same time the triplet at δ 3.03 appeared and became greater. The former is owing to α-methylene protons of *N,N*-dichloro-*n*-butylamine and the latter was ascribed to that of *N*-chloromono-*n*-butylamine.

The reaction of *N,N*-dichloro-*n*-butylamine with di-*n*-butylamine was examined in the same way. The absorption at about 270 nm in the UV spectra and the triplets at δ 2.84 and δ 2.99 in the NMR spectra appeared and increased in strength as the reaction proceeded. The absorption around 270 nm can be explained as a combined peak of two absorptions, *i.e.*, that of *N*-chlorodi-*n*-butylamine at 274 nm and that of *N*-chloromono-*n*-butylamine at 264 nm, which have the similar molar absorption coefficient of about 400 l·cm^{-1}·mol^{-1}. The peak at δ 2.84 in the NMR spectra is owing to the α-methylene protons of *N*-chlorodi-*n*-butylamine and the peak at δ 2.99 to that of *N*-chloromono-*n*-butylamine. In these reactions, the concentration of the positive chlorine of *N*-chloroamines decreased by only 5—10%, when the conversion of *N,N*-dichloroamine was 50%. The similar results were obtained in the other systems of *N,N*-dichloroalkylamines and amines. The rate of reaction was low for amines with the bulky alkyl groups. In the case of dicyclohexylamine, the replacement reaction did not take place and dicyclohexylamine hydrochloride was obtained. The details will be reported in a separate paper.

Telomerization of Ethylene with Carbon Tetrachloride using N-*Chloroalkylamines.* The results of telomerizations using *N,N*-dichloroalkylamines, *N*-chloromonoalkylamines, and *N*-chlorodialkylamines are shown in Tables 1, 2, and 3, respectively.8) When *N,N*-dichloroalkylamines were used, the yield of telomers was generally low. In the case of *N,N*-dichloro-*t*-butylamine, the yield of telomers is particularly low. The composition ratio of $n=1$ telomer was, however, very high compared with that of other cases using di-*t*-butyl peroxide (DTBP) and di-*n*-butylamine.

N-Chloromonoalkylamines were more reactive for initiation of telomerization than *N,N*-dichloroalkylamines and the following order with higher yields of telomers was observed; *t*-Bu<*s*-Bu and *n*-Bu<*i*-Bu. The same order was observed in the case of *N,N*-dichlorobutylamines. In addition, it was noticed that the yield of telomers increased and the composition ratio of $n=1$ telomer decreased when the alkyl group of *N*-chloromonoalkylamine was more bulky. The similar result was obtained in the case of *N*-chlorodialkylamines.

Table 1. Telomerization of ethylene with carbon tetrachloride using *N,N*-dichloroalkylamines a)

Dichloroamine	Total yield of telomers g	Composition of telomers mol%		
		$n=1$	$n=2$	$n\geq3$
n-BuNCl$_2$	20	77	17	6
i-BuNCl$_2$	31	78	19	3
s-BuNCl$_2$	16	80	15	5
t-BuNCl$_2$	2	—	—	—

a) Telomerization conditions: *N,N*-dichloroalkylamine, 0.02 mol; initial ethylene pressure, 20 kg/cm^2; carbon tetrachloride, 1 mol; reaction temperature, 130 °C; reaction time, 2 hr.

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6) L. K. Jackson, G. N. R. Smart, and G. F. Wright, *J. Amer. Chem. Soc.*, **69**, 1539 (1947).

7) V. L. Heasley, P. Kovacic, and R. M. Lange, *J. Org. Chem.*, **31**, 3050 (1966).

8) The telomerization using *N,N*-dichloroalkylamines has an induction period, which is about 30 min or longer and is dependent upon the concentration of dichloroamine and other reaction conditions.

TABLE 2. TELOMERIZATION OF ETHYLENE WITH CARBON TETRACHLORIDE USING *N*-CHLOROMONOALKYLAMINES a)

Chloroamine	Total yield of telomers g	Composition of telomers mol% $n=1$		
		$n=1$	$n=2$	$n\geqq3$
n-BuNHCl	36	61	34	5
i-BuNHCl	57	75	22	3
s-BuNHCl	32	67	30	3
t-BuNHCl b)	11	42	48	10
n-PrNHCl c)	21	76	20	4
i-PrNHCl c)	9	78	22	0
EtNHCl c)	6	—	—	—

a) Telomerization conditions: *N*-chloromonoalkylamine, 0.01 mol; initial ethylene pressure, 20 kg/cm^2; carbon tetrachloride, 1 mol; reaction temperature, 130 °C; reaction time, 1.5 hr.

b) Reaction time; 2.0 hr.

c) *N*-Chloromonoalkylamine: 0.02 mol.

TABLE 3. TELOMERIZATION OF ETHYLENE WITH CARBON TETRACHLORIDE USING *N*-CHLORODIALKYLAMINES a)

Chloroamine	Total yield of telomers g	Composition of telomers mol%		
		$n=1$	$n=2$	$n\geqq3$
(n-Bu)$_2$NCl	63	73	20	7
(n-Pr)$_2$NCl	30	75	22	3
Et$_2$NCl	18	79	18	3
N-Chloro-piperidine	5 b)	—	—	—

a) Telomerization conditions: *N*-chlorodialkylamine, 0.02 mol; initial ethylene pressure, 20 kg/cm^2; carbon tetrachloride, 1 mol; reaction temperature, 130 °C; reaction time, 1.5 hr.

b) Reaction time; 2.0 hr.

Telomerization of Ethylene with Carbon Tetrachloride using N,N-*Dichloroalkylamine–Amine Systems.* The effect of the composition ratio of *N*,*N*-dichloro-*n*-butylamine to *n*-butylamine is listed in Table 4. The yield of telomers decreases, but the composition ratio of $n=1$ telomer increases with the increase of the ratio of *N*,*N*-dichloroamine. The decrease in the yield of total telomers can be explained from the fact that the replacement reaction above-mentioned takes place as the amine interacts stronger with *N*,*N*-dichloroamine than carbon tetrachloride.

TABLE 4. TELOMERIZATION OF ETHYLENE WITH CARBON TETRACHLORIDE USING THE SYSTEM OF *N*,*N*-DICHLORO-*n*-BUTYLAMINE AND *n*-BUTYLAMINE a)

n-BuNCl$_2$ $\times 10^{-2}$ mol	n-BuNH$_2$ $\times 10^{-2}$ mol	Total yield of telomers g	Composition of telomers mol%		
			$n=1$	$n=2$	$n\geqq3$
0	2.0	46	57	35	8
0.5	1.5	37	57	33	10
1.0	1.0	17	73	17	10
1.5	0.5	11	72	19	9
2.0	0	4	—	—	—

a) Telomerization conditions: initial ethylene pressure, 20 kg/cm^2; carbon tetrachloride, 1 mol; reaction temperature, 130 °C; reaction time, 1.5 hr.

As is shown in Table 5, both the yield of telomers and the composition ratio of $n=1$ telomer increase by adding di-*n*-butylamine to *N*,*N*-dichloroalkylamine. This binary system is more reactive than the single system of *N*,*N*-dichloroalkylamine, *N*-chloromonoalkylamine, or *N*-chlorodialkylamine. The reactivity of this system was dependent upon the alkyl group of *N*,*N*-dichlorobutylamines and the order of reactivity was the same to that of *N*-chloromonobutylamines and *N*,*N*-dichlorobutylamines.

TABLE 5. TELOMERIZATION OF ETHYLENE WITH CARBON TETRACHLORIDE USING THE SYSTEM OF *N*,*N*-DICHLOROALKYLAMINE AND DI-*n*-BUTYLAMINE a)

Dichloroamine	Total yield of telomers g	Composition of telomers mol%		
		$n=1$	$n=2$	$n\geqq3$
n-BuNCl$_2$	60	86	12	3
i-BuNCl$_2$	91	87	12	1
s-BuNCl$_2$	70	88	9	3
t-BuNCl$_2$	23	77	18	5

a) Telomerization conditions: *N*, *N*-dichloroalkylamine, di-*n*-butylamine, 0.02 mol; initial ethylene pressure, 20 kg/cm^2; carbon tetrachloride, 1 mol; reaction temperature, 130 °C; reaction time, 1.5 hr.

TABLE 6. COMPARISON OF THE SYSTEM OF *N*-CHLOROMONO-*n*-BUTYLAMINE AND *N*-CHLORODI-*n*-BUTYLAMINE WITH THE SYSTEM OF *N*,*N*-DICHLORO-*n*-BUTYL AMINE AND DI-*n*-BUTYLAMINE a)

Initiator system	Total yield of telomers g	Composition of telomers mol%		
		$n=1$	$n=2$	$n\geqq3$
n-BuNCl$_2$/(n-Bu)$_2$NH	51	85	11	4
n-BuNHCl/(n-Bu)$_2$NCl	52	82	14	4

a) Telomerization conditions: *N*-chloroamine, amine, 0.01 mol; initial ethylene pressure, 20 kg/cm^2; carbon tetrachloride, 1 mol; reaction temperature, 130 °C; reaction time, 1.5 hr.

Table 6 shows the comparison of the result for the system of *N*,*N*-dichloro-*n*-butylamine and di-*n*-butylamine with that for the system of *N*-chloromono-*n*-butylamine and *N*-chlorodi-*n*-butylamine. The latter system is to be formed from the reaction in the former one. For the both systems, essentially the same results were obtained as expected. It was supposed that the reaction of *N*,*N*-dichloro-*n*-butylamine with di-*n*-butylamine at room temperature takes place rapidly to be almost completed within 30 min which is necessary to heat up the autoclave to the reaction temperature of 130 °C. The result for the 1 : 1 system of *N*,*N*-dichloro-*n*-butylamine–*n*-butylamine in Table 4 does not coincide with that for the *N*-chloromono-*n*-butylamine system in Table 2. This would show that the rate of the reaction of primary amines is slower than secondary amines.

Effects of Metal or Its Salts on the Telomerization Using N-*Chloroalkylamines.* The effect of iron, copper and their chlorides on the telomerization of ethylene with carbon tetrachloride using *N*-chloroalkylamines is shown in Table 7. Remarkable decreases of the yield of telomers were observed when copper, its salts, and ferric chloride are added except the case of *N*,*N*-dichloro-*n*-butylamine. The addition of iron did not affect the reactivity of *N*-chloroalkylamines. The effect of ferrous chloride varied with the kind of *N*-chloroalkylamines. Particularly, the system of ferrous chloride and *N*-chlorodi-*n*-butylamine showed a marked increase in the yield of telomers and the ethylene charged into the autoclave was completely consumed within 25 min.

TABLE 7. TELOMERIZATION OF ETHYLENE WITH CARBON TETRACHLORIDE USING THE SYSTEM OF *N*-CHLOROALKYLAMINES AND METAL OR ITS SALTS[a]

Chloroamine	Metal or its salt	Total yield of telomers g	Composition of telomers mol%		
			$n=1$	$n=2$	$n\geq3$
n-BuNCl$_2$	—	4	—	—	—
	Fe	18	83	14	3
	FeCl$_2$	22	70	27	3
	FeCl$_3$	4	—	—	—
	Cu	8	58	40	2
	CuCl	1	—	—	—
	CuCl$_2$	3	—	—	—
n-BuNHCl	—	36[c]	61	34	5
	Fe	40	85	13	2
	FeCl$_2$	38	73	23	4
	FeCl$_3$	4	—	—	—
	Cu	27	81	16	3
	CuCl	11	76	24	0
	CuCl$_2$	7	90	10	0
(n-Bu)$_2$NCl	—	63	73	20	7
	Fe	63	87	9	4
	FeCl$_2$	80[b]	87	11	2
	FeCl$_3$	35	87	9	4
	Cu	20	86	14	0
	CuCl	13	83	17	0
	CuCl$_2$	14	87	13	0

a) Telomerization conditions: chloroamine, metal, and salt, 0.02 mol; initial ethylene pressure, 20 kg/cm^2; carbon tetrachloride, 1 mol; reaction temperature, 130 °C; reaction time, 1.5 hr.
b) Reaction time, 22 min.
c) Chloroamine, 0.01 mol.

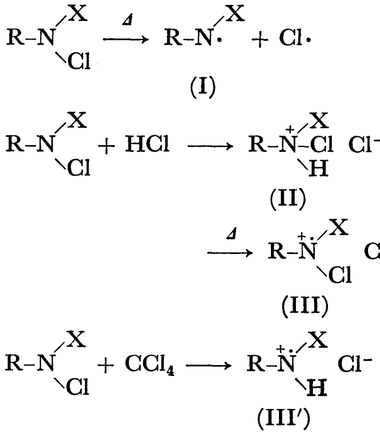
These results are to be compared with those for the systems of di-*n*-butylamine and metal or its salts. As is shown in Table 8, the high yields of telomers were obtained for all systems and the inhibition effect of copper salts or ferric chloride was not found.

TABLE 8. TELOMERIZATION OF ETHYLENE WITH CARBON TETRACHLORIDE USING THE SYSTEM OF DI-*n*-BUTYLAMINE AND METAL OR ITS SALTS[a]

Metal or salt	Total yield of telomers g	Composition of telomers mol%		
		$n=1$	$n=2$	$n\geq3$
—	63	64	18	18
Fe	84	81	16	3
FeCl$_2$	73	71	24	5
FeCl$_3$	63	88	10	2
Cu	27	85	10	5
CuCl	54	90	7	3
CuCl$_2$	52	90	8	2

a) Telomerization conditions: metal or salt, 0.02 mol; di-*n*-butylamine, 0.02 mol; initial ethylene pressure, 20 kg/cm^2; carbon tetrachloride, 1 mol; reaction temperature, 130 °C; reaction time, 1.5 hr.

Mechanism of Initiation. It is supposed that the telomerization would be initiated by *N*-chloroalkylamine through following reactions (1—3).



$$\text{R–N}\begin{smallmatrix}\text{X}\\ \text{Cl}\end{smallmatrix} \xrightarrow{\Delta} \underset{\text{(I)}}{\text{R–N}^{\cdot}\text{–X}} + \text{Cl}\cdot \qquad (1)$$

$$\text{R–N}\begin{smallmatrix}\text{X}\\ \text{Cl}\end{smallmatrix} + \text{HCl} \longrightarrow \underset{\text{(II)}}{\text{R–}\overset{+}{\text{N}}\text{(X)(H)–Cl}}\ \text{Cl}^- \xrightarrow{\Delta} \underset{\text{(III)}}{\text{R–}\overset{+\cdot}{\text{N}}\begin{smallmatrix}\text{X}\\ \text{Cl}\end{smallmatrix}}\ \text{Cl}^- + \text{Cl}\cdot \qquad (2)$$

$$\text{R–N}\begin{smallmatrix}\text{X}\\ \text{Cl}\end{smallmatrix} + \text{CCl}_4 \longrightarrow \underset{\text{(III')}}{\text{R–}\overset{+\cdot}{\text{N}}\begin{smallmatrix}\text{X}\\ \text{H}\end{smallmatrix}}\ \text{Cl}^- + \cdot\text{CCl}_3 \qquad (3)$$

X=R, H, or Cl

In Reaction 1, amino radical (I) is formed through a thermal scission of nitrogen-chlorine bond. *N*,*N*-dichloro-*n*-butylamine was utilized for the chlorination of polybutadiene by Kagiya *et al.*[9] This decomposition is probably the main process of radical formation in the case of *N*-chloro-*t*-alkylamines having no hydrogen bonded to α-carbon and *N*,*N*-dichloroalkylamines.

N-Chlorodialkylamine and *N*-chloromonoalkylamine having α-hydrogen easily undergo thermal decomposition at high temperatures to release hydrogen chloride. In the same manner as Hofmann-Loeffler reaction of *N*-chloroalkylamine in sulfuric acid,[10] hydrogen chloride maybe forms a salt (II) with *N*-chloroalkylamine and II decomposes to form aminium radical (III) and chlorine atom. Practically, II was formed stably at −60 °C and decomposed at room temperature in methanol. The decomposition products from II were amine hydrochloride and chlorine gas.

One-electron transfer from *N*-chloroalkylamine to carbon tetrachloride results in the formation of aminium radical (III′) and trichloromethyl radical (Reaction 3). It was reported that amines, such as triethylamine, and carbon tetrachloride form an *n*-σ complex which shows a charge-transfer spectrum.[11] But the basicity of *N*-chloroalkylamines is weaker than that of amines and, therefore, an electron donation is not feasible. Then, the radical formation by Reaction 3 might be excluded.

The telomerization of octene-1 instead of ethylene with carbon tetrachloride was carried out in a 20 ml glass ampule and the result was compared with that of

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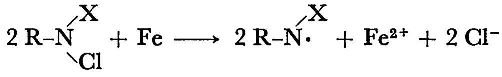
[9] H. Okamoto, S. Hagiwara, and T. Kagiya, *Kogyo Kagaku Zasshi*, **74**, 1466 (1971).

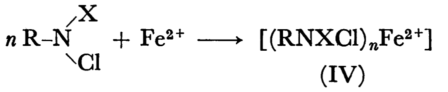
[10] M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963).

[11] D. P. Stevenson and G. M. Coppinger, *J. Amer. Chem. Soc.*, **84**, 149 (1962).

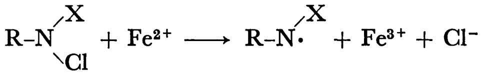
the same reaction in the 200 ml stainless steel autoclave under the same reaction conditions. The yield of telomers in the ampule was less than one fifth of that in the autoclave. This suggests that the metal surface or the trace amount of metal resolved has a large effect on the initiation of *N*-chloroalkylamine as does the case for the system of triethanolamine–carbon tetrachloride[12] or the system of cellulose–water–carbon tetrachloride.[13] The telomers in the ampule was probably produced *via* the initiations indicated by Eqs. (1)—(2). On the other hand, most part of the telomers in the autoclave was likely formed *via* the following reactions.



$$2\,\mathrm{R}\text{-}\underset{\diagdown\mathrm{Cl}}{\overset{\diagup\mathrm{X}}{\mathrm{N}}} + \mathrm{Fe} \longrightarrow 2\,\mathrm{R}\text{-}\overset{\diagup\mathrm{X}}{\mathrm{N}}\cdot + \mathrm{Fe^{2+}} + 2\,\mathrm{Cl^-} \tag{4}$$



$$n\,\mathrm{R}\text{-}\underset{\diagdown\mathrm{Cl}}{\overset{\diagup\mathrm{X}}{\mathrm{N}}} + \mathrm{Fe^{2+}} \longrightarrow \underset{\mathrm{(IV)}}{[(\mathrm{RNXCl})_n\mathrm{Fe^{2+}}]} \tag{5}$$



$$\mathrm{R}\text{-}\underset{\diagdown\mathrm{Cl}}{\overset{\diagup\mathrm{X}}{\mathrm{N}}} + \mathrm{Fe^{2+}} \longrightarrow \mathrm{R}\text{-}\overset{\diagup\mathrm{X}}{\mathrm{N}}\cdot + \mathrm{Fe^{3+}} + \mathrm{Cl^-} \tag{6}$$

$$\mathrm{IV} + \mathrm{CCl_4} \longrightarrow \underset{\mathrm{(V)}}{\begin{bmatrix}(\mathrm{RNXCl})_n\mathrm{FeCl^{2+}}\\ \cdot\mathrm{CCl_3}\end{bmatrix}} \tag{7}$$

Amino radical and ferrous ion are formed by the action of iron to *N*-chloroalkylamine, as suggested from studies by Otsu *et al.*[3] Although a part of ferrous ions is oxidized by *N*-chloroalkylamine to form ferric ion (Eq. (6)), most part of ferrous ions forms a complex (IV) with *N*-chloroalkylamine (Eq. (5)). This complex reacts with carbon tetrachloride to form trichloromethyl radical (Eq. (7)). The trichloromethyl radical thus formed seems to coordinate to iron–*N*-chloroalkylamine complex or to be trapped within the cage of this complex and carbon tetrachloride as in the system of triethyl phosphite–iron salts–carbon tetrachloride.[14]

Parts of amino radicals, aminium radicals, and chlorine atoms formed through Reactions 1, 2, 4, and 6 act as free radical initiators and give the telomers with the composition similar to that by usual radical initiators such as DTBP (Eqs. (8)—(9)).

$$\begin{aligned}\mathrm{I}\cdot + n\,\mathrm{C_2H_4} &\longrightarrow \mathrm{I(C_2H_4)}_n\cdot\\ &\xrightarrow{\mathrm{CCl_4}} \mathrm{I(C_2H_4)}_n\mathrm{Cl} + \cdot\mathrm{CCl_3}\end{aligned} \tag{8}$$

$$\begin{aligned}\cdot\mathrm{CCl_3} + n\,\mathrm{C_2H_4} &\longrightarrow \mathrm{CCl_3(C_2H_4)}_n\cdot\\ &\xrightarrow{\mathrm{CCl_4}} \mathrm{CCl_3(C_2H_4)}_n\mathrm{Cl} + \cdot\mathrm{CCl_3}\end{aligned} \tag{9}$$

On the other hand, coordinated radicals (V) react with ethylene to produce $n=1$ telomer almost selectively.[14]

$$\mathrm{V} + \mathrm{C_2H_4} \longrightarrow \mathrm{IV} + \mathrm{CCl_3C_2H_4Cl} \tag{10}$$

The telomerization of ethylene with chloroform using the system of *N*-chlorodi-*n*-butylamine and *N*-chloromono-*n*-butylamine afforded the product, a greater part of which was of chlorine abstracted type, *i.e.*, $\mathrm{CHCl_2(C_2H_4)}_n\mathrm{Cl}$. To a contrary, the product of telomerization by DTBP or di-*n*-butylamine was of hydrogen abstracted type, $\mathrm{CCl_3(C_2H_4)}_n\mathrm{H}$. This result seems to support the above suggestion.

The authors would like to express their thanks to Mr. T. Suzuki for the assistance in the experiments.

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[12] T. Asahara and J. Hirano, *Kogyo Kagaku Zasshi*, **69**, 1512 (1966).

[13] Y. Igi, N. Kinoshita, and M. Imoto, *ibid.*, **74**, 295 (1971).

[14] T. Asahara, M. Senō, and T. Sato, *ibid.*, **74**, 2288 (1971).