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Author(s)	Yoneda, Norihiko; Hasegawa, Eishi; Yoshida, Hiroshi; Aomura, Kazuo; Ohtsuka, Hiroshi
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The Catalytic Behaviors of Borontrifluoride Complex in the Alkylation of Benzene Homologues and in the Oligomerization of Propylene

Norihiko YONEDA, Eishi HASEGAWA,
Hiroshi YOSHIDA, Kazuo AOMURA,
Hiroshi OHTSUKA

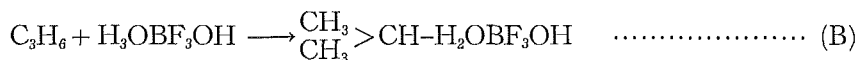
Summary

The catalytic behaviors of $\text{BF}_3\text{-H}_2\text{O}$ complex catalyst in the alkylation reaction of benzene homologues (benzene, toluene, ethylbenzene and isopropylbenzene) with propylene and in the oligomerization of propylene were studied and discussed.

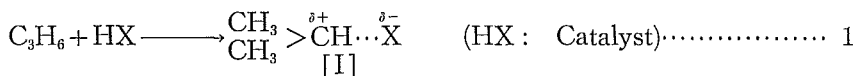
Judging from the experimental results the following conclusions were obtained.

The activity of these catalyst was very high in the initial stage of the reaction and kept almost constant for a fairly long time, but, after that time, it decreased very rapidly.

The spent catalyst, which lost its activity, was found to consist of the mixture of the under mentioned A and B.



The alkylation of benzene with propylene or the oligomerization of propylene was considered to proceed by the following scheme.



Beside the reaction 2 or 3, the reaction 4 took place, which caused the deterioration of catalyst activity.

High reaction temperature (around 50°C), large catalyst amount, high molar ratio of $\text{BF}_3/\text{H}_2\text{O}$ of the catalyst and addition of polar solvents seemed to be effective to elongate the catalyst life by retarding the ester formation (Reaction 4).

In case of the alkylation of benzene homologues, the catalyst life was influenced by the structure of the aromatics. Benzene gave the longest catalyst life. The relative reactivity of benzene homologues in the alkylation with propylene and isobutylene was also observed by competitive alkylation experiments.

1. Introduction

Borontrifluoride (BF_3) is a well known catalyst for many acid catalyzed reactions¹⁾. It has been generally used in the form of complexes with organic and inorganic substances as well as in the form of BF_3 gas²⁾. In the present report, the catalytic behaviors of BF_3 -water complex ($\text{BF}_3\text{-H}_2\text{O}$) in the alkylation reaction of benzene homologues with propylene and in the oligomerization of propylene was studied and discussed with reference to the life of the catalyst, the nature and structure of the spent catalyst, the relative alkylation reaction velocity of benzene homologues, together with the solvent effect on reactions. Comparative studies with $\text{BF}_3\text{-H}_3\text{PO}_4$ and H_2SO_4 catalysts were also carried out.

2. Apparatus and Procedure

BF_3 gas used was the product of the Hashimoto Kasei Co.. $\text{BF}_3\text{-H}_2\text{O}$ complex was readily produced by introducing BF_3 gas into water. The desired $\text{BF}_3/\text{H}_2\text{O}$ mol ratio of the complex could be obtained by adjusting the amount of BF_3 introduced. The same procedure was available for the preparation of other BF_3 complexes, such as $\text{BF}_3\text{-H}_3\text{PO}_4$.

A four necked flask of 500 cc capacity was used as the reaction vessel for the alkylation and polymerization experiments. Propylene was led into the reaction vessel containing aromatic hydrocarbon, catalyst and solvent at a constant flow rate with stirring at various reaction temperatures ($10\sim 70^\circ\text{C}$). In some experiments, a continuous flow type reaction vessel of 800 cc capacity, equipped with catalyst and product removers, was used³⁾.

The alkylation products were analyzed by means of G. L. C.. In case of the oligomerization experiments, the total amount of oligomers was measured. The structure of spent catalyst was determined by means of I. R. and n. m. r.

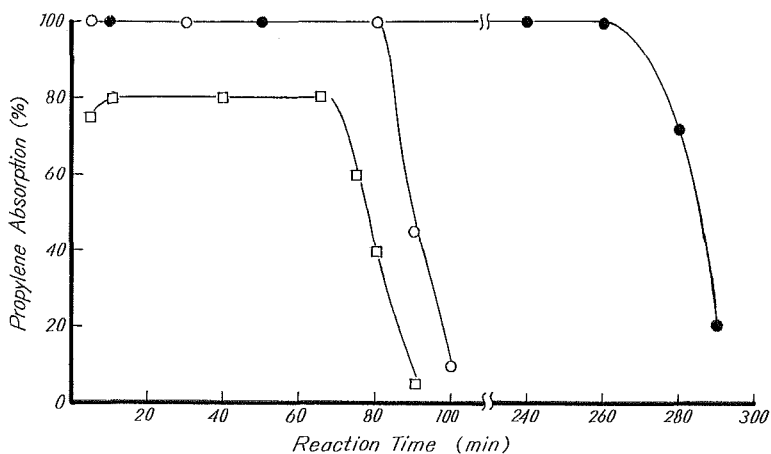


Fig. 1. Effect of Reaction Temperature on the Life of Catalyst Reaction. Conditions

React. Temp.; ○ 35°C, ● 50°C, □ 70°C

Catalyst; $\text{BF}_3\text{-H}_2\text{O}$, 8 g, Propylene Feed Rate; 0.3 l/min
Benzene; 1 mol, (Alkylate was exchanged for new benzene when 38 l propylene was conducted)

3. Results and Discussion

In the alkylation of benzene homologues with propylene, the effects of the reaction temperature, varieties of aromatic hydrocarbons (benzene, toluene, ethylbenzene, isopropylbenzene were used), $\text{BF}_3/\text{H}_2\text{O}$ molar ratio of the catalyst and varieties of solvents on the life of $\text{BF}_3\text{-H}_2\text{O}$ complex catalyst were observed. The results were shown in Fig. 1~4. The life of $\text{BF}_3\text{-H}_2\text{O}$, $\text{BF}_3\text{-H}_3\text{PO}_4$ and H_2SO_4

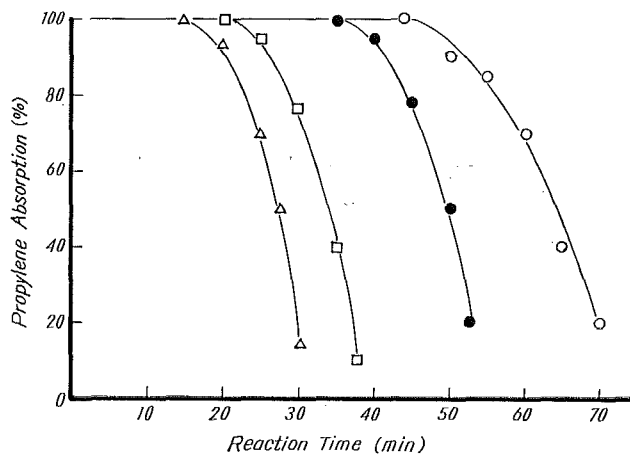


Fig. 2. Life of $\text{BF}_3\text{-H}_2\text{O}$ Catalyst in the Propylation of Aromatic Hydrocarbons
 Reaction Conditions
 Aromatics; 1.2 mol, \circ Benzene, \bullet Toluene, \square Ethylbenzene, \triangle Isopropylbenzene
 Propylene Feed Rate; 0.4 ℓ /min, Catalyst; $\text{BF}_3/\text{H}_2\text{O}$ molar ratio 0.97, 10 g, React. Temp.; 10°C

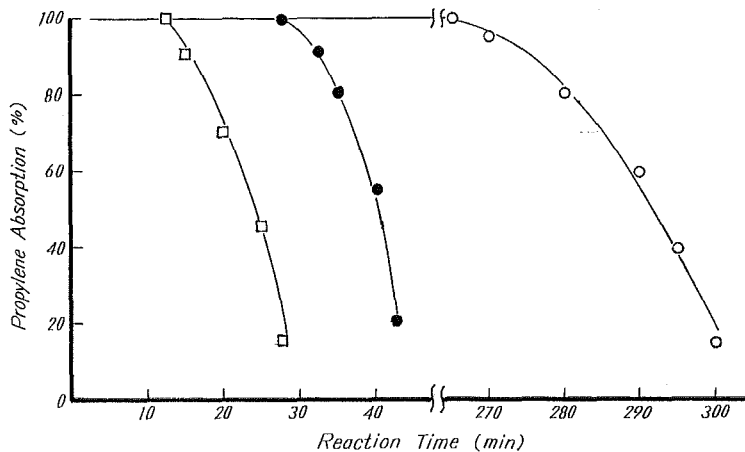


Fig. 3. Effect of $\text{BF}_3/\text{H}_2\text{O}$ Molar Ratio in the Catalyst on the Life of Catalyst
 Reaction Conditions
 $\text{BF}_3/\text{H}_2\text{O}$ molar ratio; \circ 0.97, \bullet 0.90, \square 0.80
 Continuous Reaction Vessel, Benzene/Propylene molar ratio; 4/3
 Propylene Feed Rate; 0.4 ℓ /min, Catalyst; 8 g.
 React. Temp.; 20°C

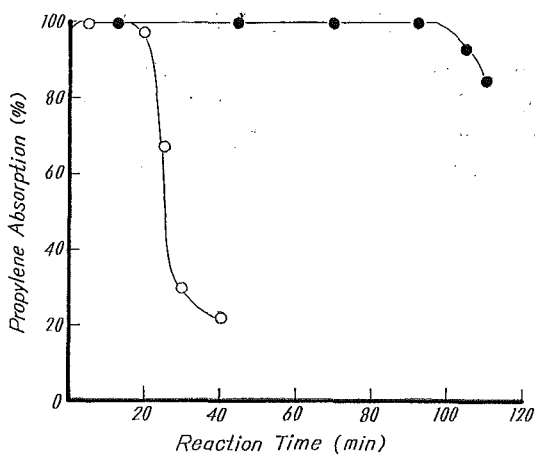


Fig. 4. Effect of Solvent on the Life of Catalyst
 Reaction Conditions
 Benzene; 0.75 mol React. Temp.; 20°C
 Propylene Feed Rate; 0.4 l/min Solvent; 50 cc
 Catalyst; $\text{BF}_3\text{-H}_2\text{O}$, 10 g ○ Cyclohexane, ● Nitrobenzene

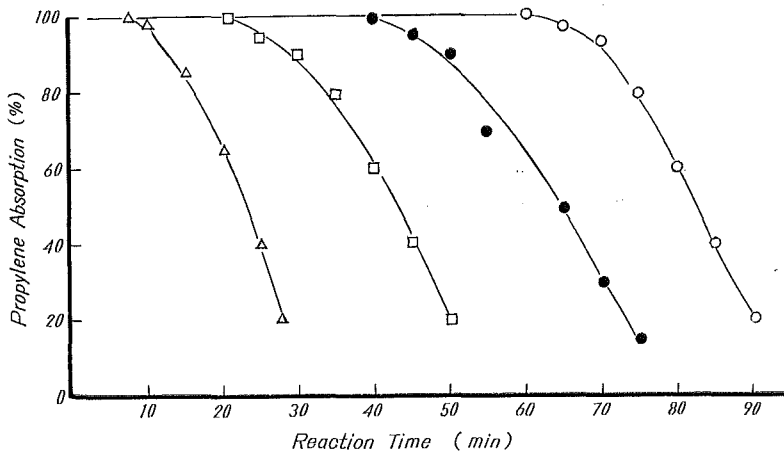


Fig. 5. Life of Catalyst in the Oligomerization of Propylene
 Reaction Conditions
 Catalyst; ● $\text{BF}_3\text{-H}_2\text{O}$ (0.23 mol), □ $\text{BF}_3\text{-H}_3\text{PO}_4$ (0.12 mol),
 △ H_2SO_4 (0.22 mol) ○ Alkylation of Benzene with
 Propylene $\text{BF}_3\text{-H}_2\text{O}$ (0.14 mol)
 Propylene Feed Rate; 0.4 l/min
 React. Temp.; 10°C, Solvent; Cyclohexane

catalysts in the oligomerization of propylene was also observed as shown in Fig. 5.

Generally speaking, the activity of these catalysts was very high in the initial stage of the reaction. It remained almost constant for a fairly long time and then a rapid decline was seen⁴⁾.

In order to obtain some useful information to elucidate the cause of the catalyst deterioration described above, the properties (nature and structure) of the spent catalyst were studied.

In the case of using $\text{BF}_3\text{-H}_2\text{O}$ catalyst having a high $\text{BF}_3/\text{H}_2\text{O}$ molar ratio, the spent catalyst had the appearance of a milky liquid. After left standing for 1~2 days, an oil layer appeared on the catalyst surface. The oil separation was accelerated by adding fresh $\text{BF}_3\text{-H}_2\text{O}$ or by heating. When water was added to the fresh spent catalyst, diisopropylether and isopropylalcohol were obtained⁴⁾.

These phenomena were also observed in the case of using $\text{BF}_3\text{-H}_3\text{PO}_4$ catalyst, but in the case of using H_2SO_4 and $\text{BF}_3\text{-H}_2\text{O}$ complex having less than 0.8 $\text{BF}_3/\text{H}_2\text{O}$ molar ratio, the spent catalysts obtained did not show these behaviors.

The n.m.r. spectrum of the spent catalyst in the case of using $\text{BF}_3\text{-H}_2\text{O}$ and

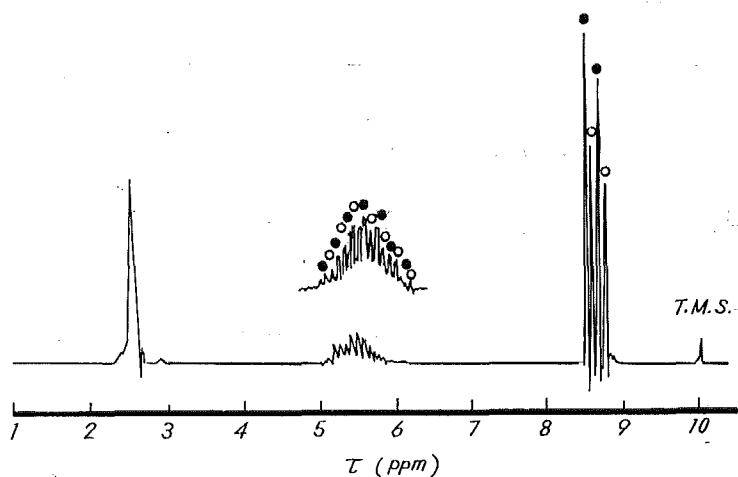


Fig. 6-1. NMR Spectrum of Spent Catalyst ($\text{BF}_3\text{-H}_2\text{O}$)

- $\text{CH}_3 > \text{CH} \cdots \text{H}_2\text{OBF}_3\text{OH}$
- $\text{CH}_3 > \text{CH} \cdots \text{BF}_3\text{OH}$

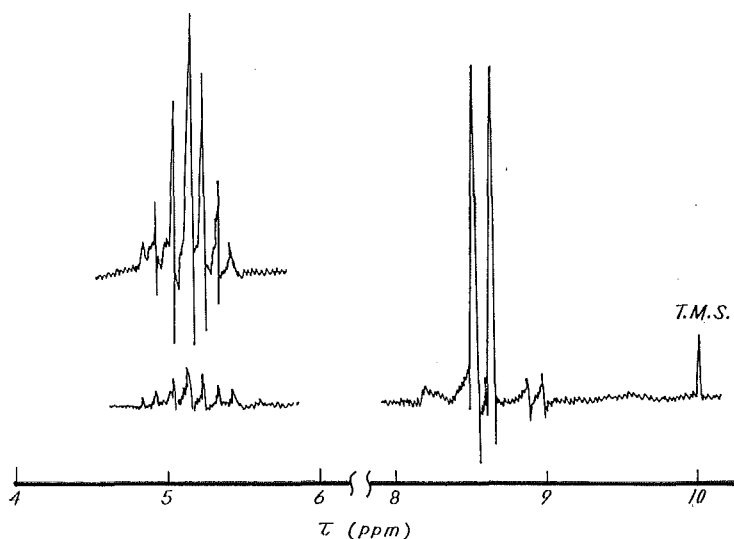
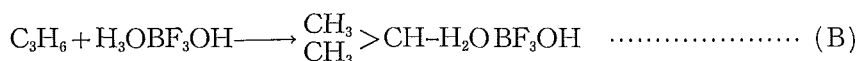


Fig. 6-2. NMR Spectrum of Spent Catalyst (H_2SO_4)

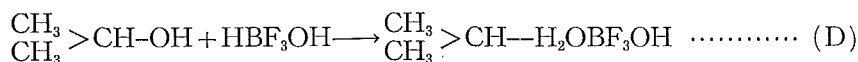
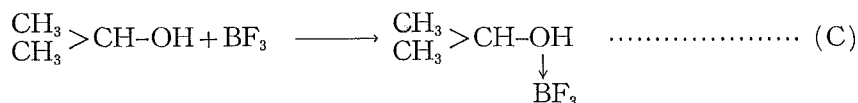
H_2SO_4 are shown in Fig. 6.

Judging from the results of measurement of m. p. of $\text{BF}_3\text{-H}_2\text{O}$ complexes, the $\text{BF}_3\text{-H}_2\text{O}$ complex was surmised to consist of two protonic acids HBF_3OH and HOBF_3OH in the region of 0.5~1.0 $\text{BF}_3/\text{H}_2\text{O}$ molar ratio⁵⁾.

In the alkylation with propylene, as well as in the oligomerization of propylene, two types of ester like substances, $\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} > \text{CH-BF}_3\text{OH}$ and $\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} > \text{CH-H}_2\text{OBF}_3$ could be formed by the following reactions:



The results of n. m. r. analysis suggested that (A) was identical with (C) and (B) was identical with (D). (C) and (D) were obtained by the following reactions.



The n. m. r. spectra of (C) and (D) and mixture of (C) and (D) are shown in Fig. 7, 8 and 9.

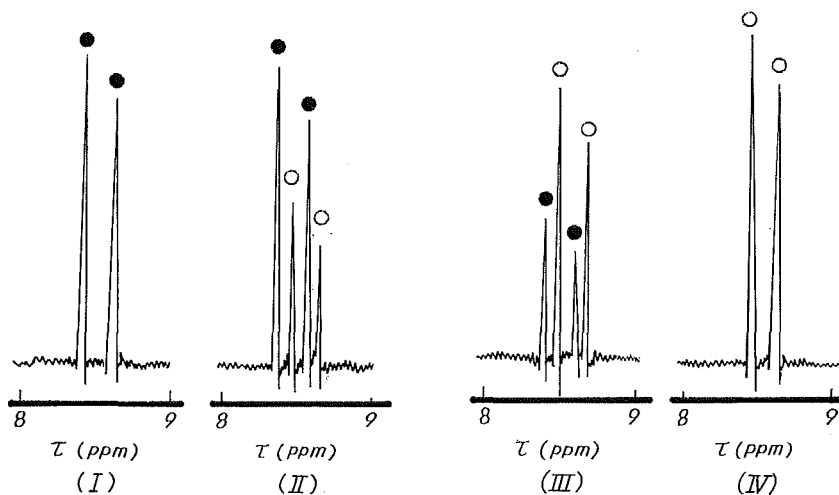


Fig. 7. NMR Spectrum of Spent Catalyst ($\text{BF}_3\text{-H}_2\text{O}$)
 $\text{BF}_3/\text{H}_2\text{O}$ molar ratio
 (I) 0.97, (II) 0.90, (III), 0.68, (IV) 0.50

The n. m. r. spectrum of the mixture of (C) and (D) (the same as the mixture of (A) and (B)) gave the same signals as shown in the spectrum of the spent catalyst with $\text{BF}_3\text{-H}_2\text{O}$ complex catalyst having 0.5~1.0 $\text{BF}_3/\text{H}_2\text{O}$ molar ratio.

From the results mentioned above, in the alkylation or oligomerization with

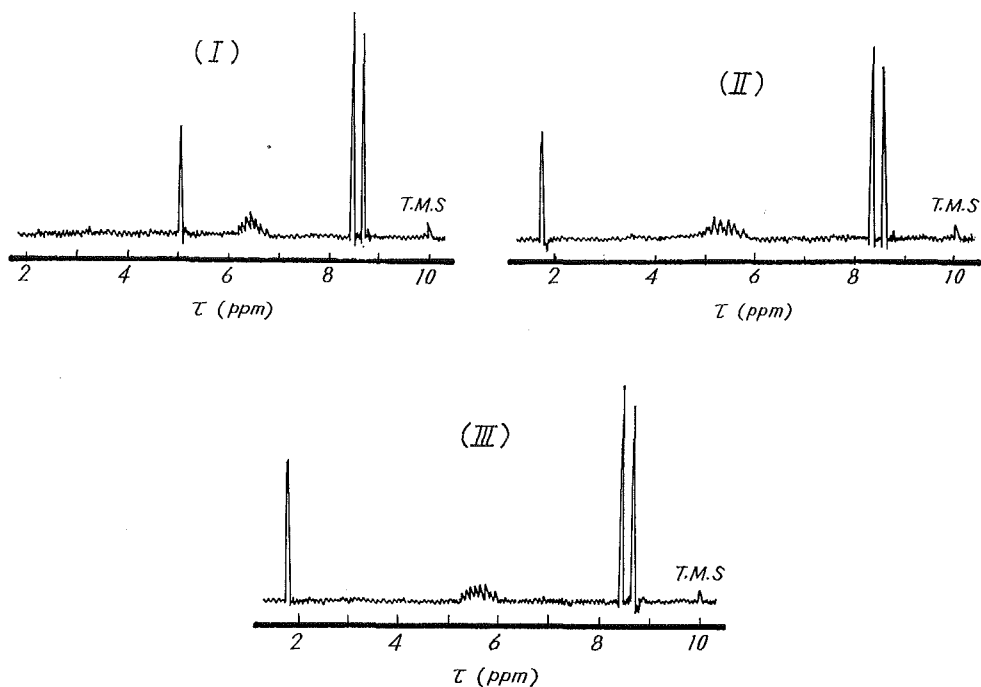


Fig. 8. NMR Spectrum of Isopropylalcohol
 (I) Isopropylalcohol
 (II) Isopropylalcohol+BF₃
 (III) Isopropyl alcohol+HBF₃OH

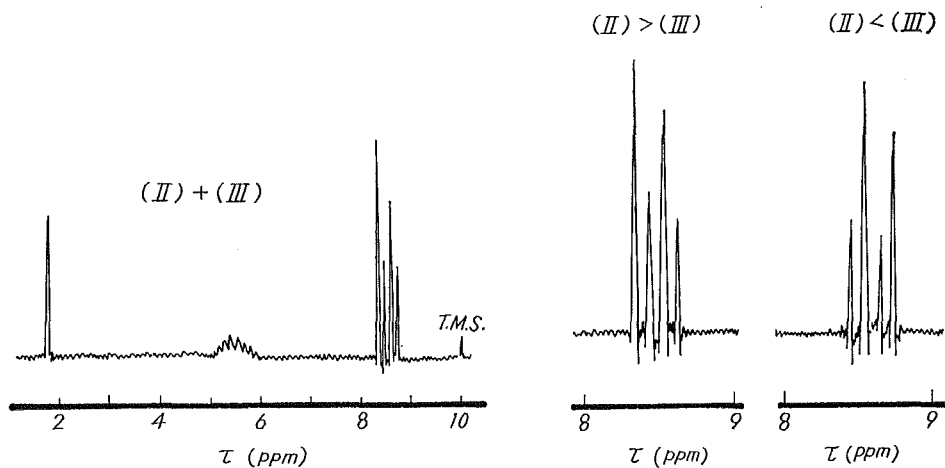
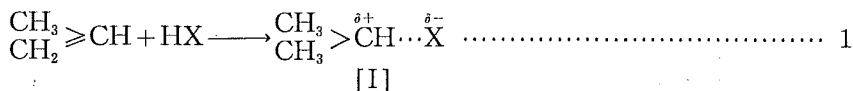
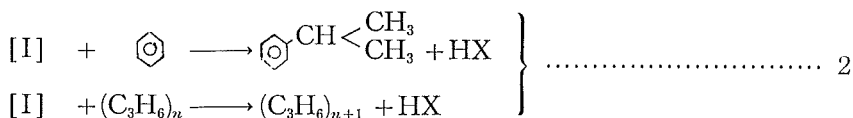


Fig. 9. NMR Spectrum of Mixtures of (II) and (III) in Fig. 8

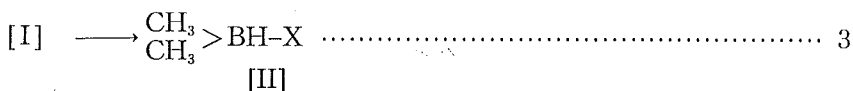
propylene in the presence of strong acid catalyst HX such as BF₃-H₂O, BF₃-H₃PO₄, H₂SO₄ etc., the first step of reaction was considered to be the formation of active olefin-catalyst complex as shown in 1.



Polarized complex [I] might react with aromatic ring or propylene to produce alkylbenzene or oligomers of propylene as shown in 2.



However, a part of the polarized complex [I] might change into more stable ester-like substances [II].



The accumulation of the ester like substance [II] in the catalyst might cause the deterioration of the catalyst. If the propylation of benzene or the polymerization of propylene in the presence of HX shown by 2 was assumed to proceed without accompanying the reaction 3, the deterioration of catalyst would not occur. (It can be observed in the reactions using isobutylene as the olefin component⁶⁾).

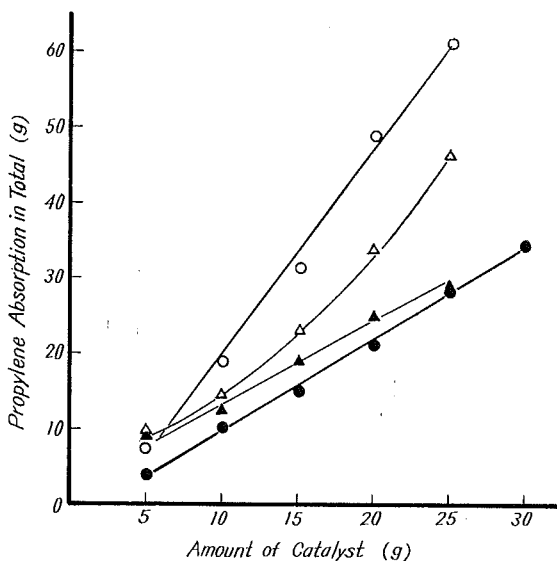


Fig. 10. Oligomerization of Propylene with $\text{BF}_3\text{-H}_2\text{O}$ Catalyst and Propylation of Benzene with H_2SO_4 Catalyst

In the Case of Oligomerization
 React. Temp.; \triangle 30°C, \blacktriangle 10°C
 Catalyst; $\text{BF}_3/\text{H}_2\text{O}$ molar ratio 0.97
 Propylene Feed Rate; 0.4 l/min
 Solvent; Cyclohexane

In the Case of Propylation
 React. Temp.; 10°C
 Catalyst; \circ 95% H_2SO_4 , \bullet 90% H_2SO_4
 Benzene; 1.5 mol.

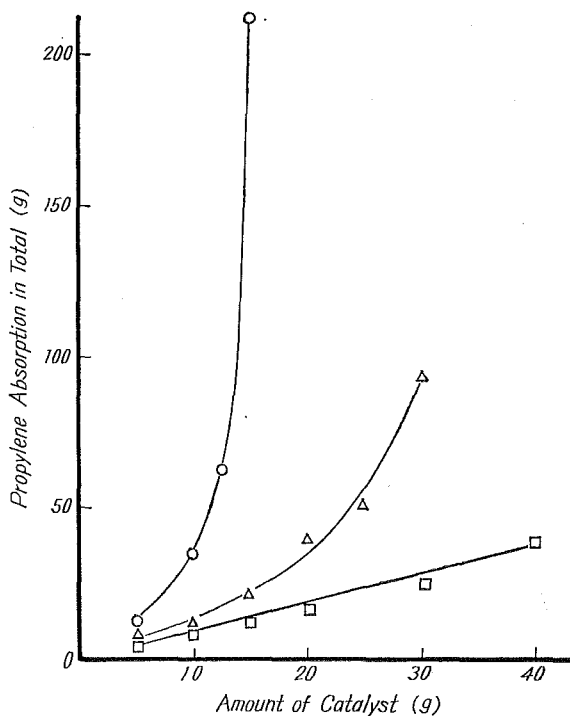


Fig. 11. Relationship between the Amount of the Catalyst and Total Propylene Absorption

Reaction Conditions (Continuous Reactor)

React. Temp.; 10°C,

Propylene Feed Rate; 0.4 l/min

Catalyst, BF₃/H₂O molar ratio; ○ 0.97,

△ 0.90, □ 0.80

Benzene/Propylene molar ratio; 4/3

In the case of using H₂SO₄ or BF₃-H₂O complex catalysts having less than 0.8 BF₃/H₂O molar ratio, a linear relationship was obtained between the amount of catalyst and the total amount of observed propylene as shown in Fig. 10 and 11, probably due to the constant rate of formation of [II], the inactive form of the catalyst complex.

However, in the case of using BF₃-H₂O catalyst having high BF₃/H₂O molar ratios, the total amount of the reacted propylene increased very rapidly with the increase of the catalyst amount as shown in Fig. 11. In these cases, a roughly linear relation seemed to hold between the catalyst amount and logarithm of the amount of total absorbed propylene.

It was also observed that, for the same catalyst amount, the total amount of absorbed propylene increased with the decrease of the feed rate of propylene.

As mentioned above, the ester like substance [II], in the case of using BF₃-H₂O, had some tendency to decompose to a mixture of propylene polymers (pentmers-hexamers) and BF₃-H₂O on long standing. It was accelerated by heating or by the addition of fresh BF₃-H₂O. It was also found that the addition of benzene homologues to the [II] favored its decomposition and, in this case, propylated

aromatics and $\text{BF}_3\text{-H}_2\text{O}$ were also produced.

On the other hand, the ester like substance was fairly stable in the dilute catalyst solution ($\text{BF}_3/\text{H}_2\text{O}$ molar ratio < 0.8). Hence, the reaction of benzene with the catalyst containing this ester like complex showed but a slight occurrence. The behaviors of the dilute $\text{BF}_3\text{-H}_2\text{O}$ catalyst were found to be quite similar to those of sulfuric acid catalyst in the alkylation or in the polymerization at low temperatures.

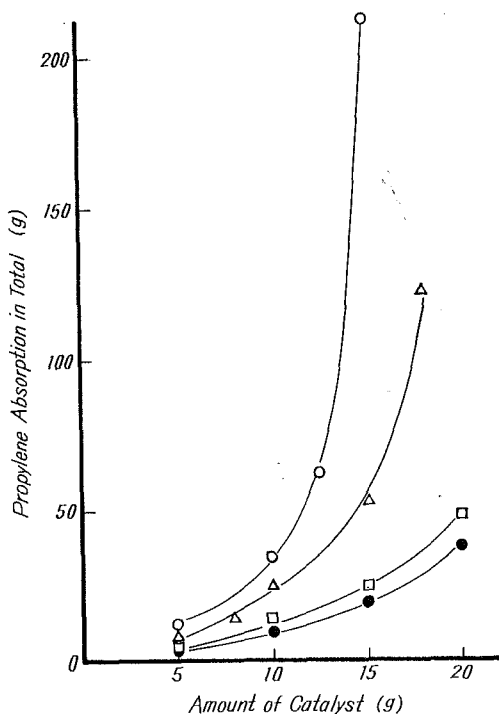


Fig. 12. Relationship between the Amount of Catalyst and Total Propylene Absorption in the Propylation of Aromatics Reaction Conditions (Continuous Reactor)

React. Temp.; 10°C
 Catalyst, $\text{BF}_3/\text{H}_2\text{O}$ molar ratio; 0.9
 Propylene Feed Rate; 0.4 l/min
 Aromatics; \circ Benzene, \triangle Toluene,
 \square Ethyl benzene, \bullet Isopropyl
 benzene
 Aromatics/Propylene molar ratio; $4/3$

TABLE 1 Competitive Alkylation of Aromatics

Propylation				
Catalyst	$\text{BF}_3\text{-H}_2\text{O}$	$\text{BF}_3\text{-H}_3\text{PO}_4$		
React. Temp. $^\circ\text{C}$	30	30		
k_T/k_B	0.43	0.53		
k_E/k_B	0.11	0.20		
k_C/k_B	0.04	0.09		
Reactivity	$\text{B} > \text{T} > \text{E} > \text{C}$	$\text{B} > \text{T} > \text{E} > \text{C}$		
$\text{C}_6\text{H}_5\text{-CH}_3$	$\left\{ \begin{array}{l} o_f \\ m_f \\ p_f \end{array} \right.$	$\left\{ \begin{array}{l} 0.54 \\ 0.29 \\ 0.90 \end{array} \right.$	$\left\{ \begin{array}{l} 0.07 \\ 0.36 \\ 1.1 \end{array} \right.$	
	$\text{C}_6\text{H}_5\text{-C}_2\text{H}_5$	$\left\{ \begin{array}{l} o_f \\ m_f \\ p_f \end{array} \right.$	$\left\{ \begin{array}{l} 0.11 \\ 0.09 \\ 0.25 \end{array} \right.$	$\left\{ \begin{array}{l} 0.22 \\ 0.17 \\ 0.43 \end{array} \right.$
		$\text{C}_6\text{H}_5\text{-iC}_3\text{H}_7$	$\left\{ \begin{array}{l} o_f \\ m_f \\ p_f \end{array} \right.$	$\left\{ \begin{array}{l} 0.03 \\ 0.05 \\ 0.10 \end{array} \right.$
Tert-Butylation				
Catalyst	$\text{BF}_3\text{-H}_2\text{O}$		$\text{BF}_3\text{-H}_3\text{PO}_4$	
k_T/k_B	1.5	1.9		
k_B/k_B	0.42	1.0		
k_C/k_B	0.21	0.46		
Reactivity	$\text{T} > \text{B} > \text{E} > \text{C}$	$\text{T} > \text{E} > \text{B} > \text{C}$		

It was also observed that the life of the catalyst in the propylation reaction varied according to the species of aromatic hydrocarbons as shown in Fig. 2 and 12.

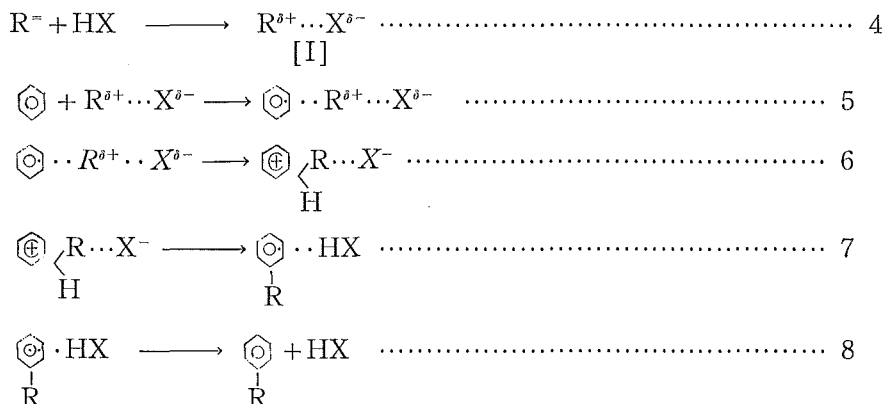
The length of the catalyst life in the propylation of individual aromatic hydrocarbons were in good parallelism with the magnitude of their reactivity in the competitive propylation reaction in the presence of $\text{BF}_3\text{-H}_2\text{O}$ complex catalyst.

The results of the competitive propylation and tertiary butylation of benzene homologues were shown in Tab. 1.

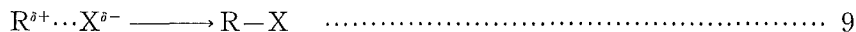
The Baker-Nathan effect usually prevailing in the electrophilic substitution of benzene homologues was not observed in the competitive propylation of benzene (B), toluene (T), ethylbenzene (E) and isopropyl benzene (C) in the presence of some acid catalysts.

These rather abnormal phenomena⁷⁾⁸⁾ have not been fully discussed as yet.

As mentioned before, in the case of alkylation with propylene with strong protonic acid catalyst HX such as BF₃-H₂O, the first step of reaction was considered to be the formation of R^{δ+}...X^{δ-}. And the second step to be the attack of the R^{δ+}...X^{δ-} on an aromatic ring as shown in 5.



And the following reaction was considered as a side reaction which caused deterioration of the catalyst.

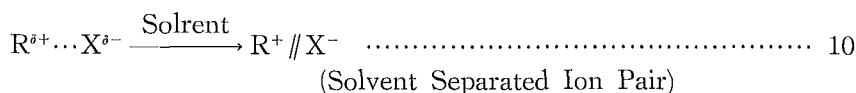


From the experimental results concerning the catalyst life, it was considered that the ratio of reaction velocity of 5 to that of 9 was larger in the reaction of benzene than in that of toluene.

The relative velocity of 5 to 9 might also be influenced by the characters of [I], such as its steric structure, the strength of bond etc. In other words, it might be influenced by the species of olfins and catalyst acids, as well as by the reaction conditions. The both extremes of [I] might be a carbonium ion + an acid anion (R⁺ + X⁻) and an ester (R-X).

By using polar solvent such as nitrobenzene etc., the catalyst life could be prolonged as shown in Fig. 4.

This fact might be explained by the formation of the solvent separated ion pair.



In the competitive propylation with BF₃-H₂O complex catalyst, the reactivity of benzene homologues was in the descending order of (B>T>E>C) as shown in Tab. 1.

However, in the case of the tertiary butylation, the order of the reactivity of benzene homologues was T>B>E>C as shown in Tab. 1.

In the case of the tertiary butylation with isobutylene, the active complex [II] would probably be in the form of carbonium ion R^+ + acid anion X^- and electronical effect on the reaction might be predominant. Hence, the reactivity of toluene became higher than that of benzene. And, the deterioration of catalyst would hardly occur as mentioned above.

In the case of propylation with propylene the active complex would be in the form of $\begin{matrix} \text{CH}_3 \\ | \\ \text{CH}_3 > \overset{\delta+}{\text{C}}\text{H} \cdots \overset{\delta-}{\text{X}} \end{matrix}$. Hence, in this case, the attacking group being a large molecule, stereochemical and probability factors would become predominant over the inductive effect in reaction 5. Therefore, benzene exhibited greater reactivity than its homologues.

In order to obtain some useful information to elucidate the above mentioned problems, the relative velocity constant was observed in the reaction temperature range of $10 \sim 40^\circ\text{C}$. The relative activation energies were calculated by the following equation.

$$\ln k_T/k_B = (\Delta S_T^\ddagger - \Delta S_B^\ddagger)/R + (\Delta H_B^\ddagger - \Delta H_T^\ddagger)/RT \dots\dots\dots 11$$

The results were shown in Fig. 13. As shown in Fig. 13, the velocity constant of benzene alkylation was larger than that of toluene alkylation ($k_B > k_T$) while the activation energy of benzene alkylation was larger than that of toluene alkylation ($\Delta H_B > \Delta H_T$). In spite of the fact that the activation energy of the propylation of B was higher than that of T, the velocity constant of B was larger than that of T. These results seemed to suggest the contribution of the entropy term of the rate constant formula to the progress of the reaction predominated over that of the enthalpy term.

However, when polar solvents, such as nitrobenzene etc., were used, the reactivity of T became larger than that of B even in the propylation with $\text{BF}_3\text{-H}_2\text{O}$ catalyst. It was also observed that the value of $(\Delta S_T^\ddagger - \Delta S_B^\ddagger)/R$ had a tendency to increase with the increase of the amount of polar solvent added as shown in Fig. 13.

This fact might explain the reason why k_T became larger than k_B in the case of solvent addition.

The mechanism of the alkylation reaction concerned might be considered as follows.

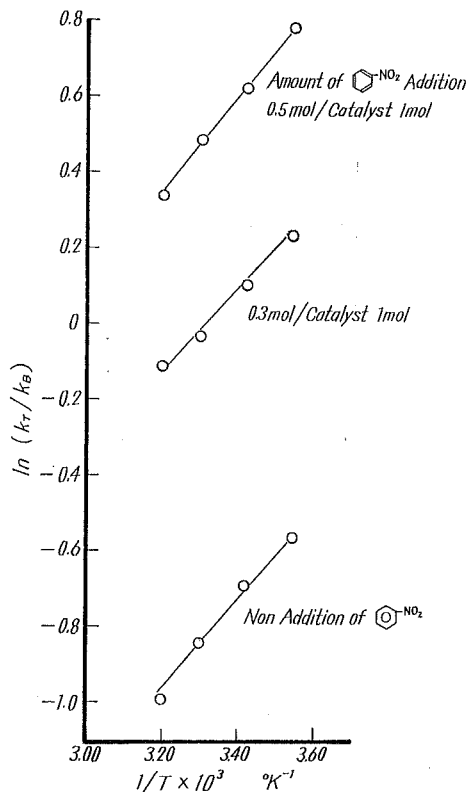
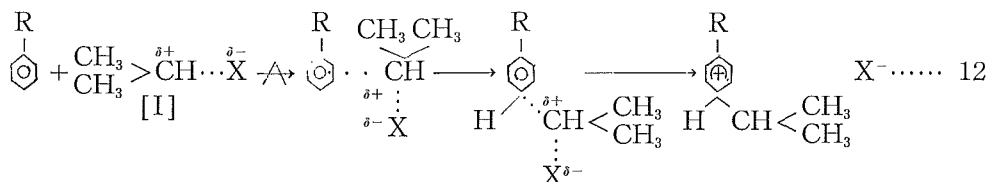


Fig. 13. Relationship between $\ln(k_T/k_B)$ and $1/T$



The rate determining step is considered to be the formation of a Dewar type π -complex where the attacking reagent [I] combined with individual aromatic hydrocarbon under the influence of some factors are represented by the entropy term.

On the other hand, partial rate factors in the ortho, meta and para position decreased with the increase of the bulkiness of the preoccupying alkylgroup (R) on the benzene ring. The decrease of the partial rate factor in the ortho position with the increase of the bulkiness of R might be due to the steric effect. However, the same tendency in the meta and para positions, where the steric effect of R seemed to be negligible, was considered to suggest that the rate determining step of the propylation of the aromatic hydrocarbons in the presence of HX such as $\text{BF}_3\text{-H}_2\text{O}$ catalyst was of a Dewar type π -complex formation step.

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