Telomerization of Ethylene and Carbon Tetrachloride Initiated by Amines*

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Summary: The telomerization of ethylene and carbon tetrachloride is initiated by various amines in the absence of metallic salts in the stainless steel autoclave. In this reaction the initiating efficiency of amines depends upon their basicity and chemical structure. In general, strong bases are excellent initiators but the strength of the basicity of amines gives only a small effect on the composition of the telomer produced. The temperature of the reaction and the dielectric constant of the solvent have pronounced effects on this reaction process. And from these observation and the other experiments, the distinction between the present initiating system and the redox system of amine-metallic salt was discussed on the basis of the reaction mechanism involved.

Introduction

In our previous work¹⁾ the catalytic system of metallic salt and ethanolamine was systematically investigated as an initiator for the telomerization reaction of ethylene and carbon tetrachloride, and it was eventually found that this reaction could be initiated by alkanolamine alone in the stainless steel autoclave. From this observation, we assumed that the metallic salt was not the reagent necessary for the formation of a $\cdot\text{CCl}_3$ radical and that the radical could be produced by the reaction of carbon tetrachloride and amine under a catalytic influence of the metallic wall of the autoclave. Several investigators²⁾ reported that the interaction between carbon tetrachloride and amine was strongly catalyzed by metallic copper to give amine hydrochloride.

In the meantime, close correlation could not be found between the composition of the produced telomer and the amount of added copper salts in this telomerization. This fact would suggest that the copper complex $\text{Cu}^+(\text{Cl})$, produced from the oxidation of cuprous salt by carbon tetrachloride under the catalytic influence of alkanolamine, did not play

such a significant role in the formation of telomers as described in Vofsi' paper³⁾, which reads as follows:

In order to clarify some questions proposed by these observations, we have undertaken a detailed research on the telomerization of ethylene and carbon tetrachloride initiated by amines.

The objective of the present paper is to disclose what effects the basicity and the chemical structure of amines exerts upon the yield and the composition of the telomers produced, and then to discuss the differences between the catalytic activity of single amines and that of the amine-metallic salt system.

Experimental

Materials: All amines used were "guaranteed grade" products. Ethylene of a 99% purity was used. Carbon tetrachloride was purified as described in our previous paper¹⁾. "Chemically pure grade" tertiary butanol was used as an inert solvent in order to increase the molar ratio of ethylene to carbon tetrachloride in a reaction system.

Apparatus and Procedure: The autoclave of a 502 ml capacity was made of SUS 27

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stainless steel and fitted with a magnetic stirrer.

A solution of a given amount of amine in 200 cc of the mixture (1:1) of carbon tetrachloride and tertiary butanol was introduced into the autoclave. After the autoclave was closed and the air was displaced by ethylene, the autoclave is heated and the reaction was carried out for 4 hours at a given temperature. The reaction product was washed with acidic water to remove soluble amine hydrochloride and treated for the analysis of the produced telomer as described in our previous paper¹⁾.

Results and Discussion

Effect of the added metal

The metallic wall of the autoclave could not initiate the telomerization reaction of ethylene and carbon tetrachloride in the range of 40°C and 120°C., if no amine was introduced into this system.

However, this reaction was broken out at 160°C or more through the thermal decomposition of carbon tetrachloride, but the conversion of carbon tetrachloride was small (lower than 10%) and more than 50% of the produced telomers was dehydrochlorinated to α, α, ω -trichloroalkene⁴⁾. The telomerization reaction also did not proceed in the presence of a catalytic amount (0.1 mole%) of cuprous, cupric, ferrous and ferric chloride up to the temperature of 100°C.

The appreciable amount of a telomer mixture could be obtained only after many hours of reaction (15~20 hours) in the presence of a large amount (5 mole% or more) of the metallic salts as described above under high temperatures of reaction (100~145°C)⁵⁾.

As metallic aluminum was used as a packing plate for the autoclave and it was reported⁶⁾ that it reacts with carbon tetrachloride at 76.7°C to give hexachloroethane, the effect of granular metallic aluminum on the telomerization was examined in the absence or the presence of *n*-butyl amine. If the amine was absent, the telomerization reaction did not proceed even at 90°C for 4 hours. In the presence of the amine (6×10^{-2} mole), the yield of the produced telomer (95.0 g) was not affected at all by the addition

of granular aluminum (0.1 g-atom) at 90°C for 4 hours under the ethylene pressure of 64 kg/cm². From these observations, it was concluded that metallic aluminum was inactive to carbon tetrachloride or the amine~carbon tetrachloride system under the above described condition, as being shown also in Beichl's work⁷⁾.

Effect of the basicity of amines

The interaction or, presumably, the complex formation between amine and carbon tetrachloride was reported to be dependent of the basicity of amines⁸⁾. By assuming that the initiating radical $\cdot\text{CCl}_3$ of the telomerization reaction is produced by the thermal disruption of the intermediate compound of amine and carbon tetrachloride and that this intermediate formation is related to the basicity of amines, a close relation is expected between the basicity of amine and the yield of the telomer. In fact, Table 1 shows that

Table 1 Influence of the basicity of amine on the yield of telomer*

Amine	pK _B value	Yield of Telomer, g/100 cc of CCl ₄
<i>n</i> -butyl amine	3.39	18.1
<i>n</i> -hexyl amine	3.36	12.8
<i>n</i> -dodecyl amine		15.1
<i>di</i> -ethyl amine	3.01	Trace
<i>di</i> -propyl amine	3.10	Trace
<i>di</i> -butyl amine	2.79	33.5
Ethylene diamine	4.07	5.0
Hexamethylene diamine		0
Pyrrolidine	2.73	16.6
Piperidine	2.80	24.5
Cyclohexyl amine	3.31	20.0
Morpholine	5.64	15.9
Pyrrolidinone		Trace
Benzyl amine	4.63	1.8
Pyridine	8.85	0
Aniline	9.42	0
<i>N, N</i> -dimethyl aniline		0
Pyrrole		0
Monoethanol amine	4.56	194.2
Diethanol amine	5.05	92.9
Triethanol amine	6.18	117.9

* Concentration of amine: 6×10^{-2} mole/1 mole of CCl₄
 Reaction press. : 50~57 kg/cm²
 Reaction temp. : 90°C
 Reaction time : 4 hours
 Volume Ratio : 0.4

such a close relation exists in the telomerization initiated by amines. As shown in Table 1, aromatic amines have only small or completely no effect on this reaction because of their low basicity, and alicyclic amines have an excellent initiating activity owing to their structural saturation. Alkanolamines were distinguished initiators in spite of their relatively low basicity. Their excellent initiating activity results presumably from their hydroxyl group, for it was said that this group has the ability of the co-ordination in a non-aqueous medium⁹⁾.

On the contrary, the composition of the produced telomer was merely affected by the basicity of amines, as shown in Fig. 1.

Fig. 1 Influence of pK_B value of amine on the content of telomer

Effect of the chemical structure of amines

The effect of the chemical structure of amines on the telomerization was shown in Figs. 2 and 3.

Figure 2 shows that the steric factor of amines gives a more pronounced effect on this reaction than their basicity and that primary amines have an unusually larger initiating activity than secondary and tertiary amines. Moreover, Figure 3 shows that branched amines are inferior to the normal ones in their initiating ability. The amines, which have the same number e.g., 6 of the carbon atoms, have the increasing catalytic activities in the following order:

- dipropyl (0%, 3.10)
- < triethyl (1.7%, 3.07)
- < *n*-hexyl (5.1%, 3.36)

Fig. 2 Influence of chemical structure on the yield of telomer

Fig. 3 Influence of chemical structure on the yield of telomer

The first numerical values in parentheses indicate the percent conversion of carbon tetrachloride in the telomerization at 90°C for 4 hours at 52 kg/cm² of ethylene pressure, and the second figures show the pK_B value of the amines. All these results suggest that the pronounced steric effect of amines should originate from the co-ordination of the amine with a bulky molecule of carbon tetrachloride.

Effect of the concentration of amine

The yield of the telomer is depended upon the amount of the added amine, as shown in Fig. 4. There is observed a maximum initiating efficiency of amines at their optimum concentration, and at higher concentrations the efficiency decreases of the amount of amine. This behavior was also observed in

Fig. 4 Influence of amine concentration on the yield of telomer

the initiating system of the triethanolamine ~copper salt¹⁾, and should be ascribed to the increasing probability of the recombination of the $\cdot\text{CCl}_3$ radical and the resulting decrease of the initiating efficiency, with the increase of the amine concentration.

Effect of the reaction temperature

The influence of the reaction temperature on the yield of telomers is shown in Fig. 5, which indicates that alkanolamine has its maximum catalytic activity even at the lower temperature of reaction and loses its activity rather abruptly with the increase of the temperature. On the other hand, the initiating activity of aliphatic and alicyclic amines increases suddenly at their optimum temperature of reaction.

The basicity of amine decreases in a re-

gular manner with the increase of temperature¹⁰⁾.

Therefore, it is anticipated that the coordination bond between amine and carbon tetrachloride becomes more unstable with the higher reaction temperature. On the other hand, Russian investigators¹¹⁾ reported that the velocity of the telomer formation coincided with that of the thermal decomposition of azobisisobutyronitrile used as an initiator.

It would seem on the basis of these results that the steep rise in the yield of telomers, as shown in Fig. 5, results from the sudden thermal decomposition of the intermediate compound of amine and carbon tetrachloride, followed by the rapid formation of the initiating radical $\cdot\text{CCl}_3$ through this disruption of the said intermediate compound.

In Fig. 5, it may be noted that the strong bases, for example, piperidine ($pK_B=2.80$), have the higher temperature of a steep rise in the telomer formation than the weak bases such as *n*-butyl ($pK_B=3.39$) and *n*-hexyl ($pK_B=3.36$) amines. This behavior suggests that the strong base requires more energy for the disruption of the intermediate compound of amine and carbon tetrachloride than the weak base.

Effect of added solvent

In the previous section, we described the pronounced influence of the basicity of amine on the yield of telomers. The basicity of amines varies with the medium in which they exist. Moreover, solvents should reveal their inhibitory action and transferring acti-

Fig. 5 Influence of reaction temperature on the yield of telomer

Table 2 Influence of dielectric constant of aprotic solvent on the yield and composition of telomer*

Solvent	Dielectric const. of solvent	Yield of telomer, g/100 cc of CCl ₄		Content of C _{≤6} telomer, wt. %	
		Monoethanol amine	<i>n</i> -Butyl amine	Monoethanol amine	<i>n</i> -Butyl amine
<i>n</i> -heptane	1.92	5.5	29.0	—	70.0
Cyclohexane	2.02	13.2	36.0	88.6	85.4
1, 4-dioxane	2.04	68.1	66.0	75.9	88.7
Carbon tetrachloride	2.22	22.5	55.5	80.9	91.1
Tetrahydrofuran	7.3	28.7	81.0	68.8	82.0
Acetone	20.7	2.0	8.9	—	—
Dimethylformamide	26.6	73.5	26.0	88.3	89.9
Benzene	2.27	12.0	9.5	—	—
Toluene	2.38	6.0	9.5	—	—
Chlorobenzene	5.62	5.0	4.0	—	—
Nitrobenzene	34.8	0	6.5	—	—

* Amount of solvent added: 100 cc/100 cc of CCl₄
 Amine concentration : 6×10^{-2} mole/1 mole of CCl₄
 Reaction press. : 60~69.5 kg/cm²
 Reaction temp. : 90°C
 Reaction time : 4 hours
 Volume ratio : 0.4

Reaction pressure : 61~70 kg cm²
 Reaction temperature : 90°C
 Reaction time : 4 hrs.
 Concn. of amine : 6×10^{-2} mole/1 mole of CCl₄
 Volume ratio : 0.4
 Amount of solvent added : 100 cc/100 cc of CCl₄
 1 : *o*-cresol   5 : cyclohexyl alcohol
 2 : phenol   6 : *n*-butyl alcohol
 3 : *t*-butyl alcohol   7 : *iso*-propyl alcohol
 4 : benzyl alcohol   8 : methyl alcohol

Fig. 6 Influence of dielectric constant of hydroxylic solvent on the yield of telomer

vity. Therefore, the effect of the solvent on the yield of telomers is interesting for investigation. The results were shown in Fig. 6 and Table 2. In these experiments, 100 cc of solvents was added to 100 cc of carbon tetrachloride. Fig. 6 shows the dielectric constant of the solvents, when hydroxylic solvents were used. Generally,

the higher dielectric constants the solvents have, the more yields of telomers is obtained.

When aprotic solvents were used, such a regular relation was not found, as shown in Table 2.

Tertiary butanol is an excellent solvent for this telomerization, probably because it has no active hydrogen atom at the α -position to the hydroxylic group. Aromatic solvents are generally inadequate for this reaction. Bagdasarian¹²⁾ explained the inhibitive action of the aromatic solvent in the polymerization of vinyl monomers through the formation of the following stable intermediate radical:

Distinction between the single amine catalyst was discussed and the redox system of amine~metallic salt.

In the telomerization of ethylene and carbon tetrachloride, we could not find any essential differences between the single amine catalyst and the redox system of amine~metallic salt, as reported in Figs. 1 and 3 of our previous paper¹⁾. The copper complex Cu⁺(Cl) in equations (1) and (2) do not reveal its inherent activity of Cl-ligand transfer in the formation of telomers.

Asscher³⁾ proposed an explanation for such an activity in the addition of chloroform to octane-1 and proposed the following scheme:

If ethylene acts as olefine in this reaction, the telomer produced should be α, α, ω -trichloroalkane.

On the contrary, the telomer of α, α, α -trichloroalkane was obtained in the telomerization initiated by peroxide through the following Kharash's mechanism¹³⁾:

In order to make clear the reaction mechanism in the present catalysis system, we carried out the telomerization of ethylene and chloroform, using the single amine or the redox system of amine+metallic salt as the initiator, under the following condition: 6×10^{-2} mole of *n*-butyl amine was used as initiator, and 5×10^{-3} mole of CuCl was admixed to the above amine in case of a redox catalyst. Telomerization was carried out at 90°C for 4 hours under the ethylene pressure of 83~70 kg/cm². From 200 cc of CHCl₃, 35 g of the telomer (I) was obtained by the redox catalyst, and 59 g (II) was obtained by the single amine. These telomers were gaschromatographed at 190°C in a 3-m column using silicone oil as the stationary phase. The result was that the telomer (I) showed only a single main peak at the retention time of 2.70 min. and the telomer (II) showed three peaks at the retention times of 1.85, 2.95 and 5.21 min. Infrared spectra of these telomers showed that the telomer (II) had two characteristic absorptions of the CCl₃ group at 775 and 695 cm⁻¹ and that the telomer (I) showed a strong absorption at 770 cm⁻¹ and a medium absorption at 642

cm⁻¹. Absorption at 642 cm⁻¹ may be assigned to the vibration of the terminal C-Cl bond. The telomer (II) has no absorption bands between 690 and 600 cm⁻¹.

From these observations, it is concluded that the telomer (I) is α, α, ω -trichloroalkane and the telomer (II) is α, α, α -trichloroalkane. Therefore, in a redox system, the metallic salt is participated in this reaction at the following two stages: (a) Cl-abstraction from chloroform and (b) Cl-ligand transfer to the growing radical. But, in case of a single amine catalyst, such a behavior was not observed and the H-abstraction from chloroform proceeds as normally as in the peroxide initiating system, presumably through the transient hydrogen-bonding state between chloroform and amine. In other words, metallic salt do not play any role in the single amine catalyst system.

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