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# The Ionic Telomerization of Conjugated Diene Compounds. III. The Effects of the Addition of Lewis Bases on the Cationic Telomerization of Butadiene with Its Hydrochlorides

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The effects of the addition of several oxygen- and nitrogen-containing compounds on the cationic telomerizations of butadiene with its hydrochloride were investigated. The addition of both acetonitrile and ethyl ether to an ethyl bromide solution of ferric chloride or a methylene chloride solution of titanium tetrachloride resulted in large decreases in the catalytic activities of the solutions at low temperatures. On the other hand, the addition of nitroethane to an ethyl bromide solution of aluminum chloride increased the activity of the catalyst, although the addition of nitrobenzene decreased it. The addition of ethyl ether to ferric chloride or titanium tetrachloride led to the formation of telomers with lower molecular weights and larger degrees of unsaturation, whereas a nitroethane - aluminum chloride catalyst gave telomers with higher molecular weights. The monomolecular addition complexes of several Lewis acids and Lewis bases were isolated, and the catalytic abilities of the complexes in halogenated hydrocarbons were investigated. The structures of the higher telomers were analyzed and will be discussed.

The telomerizations of butadiene with its hydrochloride (crotyl chloride) in the presence of Lewis acids have been investigated.[1,2] It has been found that the telomerizations in ethyl ether and nitrobenzene gave telomers with lower average molecular weights and higher degrees of unsaturation than those obtained in halogenated hydrocarbons.

It is known that the Lewis acids form addition complexes with many of the oxygen- and nitrogen-containing compounds and that the complex formation results in a decrease in acidities. These compounds are useful as solvents for alkylation and telomerization because of their strong solvent power and because they suppress undesirable side reactions. However, the actual chemical species in the solution is not clear, and the free acids and the addition compounds probably exist in an equilibrium proportion in these solvents. In order to clarify interactions between the Lewis acids and the solvents, and in order to evaluate the catalytic activities of the adducts, the effects of the addition of several oxygen- and nitrogen-containing compounds to the reaction mixtures were investigated. In this connection, it is important to investigate the effects of the addition of Lewis bases on the molecular weight and the yield of products.

## Experimental

**Chlorobutenes.** The preparation and the purification of butadiene hydrochlorides, which were used as telogens, were described in a previous paper.[1] A mixture of products consisting of about 80% 1-chloro-2-butene and 20% 3-chloro-1-butene was used for telomerizations. It has been confirmed that the two isomers give the same product when they are used as telogens.

**The Catalyst Solutions.** The purification of the solvents and the additives were described in previous papers.[1,2] Aluminum chloride, ferric chloride, and titanium tetrachloride of the first grade were used as catalysts without further purification. The catalyst solutions were prepared by adding Lewis bases to the solutions of metal halides in ethyl bromide or methylene dichloride. In some cases, equimolecular addition complexes of ferric chloride or titanium tetrachloride with oxygen- or nitrogen-containing solvents were isolated by evaporating the solutions under reduced pressure. These complexes are solid or semisolid, and the weight analyses indicate that they involve nearly equimolecular proportions of acids and solvents. Solutions of some of these complexes in ethyl bromide or methylene dichloride were used as the catalyst solutions for the telomerizations.

**Telomerization.** The apparatus and the method of telomerization are the same as those which have been described in a previous paper.[1] The reactions were stopped by the addition of a small amount of pyridine. The reaction mixtures were then washed with a dilute sodium carbonate solution, a dilute hydrochloric acid solution, and water, and dried on unhydrous sodium sulfate. Then the solvent, the unreacted butadiene, and crotyl chloride were evaporated under reduced pressure. It has been confirmed that the loss of butadiene during the telomerization is less than 5% of the initial amount at 15°C. The monomolecular adducts of butadiene and crotyl chloride were isolated by vacuum distillation; they had a boiling point of 52—65°C/10 mmHg.

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[1] T. Asahara and H. Kise, This Bulletin, **39**, 2739 (1966).
[2] T. Asahara and H. Kise, *ibid.*, **40**, 1941 (1967).

**The Analyses of the Telomers.** The molecular weights of the telomers were measured at 37°C with a Mechrolab vapor-pressure osmometer, model 301 A. The solvent was benzene or toluene, while squarane or DDT was used as the standard material. The degree of unsaturation of the telomers was determined by the Wijs method in a carbon tetrachloride solution. The infrared spectra of the telomers were taken with a Hitachi-Perkin Elmer double-beam grating spectrophotometer, model 125.

## Results and Discussion

**1) The Addition of Acetonitrile to Ferric Chloride and Titanium Tetrachloride.** The additions of acetonitrile to an ethyl bromide solution of ferric chloride and to a dichloromethane solution of titanium tetrachloride cause decreases in the catalytic activities of these solutions, as is shown in Fig. 1. The solutions were red-brownish and yellow respectively.

It is obvious that acetonitrile acts as a retarder for both the catalysts, and that the activity of titanium tetrachloride is suppressed a little more than that of ferric chloride by the addition of the same amount of acetonitrile. The average molecular weights of the telomers also decrease upon the addition of acetonitrile; this may be attributed to a decrease in the conversion of the reaction.

**2) The Addition of Nitroethane and Nitrobenzene to Aluminum Chloride.** The effects of the addition of nitroethane or nitrobenzene on the telomerization catalyzed by aluminum chloride in ethyl bromide are shown in Fig. 2. The ethyl bromide solution of aluminum chloride is yellow; no change in color is observed upon the addition of nitroethane or nitrobenzene. However, the reaction mixture which does not contain nitroethane is red-brownish; the addition of nitroethane causes it to turn yellow. In addition, a induction period is observed when nitroethane is introduced into the catalyst solution.

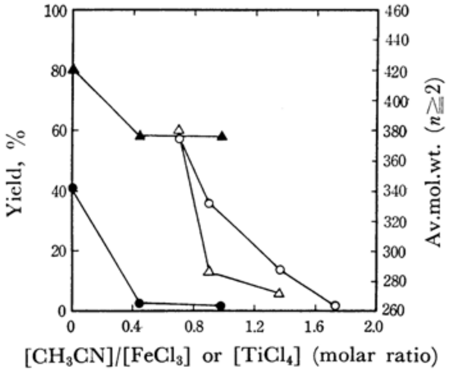


Fig. 1. Effects of addition of acetonitrile.
[CC]/[BD]=1.00
Reaction temp., −30—−35°C
Reaction time, 4 hr
○ Yield. Catalyst, FeCl$_3$
△ Av. mol. wt. Catalyst, FeCl$_3$
[FeCl$_3$]/[BD]=1.50×10$^{-2}$
● Yield. Catalyst, TiCl$_4$
▲ Av. mol. wt. Catalyst, TiCl$_4$
[TiCl$_4$]/[BD]=1.50×10$^{-2}$

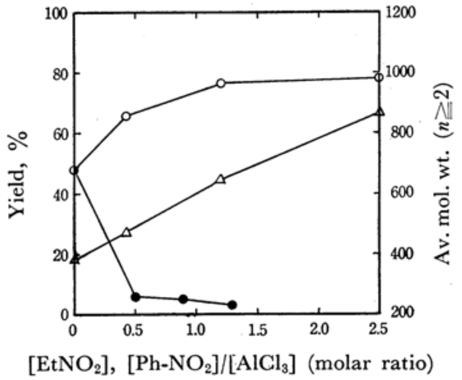


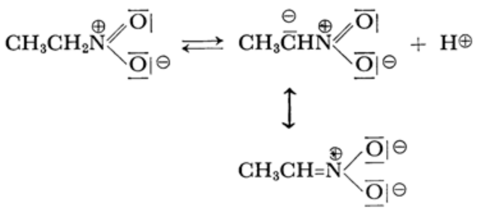
Fig. 2. Effects of addition of nitroethane and nitrobenzene.
[CC]/[BD]=1.00 [AlCl$_3$]/[BD]=1.00×10$^{-2}$
Reaction temp., −30—−40°C
Reaction time, 3 hr
○ Yield. Additive, nitroethane
△ Av. mol. wt. Additive, nitroethane
● Yield. Additive, nitrobenzene

Aluminum chloride and nitro-compounds form addition complexes, which are expected to result in a decrease in the activity of aluminum chloride.

$$AlCl_3 + xRNO_2 \rightarrow AlCl_3\cdot(RNO_2)_x \qquad (1)$$

Actually, however, the addition of nitroethane acceralates the reaction and gives telomers with higher average molecular weights than those obtained by aluminum chloride alone. On the other hand, when nitrobenzene is used in place of nitroethane, both the yield and the average molecular weight of the telomer are suppressed (Fig. 2).

The aliphatic nitro-compounds are considered to act as Brönsted acids because of the strong inductive effect of the nitro-group and the resonance stabilization of the conjugate base. Nitroethane, for example, dissociates in the solvents thus:



$$CH_3CH_2\overset{\oplus}{N}(=O)O^{\ominus} \rightleftarrows CH_3\overset{\ominus}{C}H\overset{\oplus}{N}(=O)O^{\ominus} + H^{\oplus} \updownarrow CH_3CH{=}\overset{\oplus}{N}(O^{\ominus})O^{\ominus} \qquad (2)$$

The rate and the equilibrium constant of the dissociation of nitroethane are small ($2.2\times10^{-6}$ min$^{-1}$ and $2.5\times10^{-9}$ respectively in water at 25°C).[3] However, the coordination of the Lewis acid to the

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[3] R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

nitro-group may cause an increase in the ability of proton donation. The addition of the above proton to butadiene could initiate the telomerization, causing telomers of the same structure to be obtained. On the contrary, nitrobenzene, which has no $\alpha$-hydrogen atom, acts only as a Lewis base and forms a equimolecular addition complex with aluminum chloride, resulting in a lowering of the catalytic ability of the acid. At ordinary temperatures, however, ferric chloride and aluminum chloride have considerable catalytic abilities in nitrobenzene as well as in ethyl ether.[2)]

**3) The Addition of Ethyl Ether to Ferric Chloride and Titanium Tetrachloride.** The results of telomerizations catalyzed by a methylene dichloride solution of titanium tetrachloride are shown in Fig. 3. The addition of ethyl ether to the catalyst solution causes a coloration into yellow, indicating the formation of a complex between titanium tetrachloride and ethyl ether. Both the yield and the average molecular weight of the telomers are suppressed by the addition of ether. The decrease in the average molecular weight is followed an increase in the amount of the monoadditional product of butadiene and crotyl chloride (Table1).

Ethyl ether has a basicity comparable to that of crotyl chloride and competes with it for the complex formation with acids. The formation of telomers of low-average molecular weights may be attributed to the suppression of the retelomerization of the telomers once formed and/or to some side reactions such as branching, and to an increase in the chain-transfer constants of reactions. The fact that the residual unsaturations of telomers increase with an increase in the amount of ether added indicates a suppression of branching and cyclization.

Moreover, the molecular weights of telomers depend on the relative rates of chain transfer and propagation. Without ether, titanium tetrachloride in ethyl bromide or in methylene dichloride gives telomers with average molecular weights much higher than with ether at nearly the same conversions of reaction. This indicates that the chain-transfer constant is affected also by the additives which are considered to enclose the growing cation.

The temperature effects on the telomerizations catalyzed by $FeCl_3$-$Et_2O$ and $TiCl_4$-$Et_2O$ are shown in Fig. 4. The lower activity of $TiCl_4$-$Et_2O$ suggests an extensive association between titanium tetrachloride and ethyl ether. This is comparable to the fact that titanium tetrachloride in a mixed solvent of ethyl ether and methylene dichloride is

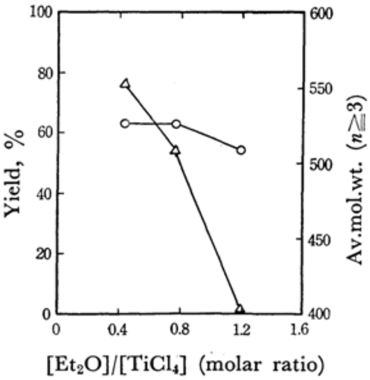

Fig. 3. Effects of addition of ethyl ether.
$[CC]/[BD]=1.00$ $[TiCl_4]/[BD]=1.00\times10^{-2}$
Reaction temp., 5—10°C
Reaction time, 4 hr
○ Yield △ Av. mol. wt.

TABLE 1. THE EFFECTS OF ADDITIONS OF ETHYL ETHER ON STRUCTURES OF TELOMERS

| $[Et_2O]/[TiCl_4]$[a)] | Total yield % | 1-1 adduct % | Av. mol. wt.[b)] | $\frac{I_{ob}}{I_{th}}$, % | $a$, % | $b$, % | $c$,[c)] % |
|---|---|---|---|---|---|---|---|
| 0 | 60.9 | 11.1 | 782 | 46.4 | — | — | — |
| 0.426 | 63.0 | 5.7 | 543 | 49.3 | 59.2 | 25.9 | 14.9 |
| 0.758 | 63.1 | 9.8 | 509 | 53.3 | 62.1 | 24.5 | 13.4 |
| 1.19 | 54.6 | 15.6 | 403 | 60.6 | 67.0 | 20.8 | 12.2 |
| $[Et_2O]/[FeCl_3]$ | | | | | | | |
| 0 | 65.8 | 13.9 | 527 | — | 53.9 | 33.0 | 13.1 |
| 1.00 | 46.0 | 25.9 | 330 | 66.9 | — | — | — |
| 1.00 | 70.8 | 9.4 | 416 | 54.6 | — | — | — |
| 1.00 | 71.3 | 10.6 | 427 | 52.3 | 60.2 | 26.5 | 13.3 |
| ∞ | 65.1 | 23.3 | 307 | 65.8 | 69.7 | 17.7 | 12.6 |

Methylene dichloride and ethyl bromide were used as solvents for titanium tetrachloride and ferric chloride respectively.

a) Molar ratio.

b) The average molecular weight of the telomers other than 1-1 adduct of butadiene and crotyl chloride.

c) *a*, *b* and *c* represent the proportion of propagation, grafting (branching) and cyclization respectively. These values were calculated by the method described in Ref. 1.

TABLE 2. PROPERTIES AND CATALYTIC ACTIVITIES OF COMPLEXES

| Lewis acid | Lewis base | Weight of complex[a) %] | Appearance | Catalytic activity[b)] |
|---|---|---|---|---|
| $FeCl_3$ | EtOH | 118.3 | Yellow solid | 15.4 |
| $FeCl_3$ | *i*-PrOH | 106.0 | Red-brownish semisolid | — |
| $FeCl_3$ | $Et_2O$ | 98.1 | Red-brownish semisolid | 36.8 |
| $FeCl_3$ | Acetone | 102.4 | Red-brownish semisolid | 14.5 |
| $FeCl_3$ | $Ph\text{-}NO_2$ | 113.1 | Red-brownish semisolid | 9.1 |
| $TiCl_4$ | $Et_2O$ | 104.8 | Yellow solid | 26.5 |

a) The weight percentage of complexes based on the theoretical value of $x=1$ in Eq. 3.

b) (Yield, %)/(Time, min) ([Catalyst]/[BD]). Reaction temperatures are 0—15°C.

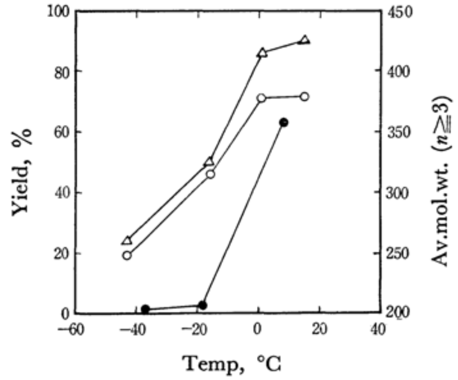

Fig. 4. Effects of reaction temperature.
Reaction time, 4 hr
○ Yield. Catalyst, $FeCl_3$
△ Av.mol.wt. Catalyst, $FeCl_3$
$[Et_2O]/[FeCl_3]=1.00$
$[FeCl_3]/[BD]=1.50\times10^{-2}$
● Yield. Catalyst, $TiCl_4$
$[Et_2O]/[TiCl_4]=1.00$
$[TiCl_4]/[BD]=1.00\times10^{-2}$

inactive, even at room temperature, whereas ferric chloride in ethyl ether shows considerable catalytic ability under the same conditions.[2)]

**4) The Isolation of the Complexes and Their Catalytic Activities.** In general, the additions of nitrile, nitro, and ether compounds to a solution of metal halides leads to the formation of complexes as follows:

$$MX_n + xB \rightarrow MX_n\cdot B_x \qquad (3)$$

$MX_n$: Metal halide
B: Lewis base

In order to evaluate $x$, several complexes were isolated by evaporating the metal halide solutions in the Lewis bases under reduced pressure until the weights of the residues reached constants. The weights of the residues indicate that they consist of metal halides and Lewis bases in nearly equimolecular proportions (Table 2).

The deviations from the round number may be due to remaining solvents. The complexes are solid or semisolid with low melting points, and the halogenated hydrocarbon solutions of these complexes have enough activities to initiate the telomerization at temperatures above 0°C. The fuming yellow solid complex, $TiCl_4\cdot Et_2O$, for example, which is obtained by evaporating an ethyl ether solution of titanium tetrachloride, is easily soluble in methylene dichloride, and the resulting solution is active for the telomerization at about 10°C.

The average molecular weights and the theoretical unsaturations of the telomers obtained by using this catalyst solution are nearly the same as those of the telomers obtained by the method described in Section 3. While the structures and the behavior of these complexes have not been proved, the formation of the carbonium ion might be expressed as follows:

$$MX_n\cdot B + RCl \rightleftarrows MX_n\cdot RCl + B \rightarrow MX_nCl^{\ominus} + R^{\oplus}\cdot B \qquad (4)$$

The concentration of the carbonium ion should depend on the relative amounts and on the basicities of RCl and B. When a strong base, such as acetonitrile, is used as a solvent or an additive, the concentration of the carbonium ion should be reduced; this results in a lower yield of the products. The basicities of ethyl ether, nitroethane, and nitrobenzene may be supposed to be nearly the same as that of crotyl chloride.

The structure and properties of B may also affect the relative rate of the propagation, the chain transfer, and the side reactions, which in turn cause changes in the average molecular weights and in the amount of the unsaturation of the telomers.