

OLIGOMERIZATION OF PERFLUOROPROPYLENE CATALYZED BY π -BIS(ARENE)CHROMIUM(0) COMPLEXES *

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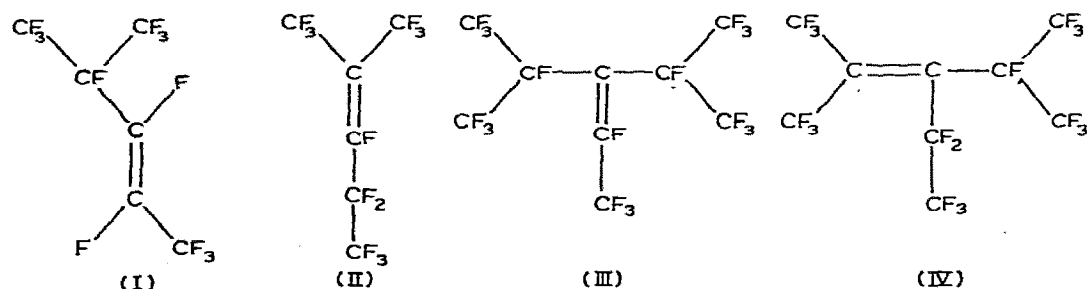
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Summary

Oligomerization of perfluoropropylene catalyzed by four π -bis(arene)chromium(0) complexes (arene = benzene, diphenyl, 1,3,5-trimethylbenzene and hexamethylbenzene) were compared. Besides dimers (I, II) and trimers (III, IV) reported previously [1], two defluorotrimers VA and VB were found to be present in the oligomer mixtures. The formation of VA and VB was shown to be derived from trimer IV by hydrogenation followed by elimination of two moles of hydrogen fluoride.

In the previous paper, we reported that zerovalent π -bis(benzene)chromium could oligomerize catalytically perfluoropropylene at room temperature to give dimers (I, II) and trimers (III, IV) [1]. We reported also, in another paper,



that the same metal complex was able to catalyze the polymerization of perfluorobut-2-yne [2]. For the above two reactions, we proposed a possible mechanism.

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TABLE 1

EFFECT OF DIFFERENT LIGANDS ON THE YIELD AND COMPOSITION OF OLIGOMERS IN π -BIS(ARENE)CHROMIUM(0)-CATALYZED OLIGOMERIZATION OF PERFLUOROPROPYLENE

Ligand	Reactant (mmol)		Oligomers (g)	Mol. of perfluoro-propylene catalyzed:	Dimers:	Composition of dimer ^a	Composition of trimer ^b
	Cr	Perfluoropropylene					
Biphenyl	3.9	172	16.6	28 : 1	3.3 : 1	4.3 : 1	1 : 2.5 : 0
Benzene	3.9	187	24.0	41 : 1	2.6 : 1	4.0 : 1	1 : 20 : 2.5
1,3,5-Tri-methylbenzene	3.9	200	28.0	48 : 1	0.6 : 1	3.0 : 1	0 : 1 : 1.1
Hexamethylbenzene	3.9	113	1.8	3 : 1	2.5 : 1	0.4 : 1	—

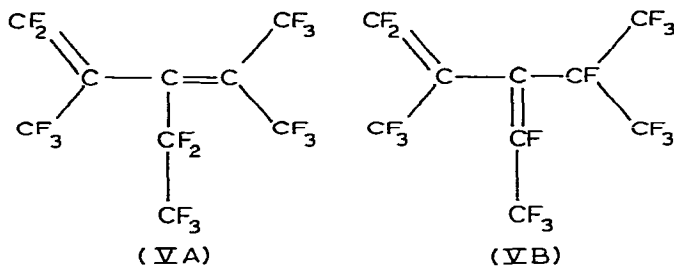
^a Estimated from integrated intensity of CF_3 in ^{19}F NMR. ^b Roughly estimated from GLC.

In this paper we deal with the oligomerization of perfluoropropylene by three other π -bis(arene)chromium(0) complexes: π -bis(diphenyl)chromium(0), π -bis(1,3,5-trimethylbenzene)chromium(0), π -bis(hexamethylbenzene)chromium(0). We found that using these different catalysts afforded a different ratio of the products as shown in Table 1 and Fig. 1. Table 1 shows that the relative activity of these four π -bis(arene)chromiums is in the order: π -bis(1,3,5-trimethylbenzene)chromium(0) > π -bis(benzene)chromium(0) > π -bis(biphenyl)chromium(0) > π -bis(hexamethylbenzene)chromium(0). Figure 1 represents the gas chromatogram of the products using perfluoroether oil on red support 202 as the stationary phase which was found to be superior to squalane used previously [1] for the separation of products.

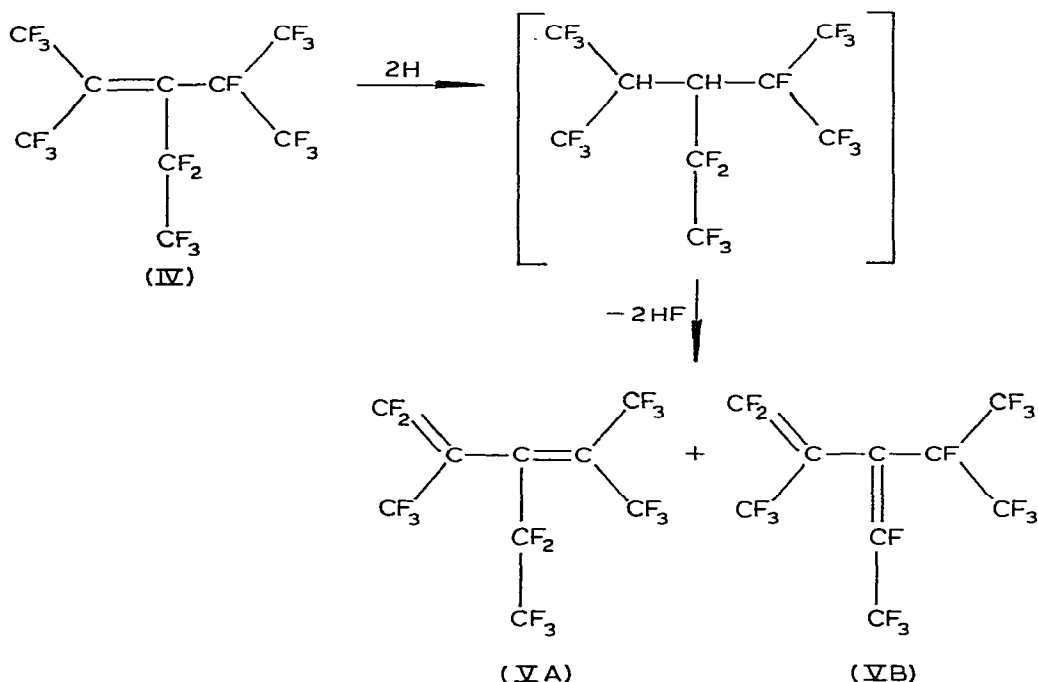
Products of the reaction catalyzed by π -bis(1,3,5-trimethylbenzene)chromium(0) were separated by preparative gas chromatography, from which both dimer I (peak 1) and dimer II (peak 2) were isolated neatly. However, they could not be separated from each other with squalane as the stationary phase reported previously [1]. The product isolated from peak 3 was found to be the trimer III, while that from peak 4 was the trimer IV. All products were identified by ^{19}F NMR spectroscopy.

It is very interesting to mention that when π -bis(biphenyl)chromium(0) was used as catalyst, the size of peak 5 increased at the expense of peak 4 (Fig. 1-C). Only when a large amount of sample was subjected to gas chromatography could peak 4 be observed. On the other hand, when π -bis(1,3,5-trimethylbenzene)chromium(0) was used as catalyst, the size of peak 4 increased and peak 5 disappeared. When a large amount of sample was subjected to gas chromatography, peak 5 could be observed. Therefore, it is reasonable to speculate that the product of peak 5 is derived from the product of peak 4 (trimer IV). Product of peak 5 was thus isolated by preparative gas chromatography. Its mass spectrum showed a parent peak 412 (fragment m/e , see experimental part); its IR showed characteristic double bond absorptions at 1640, 1690, and 1730

cm^{-1} , and its ^{19}F NMR showed it to be a mixture of defluoro-trimers VA and VB in ca. 3 : 1 ratio.



The formation of V could be due to the hydrogenation of IV to give a dihydro-IV followed by elimination of two molecules of hydrogen fluoride as shown below:



In order to verify our speculation, a mixture of trimer III and IV was subjected to hydrogenation of $\text{Pd}/\text{Al}_2\text{O}_3$ (1%) catalyst. Gas chromatogram, mass spectrum and ^{19}F NMR indicated that trimer IV was indeed converted to VA and VB in a ratio of ca. 1 : 3, while trimer III remained intact.

What is the fate of hydrogen fluoride? The low boiling fraction of the products obtained from the catalytic oligomerization was subjected to gas chromatography (Fig. 2) and examined by GC-MS. Peak A was shown to be perfluoropropylene ($M^+ = 150$, m/e 131, 100, 81, 69, 50) while peak B to be 1,1,1,2,3,3,3-heptafluoropropane ($M^+ - 19 = 151$, m/e 101, 82, 69, 51). These data are in complete coincidence with that of authentic samples. Obviously,

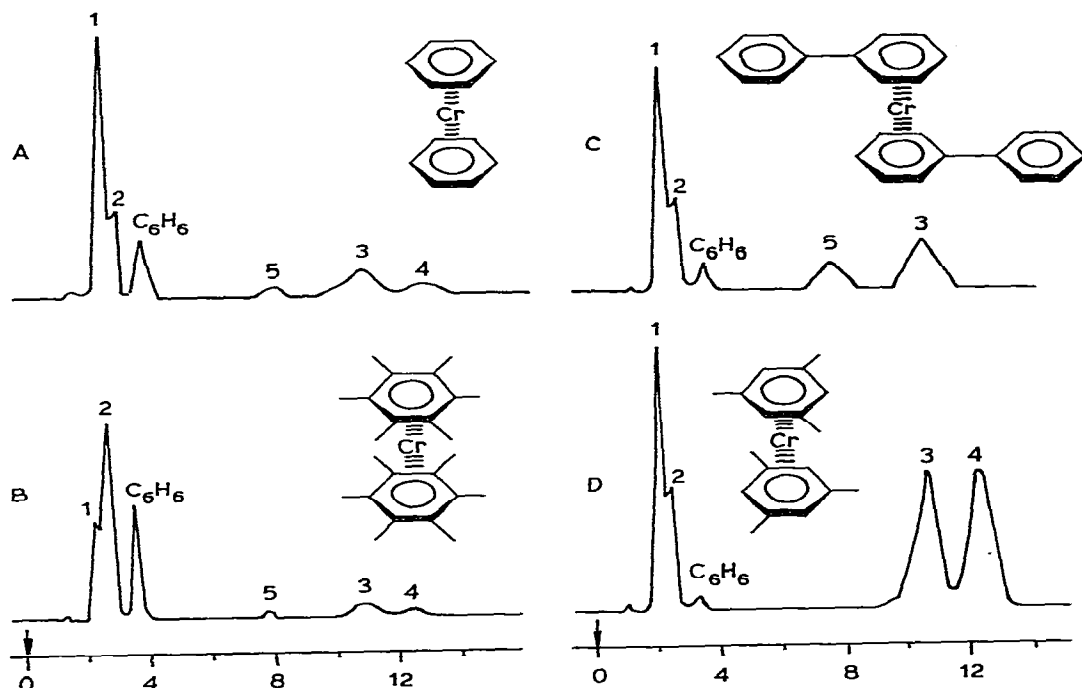


Fig. 1. Gas chromatogram of oligomers of perfluoropropylene formed by catalysis of π -bis(arene)chromium(0). Stationary phase: 30% perfluoroether oil on red support 202. Column length, 3.5 m; Temp. of column, 80°C. Flow rate of N_2 , 12 ml/min. Detector, H_2 flame ionization detector. 1. Dimer I, 2. Dimer II, 3. Trimer III, 4. Trimer IV, 5. Defluoro-trimer V.

hydrogen fluoride added to perfluoropropylene to form 1,1,1,2,3,3,3-heptafluoropropane.

Where does the hydrogen come from to hydrogenate trimer IV in oligomerization? Whether it comes from ligand through π - σ rearrangement or from sol-

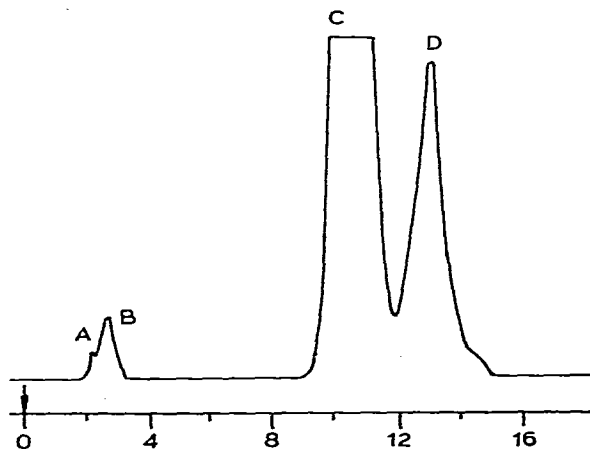


Fig. 2. Gas chromatogram of fraction, boiling below 60°C. Stationary phase: 30% perfluoroether oil on red support 202. Column length, 3.5 m; Temp. of column, 30°C. Flow rate of N_2 , 15 ml/min. Detector, Thermoconductivity. A. Perfluoropropylene. B. 1,1,1,2,3,3,3-Heptafluoropropane. C. Dimer I, D. Dimer II.

vent exchange or from both remains unknown. The mechanism is being pursued actively.

Experimental

^{19}F NMR spectra were determined with a R-32 (84.6 MHz for ^{19}F) apparatus, TFA as external standard, highfield positive.

π -Bis(arene)chromium(0)

π -Bis(biphenyl)chromium(0), π -bis(1,3,5-trimethylbenzene)chromium(0), and π -bis(hexamethylbenzene)chromium(0) were prepared by the method reported in the literature [4].

Oligomerization of perfluoropropylene by π -bis(1,3,5-trimethylbenzene)chromium(0)

According to the procedure reported in our previous paper, reaction of 40 ml of a benzene solution of π -bis(1,3,5-trimethylbenzene)chromium(0) (each ml containing 28 mg, altogether 3.9 mmol) and 30.0 g (200 mmol) of perfluoropropylene gave 28.0 g of oligomers. Fractional distillation gave two portions: one boiled below 60°C (9.8 g) and the residue (17.0 g).

Separation by preparative gas chromatography (stationary phase, 30% perfluoroether oil, boiling point 250–300°C/10⁻⁴ mmHg, on red support 202. Column length 3.5 m. Detector: Thermoconductivity. Flow rate of N₂, 15 ml/min. Temp. of column, 30°) of the former gave two products. The one corresponding to peak 1 (Fig. 1) was identified as dimer I by ^{19}F NMR, $\delta(\text{F})$ (ppm): -3 (=CCF₃), 3(2 CF₃), 84(=CF), 86 (=CF), 115(CF). Its IR spectrum showed no characteristic double bond absorption, indicating that it has *trans* structure [3]. The other, corresponding to peak 2, was identified as dimer II by ^{19}F NMR, $\delta(\text{F})$ (ppm): -16(=CCF₃), -13(=CCF₃), 10.3(CF₃), 25(=CF), 44(CF₂). It exhibits strong double bond absorption at 1680 cm⁻¹ in IR. The ^{19}F NMR spectra of both dimers mentioned above are in complete coincidence with those reported previously [1].

In the course of preparative gas chromatography of the fraction boiling below 60°C, besides dimer I (peak C) and dimer II (peak D), two small peaks (A and B) were observed (Fig. 2). By means of GC-MS (MAT 112) the compound of peak A was shown to be perfluoropropylene ($M^+ = 150$, m/e 131, 100, 81, 69, 50) and the compound of peak B to be 1,1,1,2,3,3,3-heptafluoropropane ($M^+ - 19 = 151$, m/e 101, 82, 69, 51). These data are completely consistent with those of authentic samples.

The residue, from which a fraction boiling up to 60°C had been distilled, was subjected to preparative gas chromatography (conditions identical with the above except the column temperature was 80°C). Two compounds were isolated. One is trimer III and the other trimer IV. Both were identified by ^{19}F NMR and IR. All data are identical with those reported previously [1].

Oligomerization of perfluoropropylene by π -bis(biphenyl)chromium(0)

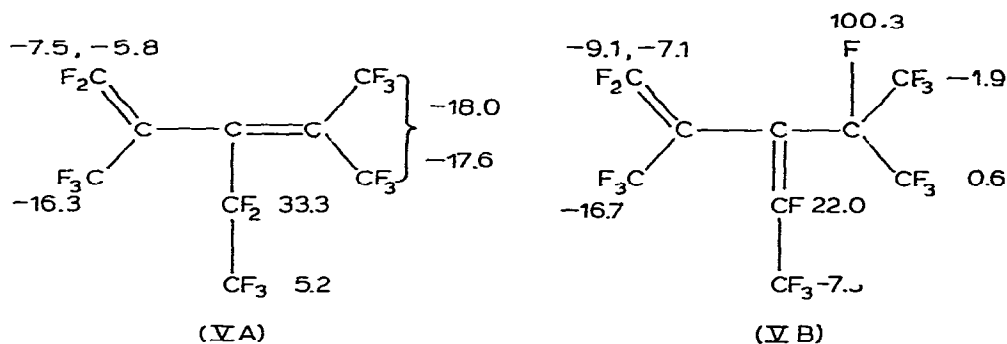
Reaction of 40 ml of benzene solution of π -bis(biphenyl)chromium(0) (each ml containing 34.6 mg, altogether 3.9 mmol) and 25.8 g (172 mmol) of

perfluoropropylene gave 16.6 g of oligomers. Fractional distillation gave two portions: distillate collected before 60°C, 12.1 g (mainly dimers) and the residue 3.7 g (mainly trimers). Dimers : trimers = 3.3 : 1.

Chromatography of the distillate showed that besides dimers I and II perfluoropropylene and 1,1,1,2,3,3,3-heptafluoropropane were also present. Preparative chromatography of the residue gave two specimens: the one corresponding to the peak 3 was identified as trimer III by ^{19}F NMR and IR, which were completely identical to that reported previously [1]. Another sample corresponding to peak 5 showed characteristic double bond absorption in IR at 1640, 1690 and 1730 cm^{-1} . Its mass spectrum showed that the parent peak 412, (m/e 412, 393, 343, 305, 293, 255, 243, 205, 181, 155, 117, 93, 69).

Anal.: Found: C, 26.08; 26.27; F, 73.21, 72.42. C_9F_{16} calcd.: C, 26.23; F, 73.77%.

^{19}F NMR showed that it was a mixture of defluorotrimer VA and VB. They could not be separated by the chromatography we adopted.



From the integrated intensities of F of $=\text{CFCF}_3$ and $-\text{CF}(\text{CF}_3)_2$ in VB and of $=\text{CCF}_2\text{CF}_3$ in VA, VA : VB was estimated as 3 : 1.

The ^{19}F NMR and IR of the compound isolated from peak 5 by preparative gas chromatography of the oligomers of perfluoropropylene obtained by catalyst π -bis(benzene)chromium(0) were found to be exactly the same as those obtained by catalyst π -bis(biphenyl)chromium(0).

Oligomerization of perfluoropropylene by π -bis(hexamethylbenzene)chromium(0)

Reaction of 40 ml of a benzene solution of π -bis(hexamethylbenzene)chromium(0) (each ml containing 36.26 mg, altogether 3.9 mmol) and 17 g perfluoropropylene (113 mmol) gave 1.8 g oligomers. Conversion, 10.8%. Its gas chromatogram was shown in Fig. 1. 1,1,1,2,3,3,3-Heptafluoropropane was also found in the low boiling fraction of the products.

Catalytic hydrogenation of trimers III and IV

A mixture of trimers III and IV obtained by the catalysis of π -bis(1,3,5-trimethylbenzene)chromium(0) was allowed to vaporize (150°C) and hydrogenated with hydrogen through the hot tube (130°C) filled with Pd/ Al_2O_3 (1%) catalyst. The tube was heated to 180°C during the reaction, and the product collected

in a trap cooled with dry-ice. The chromatogram of the hydrogenated product indicated that trimer IV was almost completely converted to defluorotrimer V and that trimer III remained intact. The mixture was subjected to preparative gas chromatography, and two compounds were isolated in pure form. The mass spectrum of one (corresponding to peak 5, Fig. 1) showed that $M^+ = 412$ (m/e 412, 393, 343, 305, 293, 255, 243, 205, 181, 155, 117, 93, 69), completely identical to that of V obtained by catalytic oligomerization of perfluoropropylene by π -bis(biphenyl)chromium(0). The ^{19}F NMR of this compound showed also the same chemical shifts. The mass spectrum and ^{19}F NMR of the other compound showed that the trimer III remained intact under the hydrogenation conditions we adopted.

Acknowledgement

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