

## The Ionic Telomerization of Diene Compounds. IV. The Cationic Telomerization of Butadiene with Its Hydrobromides

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The cationic telomerization of butadiene with its hydrobromides (1-bromo-2-butene and 3-bromo-1-butene) in the presence of metal halide was investigated. It was found that the molecular weights of the telomers depend on the conversion of the telomerization, initial bromide/butadiene ratio and the solvent used. When halogenated hydrocarbons were used as solvents, telomers with high molecular weights and low unsaturations were obtained. On the other hand, the telomerizations in ether solvents gave telomers with low molecular weights, which contained appreciable amounts of the simple adducts of butadiene and bromobutene. The infrared spectra of the telomers suggested that the addition of butadiene occurred mainly at 1,4-position. On the basis of the analyses of the telomers, the reactivities of the carbonium ion to the basic species which were present in the reaction system were estimated.

The cationic telomerization of butadiene and isoprene with alkyl and alkenyl halides have been investigated by some workers.<sup>1-5</sup> The main subject of the investigations were the development of the method of controlling the molecular weight of the telomers and the clarification of the structures of the telomers.

It was found that the cationic telomerization of butadiene and its hydrochlorides gave their simple adducts and higher telomers (telomers with more than three butadiene units), and the addition occurred both at 1,4 and 1,2 positions of butadiene molecule.<sup>1,2</sup> The structures of higher telomers were very complex because of the multiple reactivities of the carbonium ions. Thus, the telomers had lower degrees of unsaturation and higher chlorine contents as compared with telomers with the ideal formula;  $H(C_4H_6)_nCl$ .

The amount of the simple adducts of butadiene with chlorobutenes and the average molecular weight of higher telomers depended mainly on the conversion of the reaction and the solvent used.

The present paper refers to the telomerization

of butadiene with its hydrobromides in the presence of metal halides. When bromobutene is used as a telogen instead of chlorobutene, there will be some variations in the rate of initiation process; the formation of carbonium ion through the interaction between halogenated butenes and the catalyst. The carbonium ion formed may be surrounded by basic species present in the reaction system, namely, counter-anion, solvent, *etc.*, and the structure of the counter-anion may probably affect the reactivity of the carbonium ion.

### Experimental

**Materials.** Bromobutenes, which were used as telogens, were prepared by the method described in a patent.<sup>6</sup> The reaction of butadiene with hydrobromic acid in the presence of sulfuric acid at 60°C gave two isomeric bromobutenes; 1-bromo-2-butene (crotyl bromide, bp 50—51°C/128 mmHg) and 3-bromo-1-butene (bp 42—43°C/128 mmHg). The total yield of bromobutenes was about 70%, and the content of crotyl bromide in the products was about 80%. As will be described later, the two isomers give telomers with the same structure, though 1-bromo-2-butene enters into the reaction faster than 3-bromo-1-butene. Therefore, the mixture of the isomers was used as telogen except when the difference in the reactivity was estimated. In this paper the mixture of two isomeric bromobutenes is named crotyl bromide (CB).

Butadiene (BD, purity was above 99.3%) was passed before use through columns packed with calcium chloride and sodium hydroxide.

Ethyl bromide was washed several times with a chilled concentrated sulfuric acid and water, dried on

1) A. A. Petrov, Kh. V. Bal'yan, L. I. Bunina-Krivorukova and T. V. Yakovleva, *Zhur. Obshch. Khim.*, **29**, 1576 (1959).

2) T. Asahara and H. Kise, *This Bulletin*, **39**, 2739 (1966); **40**, 1941 (1967); **40**, 2664 (1967).

3) K. V. Leets, *Zhur. Obshch. Khim.*, **28**, 1823 (1958); **28**, 3090 (1958).

4) A. A. Petrov, Kh. V. Bal'yan, U. I. Kheruze, E. U. Schwarz and L. L. Cherenkova, *ibid.*, **28**, 1435 (1958); **29**, 1876 (1959).

5) L. A. Cherkasova, Kh. V. Bal'yan and L. M. Zubritskii, *ibid.*, **34**, 1917 (1964).

6) A. A. Dolnick, and H. Naidus, U. S. Pat. 2573695 (1951).

calcium chloride, and distilled. Dichloromethane was washed with a dilute aqueous sodium carbonate solution and water, dried on calcium chloride, and distilled. Ethers were dried on sodium and distilled.

**Telomerization.** Into a 300 ml round-bottomed glass flask, equipped with a sealed stirrer, a thermometer, a condenser and an inlet for gas, definite amounts of the telogen, butadiene and the solvent were placed. Then the catalyst, dissolved in part of the solvent, was slowly added under a stream of nitrogen. The reaction was exothermic, and the rate of the addition of the catalyst solution was adjusted to keep the rise in temperature within 15°C. After the reaction, a small amount of pyridine was added, and the precipitated pyridine/catalyst complex was separated. Then the solution was washed with a 5% sodium carbonate solution, a 5% hydrochloric acid solution, and then water, and dried on anhydrous sodium sulfate. The solvent and the unreacted bromobutene and butadiene were distilled off under a reduced pressure, and the residue was subjected to vacuum distillation to separate the simple adducts of butadiene with bromobutene from the other products.

**Analysis.** The molecular weights of the telomers were measured with a Mechrolab vapor-pressure osmometer, model 301A, in a benzene solution at 37°C. DDT was used as a standard material.

The infrared spectra of the telomers were taken with a Hitachi-Perkin-Elmer double beam grating spectrophotometer, model 125. The evaluation of the absorption intensity was made by the ordinary base-line method.

The adducts with a 1:1 ratio of butadiene with crotyl bromide were analyzed by a gas chromatograph with a flame ionization detector. The separation column was a stainless steel tube packed with Diasolid L; the liquid phase was tricresyl phosphate (10%).

The adducts were isolated by distillation and liquid chromatography through a column packed with activated alumina. The elution was made by carbon tetrachloride or ethyl acetate.

The amounts of unsaturation of the telomers were determined by the Wijs method in the acetic acid solution.

**The Alcoholysis of the Telomers.** The telomers of butadiene with bromobutene were treated by the 0.5N potassium hydroxide-benzyl alcohol solution at 90°C. Initial ratio of bromine to potassium hydroxide was 0.5. The amounts of the bromine which entered into the reaction were calculated from the titration of the residual alkali with a 0.5N hydrochloric acid solution.

## Results and Discussion

**1) Catalyst and Solvent.** The telomerization was carried out in several sorts of solvent in the presence of metal halides (Table I). The reaction products are yellow or brownish viscous liquid or semisolid. In halogenated hydrocarbons, the reaction is too fast to be controlled. In ethereal solvent, the reaction is mild and reproducible. When ferric chloride is used as a catalyst, the yield of the telomer decreases as follows:

*i*-Propyl ether > *n*-Butyl ether > Ethyl ether >  
Dioxane > Ethyl alcohol

A dilute dichloromethane solution of the complex of ferric chloride with ethyl ether had an absorption at 365 mμ. It is known that ethereal compounds form charge transfer complexes with ferric chloride. The result mentioned above may be explained by the differences in the basicity of the solvents. Namely, the catalytic activity of the complexes for the telomerization decreases with the increasing stabilities of the complexes. Elementary analyses and the infrared spectra of the telomers obtained in ethers confirm that any fragment of the solvent molecule is not contained in the reaction products. Accordingly, the dissociation constant,  $K_2$ , may be small, and the initiation through the formation

TABLE I. TELOMERIZATION OF BUTADIENE WITH CROTYL BROMIDE  
[CB]/[BD]=1; Reaction temperature, 5–20°C

Catalyst (C)	[C]/[BD] × 10 <sup>2</sup>	Solvent	Time (min)	Yield <sup>a)</sup> (%)	Simple adduct <sup>b)</sup> (%)	Av. mol wt <sup>c)</sup> (%)	Unsaturation <sup>d)</sup> (%)
FeCl <sub>3</sub>	1.63	( <i>i</i> -Pr) <sub>2</sub> O	150	49.0	34.8	359	55.5
FeCl <sub>3</sub>	1.60	( <i>n</i> -Bu) <sub>2</sub> O	150	—	—	319	62.8
FeCl <sub>3</sub>	3.64	Et <sub>2</sub> O	150	42.5	51.4	310	64.7
FeCl <sub>3</sub>	7.30	Dioxane	150	27.5	45.6	338	62.2
FeCl <sub>3</sub>	10.3	EtOH	310	0	—	—	—
AlCl <sub>3</sub> <sup>e)</sup>	1.00	EtBr	240	49.1	—	514	39.1
AlCl <sub>3</sub> <sup>e)</sup>	6.21	Et <sub>2</sub> O	150	0	—	—	—
AlCl <sub>3</sub> <sup>e)</sup>	10.2	Et <sub>2</sub> O	150	0	—	—	—
AlBr <sub>3</sub>	5.53	Et <sub>2</sub> O	240	0	—	—	—
SnCl <sub>4</sub>	11.6	( <i>i</i> -Pr) <sub>2</sub> O	150	14.7	36.1	298	66.8
SnCl <sub>4</sub>	20.5	CH <sub>2</sub> Cl <sub>2</sub>	310	25.5	11.4	418	50.3

a) The weight percentage of total product based on the initial butadiene and crotyl bromide.

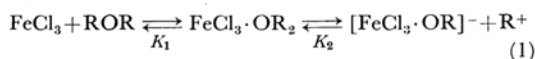
b) The weight percentage of the simple adduct based on the total product.

c) The average molecular weight of higher telomer other than the simple adducts.

d) The percentage of the iodine value of higher telomer to the theoretical iodine value.

e) Reaction temperature, –50—–30°C.

of carbonium ion from the solvent would be neglected.



When aluminum chloride and stannic chloride in halogenated hydrocarbons were used as catalysts, the telomers have high molecular weights and low degrees of unsaturation. As will be discussed later, it is presumed that some side reactions occur concurrently with the main reactions; *e. g.*, the addition of carbonium ion to the double bonds in the telomer or telogen.

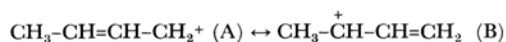
The catalytic ability of metal halides in ethers decreases in the order,  $\text{FeCl}_3 > \text{SnCl}_4 > \text{AlCl}_3$ . The result is a little different from those of Friedel-Crafts reaction and the telomerizations in halogenated hydrocarbons. The apparent rate of telomerization which is designated by total yield of the telomers would primarily depend on the rate of initiation; the formation of carbonium ion through the interaction of catalyst and crotyl bromide. The strength of the association of metal halide with the solvents may reflect on the catalytic activity of the catalyst solutions.

TABLE 2. TELOMERIZATION OF BUTADIENE WITH TWO BROMOBUTENE ISOMERS

Telogen	Yield (%)	Simple adduct (%)	Av. mol wt of higher telomers
1-Bromo-2-butene	34.8	41.5	285
3-Bromo-1-butene	25.9	51.2	308

Catalyst:  $\text{FeCl}_3$ ; Solvent:  $\text{Et}_2\text{O}$   
 Reaction time: 150 min  
 Reaction temperature: 5–15°C

Each of the two isomeric bromobutenes, which were obtained by the hydrobromination of butadiene, was used as telogens (Table 2). It was found that the primary bromide gave a larger amount of telomer than the secondary bromide under the same reaction condition. However, from the infrared spectra of the telomers and the gas chromatogram of the simple adducts, no significant difference in the structures of the telomers from respective bromides was observed. This was also confirmed in the case when chlorobutenes were used as telogens.<sup>2)</sup> The fact suggests that the two isomeric halobutenes form the same carbonium ion with the resonance structures A and B.



2) **The Effect of Initial CB/BD Ratio.** The effects of CB/BD ratio on the yield and the molecular weight of the telomer were investigated. When aluminum chloride in ethyl bromide solution is used, average molecular weight of the telomer mixture decreases monotonously with the increase

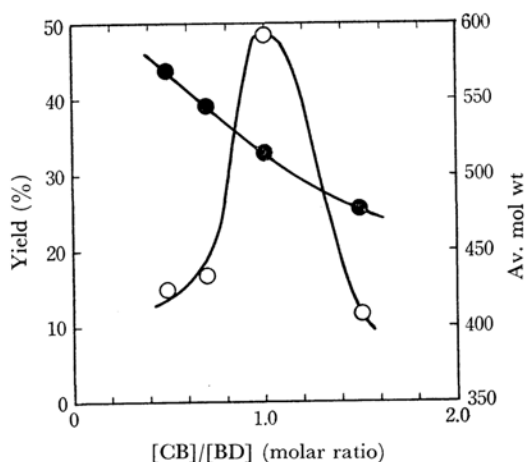


Fig. 1. Effect of the ratio of crotyl bromide to butadiene.

Catalyst,  $\text{AlCl}_3$ ; solvent, ethyl bromide.

○, Total yield of telomer; ●, average molecular weight of telomer.

$[\text{AlCl}_3]/[\text{BD}]=0.01$ ; reaction temperature,  $-50^\circ\text{C}$ ; reaction time, 4 hr.

in the ratio (Fig. 1). However, the yields of the simple adducts of butadiene with crotyl bromide were very low under the conditions. In the region of  $\text{CB/BD} < 1$ , appreciable amounts of insoluble product are obtained, which causes the decrease in the soluble telomers.

On the other hand, when ferric chloride in ether is used, considerable amounts of the simple

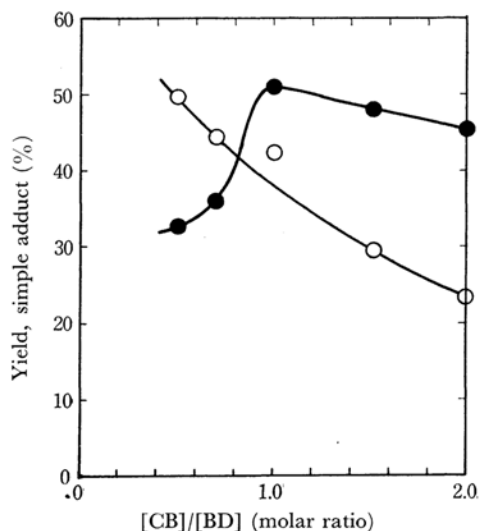


Fig. 2. Effect of the ratio of crotyl bromide to butadiene.

Catalyst,  $\text{FeCl}_3$ ; solvent, ethyl ether.

○, Total yield of telomer; ●, simple adduct of butadiene with crotyl bromide.

$[\text{FeCl}_3]/[\text{BD}]=0.0364$ ; reaction temperature,  $5^\circ\text{C}$ ; reaction time, 2.5 hr.

adducts of butadiene with bromobutene are obtained; the maximum yield of the adduct is obtained at CB/BD=1 (Fig. 2). In the region where the ratio is larger than unity, no significant change in the yield ratio of the adduct to the total product is observed. In addition, the average molecular weights of the higher telomers vary little with the variation of the initial CB/BD ratio. It appears that the excess crotyl bromide exists only as a diluent, and does not act as a chain transfer reagent.

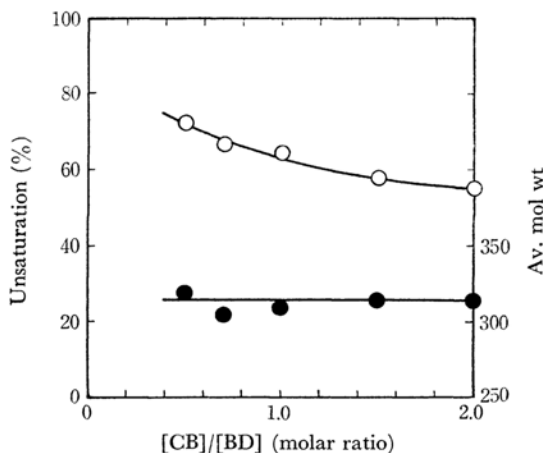


Fig. 3. Effect of the ratio of crotyl bromide to butadiene.

○, Unsaturatn of higher telomer; ●, average molecular weight of higher telomer.

Reaction condition is the same as in Fig. 2.

As Fig. 3 shows, however, the increase in the CB/BD ratio causes a decrease in the degree of unsaturation of the higher telomers. It was concluded that the excess crotyl bromide increases the proportion of side reactions (see Section 5). This may be the reason why the simple adduct of butadiene with bromobutene decreases in the region CB/BD > 1.

### 3) The Effect of Catalyst Concentration.

As Fig. 5 shows, the average molecular weight of the telomer increases with the increase in the catalyst concentration. This effect may be attributed to the increase in the conversion of the reaction (Fig. 4), because it should be presumed in general that the increase in the catalyst results in the lowering of the molecular weight of the telomer. The relation between the conversion of reaction and the amount of the simple adducts of telogen and taxogen was examined and discussed in the case of telomerizations of butadiene with crotyl chloride<sup>2)</sup> and isoprene with prenyl chloride.<sup>3)</sup>

**4) The Structure of Telomers.** The fraction with bp 35–45°C/1 mmHg (I) was separated from the telomer mixture. It was found that the fraction consists of three components from its gas chromatogram. The elementary analysis and the

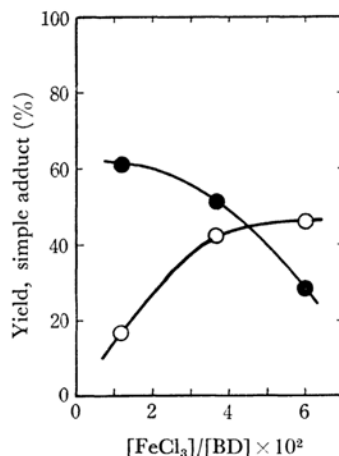


Fig. 4. Effect of the catalyst concentration.

Catalyst, FeCl<sub>3</sub>; solvent, ethyl ether.

○, Total yield of telomer; ●, simple adduct of butadiene with crotyl bromide.

[CB]/[BD]=1.00; reaction temperature, 5°C; reaction time, 2.5 hr.

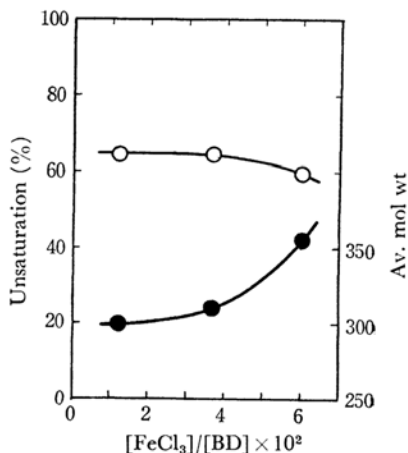


Fig. 5. Effect of the catalyst concentration.

○, Unsaturatn of higher telomer; ●, average molecular weight of higher telomer.

Reaction condition is the same as in Fig. 4.

determination of iodine value indicate that the fraction consists of the simple adducts of butadiene with crotyl bromide.

Found: C, 51.68; H, 7.18; Br, 41.14%. Iodine value, 262.2. Calcd for H(C<sub>4</sub>H<sub>6</sub>)<sub>2</sub>Br: C, 50.80; H, 6.94; Br, 42.26%. Iodine value, 268.40.

The fraction I was redistilled into two fractions; bp 35–40°C/1 mmHg (II) and 40–42°C/1 mmHg (III). From the infrared spectra (Figs. 6-2 and 6-3) and NMR spectrum (Fig. 7-2), it was concluded that the fraction II is a mixture of adducts D and E, and the fraction III is adduct C (Fig. 7). The infrared spectrum of II exhibits

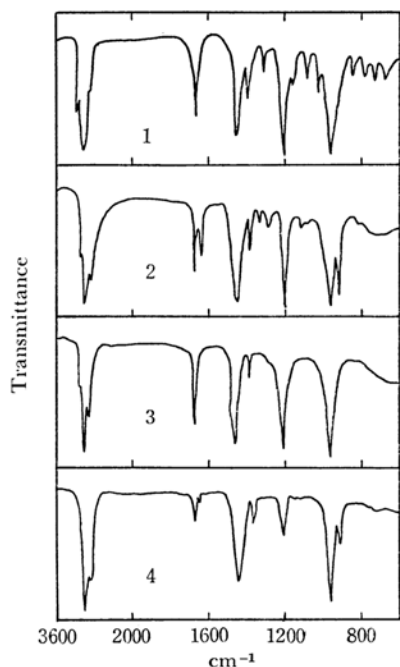


Fig. 6. Infrared spectra of crotyl bromide and telomers.

1, Crotyl bromide; 2, fraction II; 3, fraction III; 4, higher telomer.

the characteristic stretching ( $1665\text{ cm}^{-1}$ ) and deformation ( $965\text{ cm}^{-1}$ ) bands of the internal double bond, as well as the bands of vinyl grouping ( $1645$  and  $910\text{ cm}^{-1}$ ), while the spectrum of III has only the bands of internal double bond. Adducts D and E, which were contaminated a little by each other, were separated from the fraction II by liquid chromatography. The proportion of C, D and E in the fraction I can be determined from its NMR spectrum (Fig. 7-3) by using the relative intensities of the bands,  $8.35/9.00$  and  $4.55/4.22$  (in  $\tau$ ). Thus, the proportions of C, D and E were estimated to be 80%, 10% and 10% respectively. There were found small differences in the value for the adducts obtained under various reaction conditions.

The infrared spectrum of the mixture of telomers other than the simple adducts represents the bands characteristic of internal olefin and vinyl grouping (Fig. 6-4). From the absorption intensities, the ratio of the 1,4 linkage of butadiene unit was calculated to be about 90%.<sup>7)</sup>

**5) Mechanism of Telomerization.** The cationic telomerization of butadiene with crotyl bromide is assumed to proceed as follows:

Initiation:

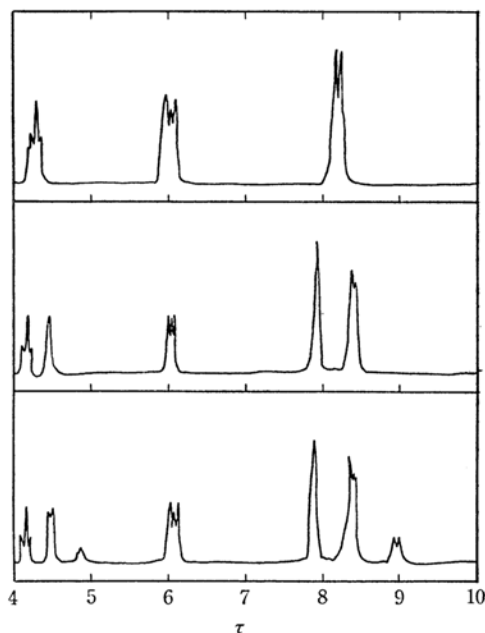
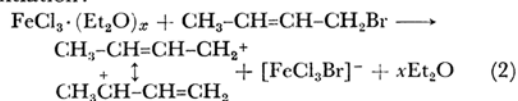
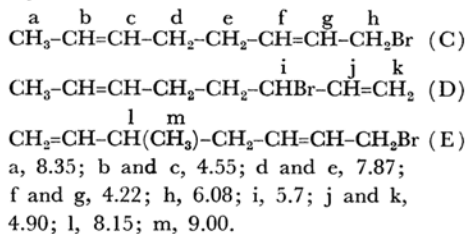
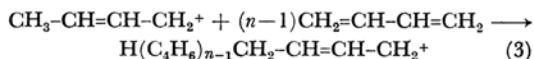


Fig. 7. NMR spectra of crotyl bromide and telomers.

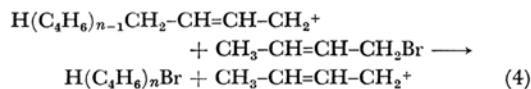
1, Crotyl bromide; 2, fraction III; 3, fraction I. Assignments:



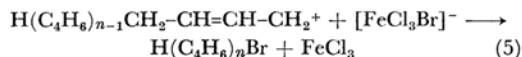
Propagation:



Transfer reaction:



Termination:



It is known that ferric chloride forms a complex with ether in about 1 : 1 ratio.<sup>2)</sup> If the solvent used has a smaller basicity than crotyl bromide, ferric chloride may form an adduct with crotyl bromide and subsequently form a carbonium ion, which initiates telomerization. It is deduced that a growing carbonium ion reacts with butadiene or crotyl bromide preferentially in the form with a positive charge on the chain end. Namely, 1,4 addition occurs more predominantly in the present system than the case of butadiene with crotyl chloride.

7) W. S. Richardson, *J. Polymer Sci.*, **13**, 229 (1954).

TABLE 4. REACTIVITY OF CARBONIUM ION

used as a catalyst, a marked increase in the proportion of side reactions was found. Namely, the telomers obtained by aluminum chloride in ethyl bromide have structures more branched and cyclized than those obtained by ferric chloride in ethers. The difference may be attributed to the difference in the basicity of the solvent, which interacts with the growing carbonium ions. In other words, reactivities of carbonium ions toward butadiene, crotyl bromide and telomers are influenced by the species of medium in which the carbonium ions exist.

**6) Reaction of Telomers with Potassium Hydroxide in Benzyl Alcohol.** In order to estimate the reactivities of bromine atoms in the telomers, the telomers were treated with potassium hydroxide in a benzyl alcohol solution. This

alcoholysis affords unsaturated ethers with benzene nucleus. As Fig. 8 shows, higher telomers enter into reaction more slowly than 1:1 adducts, which may be ascribed to the steric factor of the telomers. It was also found that the telomers with bromine are more reactive than the telomers with chlorine. That is, the ionic cleavage of carbon-bromine bond is easier than that of carbon-chlorine bond. However, no significant differences were found between the reactivities of crotyl chloride and crotyl bromide in the telomerization. The fact may be explained by the stability of the counter-anions formed through the interaction of crotyl halides and the catalyst. Namely,  $[\text{FeCl}_3\text{Br}]^-$  may be more unstable than  $[\text{FeCl}_4]^-$ , and easily recombines with carbonium ions, which results in the formation of the telomers with lower molecular weights.

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