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Telomerization of Vinyl Chloride with Carbon Tetrachloride Using Amine-Cupric Chloride. Effects of Amines and Solvents1)

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Telomerization of vinyl chloride with carbon tetrachloride was investigated in reaction systems containing amines and cupric chloride. The yield of telomers $CCl_3(CH_2CHCl)_nCl$ and the content of the telomer with $n=1$ were high when aliphatic amines with relatively long chains were used. An increase in basicity of amines raised the yield of telomers. When bifunctional amines such as diamines and alkanolamines were used, the yield of telomers was low and the content of higher telomers was high. The effect of added solvents on the yield of telomers was not so remarkable and an increase in the dielectric constant of solvents decreased the yields. The results were examined on the basis of Asscher-Vofsi mechanism, but could not be explained satisfactorily. A partly modified scheme was proposed for the radical addition in the cage complex stabilized with amine.

In a previous paper,1) we reported that the telomerization of vinyl chloride and carbon tetrachloride was initiated by *n*-butylamine in the presence of metals (cupper and iron) and metallic salts (Cu(I) or Cu(II) chloride and Fe(II) or Fe(III) chloride). While the reactions initiated by ordinary radical initiators such as benzoyl peroxide and azobisisobutyronitrile afford telomers with higher average molecular weights, the main products obtained in the *n*-butylamine - metallic salt systems were telomers lower average molecular weights. The content of $CCl_3CH_2CHCl_2$, the 1 : 1 adduct of vinyl chloride with carbon tetrachloride, is as high as 80%.

Since Collins noticed that amines change into amine hydrochlorides in carbon tetrachloride under day-light, the reaction of amines with carbon tetrachloride under mild conditions has been investigated by many authors.2) Amines form charge-transfer complexes with carbon tetrachloride. However, the formation constants are rather small. The complexes decompose with the formation of trichloromethyl radicals under the influence of light or metallic salts.3-5)

Miller5) proposed the following mechanism for the photo-decomposition:

$$RNH_2\cdot CCl_4 \xrightarrow{h\nu} RNH_2^+Cl^- + \cdot CCl_3$$

On the other hand, Asscher and Vofsi6) proposed the following redox mechanism with participation of metallic ions, *e. g.* cupper ions:

$$RNH_2\cdot CCl_4 + Cu^+ \rightarrow [Cu^{(+)}\cdot Cl]RNH_2 + \cdot CCl_3$$

When a vinyl compound is present in such a system, trichloromethyl radicals enter into polymerization. However, this mechanism has not been confirmed to be plausible through our investigation on the telomerization of vinyl compounds with carbon tetrachloride in amine-metallic salt systems.1) In the present paper, the results on the effect of amines on the reaction will be presented.

Experimental

Amines and cupric chloride of commercial special grade were used without purification. Carbon tetrachloride was purified by distillation and vinyl chloride was washed with a 5% sodium hydroxide solution and dried by passing through a calcium chloride tube.

Telomerization was carried out in a stainless steel autoclave with a magnetic stirrer. Definite amounts of carbon tetrachloride, amine and $Cu(II)Cl_2$ were placed in the autoclave chilled with dry ice-acetone, and vinyl chloride which had been liquified was added.

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5) W. J. Lautenberger, E. N. Jones and J. G. Miller, *J. Amer. Chem. Soc.*, **90**, 1100 (1968).

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TABLE 1. EFFECTS OF THE BASICITY OF AMINES ON THE YIELD AND COMPOSITION OF TELOMERS*

Run No.	Amine	pK_B	Yield g/mol CCl_4	Composition of telomers (wt%)		
				$n=1$	$n=2$	$n\geq 3$
119	*n*-Butylamine	3.39	40.1	85	10	5
180	Isobutylamine	3.59	56.4	74	5	21
181	*s*-Butylamine	—	46.8	79	7	14
201	*t*-Butylamine	3.55	43.7	79	5	16
189	*n*-Hexylamine	3.30	53.6	79	7	14
182	Cyclohexylamine	3.31	44.4	75	7	18
198	Benzylamine	4.63	53.3	69	8	23
190	Dodecylamine	3.10	50.2	77	13	10
186	Diethylamine	3.01	29.1	70	10	20
187	Di-*n*-propylamine	3.10	46.3	76	14	10
177	Di-*n*-butylamine	2.79	55.6	84	3	13
183	Dicyclohexylamine	—	46.9	73	26	1
188	Triethylamine	3.07	19.2	62	7	31
178	Tri-*n*-butylamine	4.09	44.4	74	20	6
193	Pyrrolidine	2.73	16.9	69	3	28
192	Piperidine	2.80	28.4	75	6	19
185	Pyridine	8.85	26.3	69	30	1
184	Aniline	9.42	7.1	30	26	44**
197	Pyrrole	—	7.0	9	3	88
191	Ethylenediamine	4.09	12.6	8	4	88**
202	Hexamethylenediamine	—	34.8	20	5	75
139	Monoethanolamine	4.56	9.1	17	6	77**
140	Diethanolamine	5.05	13.1	3	2	95**
141	Triethanolamine	6.18	11.1	8	3	89**
200	Diethylaminoethanol	—	12.1	60	2	38
199	2-Pyrrolidinone	—	4.1	72	2	26**

* Added amount of amine, 0.01 mol/mol CCl_4; Added amount of $CuCl_2$, 0.0025 mol/mol CCl_4; Reaction time, 2.5 hr; Reaction temperature, 130°C; Molar ratio CCl_4/vinyl chloride, 4.

** Determined by gas chromatography.

The autoclave was then sealed and the air inside was replaced several times by nitrogen gas. The autoclave was heated up to the desired temperature and kept for 2.5 hr.

The reaction conditions were as follows. The molar ratio of carbon tetrachloride to vinyl chloride was 4, cupric chloride 0.0025 mol/mol CCl_4, amine 0.01 mol/mol CCl_4, temperature 130°C and reaction time 2.5 hr.

After the autoclave was cooled to room temperature, the reaction mixture was filtered, washed with water to remove soluble amine hydrochloride and the solvent and carbon tetrachloride were recovered by distillation. The mixture of telomers was fractionated into $n=1$, $n=2$ and $n=3$ fractions by distillation. Each fraction was examined by gas chromatography, infrared and NMR spectroscopy to confirm its structure.

Results

Effect of Amines. Telomerization was carried out in the presence of various amines. The result is shown in Table 1. When the amine with lower value of pK_B is used, the yield of telomers becomes higher. The following order which gives higher yields of telomers should be noted; diethylamine< di-*n*-propylamine<di-*n*-butylamine and *n*-butylamine <tri-*n*-butylamine<di-*n*-butylamine. When amines with two functional groups such as diamines and alkanolamines are used, the yield of telomers becomes lower. The result is inconsistent with that obtained on the telomerization of ethylene with carbon tetrachloride, where the presence of alkanolamines raises the yield of telomers.[7] When the yield of total telomers is high, the composition ratio of the telomer with $n=1$ is also high in most cases. However, some heterocyclic amines such as pyridine, piperidine and pyrrolidine give lower yield of telomers, but higher ratio of telomer with $n=1$.

The effect of added amount of di-*n*-butylamine on the yield of telomers is shown in Fig. 1. We see that the yield of telomers increases rapidly at first, then slowly with the increase of added amounts

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

TABLE 2. EFFECTS OF REACTION TIME ON THE YIELD AND COMPOSITION OF TELOMERS

Run No.	Amine*	$CuCl_2$**	Temp., °C	Time, hr	Yield g/mol CCl_4	Composition (wt%) $n=1$	$n=2$
238	0.01	0.0025	130	1.0	46.8	83	4
239	0.01	0.0025	130	1.5	54.4	83	4
240	0.01	0.0025	130	2.0	55.1	83	4
177	0.01	0.0025	130	2.5	55.6	84	3

* Di-*n*-butylamine, mol/mol CCl_4; Molar ratio CCl_4/vinyl chloride, 4.
** mol/mol CCl_4

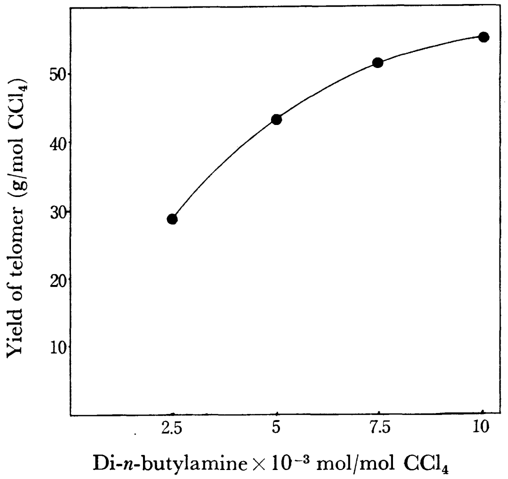

Fig. 1. Effect of added amount of amine on the yield of telomer

Reaction time, 2.5 hr; Reaction temp., 130°C; Molar ratio of CCl_4/VC=4, Added amount of $CuCl_2$: 0.0025 mol/mol CCl_4

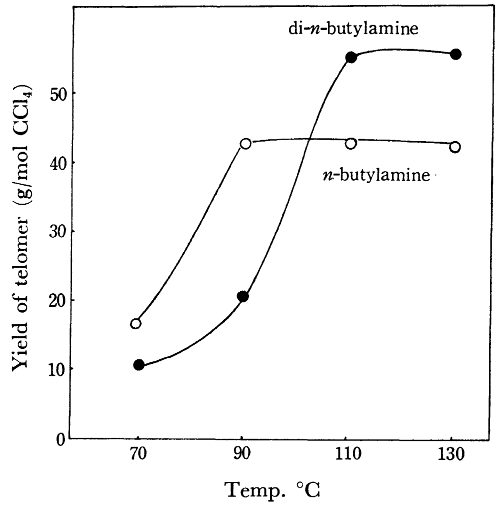

Fig. 2. Effect of temperature on the yield of telomers.

Reaction time, 2.5 hr: Molar ratio of CCl_4/VC=4, Added amount of amine, 0.01 mol/mol CCl_4; Added amount of $CuCl_2$, 0.0025 mol/mol CCl_4

of di-*n*-butylamine.

Effect of Reaction Temperature and Time. The effects of reaction temperature on the yield of telomers when di-*n*-butylamine and *n*-butylamine are used are shown in Fig. 2. The yield of telomers increases abruptly in a relatively low temperature range and shows a maximum at 90 and 120°C in the cases of *n*-butylamine and di-*n*-butylamine, respectively. The composition ratio of the 1 : 1 telomer exhibits a similar behavior.

The effect of reaction time in the system of di-*n*-butylamine and cupric chloride is shown in Table 2. The yield of telomers increases abruptly within 1 hr of the initial stage of reaction. The composition of telomers does not change remarkable during the course of the reaction.

Effect of Solvents. The basicity and ability of complex formation of amines are affected by the solvent. Thus it is probable that telomerization is affected in various stages by addition of solvents. The effect of solvent on the yield and composition of telomers was examined by using mixtures of carbon tetrachloride and various solvents. The

TABLE 3. EFFECTS OF SOLVENTS ON THE YIELD AND COMPOSITION OF TELOMERS*

Run No.	Solvent	Dielectric const.	Yield g/mol CCl_4	Composition (wt%) $n=1$	$n=2$
225	*n*-Heptane	1.92	24.5	67	9
224	Cyclohexane	2.02	50.3	72	6
228	1,4-Dioxane	2.04	42.8	67	17
119	Carbon tetrachloride	2.22	40.1	85	10
223	Benzene	2.27	39.5	75	17
216	*t*-Butyl alcohol	12.5	52.0	83	2
214	1-Butanol	17.1	66.8	73	4
212	2-Propanol	18.3	56.0	73	4
213	Methanol	32.6	43.7	85	10
218	*s*-Butanol	—	39.8	56	3

* Amount of solvent added, 100 m*l*/100 m*l* CCl_4; Amount of *n*-butylamine added, 0.01 mol/mol CCl_4; Amount of $CuCl_2$ added, 0.0025 mol/mol CCl_4; Molar ratio CCl_4/vinyl chloride, 4; Reaction time, 2.5 hr; Reaction temperature, 130°C.

results are shown in Table 3. As shown in this table, the effect of solvent is not remarkable, except for the cases where solvents take part in reactions.

Discussion

The amine-metallic salt initiating systems afford a high yield of lower telomers. This might be due to an effective chlorine-transfer mechanism. Asscher and Vofsi supposed some complexes consisting of cuprous ions and chlorine radicals or cupric ions and chloride ions with coordinated amines for a reaction intermediate to take an essential role in this chlorine-transfer mechanism. Assuming the existence of such complexes the following reaction scheme would follow.

$$\mathrm{M^{(+)}} + n\mathrm{RNH_2} \rightarrow \mathrm{M^{(+)}(RNH_2)}_n$$

$$\mathrm{M^{(+)}(RNH_2)}_n + \mathrm{CCl_4} \rightarrow [\mathrm{M^{(+)}\cdot Cl}](\mathrm{RNH_2})_n + \cdot\mathrm{CCl_3}$$

$$\cdot\mathrm{CCl_3} + \mathrm{CH_2CHCl} \rightarrow \mathrm{CCl_3CH_2CHCl}\cdot$$

$$\mathrm{CCl_3CH_2CHCl}\cdot + [\mathrm{M^{(+)}\cdot Cl}](\mathrm{RNH_2})_n \rightarrow \mathrm{CCl_3CH_2CHCl_2} + \mathrm{M^{(+)}(RNH_2)}_n$$

The result of kinetic treatments based on this scheme is inconsistent with experimental result. As an example, the increasing stability of the complex $[\mathrm{M^{(+)}\cdot Cl}](\mathrm{RNH_2})_n$ gives rise to the increase in the rate of formation of trichloromethyl radicals, and the decrease in the rate of abstraction of chlorine radical from the complex. This conflicts with the result where the increasing yield of total telomers is accompanied by the increasing content of the telomer with $n=1$.

Thus the above reaction scheme should be modified. It seems most probable that the reaction step to form the telomer with $n=1$ takes place in cages stabilized by amines. The reaction scheme is written as follows:

$$\mathrm{M^{(+)}} + n\mathrm{RNH_2} \overset{K_1}{\rightleftharpoons} \mathrm{M^{(+)}(RNH_2)}_n$$

$$\mathrm{M^{(+)}(RNH_2)}_n + \mathrm{CCl_4} \overset{K_2}{\rightleftharpoons} [\mathrm{M^{(+)}Cl\cdot\cdot CCl_3}](\mathrm{RNH_2})_n$$

$$[\mathrm{M^{(+)}Cl\cdot\cdot CCl_3}](\mathrm{RNH_2})_n + \mathrm{CH_2CHCl} \xrightarrow{k_1} \mathrm{CCl_3CH_2CHCl_2} + \mathrm{M^{(+)}(RNH_2)}_n$$

$$[\mathrm{M^{(+)}Cl\cdot\cdot CCl_3}](\mathrm{RNH_2})_n \xrightarrow{k_2} (\mathrm{M^{(2+)}Cl^-})(\mathrm{RNH_2})_n + \cdot\mathrm{CCl_3}$$

$$\cdot\mathrm{CCl_3} + \mathrm{CH_2CHCl} \xrightarrow{k_3} \mathrm{CCl_3CH_2CHCl}\cdot$$

$$\mathrm{CCl_3CH_2CHCl}\cdot + \mathrm{CH_2CHCl} \xrightarrow{k_4} \mathrm{CCl_3(CH_2CHCl)_2}\cdot$$

$$\mathrm{CCl_3CH_2CHCl}\cdot + \mathrm{CCl_4} \xrightarrow{k_5} \mathrm{CCl_3CH_2CHCl_2} + \cdot\mathrm{CCl_3}$$

The following reactions are induced by trichloromethyl radicals:

$$\cdot\mathrm{CCl_3} + \cdot\mathrm{CCl_3} \xrightarrow{k_6} \mathrm{C_2Cl_6}$$

$$\cdot\mathrm{CCl_3} + \mathrm{RNH_2} \xrightarrow{k_7} \mathrm{R\dot{N}H} + \mathrm{CHCl_3}$$

$$\mathrm{R\dot{N}H} + \mathrm{CCl_4} \xrightarrow{k_8} \mathrm{RNClH} + \cdot\mathrm{CCl_3}$$

$$\mathrm{RNClH} + \mathrm{RNH_2} \xrightarrow{k_9} \mathrm{R'CHNH} + \mathrm{RNH_3Cl}$$

By kinetic treatment of this reaction scheme, the following formulas are derived on the assumption that reaction intermediate $\cdot\mathrm{CCl_3}$, $\mathrm{CCl_3CH_2CHCl}\cdot$ and $\mathrm{R\dot{N}H}$ are in stationary states.

If the condition $k_3k_4[\mathrm{V}]^2/(k_4[\mathrm{V}]+k_5[\mathrm{C}])<4k_2k_6\times[\mathrm{com}]$ is satisfied, the rate of formation of the telomer with $n=1$ is given by

$$\frac{\mathrm{d}[\mathrm{CCl_3CH_2CHCl_2}]}{\mathrm{d}t} = k_1[\mathrm{V}][\mathrm{com}] + \frac{k_2{}^{1/2}k_3k_5[\mathrm{C}][\mathrm{V}]}{k_6{}^{1/2}(k_4[\mathrm{V}]+k_5[\mathrm{C}])}[\mathrm{com}]^{1/2} \qquad (1)$$

and the rate of formation of the telomers with $n\geq 2$, by

$$\frac{\mathrm{d}[\mathrm{CCl_3(CH_2CHCl)}_n\mathrm{Cl}]}{\mathrm{d}t} = \frac{k_2{}^{1/2}k_3k_4[\mathrm{V}]^2}{k_6{}^{1/2}(k_4[\mathrm{V}]+k_5[\mathrm{C}])}[\mathrm{com}]^{1/2} \qquad (2)$$

On the other hand, if the reverse condition

$$k_3k_4[\mathrm{V}]^2/(k_4[\mathrm{V}] + k_5[\mathrm{C}]) > 4k_2k_6[\mathrm{com}]$$

is satisfied, the corresponding equations are obtained as follows:

The rate of formation of the telomer with $n=1$,

$$\frac{\mathrm{d}[\mathrm{CCl_3CH_2CHCl_2}]}{\mathrm{d}t} = [\mathrm{com}]\left(k_1[\mathrm{V}]+\frac{k_2k_5[\mathrm{C}]}{k_4[\mathrm{V}]}\right) \qquad (3)$$

and the rate of formation of the telomers with $n\geq 2$,

$$\frac{\mathrm{d}[\mathrm{CCl_3(CH_2CHCl)}_n\mathrm{Cl}]}{\mathrm{d}t} = k_2[\mathrm{com}] \qquad (4)$$

In these equations, the following abbreviations are used,

V: $\mathrm{CH_2{=}CHCl}$, C: $\mathrm{CCl_4}$

and com: $[\mathrm{M^{(+)}Cl\cdot\cdot CCl_3}](\mathrm{RNH_2})_n$

and the concentration of this complex is

$$[\mathrm{com}] = K_1K_2[\mathrm{M^{(+)}}][\mathrm{CCl_4}][\mathrm{RNH_2}]^n \qquad (5)$$

The cage complex as a reaction intermediate would be formed through the interaction of chlorine radical with metal ion and the stabilization by coordinated amines. The attack of vinyl chloride on this cage complex affords tetrachloropropyl radical, and the resulting radical instantly abstracts chlorine radical from the complex. The presence of such cage complexes greatly decreases activation energy for the insertion of vinyl chloride into the $\mathrm{Cl{-}CCl_3}$ bond.

This scheme gives a plausible explanation for the effect of amines as shown in Table 1. The increasing basicity of amines enhances the stabilization of cage complexes and decreases the activation energy for the insertion reaction. On the other hand, bifunctional amines possess strong chelating ability to Cu(II) ions and, therefore, make the decomposition of cage complexes feasible. Bulkiness of amines do not show any steric hindrance, for the site of reaction is not on the metallic ions and mechanically stabilize the cage complex. This is the reason why the amine with two or three long alkyl chains is effective.

The slight effect of solvents is understandable if the reaction proceeds primarily in cages. However, the increase in dielectric constants might decrease the stability of cages.

Of the alternative conditions mentioned above, the latter would be satisfied in most cases, because k_2 and [com] are relatively small. In this case, from Eqs. (1) and (2), the product ratio of the telomers with $n=1$ and $n \geq 2$ is given by

$$\frac{[\mathrm{CCl_3CH_2CHCl_2}]}{[\mathrm{CCl_3(CH_2CHCl)}_n\mathrm{Cl}]} = \frac{k_1}{k_2}[\mathrm{V}] + \frac{k_5[\mathrm{C}]}{k_4[\mathrm{V}]} \simeq \frac{k_1}{k_2}[\mathrm{V}] \tag{6}$$

Table 1 shows that the ratio $k_1[\mathrm{V}]/k_2$ is 3—5.

The high reaction rate observed in this system supports the mechanism. In telomerization of vinyl chloride and chloroform, the main product of the 1 : 1 adducts is $\mathrm{CCl_3CH_2CH_2Cl}$ when benzoyl peroxide or azobisisobutyronitrile is used as an initiator, but the main product is $\mathrm{CHCl_2CH_2CHCl_2}$ when the amine-$\mathrm{CuCl_2}$ is used.[8] This observation supports the mechanism proposed in this paper. However, further examination would be necessary in order to establish this mechanism. The EPR measurement on copper ion-amine-carbon tetrachloride systems and a detailed analysis on the distribution of products in the reaction of vinyl chloride with chloroform are now in progress. The results will be presented in the near future.

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8) T. Asahara, C. C. Wu, *Kogyo Kagaku Zasshi*, **70**, 1197 (1967).