tially deuterated 1,3,5-tribenzoylbenzene, m.p. 118–119.5°, was 0.30 g. (34%). The deuterium content of the triketone was 0.87 atom per cent. deuterium or 0.157 gram atom of deuterium per mole (47% retention of the deuterium present in the epoxy ketone).

CAMBRIDGE 39, MASSACHUSETTS

Reaction of Arenes with Silver Fluoride in Hydrogen Fluoride Solution

BY D. A. McCAULAY AND A. P. LIEN

Silver fluoride, dissolved in anhydrous hydrogen fluoride, reacts with arenes to form a stable complex containing 3 moles of arene. The complex reverts to silver fluoride and arene as the hydrogen fluoride is removed by distillation. AgF–HF is therefore a useful solvent for separating arenes from other hydrocarbons. In contrast with other metal fluorides that complex with arenes, AgF in HF is a base; it inhibits rather than promotes such reactions as alkyl-group migration. The stability of the arene–silver fluoride complex is almost independent of the number and orientation of the alkyl groups on the ring. It differs from the σ-complexes formed by the action on arenes of HF plus other metal fluorides, such as BF_3, TiF_4, CbF_5, TaF_5, and acts more like a π-complex.

A few metal fluorides act as co-acids with liquid anhydrous hydrogen fluoride. A criterion used in previous work to establish such co-acid properties was whether the fluoride enabled a proton to add to a xylene molecule.[1] In the presence of a sufficiently strong co-acid, normally insoluble xylene accepts a proton and dissolves in the hydrogen fluoride. On the other hand, certain metal fluorides that are obviously bases in the hydrogen fluoride system also cause arenes to dissolve in this medium. Thus, Klatt[2] found that silver fluoride, which is soluble and ionizes in hydrogen fluoride probably according to the equation[3] can

$$AgF + HF \rightleftharpoons AgFH^+ + F^-$$
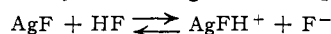
bring into solution up to four mole-equivalents of arene.

In the present study, batch extractions of hydrocarbon mixtures and petroleum fractions with AgF–HF have been used to elucidate the action of silver fluoride on arenes. Our objects were to determine how silver fluoride differs from the acidic fluorides and to learn whether it could be used to extract arenes from hydrocarbon mixtures, separate arenes from each other, or promote such reactions as alkylation and disproportionation.

Experimental

Silver fluoride, obtained from the Beta Research Laboratory, was dissolved in hydrogen fluoride and heated to 100° under vacuum to drive off any moisture present with the hydrogen fluoride. The hydrogen fluoride, a commercial grade of 99.6% purity supplied by the Matheson Co., was distilled before each experiment. The hydrocarbons, C.P. grades obtained from commercial suppliers, were used without further purification. The petroleum fractions used were typical straight-run and reformed West Texas naphthas.

The extraction runs were carried out in a 1.5-liter carbon-steel autoclave. Silver fluoride, hydrocarbon and a measured volume of hydrogen fluoride were added to the autoclave and stirred for 1 hr. After a settling period of 2 hr., the acid layer was withdrawn from the bottom of the autoclave into a polyethylene flask cooled in Dry Ice. In most cases, the extracted arenes were sprung by slowly adding water to the chilled acid phase. After a large excess of water had been added, the displaced arenes were decanted from the aqueous acid. The raffinate layer was drained from

the autoclave. Both hydrocarbon products were then washed with ammonium hydroxide and were analyzed by appropriate means, such as refractive index measurement and infrared and ultraviolet absorption.

In a few experiments designed to show whether the silver fluoride could be regenerated and used again the technique differed. After the mixing step, the autoclave was heated to 50° and the hydrocarbon and hydrogen fluoride were distilled into an evacuated flask to recover the silver fluoride residue for re-use.

Extraction of Known Mixtures.—Four mixtures of known hydrocarbons were each extracted with an equal volume of hydrogen fluoride plus silver fluoride. The results are shown in Table I.

TABLE I

EXTRACTION OF ARENES FROM SYNTHETIC MIXTURES

Arene	Benzene	Xylene[a]	C_8-Alkylbenzenes[b]	
Moles AgF per mole arene	0.17	0.17	1.0	1.0
Feed, vol. %				
Arene	40	40	32	32
n-Heptane	60	60	60	66.5
Olefin	....	...	8[c]	....
Propyl sulfide	....	...	....	1.5
Raffinate, vol. %				
Arene	22.5	25	0	0.4
Olefin	....	...	0	....
Propyl sulfide	....	...	....	0
Extract, vol. %				
Arene	97	95	97	94.5
Olefin	....	...	0	....
Propyl sulfide	....	...	....	4.5
Arene removed				
%	56.5	50	100	99
Moles per mole AgF	3.3	3.0	1.0	1.0
Separation factor, β[d]	144	57	>1000	1220

[a] Equal parts of m- and p-xylene. [b] Equal parts of all four. [c] Equal parts of n-octene and cyclohexene. [d] Quotient of the arene-to-heptane ratio in the extract phase divided by the arene-to-heptane ratio in the raffinate.

The mixture of benzene and n-heptane was about 56% dearomatized to give an extract containing 97% benzene. The separation factor, β, which measures the relative distribution of benzene and n-heptane between the two phases, has the high value of 144. Conventional solvents, such as diethylene glycol or sulfur dioxide, give β's ranging from 5

(1) D. A. McCaulay, W. S. Higley and A. P. Lien, THIS JOURNAL, 78, 3009 (1956).

(2) W. Klatt. Z. anorg. allgem. Chem., 234, 189 (1937).

(3) J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 237.

to 15. The exceptionally high selectivity of AgF–HF indicates that more than physical solution is involved; the amount extracted suggests that a coördination complex containing 3 moles of arene per mole of silver is formed. The excess 0.3 mole of benzene is probably extracted by physical solution. Xylene is known to be much less soluble in common solvents than benzene and, as expected, exactly 3 moles are extracted per mole of AgF. The excess one mole-equivalent observed by Klatt[2] could have resulted from working with pure arenes rather than with a heptane solution.

In the two runs with C_8-alkylbenzenes, two representative impurities were also present. One feed contained about 8% olefins, which alkylated the xylenes and were extracted as alkylbenzenes. The other feed contained about 1.5% propyl sulfide, which ended in the acid layer. In both these runs, excess AgF effected complete extraction. Also, the β-values jumped to well over 1000. Excess AgF changed the nature of the solvent and "salted out" the physically dissolved, uncombined hydrocarbon. The system AgF–HF is exceptional among solvents in that completeness and selectivity can be improved simultaneously.

The effect of hydrogen fluoride on extraction is summarized in Table II. Selectivity decreases as less hydrogen fluoride is used. Apparently, large amounts of arene–AgF complex change the nature of the solvent and increase the physical solubility of hydrocarbons in the acid phase. In the most concentrated solution, about 86 g. of AgF was present per 100 g. of hydrogen fluoride, whereas the measured solubility of AgF in hydrogen fluoride is only 33 g. per 100 g.[3] Because complexes form with arenes, much more than this amount of AgF goes into solution. Identical results were obtained when these runs were repeated after distilling off the HF and arenes under vacuum at 50°. Activity of the silver fluoride was unimpaired by the distillation step.

TABLE II

EFFECT OF HF CONCENTRATION

Extraction charge: 1 mole AgF, 6 moles arene, 7.5 moles n-heptane

HF, moles	111	18.5	7.4
Raffinate composition, moles			
Arene	2.97	2.93	2.77
n-Heptane	7.35	7.23	6.87
Acid-phase composition, moles			
HF	111.0	18.5	7.4
AgF	1.0	1.0	1.0
Arene	3.03	3.08	3.23
n-Heptane	0.17	0.27	0.63
Separation factor, β	50	28	13

Extraction of Petroleum Fractions.—Extraction experiments with one volume HF per volume of hydrocarbon and 1.0 mole of AgF per mole of arene were made also on two petroleum naphthas that contained a wide variety of arenes with boiling points up to 230°.

A high sulfur heavy naphtha, upon treatment with AgF–HF, formed a large amount of sludge, which interfered with phase separation. The sulfur compounds occurring in the naphtha—unlike propyl sulfide, which introduced no complication—evidently form an insoluble complex with silver fluoride. The naphtha was therefore desulfurized with HF alone before treatment with AgF–HF. No sludge formed and phase separation was good. As shown in Table III, all the arenes were extracted and the extract was almost 100% arene.

TABLE III

EXTRACTION OF LIGHT PETROLEUM STOCKS WITH HF–AgF

	Desulfurized heavy naphtha		Reformed light naphtha	
	Vol. % arene	$n^{20}D$	Vol. % arene	$n^{20}D$
Feed	23	1.4332	54.5	1.4477
Raffinate	0	1.4180	1.0	1.3873
Extract	99	1.4982	99.0	1.4968
% of aromatic removed	100		98	
Separation factor, β	>5000		4500	

A reformed naphtha was completely and selectively freed of arenes upon extraction with AgF–HF. All naturally occurring arenes boiling up to at least 230° can therefore be extracted from mixtures.

Separation of Arenes.—The possibility of separating close-boiling arenes from each other by extraction with AgF–HF was also investigated. Mixtures of two arenes in n-heptane solution were stirred with half a volume of hydrogen fluoride plus 1/6 mole AgF per mole of arene—enough to complex half of the arenes. The results are reported in Table IV. The separation factor, β, is equal to the equilibrium constant for the reaction in which both arenes compete for the silver ion

Arene B·Ag$^+$ + arene A $\rightleftarrows$ arene A·Ag$^+$ + arene B

$$\beta = K_{eq} = [A \cdot Ag^+][B]/[B \cdot Ag^+][A]$$
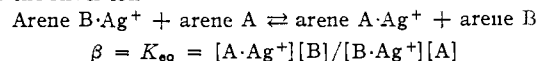
It is therefore a measure of the relative stability of the two arene complexes with AgF–HF.

Complexes of AgF with m- and p-xylene are about equally stable, the m-xylene complex being slightly stronger. The difference in stability is too small to be used in a practical process for separating these two isomers.

TABLE IV

SEPARATION OF ARENES WITH AgF–HF

Feed				
Arene A	p-Xylene		p-Xylene	
Arene B	m-Xylene		Ethylbenzene	
Raffinate				
Vol. % A	13.5	5.5	12.1	17.4
Vol. % B	11.6	20.3	13.9	7.7
Ratio A to B	1.16	0.27	0.87	2.26
Extract				
Vol. % A	47.8	25.4	50.0	69.3
Vol. % B	47.2	69.5	41.3	22.8
Ratio A to B	1.01	0.37	1.21	3.04
Separation factor, β	0.87	1.35	1.39	1.35

The experiments comparing p-xylene and ethylbenzene at three different concentrations show, first, that the p-xylene complex is stronger by a factor of 1.35 and, second, that ethylbenzene itself is unreactive. The latter effect contrasts directly with the behavior of ethylbenzene in HF–BF₃, where extensive disproportionation occurs almost instantaneously, even at temperatures as low as 0°.[4] The difference in stability between the silver complexes of p-xylene and ethylbenzene can be made the basis of a process for separating ethylbenzene from the close-boiling xylenes. Separation by distillation, because of the low value of 1.05 for the relative volatility, requires about 150 stages; extraction with AgF–HF could give the same separation in about 20 stages.

Effect of AgF on Alkylation.—Because AgF can make arenes soluble in hydrogen fluoride, it should promote alkylation by providing intimate contact between catalyst and reactants. This supposition was tested by four experiments, reported in Table V, in which ethylene and an arene were stirred with 1.5 volumes of HF for 60 minutes at 15°. When added to a stirred mixture of m-xylene and hydrogen fluoride, ethylene alkylates m-xylene at a moderate rate. But, when enough AgF is present to bring the xylene into solution, the rate of alkylation decreases and only half as much ethylene reacts. Also, as demonstrated by the toluene runs, if the olefin instead of the arene is added to the AgF–HF first, alkylation stops completely. Therefore, despite providing a homogeneous reaction medium, AgF inhibits alkylation—probably by a combination of two effects: (a) lowering the acidity of the catalyst by raising fluoride concentration and (b) tying up both olefin and arene as unreactive complexes.

Conclusion

The differences between the behavior of AgF in hydrogen fluoride and that of other metal fluorides

(4) A. P. Lien and D. A. McCaulay, THIS JOURNAL, 75, 2407 (1953).

TABLE V

ALKYLATION OF ARENES WITH ETHYLENE

	m-Xylene		Toluene	
AgF, moles per mole arene	0	——0.33——		
Ethylene, moles per mole arene	——1.0——		——0.33——	
Order of addition	——Olefin to—— arene		Arene to olefin	
Product distribution, mole %				
m-Xylene	62	77	..	..
Ethylxylene	20	16	..	..
Diethylxylene	6	2	..	..
Triethylxylene	2	1	..	..
Tetraethylxylene	10	4	..	..
Toluene	..	..	92	100
Ethyltoluene	..	..	7	0
Diethyltoluene	..	..	1	0
% of ethylene reacted[a]	78	39	27	0

[a] Unreacted ethylene appeared as ethyl fluoride.

(1) are summarized in Table VI. Silver fluoride acts as a base, decreases the acidity of the HF and inhibits acid-catalyzed reaction. The acidic fluorides markedly increase the hydrogen-ion concentration and thereby promote such acid-catalyzed reactions as alkylation and disproportionation. In forming complexes, the acidic fluoride coördinates with a fluoride ion and thereby assists a proton to add to the aromatic ring

$$\text{arene} + HF + BF_3 \longrightarrow \text{arene} \cdot H^+ BF_4^-$$
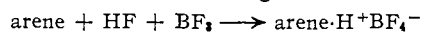
Because the metal fluoride itself is not part of the arene cation, the tendencies of the various arenes to form a complex should be independent of the metal fluoride used. Such was actually observed with the acidic fluorides.

TABLE VI

BEHAVIOR OF METAL FLUORIDES IN HYDROGEN FLUORIDE

| Property	AgF	BF₃, TiF₄, TaF₅, or CbF₅
Ionizes as	Base	Acid
Moles arene in complex	3	1
Benzene and toluene complexes	Stable	Unstable
Selectivity between m- and p-xylene	None	High
Catalytic activity		
Ethylbenzene disproportionation	Inactive	Promotes
Alkylation	Inhibits	Promotes

The arene cation is a σ-complex,[5] the stability of which is determined primarily by the number and orientation of alkyl groups on the ring.[6] The sta-

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

(6) D. A. McCaulay and A. P. Lien, ibid., **73**, 2013 (1951).

bility of the complex between arene and silver ion, however, is almost independent of the substituent groups. This cation therefore acts more like a π-complex; the silver ion combines loosely with the cloud of π-electrons around the ring.

Arenes and silver ion interact weakly[7] even in aqueous solution, but in anhydrous hydrogen fluoride the complex is many orders of magnitude more stable. Perhaps, because it is such a strong acid, hydrogen fluoride does not monopolize the vacant coördination positions around the silver ion but allows them to be filled by the arene to form complexes having the structures
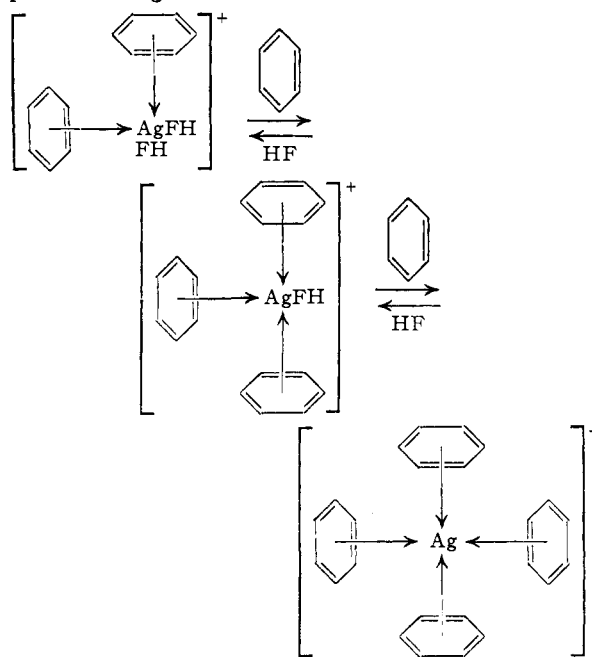
The complex containing three molecules of arene is stable even at low arene concentrations, but it shows little tendency to take on an additional molecule. The reason for the sharp cut-off at three is not clear; perhaps steric requirements prevent more than three molecules from approaching within bonding distance.

The stability of the complex depends upon hydrogen fluoride concentration. As hydrogen fluoride is removed from solution, the complex dissociates and the arene separates as a distinct organic layer. Because a strong chemical bond is formed in solution, extraction with AgF–HF is highly selective, and because this bond is easily broken by removal of a low-boiling solvent, a separation process based upon this technique is practical.

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(7) L. J. Andrews and R. M. Keefer, ibid., **71**, 3644 (1949); **72**, 3113, 5034 (1950).