[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY, RIVERSIDE, ILLINOIS]

NEW METAL HALIDE CATALYSTS FOR HYDROCARBON REACTIONS

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We have recently described[1,2,3,4,5,6,7] how different classes of hydrocarbons, such as paraffins, naphthenes, aromatics, etc., originally considered very unreactive, react among themselves in the presence of catalysts. Previously the only known reaction of this kind was the alkylation of aromatics with olefins in the presence of aluminum chloride, discovered by Balsohn[8] nearly sixty years ago.

We have found that, besides aluminum chloride, the halides of a large number of metals standing near aluminum and forming a diagonal band in the periodic table (see Table I), that is, beryllium, boron, titanium, zirconium, hafnium, thorium, columbium, and tantalum, proved effective in these reactions (and also generally in reactions of the Friedel-Crafts type). These halides all have a similar chemical nature and show similar behavior towards water and in the formation of double salts or addition compounds; they form the transition between the purely heteropolar salt-type halides and the typically homopolar covalent halides.

As a means of comparing the halides, we have chosen Balsohn's classical example, namely, the reaction between benzene and ethylene.[8] The reaction proceeds smoothly according to the equations:

$$C_6H_6 + C_2H_4 \xrightarrow{\text{Catalyst}} C_6H_5 \cdot C_2H_5,$$

$$C_6H_5 \cdot C_2H_5 + C_2H_4 \xrightarrow{\text{Catalyst}} C_6H_4(C_2H_5)_2, \text{ etc.,}$$

$$C_6H_1(C_2H_5)_5 + C_2H_4 \xrightarrow{\text{Catalyst}} C_6(C_2H_5)_6,$$

yielding a product consisting of a mixture of mono- and poly-, up to hexaethylbenzenes. All our new catalysts, like $AlCl_3$,[8] produce all ethyl-

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[1] IPATIEFF AND GROSSE, *J. Am. Chem. Soc.*, **57**, 1616, (1935).

[2] IPATIEFF, KOMAREWSKY, AND GROSSE, *ibid.*, **57**, 1722 (1935).

[3] GROSSE AND IPATIEFF, *ibid.*, **57**, 2415, (1935).

[4] IPATIEFF AND GROSSE, *Ind. Eng. Chem.*, **28**, 461 (1936).

[5] IPATIEFF AND GROSSE, *J. Amer. Chem. Soc.*, **58**, 915 (1936).

[6] IPATIEFF, GROSSE, PINES, AND KOMAREWSKY, *ibid.*, **58**, 913 (1936).

[7] GROSSE AND IPATIEFF, Reaction of Cycloparaffins with Aromatics and Paraffins, *Libr. Bull. of the Universal Oil Products Co.*, **11**, 161 (1936).

[8] BALSOHN, *Bull. soc. chim.*, [2] **31**, 539 (1879).

benzenes from mono- to hexa-. The hexaethylbenzene has been identified in all cases by determinations of the melting point of a mixture with an authentic sample. Ethylbenzene was identified by its constants and especially through oxidation to benzoic acid. The proportions of the ethylbenzenes vary to a great extent depending on the catalyst, ratio of available ethylene to benzene, time, temperature and pressure conditions. However, with most catalysts, even under conditions favoring formations of monoethylbenzene, the higher alkylated products, up to hexaethylbenzene, are formed simultaneously.[9] The details of our procedure, nature and compositions of our products, etc., are given in the experimental part.

TABLE I

DISTRIBUTION OF CATALYTICALLY EFFECTIVE HALIDES IN THE PERIODIC SYSTEM

GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V	GROUP VI
Li	**BeCl$_2$**	**BF$_3$**	C	N	O
Na	Mg	**AlCl$_3$**	Si	P	S
K	Ca	Sc	**TiCl$_4$**	V	Cr
Rb	Sr	Y	**ZrCl$_4$**	**CbCl$_5$**	Mo
Cs	Ba	La	**HfCl$_4$**	**TaCl$_5$**	W
—	Ra	Ac	**ThCl$_4$**	**EtCl$_5$**	U

TABLE II

CATALYST EFFICIENCY

METAL HALIDE	TEMPERATURE, °C.	MOLES OF ETHYLENE CONVERTED PER MOLE OF CATALYST
BeCl$_2$	200	50
BF$_3$	25	35
AlCl$_3$	75	75
TiCl$_4$	170	5
ZrCl$_4$	100	90
CbCl$_5$	75	25
TaCl$_5$	75	60

The metal halides investigated by us behave as real catalysts, as does aluminum chloride in the Balsohn reaction, though not in many other organic reactions in which it takes part. This can be seen from the fact that, even disregarding the preliminary character of our experiments, one mole of almost any of our halides can convert over fifty moles of ethylene into ethylbenzenes. In Table II the efficiencies of these catalysts are roughly compared (based on data from Table III).

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[9] See MILLIGAN AND REID, *J. Am. Chem. Soc.*, **44**, 206–10 (1922).

TABLE III

	CATALYST:				
	$BeCl_2$	$TiCl_4$	$ZrCl_4$	$CbCl_5$	$TaCl_5$
Grams of catalyst	6.62	17.1	12.37	18.2	19.71
Grams of benzene	125; 145*	148.8	126.4; 136.8	170	152.7
Grams of hydrogen chloride	$\simeq 6$; 6	$\simeq 6$	$\simeq 6$; $\simeq 6$	$\simeq 6$	$\simeq 7$
Grams of ethylene absorbed	14.6; 93.1 $\Sigma = 107.7$	12.5	58.0; 72.3 $\Sigma = 130.3$	47	37.7; 55.1 $\Sigma = 92.8$
Temperature	50–125°; 200°	120°; 170°	25–50°; 100°	25°; 75°	25–50°; 25–75°
Max. pressure, kg./cm.²	10; 35	25; 40	15; 15	10; 10	10; 10
Reaction time, hours	12; 60	6; 28	29; 48	5; 45	6; 28
Grams of total reaction product (hydrocarbon part)	142.2; 235.7	161.3	184.3; 220.9	221.4	252.5
Grams of upper layer	142.2; 224.1*	161.3	169.5; 211.3	216.5	237.5
Grams of lower layer or solid (hydrocarbon part)	142.2; 11.6	161.3	14.8; 9.6	4.9	15.0
Unreacted gas, composition	C_2H_4 (96%); (97%)	C_2H_4 (98%)	C_2H_4 (92%); (98%)	C_2H_4 (93%)	
Unreacted gas, liters (N.T.P.)	5.35; 9.20	14.5	0.30; 5.00	1.50	None
Grams C_2H_4 absorbed per 100 g. catalyst	Σ1630	73	468; 583 Σ1051	260	 Σ475
Moles C_2H_4 absorbed per mole of catalyst	47	5	40; 50 Σ90	25	61

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* Fifty grams from one period.

Tantalum pentachloride seems nearly as efficient as aluminum chloride, whereas zirconium tetrachloride appears equal or superior to the latter. Beryllium chloride has the disadvantage that it becomes active only at higher temperatures. Titanium tetra chloride is the poorest catalyst of those investigated.

The appearance of the reaction product is similar for the chlorides of the uppermost metals in each group; that is, columbium, titanium, and probably boron, chlorides form homogenous mixtures with the hydrocarbon product, whereas the other catalysts—like aluminum chloride—give rise to two liquid layers, the dark-brown viscous lower layer containing most of the chloride.

For the catalytic action of the halides the presence of hydrogen halide (in most cases hydrogen chloride) seems to be necessary, as in the conjunct polymerization of ethylene with aluminum chloride,[5] which does not take place at all in the absence of hydrogen chloride.

The action of the hydrogen halide seems to consist in its addition to the olefin to form an alkyl halide, which then reacts with the aromatic hydrocarbon whose C-H bond is activated by the metal halide with the elimination of hydrogen halide. The hydrogen halide can then repeat the same cycle indefinitely. With benzene, ethylene, and hydrogen chloride, for example, the following cycle would take place:

$$CH_2{:}CH_2 + HCl \longrightarrow CH_3{\cdot}CH_2{\cdot}Cl$$

$$H_5C_6{\cdot}\boxed{H + Cl}{\cdot}CH_2{\cdot}CH_3 \xrightarrow[\text{Chloride}]{\text{Metal}} C_6H_5{\cdot}CH_2{\cdot}CH_3 + HCl.$$

This viewpoint is supported by the fact that if larger quantities of hydrogen chloride are used ethyl chloride can be readily detected in the reaction product.

EXPERIMENTAL

Reagents.—The chlorides used were prepared either from the c.p. metals (Cb and Ta) and redistilled chlorine, or from c.p. oxides (BeO, ZrO_2, ThO_2, etc.) and c.p. phosgene, and purified by sublimation, except titanium tetrachloride which was fractionated. Ethylene was obtained from a cylinder of the gas, and was over 99% pure. Eastman's benzene "for molecular-weight determinations" was used. The hydrogen chloride was pure compressed gas stored in cylinders.

Apparatus and procedure.—All experiments were carried out in rotating Ipatieff autoclaves.[1] The benzene and the halides were placed in glass liners fitted with capillary tubes* (to avoid the catalytic effects of autoclave walls), inserted into the bombs; the latter evacuated to 2 to 5 mm. (correction being made for the evaporated benzene); the desired amounts of hydrogen chloride were passed in, and then ethylene was added up to the desired pressure. As the pressure fell, fresh ethylene was added,

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* To be described separately.

the refillings being repeated a number of times. In some cases the alkylation was allowed to take place first at one temperature range and then at a higher temperature level; in the cases of beryllium chloride and zirconium tetrachloride most of the product was decanted from the catalyst, and fresh benzene was added before going to the second temperature level.

The amounts of reagents used and the experimental conditions are recorded in Table III.

Nature of Products

Without catalysts.—Benzene and ethylene with small quantities of hydrogen chloride were heated to 25°, 125°, and 225°, respectively, for 30 hours in a glass liner. No alkylation took place, and the benzene was recovered pure, containing less than 0.5% of higher-boiling material, if any.

TABLE IV A

PRODUCTS	% BY VOLUME	n_D^{20}	REMARKS
Benzene	12.5		Contains trace of C_2H_5Cl.
Ethylbenzene	21	1.4945	All fractions olefin-free (stable to $KMnO_4$ test).
Diethylbenzenes	40	1.4999	
Triethylbenzenes and higher	16.5	1.5136	
Hexaethylbenzene	10		M.p. 128.5°; mixture (1:1) with pure sample, m.p. 128.0°.

TABLE IV B

PRODUCTS	% BY WEIGHT	n_D^{20}	REMARKS
Benzene (and possibly toluene, 80–111°)	30		
Ethylbenzene (111–160°)	23	1.4938	Olefin-free.
Di- and higher alkylbenzenes (160–265°)	24	1.5022	Olefin-free.
Fraction > 265°	20		Partly crystallized from CH_3OH; hexaethylbenzene (m.p. 128°).

From beryllium chloride.—After the first part of the experiment (50–125° during 12 hrs.) the product had the appearance of a water-white liquid with suspended white powder. A Podbielniak distillation showed it to consist of 82% benzene (containing a trace of ethyl chloride in the head fraction), 14% ethylbenzene (n_D^{20} = 1.4958; b.p. 139°/760 mm.). and 4.7% higher boiling benzenes. After the second part of the experiment (200° for 60 hrs.) the appearance of the product changed to that of a yellow liquid with blue fluorescence, containing a brownish suspended precipitate. The filtered liquid was absolutely clear, nearly water-white, and contained no beryllium. The results of a Podbielniak distillation of the filtrate are recorded in Table IV A. The precipitate (18.21 g.) was decomposed with ice in the presence of ether; the results of Podbielniak distillation of the ether extract are recorded in Table IV B.

These results show that in the presence of beryllium chloride aromatic hydrocarbons form addition compounds similar to those formed in the presence of aluminum chloride.

From boron trifluoride.—The ethylation of benzene with boron fluoride has already been described elsewhere.[10]

From titanium tetrachloride.—The product is a homogenous clear yellow-orange liquid, with a trace of black suspended powder. Water and ice decomposed the dissolved titanium tetrachloride immediately, and the liquid became water-white and clear. A Podbielniak distillation of this liquid, after washing and drying, yielded the products recorded in Table V.

From these results it can be concluded that titanium tetrachloride starts to alkylate at about 170°. On the basis of the beryllium chloride experiments it can be foreseen that at higher temperatures (*ca.* 250°) the alkylation will proceed with fair rapidity.

From zirconium tetrachloride.—After the first half of the experiment (25–50° during 29 hrs.), the product consisted of two layers, an upper, light, perfectly clear, orange-colored layer, and a deep-orange-red, pasty lower layer. The upper layer (169.5 g.) was separated, washed (washings contained only 75 mg. ZrO_2), dried, and fractioned with a Podbielniak column, with the results recorded in Table VI A. The ethylbenzene was further identified through oxidation with potassium permanganate to benzoic acid (m.p. 122°).

TABLE V

PRODUCTS	% BY VOLUME	n_D^{20}	REMARKS
Benzene (80°)	≃96	1.4964	Solidifies in ice.
Ethylbenzene (137°)	2.8	1.4960	Olefin-free.
Higher alkylbenzenes (150–250°)	1.0		Olefin-free.
Higher alkylbenzenes (>250°)	0.3		

The lower layer (27.12 g.) was used again for ethylation, after adding a fresh quantity of benzene (136.8 g.), at 100° for 48 hours. After the experiment a brown liquid product, containing a yellow-brown pasty precipitate (21.92 g.), but no lower layer was obtained. Upon filtration from the precipitate, a clear, water-white liquid (211.3 g.) was obtained (containing only 5–10 mg. ZrO_2).

The Podbielniak distillation of this product is reported in Table VI B.

The yellow-brown precipitate was readily decomposed by water. The hydrocarbons liberated (9.6 g.) consisted of small quantities of benzene and ethylbenzene and larger amounts of higher ethylbenzenes up to hexaethylbenzene; the latter was isolated in the form of crystals melting at 128°.

From columbium pentachloride.—The reaction product is a dark-brown liquid, with a dark red-brown-grayish solid suspended in it. The filtered liquid is also dark brown, similar in appearance to the titanium tetrachloride product and in contrast to those of all our other halides. Water decomposes the halide readily, forming a water-white hydrocarbon layer. From the watery layer 2.94 g. columbium pentoxide, corresponding to 5.88 g. columbium pentachloride, or about 30% of the charge, was recovered.

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[10] IPATIEFF AND GROSSE, *ibid.*, **58**, 2339 (1936).

TABLE VI A

PRODUCTS	% BY WEIGHT	n_D^{20}	REMARKS
Benzene (80°)	12.7	1.4904	Contains trace of C_2H_5Cl in head fraction; melts partly above 0°.
Ethylbenzene (138°)	41.0	1.4950	Olefin-free.
Diethylbenzenes (185°)	34.9	1.4962	Olefin-free
Tri- and higher ethylbenzenes (210–220°)	4.9	1.4979	Olefin-free
Higher ethylbenzenes (>220°)	6.6	1.5129	No hexaethylbenzene present.

TABLE VI B

PRODUCTS	% BY VOLUME	n_D^{20}	REMARKS
Benzene (80°)	37.5	1.4925	Freezes in ice.
Ethylbenzene (136°)	23.5	1.4951	Olefin-free.
Diethylbenzenes (185°)	17.0	1.4970	Olefin-free.
Higher ethylbenzenes (200–225°)	6.5	1.5005	Olefin-free.
Higher ethylbenzenes (225–245°)	8.0	1.5111	Contains also C_6Et_6.
Hexaethylbenzene (>245°)	7.5		Crystals of some C_6Et_6 (m.p. 128.5°) were separated besides a yellow oil; C, 89.38%; H, 10.58%.

TABLE VII

PRODUCTS	% BY VOLUME	n_D^{20}	REMARKS
Benzene (80°)	53.5	1.4968	Crystallizes in ice; head fraction contains trace C_2H_5Cl.
Ethylbenzene (136°)	23.5	1.4957	Olefin-free.
Diethylbenzene (183–185°)	10.0	1.4964	Olefin-free.
Higher ethylbenzenes (200–245°)	5.5	1.4996	Contains crystals of C_6Et_6; m.p. (from CH_3OH) 128.5°; mixture m.p. (1:1) 128°.
Hexaethylbenzene (>245°)	7.5	1.5040	

TABLE VIII

PRODUCTS	% BY VOLUME	n_D^{20}	d_4^{20}	REMARKS
Benzene (80°)	22.5	1.4921	0.8755	Solidifies in ice.
Ethylbenzene (138°)	25.0	1.4963	0.8671	Olefin-free.
Diethylbenzenes (183–185°)	20.5	1.4978	0.8668	Olefin-free.
Higher ethylbenzenes (200–225°)	12.0	1.5046	0.8779	Olefin-free.
Higher ethylbenzenes (225–245°)	6.5	1.5130	—	Contains some C_6Et_6.
Hexaethylbenzene (>245°)	13.5	—	—	Crystals from C_2H_5OH; m.p. 128.5°.

The water-white product (217 g.) gave, on Podbielniak distillation, the results recorded in Table VII.

The red-brown solid gave, after decomposition with water, a small quantity of higher alkylbenzenes.

From tantalum pentachloride.—After the first half of the elapsed time of treatment the product consisted of a clear yellow upper layer and a liquid red-brown lower layer; at the end of the treatment, only one layer and a sticky red-brown solid were present. The liquid product (237.5 g.) contained only very small quantities of tantalum pentachloride (150 mg. Ta_2O_5). After washing and drying a Podbielniak distillation was carried out (Table VIII).

The red-brown solid, on decomposition with water, gave hydrocarbons (15.0 g.) containing: benzene (*ca.* 17%), ethylbenzene (*ca.* 17%), higher ethylbenzenes; 165–245° (34%), and hexaethylbenzene; m.p. 128° (32%), together with small quantities of unsaturated (easily oxidizable by $KMnO_4$) hydrocarbons.

Other metal halides.—Results with other halides (thorium tetrachloride, hafnium tetrachloride) will be described later.

SUMMARY

New metal halide catalysts, including beryllium chloride, titanium tetrachloride, zirconium tetrachloride, hafnium tetrachloride, thorium tetrachloride, columbium pentachloride, and tantalum pentachloride, have been found for hydrocarbon reactions. The ethylation of benzene with these catalysts and the nature of products obtained have been described.