Reactions of Ethylene with Chloroform Initiated by Amine–Ferrous Chloride System

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The reactions of ethylene with chloroform initiated by alkylamine–ferrous chloride systems were examined in detail. Two main products, α,α,α-trichloroalkanes (I) and α,α,ω-trichloroalkanes (II), were obtained. Their composition was independent of the kind of amine but dependent upon the total carbon number of alkylamine. When amines having higher alkyl groups were used, the main product was α,α,ω-trichloropropane (II-1). When lower alkylamines were used, the main products were α,α,α-trichloroalkanes which contained considerable amounts of higher telomers. The results support the view that the reactions proceed according to the "caged free radical" process.

A number of reports on the radical reaction of olefins with polyhaloalkanes have been presented and various initiators have been explored for this reaction. The peroxides afforded telomers in most cases, whereas some transition metal complexes gave a 1 : 1 adduct in a good yield.[1] It was previously reported that amine–cupric chloride,[2] triethyl phosphite–iron chloride,[3] *N*-chloroalkylamine–ferrous chloride,[4] and others[5] also give a 1 : 1 adduct of ethylene with carbon tetrachloride as the main product. We suggested that a "caged radical" process would proceed along with the so-called "free radical" propagating process.[6] In order to confirm the above reaction mechanism, the reaction of ethylene with chloroform initiated by amine-ferrous chloride was investigated in detail and the results are given in this paper. A combination of ethylene and chloroform is suitable for this purpose, since "free" trichloromethyl radical adds readily to ethylene as compared with other higher olefins,[1g] and two products, α,α,α-trichloroalkanes (I) and α,α,ω-trichloroalkanes (II), could be derived in the reaction of ethylene with chloroform. The former is the product of the peroxide-initiated reaction and, therefore, considered to be formed *via* a "free radical" propagating process, and the latter is considered to be formed mainly *via* a "caged radical" process.

Experimental

Materials. Ethylene (purity 99.8%), amines and metallic salts of commercial special grade were used without further purification. Commercial chloroform was purified through an activated alumina column and the purity was examined by gas chromatography.

Reactions of Ethylene with Chloroform. The reaction was carried out in a 200 ml stainless steel autoclave with a magnetic stirrer. Chloroform (1 mol) and a certain amount of initiators were placed in the autoclave and the air inside was replaced several times with ethylene. After ethylene was charged to 20 kg/cm² at 30 °C, the autoclave was heated up to 130 °C. After the reaction, the autoclave was chilled to room temperature and the reaction mixture was washed with 1 M hydrochloric acid to remove amine and metallic salts.

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. Authentic samples were prepared by the following method. 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 reaction 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 purified several times by fractional distillation 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 reactions 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 weights as those of V and VI, respectively, were used.

Results and Discussion

Several initiator systems were examined and the results are summarized in Table 1. In the presence of iron particles, the reaction had an induction period (about 30 min) and proceeded very slowly. Ferrous chloride gave the same products as those in the case of iron particles at a rather slow reaction rate. *n*-Butylamine greatly accelerated the reaction, whereas di-*n*-butylamine was not effective. A combination of ferrous chloride (0.002 mol) with di-*n*-butylamine (0.02 mol), however, induced the reaction without an induction period (the decrease in ethylene pressure, $-\Delta P$= 6 kg/cm² for 90 min). An equimolar mixture of amine with iron particle or ferrous chloride increased the reaction rate. In the case of di-*n*-butylamine–iron particle system, the reaction rate changed considerably in the course of reaction; the reaction proceeded slowly at first 70 min ($-\Delta P$=4 kg/cm²) and then the rate was greatly increased. A similar stepwise change in the reaction rate was seen in the *n*–butylamine-iron particle system though the extent of change was not so large.

In the absence of amine, dichloromethyl radicals which act as initiating radicals are possibly formed:

$$Fe + 2\,CHCl_3 \longrightarrow FeCl_2 + 2\cdot CHCl_2 \quad (1)$$

$$Fe + CHCl_3 \longrightarrow FeCl_3 + \cdot CHCl_2 \quad (2)$$

The possibility of radical formation by the reaction of polyhaloalkane and amine in the absence of metal has been examined.[7] When *n*-butylamine was added

Table 1. Reaction of ethylene with chloroform[a)]

Initiator system	Time min	Conv. of chloroform %	Total yield g	$-\Delta P$ of ethylene kg/cm²	Product mol%[b)] I	II	III	IV	V	VI	VII
None	180	0	0	51—51	—	—	—	—	—	—	—
Fe	120	5	8	51—43	98	—	2	—	—	—	—
$FeCl_2 \cdot 4H_2O$	180	12	20	48—31	97	—	2	tr	—	—	—
n-$BuNH_2$	120	11	18	50—33	93	—	4	2	1	—	—
n-Bu_2NH	120	tr	tr	50—49	98	—	2	tr	—	—	—
n-$BuNH_2$/Fe	60	13	22	47—25	91	1	5	3	—	—	—
n-Bu_2NH/Fe	103	18	29	49—25	42	24	13	7	12	2	tr
n-$BuNH_2/FeCl_2 \cdot 4H_2O$	50	17	29	46—25	87	2	4	4	—	—	3
n-$Bu_2NH/FeCl_2 \cdot 4H_2O$	44	22	33	44—25	6	63	10	6	6	8	1

a) Reaction conditions: charged ethylene pressure, 20 kg/cm² at 30 °C; chloroform, 1 mol; reaction temperature, 130 °C; each initiator component, 0.02 mol. b) In all Tables, the telomers except for those contained in Experimental are omitted since their amounts were very small in all runs.

Table 2. Reaction of ethylene with chloroform using various amine-ferrous chloride systems[a)]

Amine		Time[b)] min	Conv. of chloroform %	Total yield g	Product mol% I	II	III	IV	V	VI	VII
$C_2H_5NH_2$	(**1**)	122	17	29	95	—	2	3	—	—	—
n-$C_3H_7NH_2$	(**2**)	85	17	28	90	—	3	6	—	—	1
n-$C_4H_9NH_2$	(**3**)	50	17	29	87	2	4	4	—	—	3
n-$C_6H_{13}NH_2$	(**4**)	120[c)]	12	20	59	11	9	13	4	—	4
n-$C_8H_{17}NH_2$	(**5**)	120	17	28	17	40	14	8	11	7	3
$(C_2H_5)_2NH$	(**6**)	114	16	27	60	8	9	13	4	—	6
$(n$-$C_3H_7)_2NH$	(**7**)	45	17	27	31	24	15	13	10	2	4
$(n$-$C_4H_9)_2NH$	(**8**)	44	22	33	6	63	10	6	6	8	1
$(C_2H_5)_3N$	(**9**)	46	17	27	27	20	18	13	11	5	6
$(n$-$C_3H_7)_3N$	(**10**)	26	25	39	3	71	8	5	5	8	tr
$(n$-$C_4H_9)_3N$	(**11**)	16	23	35	2	77	7	2	5	7	tr
cyclo-$C_6H_{11}NH_2$	(**12**)	30	16	27	71	9	6	9	2	—	3
$(cyclo$-$C_6H_{11})_2NH$	(**13**)	25	20	31	10	62	8	4	9	6	1
$C_5H_{11}N$	(**14**)[d)]	131	18	29	52	12	11	14	5	tr	6

a) Reaction conditions: charged ethylene pressure, 20 kg/cm² at 30 °C; chloroform, 1 mol; reaction temperature, 130 °C; amine and ferrous chloride, 0.02 mol. b) Reaction was continued until ethylene pressure fell down to 25 kg/cm² at 130 °C. c) The change of ethylene pressure was from 46 to 34 kg/cm² at 130 °C. d) Piperidine.

to ethylene and chloroform in the absence of added metal, a considerable amount of telomers of type I was obtained. Although it is uncertain whether trace of metal is necessary for the reaction or not, it is probable that the surface of the autoclave would effect the reaction. As the reaction is very low in the absence of added metal and the change of the reaction rate in the course of reaction is observed for the amine-iron particle system, it is considered that what induces the initiation reaction is not iron metal, but mainly ferrous ions. The radical formation possibly takes place, for the most part, according to Eq. 3. Through the interaction of chloroform with ferrous chloride activated by amines, dichloromethyl radical is formed.

$$Fe^{2+}L_k + CHCl_3 \rightleftharpoons [Fe^{3+}L_kCl^- \cdot CHCl_2] \quad (3)$$

X

L=amine

Results of reactions using various amine-ferrous chloride systems are shown in Table 2. The reactions were continued until the ethylene pressure fell down to 25 kg/cm² from the initial value of about 50 kg/cm² at 130 °C, and the compositions of the products were compared at the same value of ethylene conversion. It was found that the composition of products was independent of the kind of amine, but dependent upon the total carbon number of alkylamine. The main products are α,α,α-trichloroalkanes (I) when the number of alkyl carbons of amines is less than six. The ratio of α,α,ω-trichloroalkanes (II) to the total products increases as the alkyl group becomes larger, II becoming a main product for alkylamines having more than eight carbons.

The molecular weight distributions of each type product for the triethylamine–ferrous chloride system are shown in Fig. 1. The amount of the $n=2$ telomer of type I, α,α,α-trichloropentane (I-2), is comparable to that of the 1 : 1 adduct, α,α,α-trichloropropane (I-1), a considerable amount of n=3 telomers being also produced. The molar distribution of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes (IV) is similar to that of I. The distribution curves of I and IV remain unchanged when

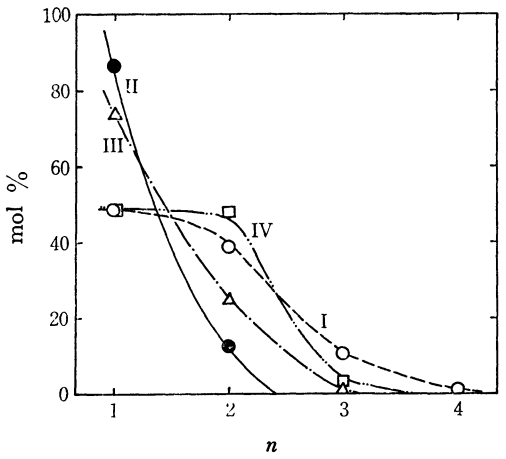

Fig. 1. Product distribution of each type telomer.

amines other than triethylamine are used. For the products of type II, however, the 1 : 1 adduct, α,α,ω-trichloropropane (II-1), is produced almost exclusively. The distribution curve of α,α-dichloroalkane (III) lies between the curve of II and that of I or IV.

The results can be explained by a reaction mechanism in which a "caged radical" process proceeds along with a "free radical" propagating process. When bulky molecules of amine coordinate ferrous ions, most of the dichloromethyl radicals formed according to Eq. 3 are trapped within a cage formed by the coordinating amine and add to ethylene invading into the cage (Eq. 4).

$$X + C_2H_4 \longrightarrow \underset{X_1}{[Fe^{3+}L_kCl^- \cdot C_2H_4CHCl_2]} \quad (4)$$

$$X_1 \longrightarrow Fe^{2+}L_k + \underset{\text{II-1}}{ClC_2H_4CHCl_2} \quad (5)$$

$$X_1 + CHCl_3 \rightarrow Fe^{3+}L_kCl^- + \underset{\text{III-1}}{HC_2H_4CHCl_2} + \cdot CCl_3 \quad (6)$$

$$X_1 + C_2H_4 \longrightarrow \underset{X_2}{[Fe^{3+}L_kCl^- \cdot (C_2H_4)_2CHCl_2]} \quad (7)$$

$$X \longrightarrow Fe^{3+}L_kCl^- + \cdot CHCl_2 \quad (8)$$

$$\cdot CHCl_2 + nC_2H_4 + CHCl_3 \rightarrow \underset{\text{III}}{CHCl_2(C_2H_4)_nH} + \cdot CCl_3 \quad (9)$$

$$\cdot CCl_3 + nC_2H_4 + CHCl_3 \rightarrow \underset{\text{I}}{CCl_3(C_2H_4)_nH} + \cdot CCl_3 \quad (10)$$

$$\underset{\text{II}}{CHCl_2(C_2H_4)_n \cdot} + Fe^{3+}L_kCl^- \rightarrow CHCl_2(C_2H_4)_nCl + Fe^{2+}L_k \quad (11)$$

$$\underset{\text{IV}}{CCl_3(C_2H_4)_n \cdot} + Fe^{3+}L_kCl^- \rightarrow CCl_3(C_2H_4)_nCl + Fe^{2+}L_k \quad (12)$$

The ω,ω-dichloropropyl radical in the cage would take part in three ways in the following steps of the reaction. For the most part, the radical abstracts chlorine atom from ferric chloride to afford II-1 (Eq. 5). The hydrogen abstraction from chloroform around the cage may partly occur and α,α-dichloropropane (III-1) and "free" trichloromethyl radical are formed (Eq. 6). The chain propagating reaction in the cage (Eq. 7) would rarely occur, because other ethylene molecules should be supplied into the cage. When smaller amines are used, the dichloromethyl radical would be relatively mobile and get out of the cage, and then a "free radical" propagating process would take place to form telomers of type III and trichloromethyl radicals (Eqs. 8 and 9).

Trichloromethyl radicals afford telomers I by the chain reaction (Eq. 10). Chloride abstraction reactions of ω,ω-dichlorolakyl radical and ω,ω,ω-trichloroalkyl radical from chloride complex give telomers II and IV, respectively (Eqs. 11 and 12).

ω,ω-Dichloroalkyl free radical is expected not to differ much from ω,ω,ω-trichloroalkyl free radical in reactivity against chloroform, ethylene, or chloride complex. According to the above reaction scheme, the product of type II is formed both in the caged radical process of Eq. 5 (mainly 1 : 1 adduct) and in the free radical process of Eq. 11 (mainly high telomers). It is seen from Fig. 2 that the ratio of II-1 to the total amount of type II products increases as the composition ratio of II to the total products increases. This can be explained by the predominant occurrence of the "caged process". Conversely, as the "free radical" process becomes predominant, the molecular weight distribution of II would gradually resemble that of I or IV with the decrease in the product ratio of II. Figure 2 shows that this is the case. The variation in total yield or the conversion of chloroform at a definite ethylene conversion in Table 2 is explained in the same way.

The effects of reaction time, ethylene pressure, and reaction temperature on the composition ratio of products were examined and the results are shown in Tables 3, 4, and 5, respectively. With the elongation

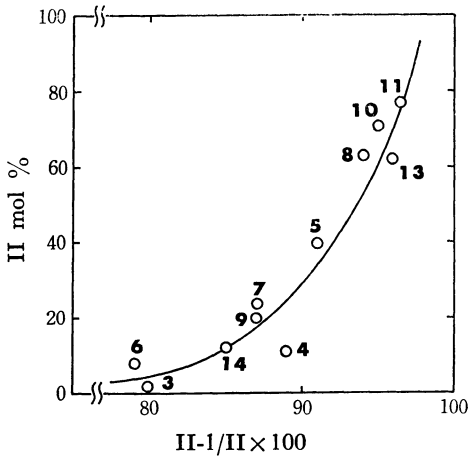

Fig. 2 Ratio of II-1 to Type II products.

Table 3. Effect of reaction time on Et_3N-$FeCl_2 \cdot 4H_2O$ system[a]

Time min	Conv. of $CHCl_3$ %	Product mol%						
		I	II	III	IV	V	VI	VII
15	8	40	21	15	15	5	1	3
30	10	30	27	16	14	7	3	3
45	12	25	29	17	13	8	4	4

a) Amount of triethylamine and ferrous chloride is 0.01 mol for both. Other reaction conditions are the same as those given in Table 2.

Table 4. Effect of ethylene pressure for n-Bu_2NH-$FeCl_2 \cdot 4H_2O$ system[a)]

Charged ethylene kg/cm² at 30 °C	Conv. of $CHCl_3$ %	Product mol%						
		I	II	III	IV	V	VI	VII
10	12	8	70	8	7	3	5	—
15	13	10	64	10	6	5	5	—
20	15	5	62	13	7	5	8	tr

a) Reaction was continued until $-\Delta P = 10$ kg/cm² at 130 °C. Other reaction conditions are the same as those given in Table 2.

Table 5. Effect of reaction temperature for Et_3N-$FeCl_2 \cdot 4H_2O$ system[a)]

Temp. °C	Time min	Conv. of $CHCl_3$ %	Product mol%						
			I	II	III	IV	V	VI	VII
110	230	15	31	25	16	11	8	3	6
120	120	15	28	24	19	11	9	3	5
130	46	17	27	20	18	13	11	5	6

a) Reaction conditions except reaction temperature are the same as those given in Table 2.

of reaction time, the composition ratios of products of types I and IV decreased, accompanied by an increase in the ratios of V, VI, and VII for all the amine–ferrous chloride systems examined. The products of types I and IV, having a trichloromethyl group, may react as a telogen in the same manner as for chloroform and give products of types V, VI, and VII.[1f)] The slight increase of II with an increase in reaction time seems to be connected with the change in ethylene pressure. The ratio of II is slightly greater at a low ethylene pressure compared with that at a high pressure as is shown in Table 4. The increase in reaction temperature scarcely affects the composition ratio of products. The ratio of II tends to increase somewhat at lower temperatures.

It should be noted that the amine–cuprous chloride system shows a similar tendency to the amine–ferrous chloride system. The main products in the case of $EtNH_2$–CuCl were of type I, whereas those in the case of $BuNH_2$–CuCl and Bu_2NH–CuCl were of ty peII. The reactions in the amine–cuprous chloride system probably proceed according to a similar mechanism to that in the amine–ferrous chloride system.

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