TABLE I

RATE OF DIMERIZATION OF HYDROXYDIOXALATOAQUOCHROMATE(III) AS A FUNCTION OF TEMPERATURE AND IONIC STRENGTH

Rate constants given in sec.$^{-1}$ × 10^5.

Ionic strength	Temperature, °C. 25	30	35	40	45	50
0.10	0.277	0.87	1.66	2.52	3.78	6.5
0.35	0.75	1.30	2.40	4.28	6.9	10.6
0.60	0.85	1.83	3.25	5.1	8.9	12.6
0.85	1.08	2.12	3.68	5.6	10.3	14.4
1.10	1.21	2.27	4.08	6.5	11.0	17.1
2.10	1.80	2.80	4.84	8.0	12.6	20.4

activation were determined for each ionic strength by using the method of least squares. The heats and entropies of activation obtained are given in Table II. The plot of these values against the square root of the ionic strength was such that the method of least squares was used to evaluate the extrapolated values at zero ionic strength of $\Delta H^{\ddagger}$ = 22.5 kcal./mole and $\Delta S^{\ddagger}$ = −8 cal./mole degree.

TABLE II

HEATS OF ACTIVATION AND ENTROPIES OF ACTIVATION

Ionic strength	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, cal./mole degree
0.10	22.1	− 9.3
0.35	20.1	−14.7
0.60	19.9	−14.8
0.85	19.3	−16.4
1.10	19.6	−15.1
2.10	18.2	−19.4

The considerably lower values of the heat of activation at higher values of ionic strength are in accord with the idea that it should be much easier for a polar water molecule to leave the ion in the dissociation process.

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[CONTRIBUTION FROM RESEARCH DEPARTMENT, STANDARD OIL COMPANY]

Metal Fluorides as Acids in the Hydrogen Fluoride System

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Various metal fluorides and other metal salts were evaluated as acids in the hydrogen fluoride system. In each test, a mixture of *m*- and *p*-xylene was treated with hydrogen fluoride plus the metal salt. In this medium, a fluoride may act as a Lewis acid and coördinate with a fluoride ion. The proton released then adds preferentially to *m*-xylene. Three fluorides proved to be strong acids: titanium tetrafluoride, columbium pentafluoride and tantalum pentafluoride. Phosphorus pentafluoride acted as a weak acid. The acidity of the fluorides was attributed to the high positive valence of the metal and its ability to form covalent bonds with fluorine. All acidic fluorides show about the same preference for *m*-xylene *vs.* *p*-xylene as does BF_3. The acid $HF-TiF_4$ also extracts, isomerizes and disproportionates arenes in the same manner as $HF-BF_3$. The arene cation is therefore the same regardless of the metal fluoride present.

Hydrogen fluoride, when promoted by boron trifluoride, is a strong acid. It is capable of donating a proton to even as weak a base as an alkylbenzene molecule.[1] The hydrogen fluoride, present in excess, acts as an ionizing solvent and furnishes the proton. The boron trifluoride participates by coördinating with the fluoride ion to form the fluoroborate ion

$$\text{Arene} + \text{HF} \rightleftarrows [\text{Arene}\cdot\text{H}]^+ + \text{F}^-$$

$$\text{BF}_3 + \text{F}^- \rightleftarrows \text{BF}_4^-$$

There is no reason why this property should be limited to boron trifluoride, and, therefore, other prospective fluoride ion acceptors were examined.

As many fluorides as could be readily purchased or easily prepared were tested. The fluorides rather than other salts were chosen to avoid reaction of the salt anion with hydrogen fluoride. If the fluoride could not be prepared, the chloride, oxide or carbonate was used with the hope that enough metal ion would go into solution for a test. The test procedure consisted of attempting to extract the weak bases, *m*- and *p*-xylene, from a solution in *n*-heptane by means of a mixture of hydrogen fluoride and the metal salt. The resulting composition of the hydrocarbon furnished a measure of the effectiveness of the fluoride. One of the acidic fluorides, titanium tetrafluoride, was examined in more detail for comparison with boron trifluoride in conversion reactions.

Experimental

Preparations of the fluorides, extraction experiments and conversion reactions were carried out in a 1570-ml. carbon-steel autoclave.[2] The hydrogen fluoride used, a commercial grade of 99.6% purity supplied by the Matheson Company, was distilled before each experiment. No effort was made to remove the last traces of water.

Lead fluoride (PbF_2), zirconium tetrafluoride, zinc fluoride, bismuth trifluoride, silicon tetrafluoride and antimony trifluoride were purchased as such and were used without purification.

Titanium tetrafluoride, tantalum pentafluoride and columbium pentafluoride were prepared from the corresponding chlorides by stirring with two equivalents of hydrogen fluoride for 1 hr. at room temperature. Conversion was rapid, as shown by a rapid rise in pressure due to liberation of hydrogen chloride. After the pressure had leveled off, the liberated hydrogen chloride and the excess hydrogen fluoride were removed by pumping. The metal fluorides were left in the reactor for use in the extraction experiments. Tungsten hexafluoride was prepared from tungsten hexachloride in a similar manner, except that the liberated hydrogen chloride was not pumped off because of the high volatility of tungsten hexafluoride, which boils at 17.5°.

Cadmium fluoride was prepared from the carbonate by stirring with two equivalents of hydrogen fluoride for 1 hr. at room temperature. Pumping for 1 hr. at 100° removed the carbon dioxide, water of reaction and excess hydrogen fluoride.

Phosphorus pentafluoride was prepared from benzene dia-

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[1] D. A. McCaulay and A. P. Lien, THIS JOURNAL, **73**, 2013 (1951).

[2] D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

zonium fluorophosphate, produced by treating benzene diazonium chloride with 65% HPF_6 acid. The salt, $C_6H_5N_2PF_6$, was dried and then was decomposed thermally. The PF_5 was separated from the nitrogen by pumping the latter away from the PF_5 in a stainless-steel bomb at liquid nitrogen temperatures.

Attempts to prepare stannic fluoride, germanium fluoride and molybdenum pentafluoride from the corresponding chlorides by stirring with hydrogen fluoride were unsuccessful, even at 100° for extended periods. Likewise, fluorides could not be prepared from thorium oxide and copper oxide by agitating the oxide with hydrogen fluoride. Probably the fluorides which formed at first were insoluble in the acid and protectively coated the oxide. Methods of preparing these fluorides are described in the literature,[3] but the procedures were too involved for the purpose of this study. Therefore, these salts were used as such in the extraction experiments in the hope that enough metal ion would dissolve to give some indication of its activity.

The synthetic hydrocarbon feed was an equimolar mixture of *m*-xylene and *p*-xylene dissolved in enough *n*-heptane to give a solution containing 40% xylenes by volume. This solution and an equal volume of hydrogen fluoride were added to the autoclave containing 0.2 to 1.0 mole of metal fluoride per mole of xylene. The mixture was stirred for 1 hr. at 20 to 25°. After the mixture had settled for 2 hr., the acid layer was withdrawn into a polyethylene flask cooled in Dry Ice. The extracted xylenes were sprung by adding water, slowly and with cooling, to the acid phase. Each mole of water displaced one mole of xylene. After a large excess of water had been added, the displaced xylenes were decanted from the aqueous acid. The raffinate layer was drained from the reactor. Both hydrocarbon products were washed with ammonium hydroxide. The total arene contents and the distribution of isomers in both products were determined by refractive index and ultraviolet absorption.

Further tests of titanium tetrafluoride with other hydrocarbons followed a similar pattern. The titanium tetrafluoride was prepared *in situ* and the hydrocarbon was charged as before. Some of these experiments were carried out at either a higher temperature or with a more reactive hydrocarbon so that the arenes were isomerized and disproportionated as well as extracted. The hydrocarbon products were analyzed by appropriate means, such as fractional distillation and infrared and ultraviolet absorption.

Results

The results of the experiments made with hydrogen fluoride[4] plus the various metal fluorides are given in Table I. Four compounds, titanium, columbium, tantalum and phosphorus fluorides, show activity by extracting xylene from the hydrocarbon layer; the others are relatively inactive. Titanium tetrafluoride extracts about 0.5 mole of xylene per mole of salt; tantalum and columbium fluorides extract about 1 mole. Phosphorus pentafluoride is much weaker and extracts only 0.3 mole of xylene in spite of being used at a partial pressure of 10 atmospheres. The titanium, tantalum and columbium fluorides are white solids, by themselves not very soluble in HF; but in the presence of xylene they rapidly co-dissolve with the xylenes in the acid layer.

In Table II are the results obtained with hydrogen fluoride plus the various salts that were not successfully converted to fluorides. None of these salts is active.

TABLE I

EXTRACTION OF XYLENE FROM *n*-HEPTANE MIXTURE BY HF PLUS METAL FLUORIDES

Feed: Equimolar mixture of *m*- and *p*-xylenes (40 vol. %) in *n*-heptane (60 vol. %)

Metal fluoride	*V*, % Xylene Raffinate	Extract	Ratio: *meta/para* Raffinate	Extract	Moles xylene extracted per mole fluoride used	α (*m/p*)
TiF_4	28	94.2	0.35	5.1	0.44	15
TaF_5	25	98.2	.54	6.7	.99	12
CbF_5	26	97.0	.51	6.5	.93	13
PF_5[a]	33	95.0	.64	6.5	.3	10
SiF_4[b]	40	..	1.0	..	.0	..
BaF_2	40	..	1.0	..	.0	..
PbF_2	37	..	1.0	..	.2	..
BiF_3	40	..	1.0	..	.0	..
SbF_3	39	..	1.0	..	.2	..
CrF_3	40	..	1.0	..	.0	..
ZrF_4	39	..	1.0	..	.1	..
WF_6	40	..	1.0	..	.1	..
ZnF_2	39	..	1.0	..	.1	..

[a] Partial pressure 10 atmospheres. [b] Partial pressure 20 atmospheres.

TABLE II

EXTRACTION OF XYLENE FROM *n*-HEPTANE MIXTURE BY HF PLUS METAL SALT

Salt used	Time, min.	Temp., °C.	Moles xylene extracted per mole metal used
$SnCl_4$	480	105	0
$GeCl_4$	60	20	0.02
$MoCl_5$	120	100	0
ThO_2	90	100	0.02
CuO	30	25	0.15
$CdCO_3$	60	20	0

Because titanium tetrafluoride, one of the active fluorides, is potentially available in large quantities from the commercial titanium tetrachloride, it was studied more intensively. This study is summarized in Tables III and IV which show that titanium fluoride separates alkylbenzenes and promotes alkylbenzene reactions in the same manner as BF_3.

Discussion

All active fluorides—titanium, tantalum, columbium and phosphorus—have a marked preference for *m*-xylene over *p*-xylene. A measure of this preference toward *m*-xylene is provided in the last column of Table I by the function *m/p*, the mole ratio of *m*-xylene to *p*-xylene in the extract divided by the mole ratio in the raffinate. Titanium, tantalum, columbium and phosphorus fluorides give $\alpha(m/p)$ in the range of 10 to 15, about the same as does boron trifluoride.[2] The mechanism of extraction is probably the same in all cases. The xylene takes on a proton, to form a sigma-complex[5] as was postulated for boron trifluoride.[1]

The conversion reactions catalyzed by titanium tetrafluoride, in Table IV, also indicate sigma-complex formation. Neither ethylbenzene nor *p*-xylene is affected by HF alone. But in the pres-

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[3] J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950.

[4] Although the hydrogen fluoride used undoubtedly contained traces of moisture, it is believed that strictly anhydrous acid would not give noticeably different results. Small amounts of water, when added to the HF–xylene–metal fluoride solution, liberated mole equivalent portions of xylene. As expected, the water molecule, being much more basic than the arene, took the added proton away from the xylene. Otherwise it did not effectively change the nature of the solvent in the range of 99.9 to 98% HF. The small extrapolation from 99.9 to 100% HF is thereby justified.

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

TABLE III

EXTRACTION OF ARENES WITH HF–TiF_4

Temperature 15°; 2.5 volumes HF per volume hydrocarbon.

Composition of feed, mole %			
n-Heptane	70	71	55
o-Xylene	..	..	15
m-Xylene	..	..	15
p-Xylene	..	..	15
Mesitylene	30	29	..
TiF_4, moles/mole arene	0	1	1
Composition of products, mole %			
Raffinate			
n Heptane	72	88	71
o-Xylene	..	..	11
m-Xylene	..	..	5
p-Xylene	..	..	13
Mesitylene	28	12	..
Extract			
n-Heptane		1	2
o-Xylene		..	19
m-Xylene		..	69
p-Xylene		..	10
Mesitylene		99	..
Moles arene extracted/mole of TiF_4		0.6	0.4
Separation factors[a] α *meta/para*	..	..	18
Separation factors[a] α *meta/ortho*	..	..	8

[a] Defined as the isomeric ratios in the extract phase divided by the same ratio in the raffinate phase.

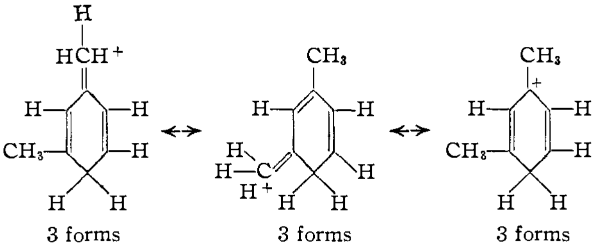
TABLE IV

CONVERSION OF ARENES WITH HF–TiF_4

2.5 volumes HF per volume of arene; reaction time 30 minutes.

Arene	Ethylbenzene	*p*-Xylene	*p*-Xylene
TiF_4, moles per mole arene	2	0.2	2
Temperature, °C.	30	66	66
Product composition, mole %			
Benzene	44	0	0
Monoalkylbenzene	14	8	15
Dialkylbenzene	40	85	72
Trialkylbenzene	2	6	10
Tetraalkylbenzene	0	1	3
Composition of dialkylbenzene fraction, %			
Ortho-	0	6	7
Meta-	100	36	86
Para-	0	58	7

ence of excess titanium tetrafluoride ethylbenzene is 85% disproportionated into benzene and 1,3-diethylbenzene; *p*-xylene isomerizes to *m*-xylene and disproportionates to toluene and trimethylbenzene. The same effects occur in HF—BF_3.[6]



All these reactions involve replacement of an alkyl group by a proton and therefore are best explained by the addition of a proton to an arene to form a sigma-complex intermediate. The function of the metal fluoride is to increase proton availability, and this it does by coördinating with the fluoride ion

$$F^- + BF_3 \rightleftarrows BF_4^-$$

$$F^- + 2TiF_4 \rightleftarrows Ti_2F_9^-$$

$$F^- + TaF_5 \rightleftarrows TaF_6^-$$

$$F^- + CbF_5 \rightleftarrows CbF_6^-$$

These acceptors for fluoride ion have two common characteristics. First, the central atom is not extremely electropositive. The metal–fluorine bonds have considerable covalent character, as is indicated by the low boiling and sublimation points of the compounds. When dissolved in hydrogen fluoride they therefore do not dissociate as bases into a metal cation and a fluoride ion, as for example to the alkali or alkaline earth fluorides. Second, the central atom is in a high positive valence state and can form a partially covalent bond with an additional fluoride ion without a net negative charge residing on the central atom.

Tantalum and columbium fluorides show the strongest tendency to accept a fluoride ion presumably because, by use of an available d orbital in the shell below the valence shell, they can thereby assume the very stable octahedral hexafluoro configuration. Phosphorus pentafluoride is a weaker acceptor probably because it must expand its valence shell to take on the octahedral configuration.

Since the acid properties of titanium, columbium, tantalum and phosphorus fluorides stem from an ability to coördinate with fluoride ion, they will promote the whole host of reactions in hydrogen fluoride that are known to be promoted by boron trifluoride. Therefore, it may be possible in individual cases to choose a promoter that is particularly suited for a given task, instead of depending exclusively on boron trifluoride.

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(6) A. P. Lien and D. A. McCaulay, THIS JOURNAL, **75**, 2404 (1953).