Selective Synthesis of Isobutene Trimers and Hexamers with Oxo Acid Catalysts

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Synopsis

The reaction of isobutene (IB) with its dimers (IB_2) catalyzed by CF_3SO_3H yielded isobutene trimers (IB_3) in high yield in nonpolar solvents at 0°C. The initial feed of isobutene, in the presence of equimolar IB_2 or more, was selectively converted into IB_3 without loss or accumulation of IB_2. After complete consumption of the isobutene, however, the remaining IB_2 rapidly dimerized to isobutene tetramers (IB_4). ^{13}C-NMR analysis of the products showed that the IB_3 was formed via addition of the t-butyl cation (protonated isobutene to 2,4,4-trimethyl-1-pentene (an IB_2 isomer); the trimer fraction was free from isomers arising from addition of the t-butyl cation to 2,4,4-trimethyl-2-pentene (another IB_2 isomer) or addition of the IB_2 cation to isobutene. The IB_3 thus obtained was further oligomerized with CF_3SO_3H catalyst in nonpolar media in the range of 0 to −25°C to give a mixture of IB_5, IB_6, and IB_7 in high yield. With $EtAlCl_2$ as catalyst, reaction of isobutene with IB_2 and oligomerization of IB_3 both resulted in products with a broad molecular weight distribution containing higher oligomers and complex hydrocarbons formed via cracking of the intermediate carbocations.

INTRODUCTION

Oligomers of unsaturated hydrocarbons (e.g., isobutene) have found extensive application in many industrial fields. However, those obtained with an acid catalyst, in spite of their potential usefulness, have been less attractive for practical use because of their ill-defined structure and uncontrolled molecular weight distribution (MWD). Development of acid-catalyzed selective synthesis of oligomers with desired structure and molecular weight will considerably widen the range of their application.

Although cationic oligomerization of isobutene has a long research history,[1] it has been beyond our reach to selectively synthesize isobutene oligomers of controlled molecular weight (except for dimers IB_2). According to the kinetic study by Haag[2], for example, oligomerization with a cationic ion exchange resin gives a mixture of isobutene oligomers ranging from dimers to tetramers. These results indicate that "homo-oligomerization" of isobutene is not suitable for the selective synthesis of its oligomers other than dimers.

We have thus started a series of studies on cationic "oligomerization" of isobutene oligomers of low molecular weight (e.g., IB_2) in an attempt to obtain higher oligomers selectively. We have already found that treatment of IB_2 with an oxo acid (e.g., CF_3SO_3H) leads to isobutene tetramers (IB_4) in a very high yield.[3] This study focuses on the synthesis of isobutene trimers (IB_3) and hexamers (IB_6) by "co-oligomerization" of IB_2 and isobutene and by "dimerization" of IB_3, re-

spectively. We wish to report that IB_3 and IB_6 can be prepared in high yields by the use of a strong oxo acid (CF_3SO_3H) as catalyst.

EXPERIMENTAL

Materials

Isobutene (Tokyo Kasei, purity 99%) was dried by passing it through a 1-m column packed with KOH pellets immediately before use. 2,4,4-Trimethyl-1-pentene (IB_2, 1) and 2,2,4,6,6-pentamethyl-3-heptene (IB_3, 3), both commercially obtained (Tokyo Kasei, purity 99%), were distilled twice over calcium hydride. Catalysts (CF_3SO_3H, CH_3COClO_4, and $EtAlCl_2$) and solvents were purified as previously reported.[3]

Procedures

Oligomerizations were carried out under dry nitrogen as described previously.[3] Consumption of hydrocarbon monomers (isobutene, IB_2, etc.) was followed by gas chromatography. Yields of IB_3 and IB_4 were obtained on a temperature-programmed gas chromatograph (Shimadzu GC-6A) equipped with a 3-m column of silicon DC 550, n-octane being the internal standard. Isobutene oligomers higher than pentamer were determined by high-performance liquid chromatography (HCL).[3] The structure of the products was analyzed primarily by ^{13}C-NMR spectroscopy.

RESULTS AND DISCUSSION

Reaction of IB_2 with Isobutene—Synthesis of IB_3

Time Course of the Co-oligomerization

For the selective synthesis of IB_3, an equimolar mixture of isobutene and IB_2 (2,4,4-trimethyl-1-pentene, 1) was treated with CF_3SO_3H as catalyst. Figure 1 shows the time course of the co-oligomerization in CCl_4 at 0°C. Isobutene was consumed rather slowly up to 100% conversion in ca. 8 h, while a small amount of 1 reacted and 2,4,4-trimethyl-2-pentene (2), an isomer of 1, formed concurrently. As long as unreacted isobutene remained in the reaction mixture, the combined concentration of IB_2 (1 + 2) was almost constant.

Immediately after complete consumption of the isobutene however, the IB_2 rapidly reacted. A similar phenomenon, i.e., rapid disappearance of IB_2 left intact in the presence of isobutene, has been observed in homo-oligomerization of this monomer.[2]

Figure 2 illustrates the gas chromatograms for a series of the co-oligomerization products obtained at different reaction times. During the first 7 h in which isobutene was present in the reaction mixture, the amount of IB_3 (two isomers) increased with time; neither IB_4 nor higher oligomers were produced during this period. The total concentration of IB_3 at 7 h was 0.14 M, which means that all of the initial isobutene feed (0.50 M) was apparently converted into IB_3.
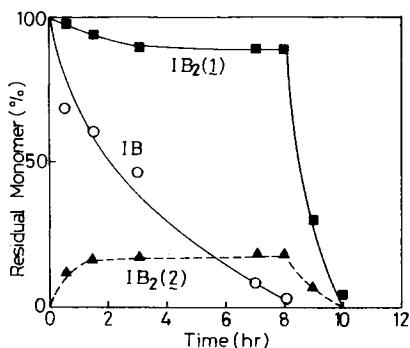
Fig. 1. Reaction of IB_2 with isobutene (IB) catalyzed by CF_3SO_3H at 0°C in CCl_4: $[IB_2]_0 = [IB]_0$ = 0.50 M; $[C]_0$ = 10 mM. **1**, 2,4,4-trimethyl-1-pentene; **2**, 2,4,4-trimethyl-2-pentene.

Therefore, if one quenches the co-oligomerization of IB_2 and isobutene just when the latter has completely reacted, then one can obtain IB_3 selectively without any apparent loss of IB_2 initially charged.

   The complete consumption of isobutene triggered the rapid formation of IB_4 that amounted to ca. 0.2 M at 10 h, at which time almost all IB_2 feed (0.50 M) had reacted.   Thus, IB_2 dimerizes to IB_4 nearly quantitatively.
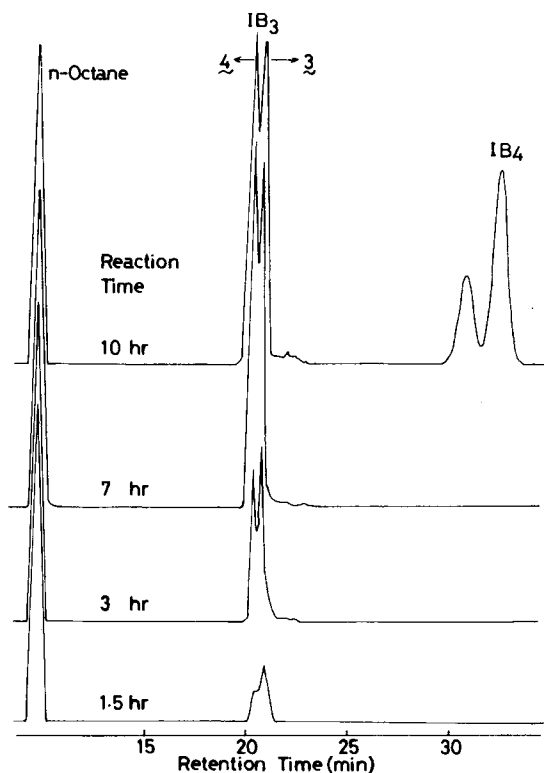

Fig. 2. Gas chromatograms for the reaction mixtures in the co-oligomerization of IB_2 and isobutene. n-Octane as internal standard.   See Fig. 1 for reaction conditions.

Effect of Reaction Conditions

Table I summarizes the effects of catalysts, solvents, and reaction temperature on the co-oligomerization of IB_2 and isobutene. Among the three catalysts examined (CF_3SO_3H, CH_3COClO_4, and $EtAlCl_2$), the aluminum compound was the most active, leading to complete consumption of isobutene within a few minutes in CCl_4 at $0°C$. In spite of the high catalytic activity, $EtAlCl_2$, a metal halide, was a poorly selective catalyst for IB_3 synthesis. The products consisted of isobutene oligomers and polymers with a broad MWD extending in the molecular weight range of 100–3000; the IB_3 content was very small. Among the oligomer fractions were not only IB_3 and IB_4 but hydrocarbons with 13–20 carbons (by mass spectroscopy) that formed via cracking of the intermediate carbocations. Similar extensive cracking has also been observed for the dimerization of IB_2 by the same catalyst.[3]

CH_3COClO_4 (the data are not given in Table I) was unsuitable for the synthesis of IB_3 because of its low activity.

With CF_3SO_3H catalyst, the use of a polar solvent, CH_2Cl_2, gave greater reaction rate and higher IB_3 yield than those obtained in CCl_4. However, the co-oligomerization in this solvent was less selective for IB_3, yielding, in addition to IB_3, IB_4 and other hydrocarbons of 13–20 carbons even in the presence of unreacted isobutene. At a lower temperature ($-20°C$) in CCl_4, the concentration of IB_2 in the reaction mixture increased with increasing isobutene conversion, and thus the yield of IB_3 was smaller than that at $0°C$.

Figure 3 shows the dependence of the IB_3 yield at 90–100% isobutene conversion upon the initial concentration of isobutene ($[IB]_0$) (catalyst CF_3SO_3H). The solid line indicates the IB_3 yields calculated with the assumption that the initial isobutene feed is quantitatively converted into IB_3. When $[IB]_0$ was smaller than the initial concentration of IB_2, the IB_3 yields were in close agreement with the calculated values, indicating selective conversion of isobutene into its trimers. When isobutene was in excess over IB_2 ($[IB]_0 > [IB_2]_0$), on the other hand, the IB_3 yield was smaller than the calculated values. This implies that a part of the isobutene feed dimerizes to IB_2 instead of reacting with it.

The results described above show that clean, efficient synthesis of IB_3 from isobutene requires a strong oxo acid (CF_3SO_3H) as catalyst employed in a nonpolar medium around $0°C$ at an appropriate $[IB]_0/[IB_2]_0$ feed ratio.

TABLE I
Effect of Reaction Conditions on the Co-oligomerization of IB_2 and Isobutene ($[IB_2]_0 = 0.50\ M$; $[IB]_0 = 0.50\ M$)

Catalyst	Solvent	Temp, °C	Reaction time	Conversion of isobutene, %	Products	
					IB_3, M	Remainder
$EtAlCl_2$[a]	CCl_4	0	6 min	100	0,017	Higher oligomers
CF_3SO_3H[b]	CCl_4	0	8 h	100	0.14	None
CF_3SO_3H[b]	CCl_4	−20	12 h	54	0.048	IB_2
CF_3SO_3H[b]	CH_2Cl_2	0	10 min	85	0.20	IB_4 (trace) + higher oligomers

[a] 10 mM with 5.0 mM H_2O.

[b] 10 mM.

Structure of the IB_3 and Reaction Pathway

As seen in Figure 2, the IB_3 obtained with CF_3SO_3H consists of two isomers. The formation of IB_3 from IB_2 and isobutene may involve two pathways: addition of the isobutene cation (IB^+) to 1, eq. (1), and addition of the protonated form of 1 or 2 (the identical cation) to isobutene, eq. (2).

$$
\begin{array}{c}
\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\text{C}^{\oplus}}} \;+\; \underset{\underset{\underset{\underset{\underset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\text{C}\!-\!\text{CH}_3}}{|}}{\text{CH}_2}}{\overset{\overset{\text{CH}_3}{|}}{\text{CH}_2\!=\!\text{C}}} \;\longrightarrow\; \underset{\underset{\underset{\underset{\underset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\text{C}\!-\!\text{CH}_3}}{|}}{\text{CH}_2}}{\overset{\overset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\overset{\overset{|}{\text{CH}_3}}{\text{C}}\!-\!\text{CH}_2\!-\!\text{C}^{\oplus}}} \quad \overset{-\text{H}^{\oplus}}{\longrightarrow}
\end{array}
$$

1

$$
\underset{\underset{\underset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\overset{|}{\text{C}}\!-\!\text{CH}_3}}{\overset{\overset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\overset{\overset{|}{\text{CH}_2}}{\text{C}}\!-\!\text{CH}}}\!=\!\underset{\overset{\text{CH}_2}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}} \quad + \quad \underset{\underset{\underset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\overset{|}{\text{C}}\!-\!\text{CH}_3}}{\overset{\overset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\overset{|}{\text{C}}\!-\!\text{CH}_2\!-\!\overset{\overset{\text{CH}_2}{\parallel}}{\underset{\text{CH}_2}{\text{C}}}}} \qquad (1)
$$

3   **4**

$$
\begin{array}{c}
\underset{\underset{\underset{\underset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\text{C}\!-\!\text{CH}_3}}{|}}{\underset{\text{CH}_2}{\overset{\overset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\text{C}^{\oplus}}}} \;+\; \underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{CH}_2\!=\!\text{C}}} \;\longrightarrow\; \underset{\underset{\underset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\text{C}\!-\!\text{CH}_3}}{\underset{\text{CH}_2}{\overset{\overset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\text{C}\!-\!\text{CH}_2\!-\!\overset{\overset{\text{CH}_3}{|}}{\underset{\text{CH}_3}{\text{C}^+}}}}} \quad \overset{-\text{H}^{\oplus}}{\longrightarrow}
\end{array}
$$

$(1^{\oplus}, 2^{\oplus})$

$$
\underset{\underset{\underset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\text{C}\!-\!\text{CH}_3}}{\overset{\overset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\overset{\overset{|}{\text{CH}_2}}{\text{C}}\!-\!\text{CH}}}\!=\!\underset{\text{CH}_3}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}} \quad + \quad \underset{\underset{\underset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\overset{|}{\text{C}}\!-\!\text{CH}_3}}{\overset{\overset{\text{CH}_3}{|}}{\text{CH}_3\!-\!\overset{|}{\text{C}}\!-\!\text{CH}_2\!-\!\overset{\overset{\text{CH}_2}{\parallel}}{\underset{\text{CH}_3}{\text{C}}}}} \qquad (2)
$$

5   **6**
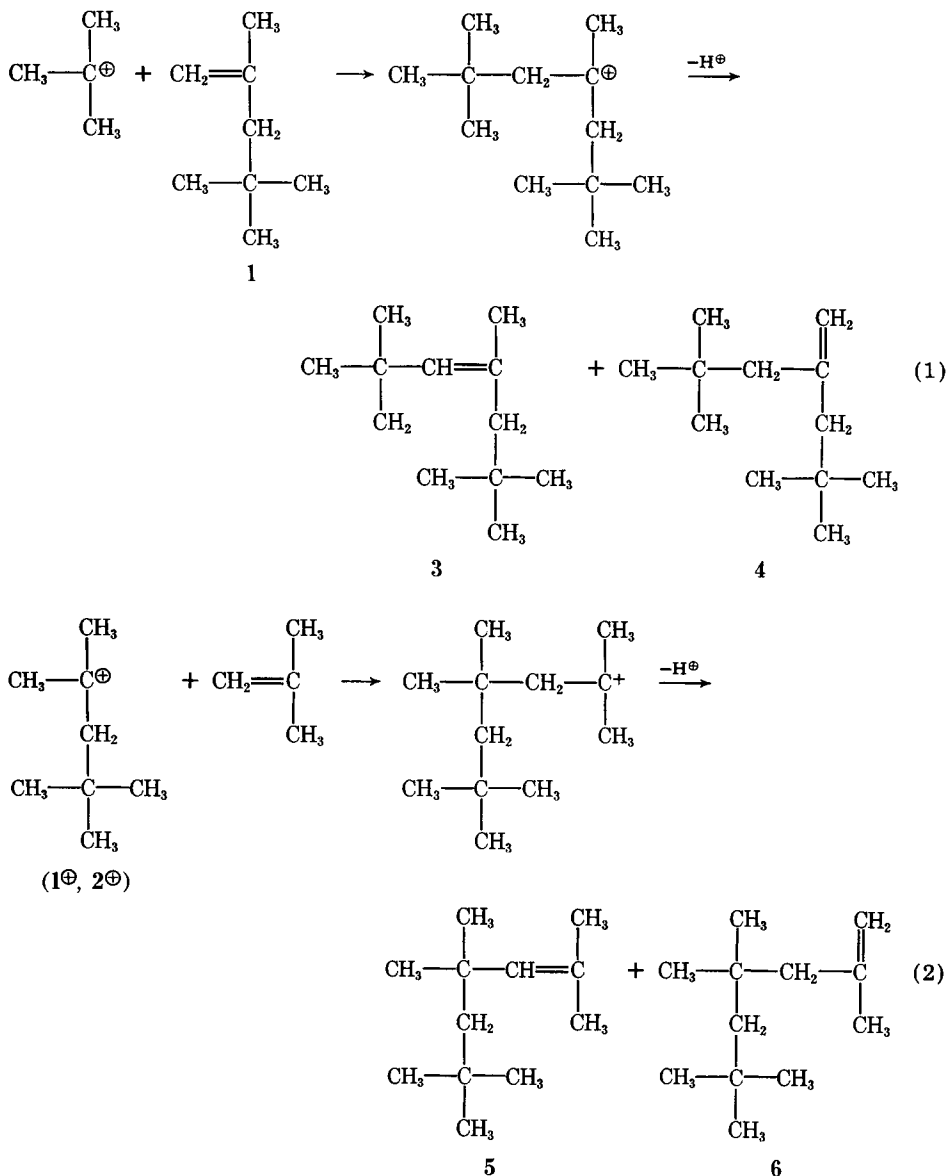
We neglected the addition of IB^+ to **2**, which would also give IB_3, because **2** remains intact in the presence of $EtAlCl_2$[3] and protonated IB_2 (IB_2^+) does not react with **2**.[3] This assumption was supported by ^{13}C-NMR analysis of the co-oligomerization products (see below). In the presence of CF_3SO_3H (oxo acid), **2** isomerizes to **1**, which subsequently reacts with IB^+, as we have reported for dimerization of IB_2.[3]

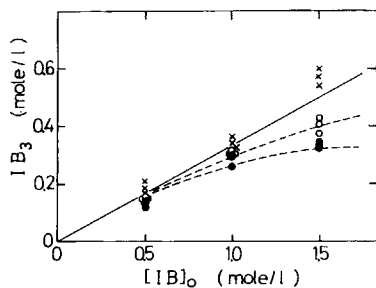Fig. 3. Yield of IB$_3$ as function of the initial isobutene concentration [IB]$_0$ in the co-oligomerization of IB$_2$ and isobutene with CF$_3$SO$_3$H catalyst at 0°C in CCl$_4$. Conversion of IB$_2$ = 90–100%; [IB$_2$]$_0$: (●) 0.50 M; (○) 1.00 M; (×) 1.50 M.

Figure 4(A) presents the ^{13}C-NMR spectrum of the IB$_3$ produced with CF$_3$SO$_3$H in CCl$_4$ solvent. The four resonances due to olefinic carbons between δ 115 and 145 ppm show the presence of two IB$_3$ isomers having a C═C double bond. Upon off-resonance decoupling from protons [Fig. 4(B)], the peak at δ 116 ppm split into a triplet and the one at 139 ppm into a doublet, whereas the other two remained as singlets.

2,2,4,6,6-Pentamethyl-3-heptene (3), an isomer of IB$_3$, exhibits the ^{13}C-NMR spectrum shown in Figure 4(C). Comparison of Figures 4(A) and 4(C) indicates that one of the two IB$_3$'s obtained is isomer 3, which has a trisubstituted double bond (—CH═C<).

Trimer 3 is known to isomerize to 4 under acidic conditions.[4] Figure 4(D) shows the ^{13}C-NMR spectrum of an authentic mixture of 3 and 4, which was prepared by partial isomerization of 3 to 4 with CF$_3$SO$_3$H in CCl$_4$ and subsequent separation by HLC. The spectrum exhibits all the peaks seen in Figure 4(A); no signals assignable to other IB$_3$ isomers [e.g., 5 and 6; eq. (2)] were detected. The absence of 5 and 6 is in contrast to the fact that the IB$_3$ fraction obtained
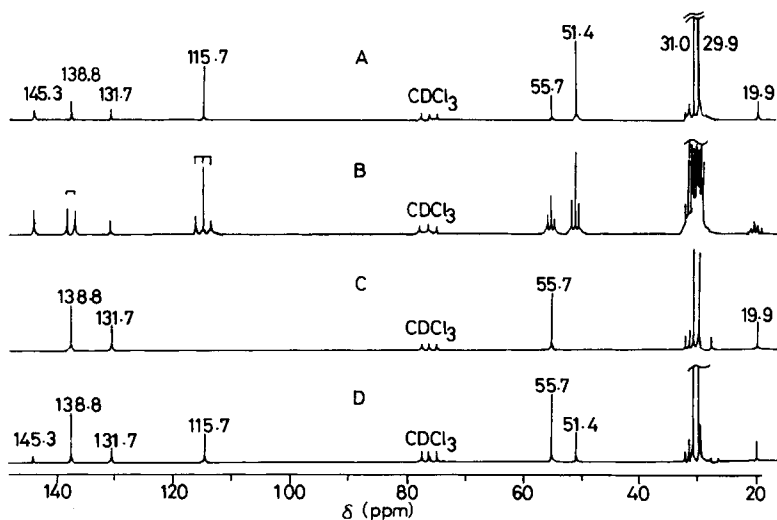

Fig. 4. ^{13}C-NMR spectra of IB$_3$ and related authentic samples: A, IB$_3$ obtained by the co-oligomerization of IB$_2$ and isobutene with CF$_3$SO$_3$H (cf. Fig. 1); B, off-resonance decoupled spectrum of sample A; C, authentic 2,2,4,6,6-pentamethyl-3-heptene (3); D, authentic mixture of 3 and 4.

by dehydration of t-butanol with sulfuric acid contains ca. 10% of these isomers.[5] It was therefore found that the IB_3 produced by the reaction of IB_2 with isobutene is a mixture of **3** and **4** only. This conclusion was supported by agreement of the observed ^{13}C-NMR chemical shifts with those calculated by Roberts' method.[6]

Scheme I visualizes the pathway of acid-catalyzed co-oligomerization of IB_2 and isobutene. The absence of **5** and **6** in the IB_3 fraction indicates that the trimers are formed via path (a) instead of path (c). Scheme I also explains the disagreement between the observed and calculated IB_3 yields when isobutene was in excess over IB_2 (Fig. 3). At low $[IB_2]_0$, IB^+ reacts not only with IB_2 but with isobutene [path (e)] to form IB_2, and thus the relative content of IB_3 in the product is decreased. In the reverse case ($[IB]_0 < [IB_2]_0$), the concentration of IB_2 (**1 + 2**) remained constant during the reaction (Fig. 1). It follows that the consumption of IB_2 via path (a) and its production via path (e) (dimerization of isobutene) are nearly balanced; i.e., IB^+ reacts with isobutene and IB_2 at similar rates.

Scheme I.
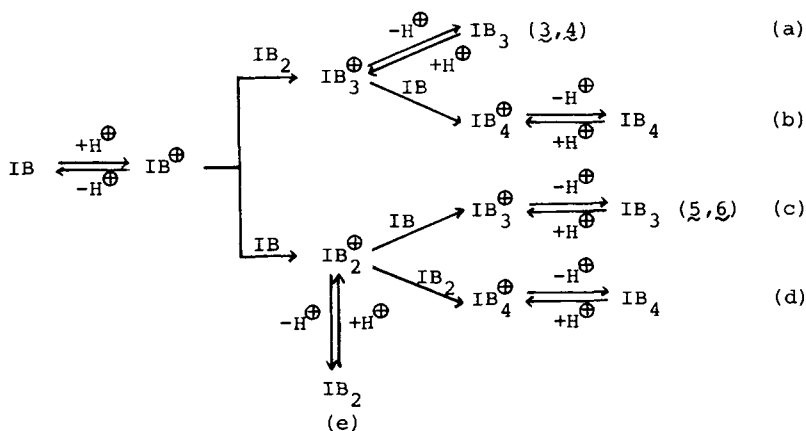
Another characteristic of the IB_2–isobutene co-oligomerization is the rapid formation of IB_4 triggered by complete consumption of isobutene (Figs. 1 and 2). This fact suggests that IB_4 forms only through path (d) instead of path (b), which involves isobutene as a reactant. Path (b) seems difficult because of the bulkiness of the intermediate, IB_3^+. Our data however cannot interpret the suppression of path (d) in the presence of unreacted isobutene. Haag has reported[2] that in the isobutene oligomerization catalyzed by a cationic ion exchange resin, dimerization of IB_2 is about 30 times faster than that of isobutene; and he explained this rate difference in terms of inhibition of isobutene dimerization by preferential adsorption of the monomer onto the catalyst resin. Apparently, this explanation is irrelevant to our system in which a soluble protonic acid was the catalyst.

Dimerization of IB₃—Synthesis of IB₆

Homo-oligomerization of isobutene cannot give isobutene hexamer (IB_6) in high yield.[1] Encouraged by the successful preparation of IB_4 from IB_2,[3] we studied the synthesis of IB_6 by dimerizing IB_3 obtained as above.

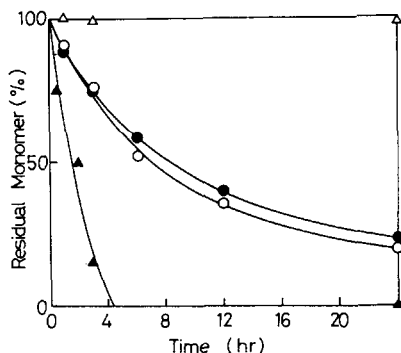Fig. 5. Oligomerization of IB_3 (3/4 = 6/4) with CF_3SO_3H (O, ●) or $EtAlCl_2$ (△, ▲) as catalyst in CCl_4 at 0°C: $[IB_3]_0 = 0.50\ M$; $[C]_0 = 10\ mM$; (O, △) 3; (●, ▲) 4.

Time Course of IB_3 Dimerization and MWD of the Products

A sample of IB_3 (a mixture of 3 and 4 at a 6:4 molar ratio) was treated with CF_3SO_3H or $EtAlCl_2$ catalyst in CCl_4 (Fig. 5). With the oxo acid catalyst, 3 and 4 were consumed at nearly the same rates. With $EtAlCl_2$, on the other hand, only 4 reacted and no further reaction took place after its complete consumption.

Treatment of pure 3 with CF_3SO_3H in CCl_4 led to isomerization to 4; no oligomers were formed during the early stages of the reaction. Therefore, even when the mixture of 3 and 4 was treated with CF_3SO_3H, only 4 gives oligomers; the concurrent disappearance of 3 is due to its isomerization to 4.

Figure 6 shows the HLC charts of the products obtained with CF_3SO_3H and $EtAlCl_2$. The figures attached to each peak indicate the degree of polymerization in isobutene units. The main product with CF_3SO_3H was IB_6 accompanied by isobutene pentamers (IB_5) and heptamers (IB_7) [Fig. 6(A)]. These by-products

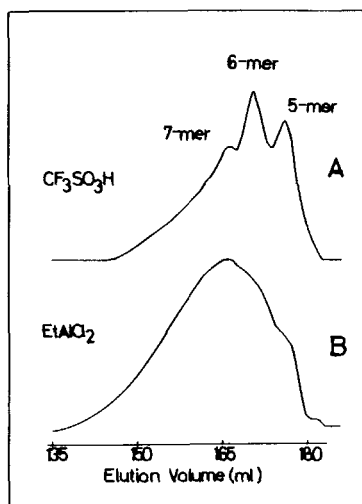Fig. 6. MWD of the products obtained in the oligomerization of IB_3. Catalysts as indicated. See Fig. 5 for reaction conditions.

are probably formed via displacement of the t-butyl cation from protonated IB_3, which carries bulky substituents around its cationic center.

The product with $EtAlCl_2$ showed a broad MWD centered in the IB_6–IB_7 region [Fig. 6(B)]. The poor resolution of IB_5, IB_6, and IB_7 suggests that the product is a complex mixture of hydrocarbons with various carbon numbers which arose from cracking of the intermediate carbocations.[3]

Effect of Reaction Conditions

Figure 7 compares the MWDs of the products obtained with CF_3SO_3H under different reaction conditions. IB_6 amounted to as much as ca. 40% of the oligomers produced in nonpolar media (n-hexane and CCl_4). Especially, with n-hexane solvent [Fig. 7(C)] the MWD of the product was narrow and the content of IB_7 and higher oligomers was small.

The products obtained in a polar solvent (CH_2Cl_2) [Fig. 7(A)] contained more IB_5 than IB_6, and the content of IB_7 and higher oligomers was greater than that for the nonpolar media. Higher reaction temperature ($+30°C$) increased IB_5 and decreased higher oligomers in the product [Figs. 7(D) and 7(E)]. The increase in IB_5 content is due to cracking of the intermediate carbocations promoted at higher temperature.

Decreasing the initial IB_3 concentration from $0.50\ M$ to $0.10\ M$ led to broadening of the MWD of the product; a decrease of higher oligomers [Fig. 7(F)] was observed at a very high IB_3 concentration ($2.0\ M$).

CH_3COClO_4 was much less active as catalyst than CF_3SO_3H (ca. 10% conversion of IB_3 after 24 h under the same conditions as shown in Fig. 5), although the two catalysts gave similar products.

Structure of the IB_6

The IB_6 fraction obtained with CF_3SO_3H at $0°C$ in CCl_4 was separated by HLC for structural analysis by ^{13}C-NMR spectroscopy. The spectra were too com-
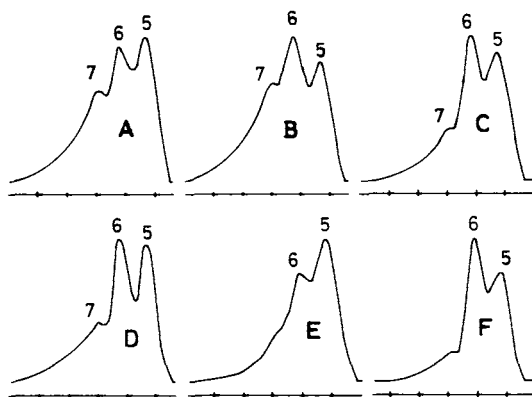

Fig. 7. MWD of the products obtained in the oligomerization of IB_3 with CF_3SO_3H. Solvents, temperature, and $[IB_3]_0$ (M): A, CH_2Cl_2, $-25°C$, 0.50; B, CCl_4, $-25°C$, 0.50; C, n-hexane, $-25°C$, 0.50; D, CCl_4/CH_2Cl_2 (3/1), $-25°C$, 0.50; E, CCl_4/CH_2Cl_2 (3/1), $30°C$, 0.50; F, CCl_4/CH_2Cl_2 (3/1), $-25°C$, 2.0. Numbers indicate the degree of polymerization.

plicated to be fully assigned, but the peaks in the olefinic region indicated the presence of four to five unsaturated hydrocarbons in the IB_6. Among the olefinic resonances, those at δ 140.0 and 138.4 ppm were the greatest in intensity, comprising 30–40% of the whole olefinic carbons. The former peak split into a doublet on off-resonance decoupling from protons, and hence the compound assignable to it has a —CH=C< group.

Analogous to dimerization of IB_2,[3] IB_3 may dimerize primarily through the following pathway:

$$\mathbf{3^+,\ 4^+} \quad + \quad \mathbf{4} \quad \longrightarrow \quad \xrightarrow{-H^\oplus}$$

$$\mathbf{7} \quad + \quad \mathbf{8} \tag{3}$$
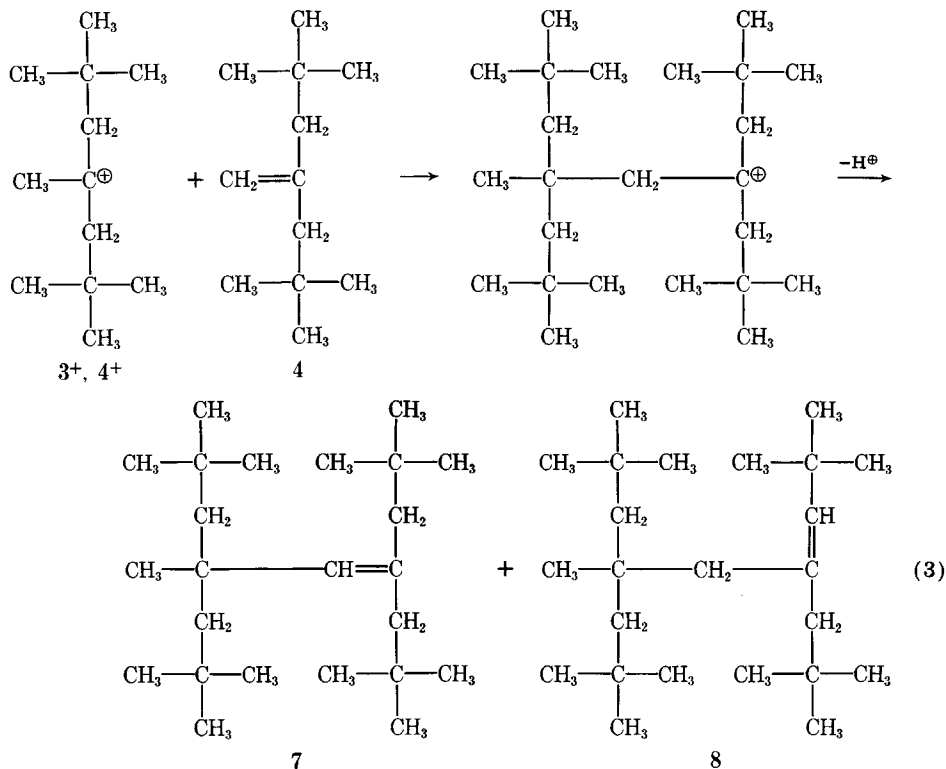
Therefore, the IB_6 showing the major olefinic peaks (140.0 and 138.4 ppm) should be **7** and/or **8**.

The fact that **4** dimerizes whereas **3** does not mean the absence of addition of IB_3^+ to **3**. Cation IB_3^+ may isomerize via intramolecular hydride transfer, so that reactions of the isomerized IB_3^+ with **4** give various IB_6 isomers that lead to the complicated ^{13}C-NMR spectra. Furthermore, cations IB_3^+ and IB_6^+ are prone to crack because of their sterically crowded cationic centers, and this cracking results in IB_5 and IB_7.

This study showed that the oligomerization of IB_3 with CF_3SO_3H can effectively yield a mixture of IB_5, IB_6, and IB_7 in a nonpolar solvent at low temperature; IB_6 was obtained, though no selectively, as a major product.

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