ethyl acetate (40 g., 0.24 mole) with stirring at 100° in a nitrogen atmosphere during 30 minutes. The mixture was slowly heated to 160°. It was then heated at 160–170° for 3 hr. and finally at 175° for two hr. The reaction mixture was distilled to yield $\beta$-acetoxyethyl phenyl-(methyl)-phosphinate (33.2 g., 59%), b.p. 155–160° (0.9 mm.), $n^{25.8}\text{D}$ 1.5073–1.5093.[27] The ester gave a single peak on vapor chromatography.

*Anal.* Calcd. for $C_{11}H_{15}PO_4$ (242.2): C, 54.54; H, 6.24; P, 12.50. Found: C, 53.94; H, 6.53; P, 12.47.

Further distillation of the reaction mixture yielded a light-yellow viscous liquid (10.5 g.), b.p. 214–217° (0.15 mm.), $n^{25}\text{D}$ 1.5600.

*Anal.* Calcd. for $C_{16}H_{20}P_2O_4$ (338.3): C, 56.87; H, 5.95; P, 18.24; sapon equiv., 169. Found: C, 56.79; H, 5.85; P, 18.82; sapon. equiv., 167.

A sample of the high boiling ester (2.45 g., 14.9 mmoles) was refluxed for 2 hr. with 10% NaOH (20 ml.). The solution was chilled to 0° and was then shaken with benzoyl chloride (2.7 g., 19.2 mmoles). The precipitate which formed was ethylene dibenzoate, 0.9 g. (50%), m.p. 69–70.5°.

Hydrolysis of a 1.02-g. sample of the high boiling ester with dilute alkali, as described above, followed by acidification yielded 0.76 g. (82%) of phenyl-(methyl)-phosphinic acid. No ethylene bis-(phenylphosphinic acid) was found. The high boiling ester was therefore ethylene bis-[phenyl-(methyl)-phosphinate].

**Reaction of Dimethyl Phenylphosphonite with Ethylene Dibromide.**—Dimethyl phenylphosphonite (54 g., 0.37 mole) was slowly added with stirring to ethylene dibromide (30 g., 0.16 mole) at 130° during 4 hr. After heating for an additional 2 hr. at 150–160°, the mixture was distilled to yield methyl phenyl-(methyl)-phosphinate (20.3 g., 38%), b.p. 123° (5 mm.), $n^{25}\text{D}$ 1.5164–1.5252, and a mixture of the higher boiling bisphosphinic esters VI and VIII (30.7 g., 56%), b.p. 205–220° (0.2–0.4 mm.), $n^{25}\text{D}$ 1.5630.

*Anal.* sapon. equiv., 164.8; Br, 0.38.

Unreacted ethylene dibromide (9.1 g., 30%), $n^{26}\text{D}$ 1.5328, was recovered from the Dry Ice trap.

Vapor chromatography of the methyl phenyl-(methyl)-phosphinate fraction showed that traces of water and alcohol were the only impurities present. There was no evidence for the presence of either methyl phenyl-($\beta$-bromoethyl)-phosphinate or $\beta$-bromoethyl phenyl-(methyl)-phosphinate.

**Composition of Diester Mixture by Hydrolysis.**—A sample of the diester fraction (19.4 g., 0.058 mole) was dissolved in 2.5% NaOH solution (400 ml.) and the solution was acidified with concd. HCl. A mixture (11.7 g.) of phenyl-(methyl)-phosphinic acid and ethylene bis-(phenylphosphinic acid) precipitated, m.p. 128–205°. Extraction with ethanol yielded ethylene bis-(phenylphosphinic acid) (0.74 g., 0.024 mole, 4%), m.p. 252–260°. After recrystallization from glacial acetic acid, the product melted 267–269°.[30]

*Anal.* Calcd. for $C_{14}H_{16}P_2O_4$ (310.5): C, 54.1; H, 5.2; P, 20.0. Found: C, 53.60; H, 5.85; P, 19.78.

Evaporation of the ethanol extract to dryness yielded phenyl-(methyl)-phosphinic acid, m.p. 132–133.5°, neut. equiv. 157 (calcd. 156).

A sample of the diester mixture (5.1 g., 0.015 mole) in 10% NaOH solution (50 ml.) was boiled to distil off methanol. The solution was chilled and then treated with four 1-ml. portions of benzoyl chloride. There was obtained ethylene dibenzoate (1.97 g., 0.0073 mole, 48.7%), m.p. 70–72°. The infrared spectrum was identical with that of ethylene dibenzoate. A mixed m.p. was undepressed.

**Acknowledgments.**—Spectroscopic and vapor chromatography analyses were made by Messrs. D. R. Beasecker, R. B. Coffey, J. W. Cooper, J. V. Pustinger, J. M. Schlater and W. D. Ross of our instrumental laboratory; chemical analyses were made by Messrs. R. Knotts, A. Wheeler and Mrs. W. Harden of our analytical department and by Galbraith Microanalytical Laboratories.

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[30] This reaction is regarded as an independent synthesis of ethylene bis-(phenylphosphinic acid) even though the product was obtained in very low yield. An alternate procedure for preparing this acid in high yield will be published subsequently.

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[CONTRIBUTION NO. 16 FROM THE EXPLORATORY RESEARCH LABORATORY, DOW CHEMICAL OF CANADA, LTD.]

# Ionic Polymerization. I. Reaction Mechanism Investigation of the Cationic Polymerization of $\alpha$-Olefins through Intermediate Carbonium Ion Complexes[1]

BY G. A. OLAH, H. W. QUINN AND S. J. KUHN

RECEIVED MAY 1, 1959

The reaction mechanism of the ionic polymerization of $\alpha$-olefins was investigated in the olefin:HF:$BF_3$, olefin:DF:$BF_3$, olefin:alkyl fluoride:$BF_3$, olefin:acyl fluoride:$BF_3$ and olefin:nitryl fluoride:$BF_3$ systems. Olefin:anhydrous silver tetrafluoroborate:organic chloride or bromide systems were similarly used. Electrophilic aromatic alkylation and cationic polymerization of olefins as consecutive and concurrent reactions were investigated by treating protonated alkylbenzene tetrafluoroborates with olefins.

The polymerization of $\alpha$-olefins and certain vinyl monomers with small amounts of catalyst of the Friedel–Crafts type is well known.[2] Effective polymerization catalysts in this class include $AlCl_3$, $AlBr_3$, $BF_3$, $TiCl_4$, $SnCl_4$, etc. All of them are strong acids in the terminology of G. N. Lewis, *i.e.*, they are strong electron acceptors. Isobutylene, styrene, $\alpha$-methylstyrene, butadiene and vinyl alkyl ethers are representatives of the monomer types readily converted to polymers of high molecular weight by catalysts among those mentioned. However, these reactions are generally too fast to be suitable to follow. Propylene, butenes and other olefins may also be polymerized, but the products tend to be relatively low in molecular weight. The formation of these liquid polymers is however more easily followed in reaction mechanism investigations.

The mechanism of the Friedel–Crafts polymerization of $\alpha$-olefins was originally proposed[3] as the direct interaction of the Lewis acid-type catalyst with the corresponding olefin.

The inactivity of a pure Friedel–Crafts catalyst for polymerization was first reported by Ipatieff

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[1] Presented partly as a paper at the 8th Canadian High Polymer Forum, St. Anne de Bellevue (Quebec), Canada, May 13, 1958.

[2] D. C. Pepper, *Sci. Proc. Roy. Dublin Soc.*, **25**, 131 (1950) (a discussion ed. by D. C. Pepper); P. H. Plesch, "Cationic Polymerization and Related Complexes," W. Heffer and Sons, Cambridge, England, 1953; P. H. Plesch, *Research* (*London*), **2**, 267 (1949).

[3] W. Chalmers, *Can. J. Research*, **7**, 113, 472 (1932); THIS JOURNAL, **56**, 912 (1934).

and Grosse[4] in 1936. They reported their experimental discovery that aluminum chloride, when really pure, does not react with pure ethylene. However, the necessity for an additional component for Friedel–Crafts catalytic activity was not discussed in the literature until ten years later.

Polanyi, Evans, Plesch, Meadows, Skinner, Norrish, Russell, Dainton, Pepper and others have proved,[5] however, that to achieve polymerization with a Friedel–Crafts-type catalyst the presence of a co-catalyst is also always needed. Accordingly, the catalyst–co-catalyst system interacts as a strong protonating acid and the electrophilic polymerization proceeds through the simple protonating mechanism.

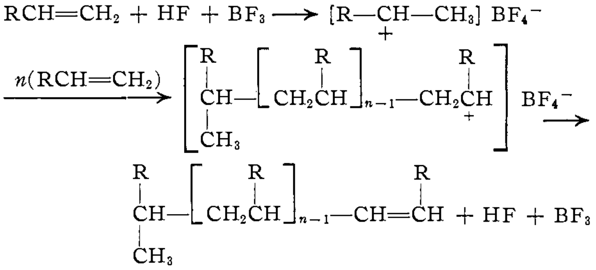
In recent work we have investigated the acyl fluoride:boron trifluoride,[6] nitryl fluoride:boron trifluoride[7] and alkyl fluoride:boron trifluoride binary[8] and also the alkylbenzene:hydrogen fluoride:boron trifluoride ternary complexes.[9] It was found that the intermediate protonated alkylbenzene tetrafluoroborates, already postulated by McCaulay and Lien,[10] could be isolated at low temperatures. Similarly ternary complexes of the composition 1:1:1 were prepared from alkylbenzenes:alkyl fluorides:boron trifluoride and alkylbenzenes:acyl fluorides:boron trifluoride. These complexes are indeed the intermediate σ-complexes proposed by Brown[11] for the electrophilic aromatic substitutions.

Theoretically the intermediate complexes of an electrophilic aromatic substitution and a electrophilic olefin addition (and subsequently the electrophilic polymerization) must be identical. We have extended now our investigations on the reaction mechanism to cationic polymerizations of α-olefins.

By replacing the alkylbenzenes as the nucleophilic agents by α-olefins we have observed a close similarity with the hydrogen fluoride:boron trifluoride system. α-Olefins are generally only slightly soluble in anhydrous hydrogen fluoride at temperature between −80 and 0°. (The solubility is in the order of magnitude of 1% or less.) However, anhydrous hydrogen fluoride adds to olefins to form alkyl fluorides and this makes the measurement of the solubilities difficult. At −80° the addition reaction is generally slow and most of the simple α-olefins were found insoluble in anhydrous hydrogen fluoride without adding to it for some hours. Boron trifluoride is not absorbed by either α-olefins or hydrogen fluoride under absolutely anhydrous conditions and as proved by Evans and Polanyi[5c] under these anhydrous conditions even isobutylene is not polymerized by boron trifluoride at −80°. However, if we introduced boron trifluoride into the heterogeneous equimolecular α-olefin:hydrogen fluoride mixtures, it was absorbed vigorously up to a weight increase of one mole equivalent. On the basis of this result the formation of an intermediate α-olefin:hydrogen fluoride:boron trifluoride complex approximating the molar composition 1:1:1 is to be expected. The investigation of the intermediate complexes is more difficult in this case than with the corresponding aromatic:hydrogen fluoride:boron trifluoride complexes due to the fact that the carbonium ion formation is followed by polymerization. The intermediate complex formation can be represented as

$$RCH{=}CH_2 + HF + BF_3 \longrightarrow [R{-}\underset{+}{C}H{-}CH_3]\ BF_4^-$$

The polymerization of simple α-olefins initiated by the intermediate olefin:HF:BF$_3$ complex most probably follows the mechanism, in which proton elimination is taken as the simplest chain termination reaction



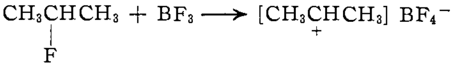
$$RCH{=}CH_2 + HF + BF_3 \longrightarrow [R{-}\underset{+}{C}H{-}CH_3]\ BF_4^-$$

$$\xrightarrow{n(RCH=CH_2)} \left[\underset{CH_3}{\overset{R}{CH}}{-}\left[CH_2\overset{R}{CH}\right]_{n-1}{-}CH_2\underset{+}{\overset{R}{CH}}\right] BF_4^- \longrightarrow$$

$$\underset{CH_3}{\overset{R}{CH}}{-}\left[CH_2\overset{R}{CH}\right]_{n-1}{-}CH{=}\overset{R}{CH} + HF + BF_3$$

This mechanism is basically identical with Whitmore's earlier proposed proton-catalyzed mechanism.[12] As a matter of convenience, we have not considered in writing this mechanism any possible isomerization undergone by the carbonium ions.

Alkyl fluorides themselves form with boron trifluoride at low temperatures, as shown by us previously, 1:1 addition complexes.[8] Measurement of the electric conductivities suggest that the methyl and ethyl fluoride:boron trifluoride complexes are only polarized covalent addition compounds; however, the isopropyl and *t*-butyl fluoride:boron trifluoride complexes are highly ionized complexes approximating the ionic alkyl carbonium tetrafluoroborates.



$$CH_3\underset{F}{C}HCH_3 + BF_3 \longrightarrow [CH_3\underset{+}{C}HCH_3]\ BF_4^-$$

The alkyl fluoride:boron trifluoride complexes are effective catalysts for polymerizing such α-olefins as propylene, 1-butene, 2-methyl-1-butene, isobutylene, etc.

Similarly alkylcarbonium tetrafluoroborate complexes were also prepared by our tetrafluoroborate complex preparation method[13] using silver tetrafluoroborate and the corresponding chlorides or bromides (this method eliminates the use of HF or alkyl (acyl) fluorides).

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(4) J. N. Ipatieff and A. V. Grosse, THIS JOURNAL, **58**, 915 (1936).

(5) (a) A. G. Evans, B. Holden, P. Plesch, M. Polanyi, H. A. Skinner and M. A. Weinberger, *Nature*, **157**, 102 (1946); (b) A. G. Evans, G. W. Meadows and M. Polanyi, *ibid.*, **158**, 94 (1946); (c) A. G. Evans and M. Polanyi, *J. Chem. Soc.*, 252 (1947); (d) P. H. Plesch, M. Polanyi and H. A. Skinner, *ibid.*, 257 (1947); (e) A. G. Evans and G. W. Meadows, *J. Polymer Sci.*, **4**, 359 (1949); (f) F. S. Dainton and G. B. B. M. Sutherland, *ibid.*, **4**, 37 (1949); (g) R. G. W. Norrish and K. E. Russell, *Trans. Faraday Soc.*, **48**, 91 (1952); (h) D. C. Pepper, *ibid.*, **45**, 397 (1949).

(6) G. Olah and S. Kuhn, *Chem. Ber.*, **89**, 866 (1956).

(7) G. Olah, S. Kuhn and S. Mlinko, *J. Chem. Soc.*, 4257 (1956).

(8) G. Olah, S. Kuhn and J. Olah, *ibid.*, 2174 (1957).

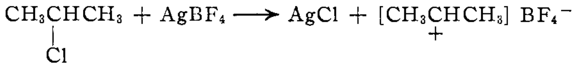
(9) G. A. Olah and S. J. Kuhn, THIS JOURNAL, **80**, 6535 (1958); **80**, 6541 (1958).

(10) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951); **74**, 6246 (1952); D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

(11) H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

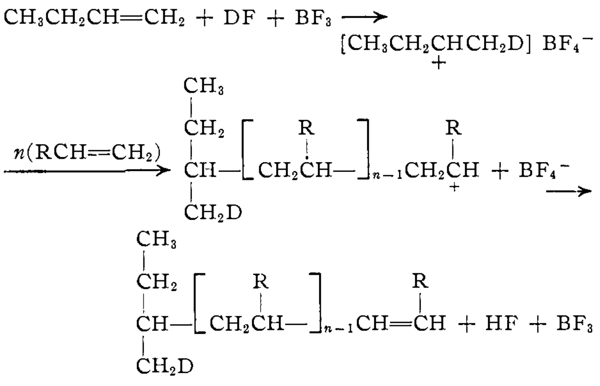
(12) F. C. Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

(13) G. Olah, A. Pavlath and S. Kuhn, *Chemistry & Industry*, 50 (1957).



$$\mathrm{CH_3\underset{\substack{|\\ Cl}}{C}HCH_3 + AgBF_4 \longrightarrow AgCl + [CH_3\underset{+}{C}HCH_3]\ BF_4^-}$$

When anhydrous DF + $BF_3$ was used in the complex formation and subsequent polymerization, we have obtained deuterated polymers as a further proof of the protonating mechanism postulated by Whitmore.[12]

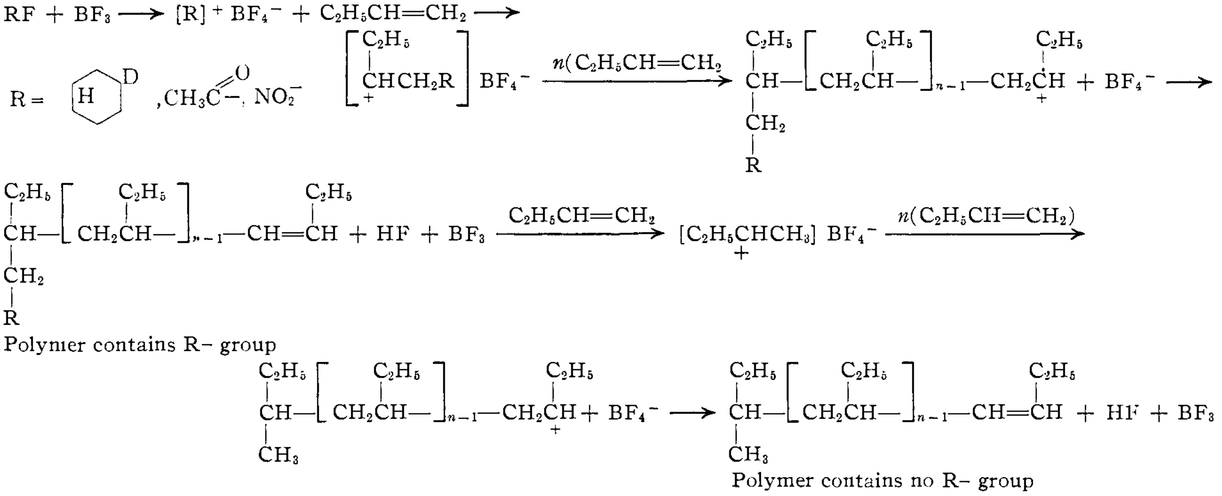


$$\mathrm{CH_3CH_2CH{=}CH_2 + DF + BF_3 \longrightarrow [CH_3CH_2\underset{+}{C}HCH_2D]\ BF_4^-}$$

$$\xrightarrow{n(\mathrm{RCH{=}CH_2})} \mathrm{\underset{\substack{|\\ CH_2D}}{\overset{\substack{CH_3\\ |\\ CH_2\\ |}}{CH}}—\left[CH_2\overset{\substack{R\\ |}}{C}H—\right]_{n-1}CH_2\underset{+}{\overset{\substack{R\\ |}}{C}}H + BF_4^- \longrightarrow}$$

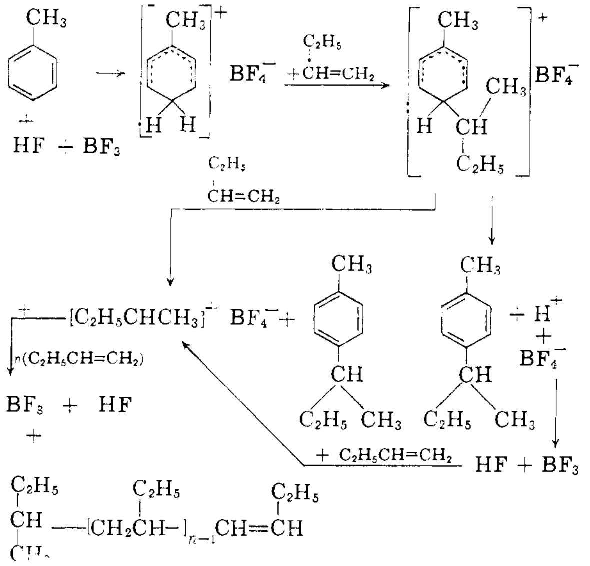
$$\mathrm{\underset{\substack{|\\ CH_2D}}{\overset{\substack{CH_3\\ |\\ CH_2\\ |}}{CH}}—\left[CH_2\overset{\substack{R\\ |}}{C}H—\right]_{n-1}CH{=}\overset{\substack{R\\ |}}{C}H + HF + BF_3}$$

The polymerization of α-olefins with alkyl fluoride: boron trifluoride catalysts is furthered not only by the direct interaction of the cation complex with the olefins but also by the termination reactions of polymer chains with release of protons. By performing the polymerization of 1-butene with cyclohexyl-*d* tetrafluoroborate, two fractions of the polymers were isolated, one of which contained (as proved by infrared spectrum) cyclohexyl-*d* groups while the other was free of spectroscopically detectable cyclohexyl-*d* groups.



Similar to the HF or DF + $BF_3$ and alkyl fluoride + $BF_3$ systems, acyl fluoride + $BF_3$ systems, which produce stable acyl tetrafluoroborate complexes, can also be used as polymerization catalysts. In this case too it was possible to isolate two fractions of liquid polymers: an acyl group containing fraction identified through the carbonyl frequency in the infrared spectrum and a second polymer fraction completely free of carbonyl absorption.

The isolation of these two fractions of polymer is a further direct proof of the postulated reaction mechanism: polymerization is initiated partly through acyl cations and partly through released protons from terminating polymer chains. Applying the same principle, nitronium tetrafluoroborate, previously described by us as effective aromatic nitrating agent,[7] was found to polymerize olefins. Again it was possible to isolate a liquid polymer fraction free of nitro groups and another, more viscous fraction showing in the infrared absorption the presence of nitro groups.

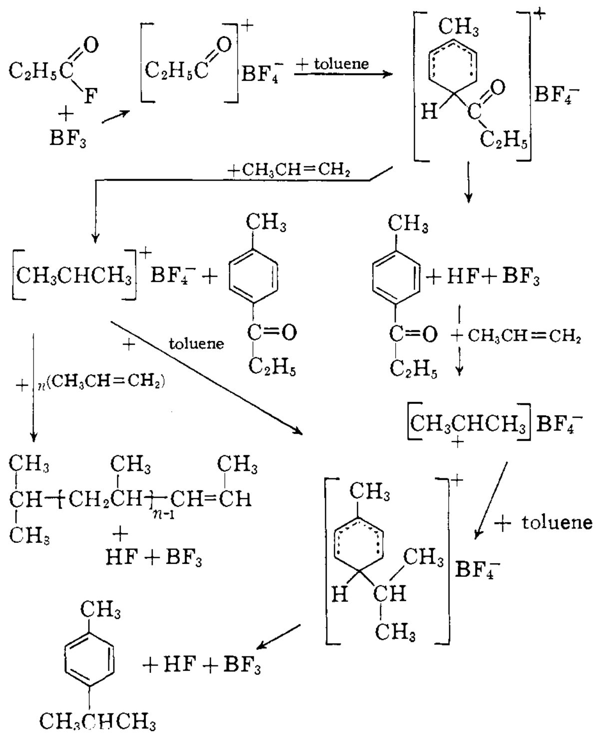


We have found that protonated aromatic tetrafluoroborate σ-complexes are also effective cationic polymerization catalysts. It was possible to follow the reaction mechanism of electrophilic polymerizations in this case too, isolating the products of the reactions. If we used a protonated toluene tetrafluoroborate complex as the polymerization catalyst for 1-butene, the main reaction products were liquid polymer and butyltoluenes (depending on the aromatic: olefin ratio) (as above chart shows). The equations as written are not meant to imply that a simple one-step addition process is involved in the interaction of the protonated tetrafluoroborate σ-complex with the olefin to produce the alkylated σ-complex. More likely the protonated σ-complex itself acts as a protonating agent toward the olefin which then alkylates the aromatic ring in the usual way. Investigation of the chemical reactivity of the σ-complexes will be reported later.

By carefully fractionating the reaction products and investigating the fractions by infrared spectroscopy it was found that also longer chain alkylated toluenes were formed, *i.e.*, the low molecular weight polymers formed were able also to alkylate in the presence of the Friedel–Crafts system and so to form aromatics containing longer side chains. Similar results were also obtained by using as polymerization initiators (1) alkylated aromatic tetrafluoroborate σ-complexes, formed by the reaction of toluene with isopropyl fluoride and boron trifluoride, and (2) acylated aromatic tetrafluoroborate complexes formed from toluene, propionyl fluoride and boron trifluoride.

In this latter reaction the fractionation of the products yielded methylpropiophenone and liquid polymer not containing the aromatic initiating group (all fractions were identified through infrared spectra).

If the reaction is carried out with propylene in the presence of excess toluene, aromatic alkylation and polymerization take place as competitive reactions and the isolated products are methylpropiophenone, liquid polymer free of the initiating aromatic group and cymene (methylisopropylbenzene). Also a small amount of longer side chain alkylated toluene is formed.



It will be noted that after the initial reaction step of the corresponding olefin with HF + $BF_3$, DF + $BF_3$, alkyl fluoride + $BF_3$, acyl fluoride + $BF_3$ or the corresponding aromatic σ-complex tetrafluoroborates, the reaction mechanism is the same. The once-formed active cation or the subsequently released proton initiates a simple electrophilic chain-growing reaction. The isolation of ring-substituted compounds and lower molecular weight liquid polymers from the same reaction mixtures proves in a direct way the theoretical suggestion that Friedel–Crafts polymerizations and aromatic substitutions proceed through identical cationic complexes. The infrared spectra of the obtained liquid polymers always give evidence of the presence of olefinic unsaturation, due to chain termination by proton elimination.

## Experimental

**Materials.**—The olefins used were Phillips 66 research grade with a minimum purity between 99.65 and 99.95%. Boron trifluoride was obtained from the Harshaw Chemical Corp. with a purity of 99%. Anhydrous hydrogen fluoride was a commercial grade of minimum purity of 99.5%. For anhydrous state experiments it was purified as described previously by Olah and Kuhn.[9] Anhydrous silver tetrafluoroborate was prepared according to Olah and Quinn[14] from argentous fluoride and boron trifluoride in nitromethane. The alkyl fluorides and acyl fluorides were prepared as described by Olah and Kuhn.[9] Anhydrous DF was prepared according to Olah and Kuhn.[15]

The infrared spectra of the liquid polymers obtained in the course of our experimental work revealed the presence of olefinic unsaturation. These polymers were of an average molecular weight between 150 and 400 (based on boiling ranges), thus enabling in most cases fractionation by vacuum distillation. In this work, there was no attempt to investigate any other properties (physical or chemical) of the polymers obtained.

**Olefin: HF:BF$_3$ Complexes.**—To 5 g. (0.25 mole) of anhydrous liquid hydrogen fluoride was added 16.5 g. (0.25 mole) of 2-methyl-1-butene, in an all-silica apparatus at −80°. No interaction was observed. The heterogeneous two-phase system was saturated thereafter with boron trifluoride. Upon introduction of $BF_3$ a yellow colored complex was formed. After removing excess $BF_3$ by evaporation at low temperature a weight increase of 14 g. was observed, approximately the equimolar (0.25 mole = 17 g.) quantity needed for a 1:1:1 complex formation. The olefin or anhydrous hydrogen fluoride alone do not absorb boron trifluoride to any extent. However, the complex formation is inevitably followed by partial polymerization and therefore no exact determination of the complex layer composition was possible. Similar complex formation experiments were carried out with propylene and butene-1.

**Polymerization of Olefins with Olefin:HF:BF$_3$ Complexes.**—The olefin:HF:$BF_3$ complexes were prepared from 2-methyl-1-butene and 1-butene as described previously. The complexes of the approximately molar compositions of 1:1:1 were frozen with liquid nitrogen and small quantities (0.2 g.) of the solid complex was added at −80° to the following liquid olefins: propylene, 1-butene, isobutylene, 2-methyl-1-butene, 3,3,3-trifluoro-1-propene and styrene. Propylene, isobutylene and styrene were immediately polymerized with great velocity. 1-Butene and 2-methyl-1-butene gave liquid polymers after the mixture was allowed to stand for two hours while 3,3,3-trifluoro-1-propene gave no polymer.

**Polymerization of Olefins with Olefin:DF:BF$_3$ Complexes.**—To 112 g. (2.0 moles) of liquid 1-butene and 138 g. of 2-methyl-1-butene, respectively, was added 42 g. (2.0 mole) of anhydrous deuterium fluoride. No interaction was observed. Thereafter boron trifluoride was introduced in an equimolar quantity based on the deuterium fluoride. A lower yellow complex layer separated. On standing, the whole reaction mixture became viscous and a liquid polymer was formed. Infrared spectra revealed the presence of C–D bonds by absorption in the 2200 cm.$^{-1}$ region.

**Polymerization of Olefins with Alkyl Fluoride:Boron Trifluoride Complexes.**—Into 0.25 mole of the corresponding alkyl fluoride (isopropyl, *t*-butyl and cyclohexyl fluoride) boron trifluoride was introduced at −80°. The corresponding addition complexes were obtained as described previously.[8] The complexes were frozen at liquid nitrogen temperature and small amounts (0.2 g.) were added at −80° to the following liquid olefins: propylene, 1-butene, isobutylene, 2-methyl-1-butene. Liquid polymers were obtained in all cases in accord with the previous experiments.

(14) G. A. Olah and H. W. Quinn, unpublished work.

(15) G. Olah and S. Kuhn, *Z. anorg. allgem. Chem.*, **287**, 282 (1956); *J. Inorg. and Nuclear Chem.*, **10**, 164 (1959).

**Polymerization of Olefins with Anhydrous Silver Tetrafluoroborate + Organic Chloride (or Bromide) Catalyst.**—To 0.5 mole of liquid olefin (propylene, 1-butene, isobutylene, 2-methyl-1-butene, styrene) was added 1 g. (0.005 mole) of anhydrous AgBF generally at −80° while stirring with a magnetic stirrer. Thereafter 0.005 mole of alkyl (isopropyl, *n*-butyl, *t*-butyl) or acyl (acetyl-, propionyl-) chloride (or bromide) was added. Immediately a white silver halide precipitate was observed and simultaneously heat evolution took place, due to the polymerization of the olefin. The mixture was maintained for 15 minutes at Dry Ice temperature. Thereafter it was allowed to warm up to room temperature. Similar liquid polymers as in the previous experiments were formed.

**1-Fluoro-2-deuteriocyclohexane.**—After cooling 82 g. (1.0 mole) cyclohexene to −80°, 21 g. (1.0 mole) of liquid deuterium fluoride was added rapidly, while the reaction mixture was stirred with a Teflon covered magnetic stirrer. The reaction mixture was then allowed to warm up and was poured over cracked ice. The organic layer was separated, dried over anhydrous potassium carbonate and distilled at slightly reduced pressure; 66.5 g. (64.5% of the theoretical yield) of 1-fluoro-2-deuteriocyclohexane was obtained, b.p. 58–65° (200 mm.), and 23 g. of higher boiling (polymer) residue.

**Polymerization of Olefin with 1-Fluoro-2-deuteriocyclohexane–$BF_3$ Complex.**—A solution of 5 g. (0.05 mole) of 1-fluoro-2-deuteriocyclohexane in 56 g. (1.0 mole) of 1-butene was cooled to Dry Ice temperature and $BF_3$ passed in. An orange complex lower layer appeared and on standing for two hours the whole system became viscous. The orange viscous layer was separated from the remaining material, which was pale yellow in color, and both fractions were washed with water and dried. The infrared spectrum of each fraction was obtained. That of the orange layer revealed the presence of carbon–deuterium bonds in fairly high concentration by absorption in the 2200 cm.$^{-1}$ region while that of the pale yellow layer was practically free of these bonds.

**Acetyl Tetrafluoroborate.**—A solution of 31 g. (0.5 mole) of acetyl fluoride at −80° in 100 ml. of Freon 12 was saturated with boron trifluoride. A white, crystalline precipitate ($CH_3CO^+BF_4^-$) separated. The excess of boron trifluoride was evaporated together with the solvent at ice-bath temperature and the acetyl tetrafluoroborate was kept in a vacuum desiccator; yield 59.5 g. (90%), decomposition point ∼20°.

**Polymerization of Olefin with Acetyl Tetrafluoroborate Complex.**—To 112 g. (2.0 moles) of 1-butene at −80° was added 26 g. (0.2 mole) of crystalline acetyl tetrafluoroborate. No interaction was observed. The mixture was then allowed to warm up slowly. At −20° the white crystalline acetyl tetrafluoroborate became covered with a yellow sticky mass. By cooling the mixture again to −80° and maintaining at this temperature a continuous heat evolution was observed and after about 30 minutes the clear, colorless olefin had become very viscous. The colorless polymer layer was separated from the lower yellow layer at −80° and each layer was treated separately.

The lower yellow layer was washed acid-free, dried and distilled. The fraction collected up to 200° at 30 mm. pressure and the residue both had a strong absorption in the infrared spectrum at about 1725 cm.$^{-1}$, indicating the presence of carbonyl group.

The colorless upper polymer layer after having been washed and dried produced an infrared spectrum showing no carbonyl absorption frequencies.

**Nitronium Tetrafluoroborate.**[7,16]—To a solution of 108 g. (1.0 mole) of freshly prepared dinitrogen pentoxide in 150 g. of nitromethane was added at −20°, 20 g. (1.0 mole) of anhydrous hydrogen fluoride. The solution was then saturated with boron trifluoride. Nitronium tetrafluoroborate separated as a white crystalline material, was collected and dried in vacuum over phosphoric oxide at 100°; yield 125 g. (94%).

**Polymerization of Olefin with Nitronium Tetrafluoroborate Complex.**—To 112 g. (2.0 mole) of 1-butene at −80° was added 27 g. (0.2 mole) of crystalline nitronium tetrafluoroborate in small portions. A vigorous reaction was observed and a highly colored, viscous layer was formed. The reaction mixture was allowed then to warm up slowly to −20°, while the main part of the olefin formed a viscous liquid and boron trifluoride was evolved. The reaction mixture was then poured on cracked ice, washed acid-free. The lower more viscous and colored layer was separated and distilled under reduced pressure (boiling up to 170° at 5 mm. pressure). The infrared spectrum indicated strong absorption in the 1600–1550 and 1350 cm.$^{-1}$ region and thus revealed the presence of nitro groups. The upper liquid polymer layer when investigated in the infrared was practically free of nitro groups.

**Reaction of Olefins with Toluene–HF–$BF_3$ Complex.**—Reactions were carried out in a vessel immersed in a bath at Dry Ice temperature and at atmospheric pressure. The catalyst complex was formed according to Olah and Kuhn,[9] by passing $BF_3$ into colorless two-phase equimolar system of toluene and liquid HF, whereupon a single yellow phase was formed which contained an equimolar quantity of $BF_3$.

(a) To 1.0 mole of liquid 1-butene at −80° was added 0.15 mole of the complex. Heat evolution was quite vigorous for a sustained period of time and the system became very viscous. After washing with water and drying, the organic layer was vacuum fractionated, approximately one-half of it boiling above 200° at 10 mm. pressure. The product, as identified by its infrared spectrum, was largely liquid polymer of butene. The higher boiling fractions showed also the presence of *p*-substituted toluene with side chains of varying length.

(b) To 0.5 mole of the complex in the presence of 0.5 mole of toluene at −80° was added 0.5 mole of liquid 1-butene. There was a quite marked heat evolution and the complex layer became orange in color. The mixture was poured over cracked ice, the organic layer washed, dried over an anhydrous $K_2CO_3$–$Na_2SO_4$ mixture and fractionated. The product was largely a mixture of the isomers of *sec*-butyltoluene, the *o*-isomer predominating, but there was also a small quantity of liquid polymer not containing aromatic groups plus some material identified by its infrared spectrum as a *p*-substituted toluene with a side chain of considerable length, consisting probably of three or four butene units.

**Reaction of Propylene with Toluene–Propionyl Fluoride–$BF_3$ Complex.**—Boron trifluoride was passed into a solution of 0.1 mole of propionyl fluoride in 0.3 mole of toluene at −80°. A yellow solid complex was precipitated which on warming somewhat became orange in color. Propylene (0.5 mole) was passed in at ice-bath temperature. The system became deep orange in color, but the solid remained. The mixture was allowed to stand for an hour and was then slowly allowed to warm up. Addition of water decomposed the complex and the organic layer was washed, dried and fractionated. The fraction collected at 160–200° (760 mm.) was treated with 2,4-dinitrophenylhydrazine to remove carbonyl compounds and the residue from this treatment was redistilled. The fraction collected at 170–185° (760 mm.) was identified from its infrared spectrum as isopropyltoluene, the three isomers being present. Also a small liquid polymer fraction free of aromatic and carbonyl groups was isolated. The carbonyl compound was identified from the 2,4-dinitrophenylhydrazone (m.p. 200–203°) as *p*-methylpropiophenone.

**Reaction of Propylene with Toluene–Isopropyl Fluoride–$BF_3$ Complex.**—A solution of 0.1 mole of isopropyl fluoride in 0.1 mole of toluene was cooled in a Dry Ice-bath and 0.1 mole of boron trifluoride was introduced under previously described conditions.[17] Thereafter 0.5 mole of propylene was passed into the homogeneous yellow complex at Dry Ice temperature. The mixture was allowed to stand for an hour and then slowly warmed. The complex layer was decomposed by water and the organic layer was washed, dried and fractionated as in previous experiments.

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