again for 4 hours and was then allowed to stand overnight. The reaction mixture was thereafter filtered and the carbon tetrachloride distilled off at 0.1 mm. pressure. A yellow oily residue remained. This oil could not be distilled by means of a normal vacuum distillation even at 0.001 mm. pressure without decomposition. It could be purified only be sealing it in a flask connected by a wide tube to a receiver flask at 10^{-5} mm. pressure at room temperature, while the receiver flask was cooled to liquid air temperature. In 48 hours about 1.6 g. of 1-methylcyclohexadiene-1,4 monobromide distilled over in this way. It was colorless but rapidly turned yellow on standing; $n^{20}\text{D}$ 1.5670. *Anal.* Calcd. for C_7H_9Br (172.9): Br, 46.21; C, 48.58; H, 5.21. Found: Br, 47.7; C, 48.49; H, 4.81. The high bromine and the low hydrogen value indicated contamination with dibromocyclohexadiene derivatives, which was to be expected from the method of separation used.

1-Methylcyclohexa-1,4-diene Monofluoride.—1-Methylcyclohexadiene-1,4 monobromide (17.3 g. 0.1 mole) was dissolved in 35 ml. of acetonitrile and at room temperature with effective stirring a saturated solution of 14 g. (0.11 mole) of silver fluoride in acetonitrile was added. A white precipitate could be instantly observed, which increased in amount as the reaction continued. The reaction mixture was stirred for another 6 hours, during which time the yellow-brown silver fluoride was almost completely dissolved and a white silver bromide precipitate was formed. After standing overnight the mixture was filtered and the acetonitrile distilled over at 0.01 mm. pressure. The remaining product could not be distilled with decomposition even at 10^{-3} mm. pressure. It was purified in a similar way to that described for the 1-methyl-cyclohexadiene-1,4-monobromide at 5×10^{-4} mm. pressure at around 0°. In 48 hours about 1.9 g. of distillate was collected, as a colorless liquid, rapidly turning yellow-brown on standing, $n^{20}\text{D}$ 1.4971. *Anal.* Calcd. for C_7H_9F (112): C, 75.00; H, 8.03; F, 16.95. Found: C, 74.83; H, 7.90; F, 17.12.

The acetonitrile distilled over contained toluene, the presence of which was shown by preparing the 2,4-dinitrotoluene, m.p. 71°. (The acetonitrile–toluene azeotrope has a boiling point at atmospheric pressure of 81.1°).

Reaction of 1-Methylcyclohexa-1,4-diene Monofluoride with Boron Trifluoride.—1-Methylcyclohexa-1,4-diene monofluoride (5.6 g. 0.05 mole) was saturated with boron trifluoride, starting at −50° and gradually decreasing the temperature to −65° as the boron trifluoride was introduced. An all-glass apparatus was used to avoid atmospheric moisture. A bright brown color appeared with evolution of heat (possibly through the partial polymerization of the cyclohexadiene by boron trifluoride); 2.9 g. of boron trifluoride was taken off. The specific conductivity of the complex so formed at the melting point (−65°), $\kappa = 1.0 \times 10^{-3}\ \Omega^{-1}$ cm.$^{-1}$. *Anal.* Calcd. for $C_7H_9BF_4$ (179.8): BF_4, 48.3. Found: BF_4, 43.1.

The complex, when warming up, began to decompose at −50° with strong boron trifluoride evolution while it separated into two phases: a lower phase miscible with water and containing hydrogen fluoride and an upper, organic layer, not miscible with water. The organic layer after separation, drying and distillation consisted of 1.1 g. of toluene, b.p. 110°, $n^{20}\text{D}$ 1.4967, and some resinous material.

Reaction of 1-Methylcyclohexa-1,4-diene Monobromide with Silver Tetrafluoroborate.—To 3.5 g. (0.002 mole) of 1-methylcyclohexa-1,4-dienemonobromide 3.9 g. (0.02 mole) of anhydrous silver tetrafluoroborate was added in small portions with effective stirring and avoiding atmospheric moisture at −60°. The silver tetrafluoroborate dissolved in the organic layer followed by an immediate quantitative precipitation of silver bromide. The organic complex so formed melted at −65 −64°, $\kappa = 1.10^{-3}\ \Omega^{-1}$ cm.$^{-1}$. On heating the complex, boron trifluoride was evolved and again two phases were formed: the organic upper layer was toluene and the lower layer hydrogen fluoride. One and six-tenth grams of toluene was formed (90%). The filtered silver bromide was 3.72 g. (about 100%).

SARNIA, ONTARIO, CANADA

[CONTRIBUTION NO. 6 FROM THE EXPLORATORY RESEARCH LABORATORY OF DOW CHEMICAL OF CANADA, LTD.]

Aromatic Substitution. VI. Intermediate Complexes and the Reaction Mechanism of Friedel–Crafts Alkylations and Acylations[1]

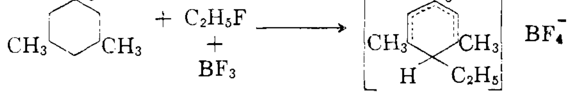
BY G. A. OLAH AND S. J. KUHN

RECEIVED JULY 7, 1958

σ-Complex type intermediates of Friedel–Crafts alkylations and acylations with a molar ratio of 1:1:1 were isolated by the low temperature interaction of methylbenzenes, alkyl fluorides and boron trifluoride, and alkylbenzenes, acyl fluorides and boron trifluoride, respectively. On the basis of the intermediate complexes the reaction mechanism is discussed.

From our experience gained during the isolation and investigation of the protonated and deuterated alkylbenzene tetrafluoroborate complexes,[2] we were encouraged to examine the structure of the intermediate complexes of other electrophilic aromatic substitutions of such common interest as the Friedel–Crafts alkylations and acylation.

Alkyl fluorides are quite soluble in methylbenzenes. When, for example, an equimolecular amount of ethyl fluoride is dissolved in toluene at −80° (or in other methylbenzenes at low temperatures which are determined by the freezing points of the hydrocarbons) a homogeneous solution is obtained. When boron trifluoride is introduced into this homogeneous solution at low temperature, a lower, brightly colored phase separates immediately. The amount of this phase is increased by introducing more boron trifluoride. One mole of boron trifluoride is taken resulting in a homogeneous solution. In this way it was possible to isolate the methylbenzene:boron trifluoride complexes with a molar ratio of 1:1:1.



Some of the properties of these complexes are listed in Table I.

TABLE I

$ArHC_2H_5{}^+BF_4{}^-$ COMPLEXES

Ar	M.p. dec., °C.	κ(Ω⁻¹ cm.⁻¹) × 10³	Color	Formula	BF₄, % Calcd.	BF₄, % Found
$CH_3C_6H_5$	−80	0.2	Yellow	$C_9H_{14}BF_4$	41.6	40.8
m-$(CH_3)_2C_6H_4$	−75	.1	Red	$C_{10}H_{16}BF_4$	39.0	37.7
sym-$(CH_3)_3C_6H_3$	−15	.2	Orange	$C_{11}H_{18}BF_4$	37.8	36.4

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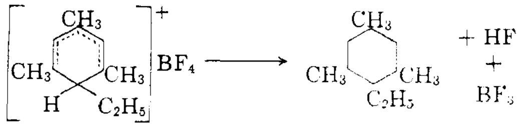
(1) The work was started in the author's earlier laboratory, the Chemical Central Research Institut of the Hungarian Academy of Sciences, Budapest (Hungary). Preliminary communications appeared in *Nature*, **178**, 1344 (1956); **179**, 146 (1957). Partly delivered as a paper at the XVI International Congress of the International Union of Pure and Applied Chemistry in Paris, July 18, 1957.

(2) G. A. Olah and S. J. Kuhn, THIS JOURNAL, **80**, 6540 (1958).

On heating the complexes we obtained the corresponding ethylmethylbenzenes in high yields



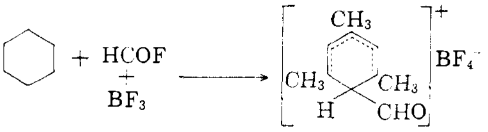
During the decomposition reaction a smaller additional amount of polyethyl derivatives always was formed.

In a similar way we isolated the methyl, *n*-propyl and isopropyl fluoride:toluene:BF_3 complexes. The isolation of these complexes of unambiguous composition was impossible in the case of methyl fluoride on account of its low boiling point and consequent preparative difficulties, but in the case of the propyl fluorides we were able to isolate complexes with a molar ratio of 1:1:1.

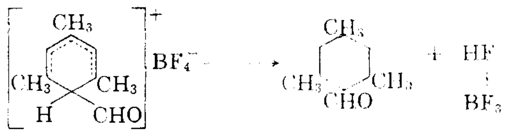
The *n*-propyl as well as the isopropyl fluoride–toluene–boron trifluoride complexes are yellow colored, their melting points (with decomposition) are -80 $-78°$ and they have a specific conductivity of $0.2 \times 10^{-2}\ \Omega^{-1}\ \text{cm.}^{-1}$. (We wish to point out that in the case of the propyl fluoride–boron trifluoride complexes and the toluene–propyl fluoride–boron trifluoride complexes the investigation of the *n*-propyl → isopropyl isomerization will be discussed in a future paper.)

By the isolation of the methylbenzene–alkyl fluoride–boron trifluoride complexes we were essentially able to investigate the intermediate complexes in a Friedel–Crafts alkylation reaction.

With a similar purpose further investigations were carried out on the isolation of the methylbenzene:boron trifluoride-acyl fluorides complexes, to investigate the Friedel–Crafts acylation. By investigating first the Friedel–Crafts formylation reaction with formyl fluoride,[3] the first member of the acyl fluoride series, we were able to isolate the formyl fluoride:methylbenzene:boron trifluoride complexes with the molar ratio of 1:1:1 at low temperatures. Some of the properties of these complexes are shown in Table II.



During the thermal decomposition of the complexes (when carefully warmed beyond their melting points) the corresponding aldehydes were obtained in 80-90% yields



The formation of the aldehydes was followed by a certain amount of resinification as a consequence of the boron trifluoride and hydrogen fluoride evolved. Therefore, it was preferable to separate the aldehydes quickly by washing them acid-free with water and then drying and distilling.

TABLE II

$ArHCHO^+BF_4^-$ COMPLEXES

Ar	M.p., dec., °C.	κ(Ω⁻¹ cm.⁻¹ × 10²)	Color	Brutto formula	—BF₄, %— Calcd.	Found
$CH_3C_6H_5$	−70	0.3	Red	$C_8H_9OBF_4$	41.8	40.4
m-$(CH_3)_2C_6H_4$	−52	.5	Cherry red	$C_9H_{11}OBF_4$	39.2	37.7
sym-$(CH_3)_3C_6H_3$	−16	.7	Red	$C_{10}H_{13}OBF_4$	36.6	35.0
asym-$(CH_3)_4C_6H_2$	−10	.7	Red	$C_{11}H_{15}OBF_4$	34.4	32.8

Our attempt to isolate in a similar way the onium ion complex in the case of acetyl fluoride: methylbenzene:boron trifluoride failed. The essentially more stable acetyl tetrafluoroborate complex separated first from the interaction of acetyl fluoride and boron trifluoride[4a,b]

$$CH_3COF + BF_3 \rightleftarrows CH_3CO^+BF_4^-$$

When the reaction mixture was allowed to warm up to a higher temperature, the acetyl tetrafluoroborate complex acetylated the aromatic compound in a secondary reaction

$$ArH + CH_3CO^+BF_4^- \longrightarrow ArCOCH_3 + HF + BF_3$$

but the intermediate complex of this reaction could not be isolated.

When propionyl fluoride was treated with toluene and boron trifluoride at $-80°$, we were able to isolate the $CH_3\ C_6H_6\ COC_2H_5^+\ BF_4^-$ complex (dec. point $\sim -2°$, $\kappa = 0.2 \times 10^{-2}\ \Omega^{-1}\ \text{cm.}^{-1}$). In the case of *m*-xylene, mesitylene or isodurene propionyl tetrafluoroborate again was formed first and we were not able to isolate the ternary complexes. On account of the higher freezing points of these hydrocarbons we were unable to work at low temperatures as in the toluene case and remain in the liquid phase region.

As we were now able, from the foregoing investigations, to isolate intermediate complexes of Friedel–Crafts acylations, a further attempt was made to investigate the intermediates of nitration, as in the case of the boron trifluoride-catalyzed Friedel–Crafts nitration with nitryl fluoride.[5,6]

$$ArH + NO_2F \xrightarrow{BF_3} ArNO_2 + HF$$

As a consequence of the high reactivity of nitryl fluoride, the preparative difficulties were considerably greater in this case than with the aliphatic acid fluorides hitherto discussed. As nitryl fluoride is a powerful oxidating and fluorinating agent too, methylbenzenes could not be used in this nitration reaction, because the side chain was attacked. As the reaction may be very violent even at low temperatures, a compound having a deactivated aromatic ring was preferred. Benzotrifluoride was found to be a suitable compound.[7] The fluorinated side chain was not attacked by the nitryl fluoride, and the ring itself was greatly deactivated.

It was possible to prepare by the low temperature reaction the benzotrifluoride:nitryl fluoride:boron trifluoride complex with a molar ratio of 1:1:1

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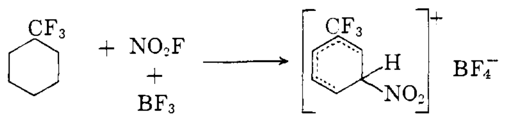
(3) G. Olah and S. Kuhn, *Chem. Ber.*, **89**, 866 (1956); *Acta Chim. Ac. Sci. Hung.*, **10**, 233 (1956).

(4) (a) F. Seel, *Z. anorg. allgem. Chem.*, **250**, 331 (1943); (b) G. Olah, A. Pavlath, S. Kuhn and G. Varsanyi, "Elektronentheorie der homeopolaren Bindung," Akademie Verlag, Berlin, 1955, pp. 79-94

(5) G. Olah and S. Kuhn, *Chemistry & Industry*, 98 (1956).

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

(7) G. Olah, L. Noszko and A. Pavlath, *Nature*, **179**, 146 (1957).

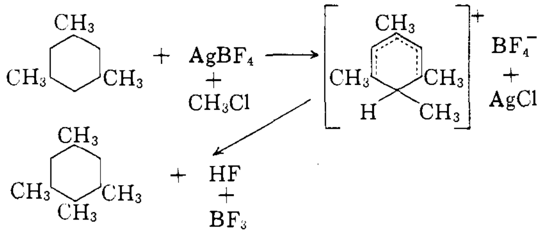


This complex was stable at temperatures below −50°. Above −50° it decomposed without melting, whilst boron trifluoride and HF were liberated and *m*-nitrobenzotrifluoride was formed with nearly quantitative yield. The existence of the intermediate complex was indirectly further proved by the fact that nitronium tetrafluoroborate, which itself was found by us[8] to be a very effective nitrating agent, did not react with benzotrifluoride even up to +100° and nitryl fluoride alone nitrated benzotrifluoride only very slowly at −50°.

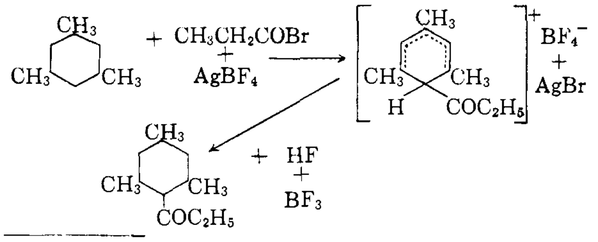
By the preparation of the intermediate σ-complexes we have followed our general method of treating an aromatic hydrocarbon (preferably a methylbenzene) with a fluoride (inorganic or organic) in the presence of boron trifluoride. The use of the fluoride technique was an essential part of the work. In many cases, however, it was inconvenient to use fluoride compounds and especially hydrofluoric acid as the starting material. To overcome this difficulty, we have found silver tetrafluoroborate, previously suggested by us[9] as a new cation forming agent, as a very suitable reagent for preparing the intermediate tetrafluoroborate complexes.

To prepare the intermediate σ-complexes with silver tetrafluoroborate, the silver salt is added to the aromatic compound and then the cold solution (it is also possible to work with only a partly dissolved material by stirring the suspension of silver tetrafluoroborate in the aromatic) is treated with an alkyl or acyl chloride or bromide, respectively.

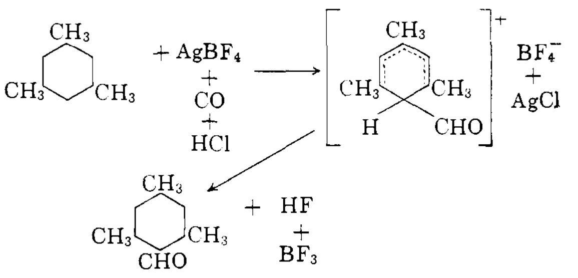
Using an alkyl halide the alkylation intermediate σ-complexes were formed in the following way, represented by the alkylation of mesitylene with methyl chloride



With an acyl halide the acylation intermediate σ-complexes were formed in the following way, represented by the acylation of mesitylene with propionyl bromide



In a similar way it was possible to prepare the intermediate σ-complex of a modified Gattermann–Koch reaction



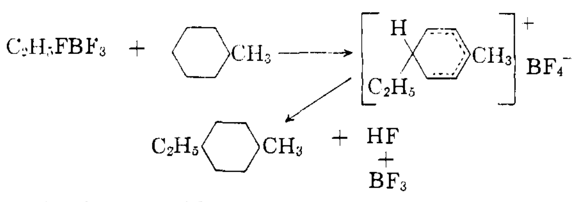
This complex was found to be identical to the previously prepared σ-complex of mesitylene with formyl fluoride + boron trifluoride.

The isolation of the intermediate complexes of electrophilic aromatic substitutions, performed in earlier work with the cation reagent complexes[9,10] and the cation reagent–aromatic ring complexes reported earlier in this paper, made it possible for us to investigate the reaction mechanism of aromatic substitutions by chemical methods by division into elementary steps. We have investigated in this way the mechanism of Friedel–Crafts alkylation and acylation. The reactions investigated were: the boron trifluoride-catalyzed ethylation of toluene with ethyl fluoride and the boron trifluoride-catalyzed formylation of toluene with formyl fluoride.

As previously reported[11] ethyl fluoride forms a 1:1 molar complex with boron trifluoride whose low specific conductivity ($\kappa = 1.0 \times 10^{-5}\ \Omega^{-1}\ \text{cm.}^{-1}$) indicates merely a polarized covalent addition complex is formed between the alkyl halide and the Lewis acid type catalyst and its ionization is only very small

$$C_2H_5\text{-}F + BF_3 \longrightarrow \overset{\delta^+}{C_2H_5} \longrightarrow F \longrightarrow \overset{\delta^-}{BF_3}$$

To the prepared ethyl fluoride–boron trifluoride complex, after measuring its conductivity, we have added, at −80°, an equimolar amount of toluene also at −80°. On addition of the toluene the hitherto white complex mixed complete with the toluene while a bright yellow color appeared. After addition of the equimolar quantity of toluene the ethyl borofluoride complex was quantitatively converted into the $CH_3C_6H_5C_2H_5{}^+BF_4{}^-$ onium ion salt or σ-complex previously discussed. The value of the specific conductivity increased to $\kappa = 0.2 \times 10^{-2}\ \Omega^{-1}\ \text{cm.}^{-1}$. So the second step of the ethylation reaction can be written



The boron trifluoride catalyzed formylation of toluene with formyl fluoride can be performed in a similar way. As we have described previously[3]

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(8) G. Olah and S. Kuhn, *Naturwissenschaften*, **43**, 59 (1956).

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

(10) G. Olah Summary of papers, Division of Organic Chemistry, XVIth International Congress of Pure and Applied Chemistry, Paris, 1957, pp. 12–13.

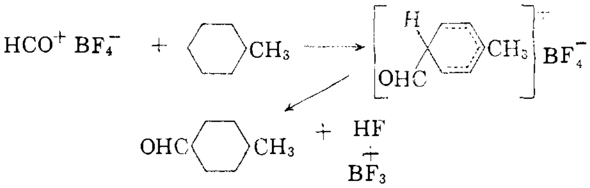
(11) G. Olah, S. Kuhn and J. Olah, *J. Chem. Soc.*, 4257 (1957).

formyl fluoride and boron trifluoride forms a stable ion complex, the formonium tetrafluoroborate (κ = 0.1 × 10^{-2} Ω^{-1} cm.$^{-1}$) at low temperature

$$HCOF + BF_3 \rightleftarrows HCO^+BF_4^-$$

When the formonium tetrafluoroborate complex was mixed with an equimolar amount of toluene at low temperature, the white complex was quantitatively converted in the vivid red $CH_3C_6H_5$ CHO^+ BF_4^- onium ion or σ-complex leaving a homogeneous solution. The specific conductivity increased to κ = 0.3 × 10^{-2} Ω^{-1} cm.$^{-1}$ and the complex so formed was identical to the complex made from toluene:formyl fluoride:boron trifluoride.

The second step of the formylation reaction thus be written



Experimental

Materials.—The alkylbenzenes were the purest available commercial products. They were fractionated in a column rated at 55 theoretical plates. Center fractions which exhibited constant boiling point and refractive index were utilized. They were stored over calcium hydride and redistilled before use. (For the physical constants of the alkylbenzenes used see Part IV of this series.) Anhydrous hydrogen fluoride and boron trifluoride were of a minimum purity of 99.5 and 99%, respectively. Anhydrous silver tetrafluoroborate was prepared according to Sharpe[12] Methyl and ethyl fluoride were prepared from the alkyl sulfates by the method of Fremy[13] using anhydrous KF as the fluorinating agent. n-Propyl fluoride was prepared by the silver fluoride method according to Moissan.[14] Isopropyl fluoride was prepared by HF addition to propylene according to Grosse and Linn.[15] The acyl fluorides were prepared according to Olah, Kuhn and Beke.[16]

Nitryl fluoride and nitronium tetrafluoroborate were prepared according to Schmeisser and Elischer[17] and Olah, Kuhn and Mlinko.[6] The alkyl and acyl chlorides and bromides were the purest commercial products available and were redistilled before use. The 1:1 ratio mixture of CO:HCl used in the Gattermann–Koch reactions was prepared from chlorosulfonic acid and anhydrous formic acid according to Bert.[18] The alkyl tetrafluoroborate complexes were prepared according to Olah, Kuhn and Olah.[19] The acyl tetrafluoroborate complexes were prepared according to Olah and Kuhn.[8]

Procedure for the Preparation of $ArHR^+BF_4^-$ Complexes (R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7). (A) **Fluoride Method.**—Alkyl fluoride (0.5 mole, methyl, ethyl, n-propyl and i-propyl) was dissolved in 0.5 mole of alkyl benzene (toluene, m-xylene and mesitylene). The solution was cooled in a Dry Ice-bath and 0.5 mole of boron trifluoride was introduced under conditions precluding the entrance of atmospheric moisture. The apparatus was made of silica, polyethylene and Teflon. The amount of boron trifluoride was measured by weight increase; BF_3 was absorbed and the solution became brightly colored. (Excess of volatile material was pumped off at Dry Ice temperature and introduction of BF_3 was discontinued after no more weight increase was observed after twice pumping the system). Freezing and decomposition points of the resulting homogeneous complexes were determined with a calibrated Pt thermocouple. Electrical conductivities were measured as described previously (Part 4).

The tetrafluoroborate determinations were carried out in the form of nitron tetrafluoroborate $C_{20}H_{16}HBF_4$ according to the method of Lange.[20] The properties of the prepared complexes are shown in Table I.

The complexes, when allowed to warm up over their decomposition points, separated into two phases with vigorous evolution of BF_3: a lower hydrogen fluoride and an upper organic phase, containing the alkylated methylbenzenes. After the thermal decomposition of the complexes was completed and no more boron trifluoride was evolved, the organic phase was separated, washed free from acid, dried and distilled. After distilling off any excess of the starting methylbenzene the fraction containing the monoalkylated isomers was isolated. No attempt was made in general to isolate the isomers by distillation. The monoalkylated products were obtained with a yield above 90%, besides small amounts of di and higher alkylated products.

(B) **Silver Tetrafluoroborate Method.**—Two-tenths mole of anhydrous silver tetrafluoroborate was added to an excess of alkyl benzene (toluene, m-xylene, mesitylene) with efficient stirring. The stirred mixture then was cooled (−40 to −80°) and 0.2 mole of alkyl chloride or bromide (methyl, ethyl, n-propyl and isopropyl) was introduced into the stirred mixture. The amount of alkyl halide taken up by the system was equivalent to the quantity of silver tetrafluoroborate present in the system. Silver halide was precipitated and a colored complex layer formed. The complex layer was separated after removing the silver halide (preferably in a cooled centrifuge). The complexes were found to be identical with these prepared by the fluoride method.

Procedure for the Preparation of $ArHCOR^+BF_4^-$ Complexes (R = H, CH_3, C_2H_5). (A) **Fluoride Method.**—To 0.5 mole of alkylbenzene (toluene, m-xylene, mesitylene, isodurene) 0.5 mole of acyl fluoride (formyl, or propionyl) was added at −20 to −80° (depending on the melting point of the hydrocarbon). With further cooling in a Dry Ice-bath, and allowing the reaction mixture to remain in the liquid phase, 0.5 mole of BF_3 was introduced under conditions precluding the entrance of atmospheric moisture; BF_3 was absorbed and the solution became homogeneous and brightly colored. The amount of BF_3 introduced was measured by weight increase. Excess of volatile material was pumped off and introduction of BF_3, was discontinued after no more weight increase was observed after twice pumping the system. Freezing and melting points of the resulting homogeneous complexes were determined with a calibrated thermocouple. Electrical conductivities were measured as described earlier. Properties of the prepared complexes are shown in Table II.

The complexes, when allowed to warm up over their decomposition points, separated into two phases with vigorous evolution of BF_3: a lower hydrogen fluoride and an upper organic phase, containing the acylated (formylated) methylbenzenes. After the thermal decomposition of the complexes was completed and no more boron trifluoride was evolved, the mixture was poured on ice-water, the organic layer separated, washed acid free and distilled. After distilling off any excess of the starting methylbenzenes the acyl (formyl) methylbenzenes were obtained with over 90% yields. In the case of the formyl derivatives the resulting HF must be removed as fast as possible to avoid polymerization of the formed aldehydes.

(B) **Silver Tetrafluoroborate Method.**—Two-tenths mole of anhydrous silver tetrafluoroborate was added to an excess of alkylbenzene (toluene, m-xylene, mesitylene, isodurene) with efficient stirring. The stirred mixture then was cooled (−20 to −80°) and 0.2 mole of acyl chloride or bromide (acetyl, propionyl) was dropped into the stirred mixture. It is also possible to effect the reaction with formyl fluoride, the only stable formyl halide. Silver halide was precipitated and a colored complex layer formed. The complex layer was separated after removing the silver halide. The complexes were found to be identical with those prepared by the fluoride method and decomposed in a similar way.

Preparation of the $CF_3C_6H_5NO_2^+BF_4^-$ Complex. (A) **Fluoride Method.**—To 14.5 g. (0.1 mole) α,α,α-trifluorotoluene, cooled in a Dry Ice–acetone-bath 6.5 g. (0.1 mole) nitryl fluoride was added. No reaction was observed. The mixture was cooled with liquid nitrogen and 0.2 mole of

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[12] A. G. Sharpe, *J. Chem. Soc.*, 4538 (1952).

[13] E. Fremy, *Ann.*, **92**, 246 (1854); *Compt. rend.*, **38**, 393 (1854); *Chem. Gazette*, **12**, 138 (1954).

[14] H. Moissan, *Compt. rend.*, **110**, 952 (1890).

[15] A. V. Grosse and C. B. Linn, *J. Org. Chem.*, **3**, 26 (1938).

[16] G. Olah, S. Kuhn and S. Beke, *Chem. Ber.*, **89**, 862 (1956).

[17] M. Schmeisser and S. Elischer, *Z. Naturforsch.*, **76**, 583 (1952).

[18] L. Bert, *Compt. rend.*, **221**, 77 (1945).

[19] G. Olah, S. Kuhn and J. Olah, *J. Chem. Soc.*, 2174 (1957).

[20] W. Lange, *Ber.*, **59**, 2107, 2432 (1926).

boron trifluoride was condensed onto it. After mechanical mixing of the solid mixture it was allowed to warm up to −100° while the excess of boron trifluoride distilled off. In the mixture 0.1 mole of boron trifluoride remained (measured by weight absorbed). The homogeneous, yellow colored, crystalline complex of the mole ratio 1:1:1 was stable up to −50°. About −50° the complex decomposed without melting, while BF_3 was evolved and hydrogen fluoride and *m*-nitro-α,α,α-trifluorotoluene (b.p. 93–95° (35 mm.) were formed in almost quantitative yield.

(B) Silver Tetrafluoroborate Method.—One-tenth mole of anhydrous silver tetrafluoroborate was added to an excess of α,α,α-trifluorotoluene with efficient stirring. The stirred mixture was cooled to Dry Ice temperature and 8.15 g. (0.1 mole) of nitryl chloride added. Silver chloride was precipitated and a colored complex layer formed. After removing the silver halide the complex layer was separated. It was found to be identical to the complex formed by the fluoride method and decomposed in a similar way.

Preparation of the $ArHCHO^+BF_4^-$ Complexes with CO +HCl.—Two tenths mole of anhydrous silver tetrafluoroborate was added to an excess of alkylbenzene (toluene, *m*-xylene, mesitylene) with efficient stirring. The stirred mixture then was cooled (−20 to −80°) and a 1:1 ratio mixture of CO:HCl introduced until no more weight increase was observed. The amount of CO:HCl taken off was equimolar with the amount of silver tetrafluoroborate present in the system. Silver chloride was precipitated and a colored complex layer formed. The complex layer was separated after removing the silver halide. The complexes were found to be identical with those prepared from methylbenzenes with formyl fluoride and boron trifluoride and decomposed to the corresponding aldehydes in a similar way.

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Polymerization of Ethylene with Titanium Tetrachloride–Aluminum Triisobutyl

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RECEIVED JUNE 30, 1958

An investigation has been made of the polymerization of ethylene, using titanium tetrachloride–aluminum triisobutyl catalyst, at atmospheric pressure and at 10–70°. Linear polyethylenes in the viscosity molecular weight region 3500 to 940,000 are formed. The molecular weight is decreased by raising the reaction temperature, increasing the ratio $TiCl_4$:$Al(i\text{-}C_4H_9)_3$ and increasing the quantity of catalyst. At a catalyst ratio of 2:1, a quantitative estimate of the apparent activation energy is 10 kcal. per mole.

Within recent years a considerable quantity of literature has appeared on olefin polymerization catalyzed by a mixture of a metal halide of a transition element (*e.g.*, titanium tetrachloride) and a metal alkyl. The unique feature of such a catalyst system is that polymerization to high molecular weight linear polymers may be carried out at atmospheric pressure and at relatively low temperature.

Earlier results contain information regarding polymerizations catalyzed by either of the two catalyst components. For example, polymerization of olefins such as isobutene was carried out[1,2] at low temperatures and atmospheric pressure by using titanium tetrachloride with traces of water or trichloroacetic acid as cocatalyst. Use of metal alkyls alone as polymerization catalyst for olefins at relatively low pressures also has been observed. Friedrich and Marvel[3] found that gaseous ethylene in contact with lithium butyl over a period of days resulted in formation of a solid polymer.

The use of the two component system, titanium tetrachloride–aluminum alkyl, was recorded by Ziegler.[4] Subsequent papers by Natta[5] and coworkers using a similar catalyst have reported results in which the study has been extended to olefins other than ethylene and the concept of regularity of structure has been introduced.

In this paper a brief summary is presented of some results dealing with the polymerization of ethylene, using titanium tetrachloride–aluminum triisobutyl catalyst, at atmospheric pressure and in the temperature range 10–70°.

Experimental

Experiments were carried out in one liter creased flasks equipped with gas inlet tube, thermometer, condenser and stainless steel stirrer. A high speed electric motor adjusted at about 8000 no load r.p.m. was used in all experiments. All glassware was cleaned and oven dried at 110° for at least 3 hours. No solvent other than water was used before drying. Prior to an experiment the flask was heated to 160° during which time a stream of prepurified nitrogen (Matheson Co.) passed through the apparatus. The flask then was allowed to cool to 30°. The solvent (400 ml. sodium-dried, distilled cyclohexane) was then added to the flask and stirred in a nitrogen atmosphere for 10 minutes.

Catalyst addition was made by pipetting in a solution of the aluminum triisobutyl (Hercules Powder Co.) (1.00 molar solution in cyclohexane) followed by addition of titanium tetrachloride (Matheson, Coleman and Bell Co.) (1.82 molar solution in cyclohexane). The aluminum triisobutyl analyzed for 14.0% aluminum and contained a small quantity (*ca.* 7% based on aluminum analysis) of aluminum diisobutyl hydride. Addition of titanium tetrachloride to aluminum triisobutyl led to formation of a finely divided black to brownish black precipitate and was accompanied by some heat evolution.

Immediately after addition of the two catalyst materials, the nitrogen was turned off and ethylene was introduced through a calibrated flowmeter. Pyrex capillary-type flowmeters (manometer fluid Silicone) were used. Addition of ethylene to the catalyst slurry led to heat evolution. In certain experiments without cooling baths this could account for a temperature rise of from 30 to 60° within a few minutes. Throughout an experiment temperatures were maintained to within ± 1° by means of ice-water or water-baths. Tank ethylene (Matheson, C.P. grade) was used without further purification.

At the end of each experiment 200 ml. of methanol containing 3% concentrated hydrochloric acid was added directly to the reaction flask. This was followed by filtration of the polymer, water washing and washing with dry methanol. In some cases washing of the polymer was carried out by vigorous stirring using a Waring Blendor. The polymer then was dried at a temperature below 100°.

Melting points were obtained using a Fisher–Johns ap-

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[2] M. Polanyi, *ibid.*, **157**, 520 (1946).

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[4] K. Ziegler, Belgian Patent 533,362 (1953); K. Ziegler, Holzkamp and Briel, *Angew. Chem.*, **67**, 541 (1955).

[5] G. Natta, paper presented at meeting of Gesellschaft Deutscher Chemiker, Bad Nauheim, Germany, April, 1956.