acid hydrolysis of the product in the presence of 2-naphthol fails to yield the coupling product. Second, the compounds do not yield 8-arylguanines after acid hydrolysis; hence they are not 8-aryl-5′-guanylic acids. Third, the compounds are not hydrolyzed in acidic or basic solution to yield phenols. One product that has not been rigorously excluded is the 2′- or 3′-phenyl ether.

About 90% of the 5′-guanylic acid was accounted for in these experiments.

Comparison of the Reactivity of 5′-Adenylic Acid and 5′-Guanylic Acid. Solutions of 5′-adenylic acid (2.85×10^{-3} M), 5′-guanylic acid (2.85×10^{-3} M), and 4-sulfobenzenediazonium ion (5.71×10^{-3} M) was prepared at pH 8.0 and 10.5.

The solutions were stirred for 15 min at room temperature. The electronic spectra of aliquots of the reaction mixture which had been diluted with the buffer were recorded. Only the absorption at 390 nm could be detected. 6-[3-(4-Sulfophenyl)-2-triazen-1-yl]purine ribonucleoside 5′-phosphate and 2-[3-(4-sulfophenyl)-2-triazen-1-yl]-6-hydroxypurine ribonucleoside 5′-phosphate exhibit absorption maxima at 390 and 360 nm, respectively, at pH 8.0.

The same experiment was carried out at pH 10.5, only the absorption at 398 nm, which is characteristic of 6-[3-(4-sulfophenyl)-2-triazen-1-yl]purine ribonucleoside 5′-phosphate,[6] was observed.

Phenylation of 5′-Guanylic Acid. The reaction mixtures prepared from 4-bromo- and 4-sulfobenzenediazonium ion and 5′-guanylic acid were also heated for 95 °C for 8 h. The solution was neutralized with 1.0 N hydrochloric acid to precipitate the products and residual 5′-guanylic acid. The solid was suspended in 0.1 N hydrochloric acid and heated at 100 °C for about 1 h. The mixture was cooled rapidly, and the solids were collected, washed with cold chloroform and ice water, and dried to yield 8-(4-bromophenyl)- and 8-(4-sulfophenyl)guanine in 18 and 10% yields, respectively. These products were identical in all respects with the materials obtained in the hydrolysis of the 8-arylguanosine.

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Registry No. 1a, 79953-00-7; **1b**, 79953-01-8; **1c**, 79953-02-9; **1d**, 75056-37-0; **2a**, 79953-03-0; **2b**, 79953-04-1; **2c**, 79953-05-2; **2d**, 79953-06-3; **2e**, 79953-07-4; **3a**, 7780-10-1; **3b**, 79953-08-5; **3c**, 79953-09-6; **3d**, 14677-69-1; **3e**, 14173-37-6; **4d**, 79953-10-9; **4e**, 79953-11-0; 4-bromobenzenediazonium chloride, 2028-85-5; guanine, 73-40-5; benzenediazonium tetrafluoroborate, 369-57-3; 4-methylbenzene diazonium tetrafluoroborate, 459-44-9; 8-aminoguanine, 28128-41-8; adenine, 73-24-5; guanosine, 118-00-3; 2-aminopyrimidine, 109-12-6; 2-[3-(4-bromophenyl)-2-triazen-1-yl]pyrimidine, 79953-12-1; 5′-guanylic acid, 85-32-5; 4-sulfodiazonium chloride, 6118-33-8; 4-nitrodiazonium chloride, 100-05-0; 5′-adenylic acid, 61-19-8; 6-[3-(4-sulfophenyl)-2-triazen-1-yl]purine ribonucleoside 5′-phosphate, 79982-46-0.

Evaluation of Superacid Strength from the Protonation of Benzene. Comparison of $HF-SbF_5$, $HF-TaF_5$, and $HBr-AlBr_3$ Systems[1]

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The degree of protonation of benzene in $HF-SbF_5$, $HF-TaF_5$, and $HBr-AlBr_3$ solutions has been investigated by carbon-13 NMR spectroscopy. Both 30:1 $HF-SbF_5$ and $HBr-AlBr_3$ are much stronger acids than 30:1 $HF-TaF_5$ (55% protonation at a TaF_5/benzene ratio of 3) or 4:1 $HF-TaF_5$ (68% protonation at a TaF_5/benzene ratio of 2.5). $HBr-AlBr_3$ protonates benzene completely down to a $AlBr_3$/benzene ratio of 2. Under HBr pressure, 3.5–4 mol of HBr for each mole of $AlBr_3$ are taken into the benzenium bromoaluminate solution. The "sludge" catalysts commonly encountered in hydrocarbon conversions are actually solutions of carbocations in the $HBr-AlBr_3$ superacid. The high acidity revealed by the benzene protonation is representative for such sludges. The acidity measurement by benzene protonation can in principle be extended to other superacid systems.

Protonation of mono- and polyalkylbenzenes and the NMR spectra of the corresponding cations in various acidic media have been extensively investigated.[3–7] Although all these acidic systems are classified as superacids,[8] their acid strengths vary widely. Thus, a small amount of mesitylene was indicated in addition to its protonated form in $HF-BF_3$,[9] while $HF-SbF_5$ was found to convert benzene

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(1) A part of the work on the protonation of benzene in $HF-TaF_5$ and 30:1 $HF-SbF_5$ had been presented at the 173rd National Meeting of the American Chemical Society, New Orleans, LA, Mar 24, 1977; Abstract No. ORGN 188.

(2) (a) Corporate Research Laboratories. (b) Summer Intern under the Summer Employment Program in Corporate Research. (c) Analytical and Information Division.

(3) $HF-BF_3$: (a) McLean, C.; van der Waals, J. H.; Mackor, E. L. *Mol. Phys.* **1958**, *1*, 247. (b) Brouwer, D. M.; Mackor, E. L.; MacLean, C. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 1564 and references therein.

(4) $HF-SbF_5$: (a) Olah, G. A.; Schlosberg, R. H.; Kelly, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 2546. (b) Olah, G. A.; Schlosberg, R. H.; Porter, R. D.; Mo. Y. K.; Kelly, D. P.; Mateescu, G. D. *Ibid.* **1972**, *94*, 2034. (c) Olah, G. A.; Spear, R. J.; Messina, G.; Westerman, P. *Ibid.* **1975**, *97*, 4051 and references therein. (d) Reference 3b.

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(8) (a) Gillespie, R. J. *Acc. Chem. Res.* **1968**, *1*, 202. (b) Gillespie, R. J. *Endeavour* **1973**, *32*, 3.

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Table I. Carbon-13 Chemical Shift of Benzene in Solution

no.	solvent or acid system	MX_n/PhH ratio	HBr in the upper layer[a]	temp, °C	$\delta(^{13}C)$[b]	% **2**
1	$CHCl_3$[c]			0	128.5	0
2	CF_3COOH[d]			0	127.3	0
3	$HF-SbF_5$ (1:1)[e]	≥5		−78	145.7	100
4	$HF-SbF_5$ (30:1)	2.85		−10	144.8	(100?)
5	$HF-TaF_5$ (4.2:1)	2.5		30	139.9	68[f]
6	$HF-TaF_5$ (4.9:1)[g]	2.1		23	138.0	58[f]
7	$HF-TaF_5$ (4.3:1)	1.7		30	137.4	55[f]
8	$HF-TaF_5$ (30:1)	3		0, 10, 30[h]	137.5[i]	55[f]
9	$HF-TaF_5$ (28:1)	1.7		30	134.9	41[f]
10	HF[j]	0		4	127.5	0
11	$HBr-AlBr_3$ (3.2:1)	3.0	0.34	−5, 5[h]	144.4	100
12	$HBr-AlBr_3$ (3.9:1)	2.5	3.1	0	144.6	100
13	$HBr-AlBr_3$ (4.0:1)	2.1	1.0	0	144.5	100
14	$HBr-AlBr_3$ (3.9:1)	2.0	5.6	0	144.2	100
15	$HBr-AlBr_3$ (3.7:1)	1.8	1.35[k]	0	143.0	89
16	$HBr-AlBr_3$ (4.1:1)	1.55	0.74[k]	4	141.5	79
17	HBr[l]	0		0	129.1	0

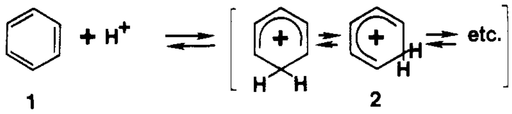
[a] Moles per mole of $AlBr_3$ (see the Experimental Section). [b] In parts per million from external (coaxial) Me_4Si in CD_2Cl_2 or $CDCl_3$ as the lock solvent; the CD_2Cl_2 and $CDCl_3$ multiplets (δ 53.8 and 76.9, respectively) served as a second calibration signal. [c] 14% v/v, δ $CHCl_3$ 77.5. [d] 14% v/v, δ (CF_3COOH) 161.7 (J = 43.7 Hz) and 113.7 (J = 283.2 Hz). [e] In SO_2FCl.[4a,b] [f] If $\delta(^{13}C)$ for **2** is taken from entry 4, the values become 72%, 61%, 58%, 58%, and 43%, respectively. [g] The HF/TaF_5 ratio might be somewhat lower due to evaporation during the sample transfer (see the Experimental Section). [h] Spectra run at more than one temperature. [i] Somewhat broad signal at 0 and 10 °C. [j] Saturated at 0 °C (2.5 % v/v).[36] [k] The presence of 1 in the upper layer was not tested for this particular sample, but its amount should be small (see text). [l] 10% v/v.

(**1**) into the benzenium cation (**2**),[4a,b,10] the simplest Pfeiffer–Wizinger complex,[11] although benzene is a base 10^9 times weaker than mesitylene.[12]

We report here on a study of the degree of protonation of benzene (**1**) and its use to measure the acid strength of various superacids.[1]

Hammett's classical method of acidity measurements,[13] as applied to superacids which consist of a solution of a Lewis acid in a Brønsted acid,[14] is limited to low concentrations of Lewis acid in the system.[14-16] Also, these measurements, as well as the newer methods, whether based on protonation–deprotonation equilibria,[15a] kinetics,[15b,17a] or mechanistic studies,[17b] are all based on protonation of oxygen bases. Since the relative acidities are determined by the nature of the indicator base,[13b] the values deduced in the literature so far might not be relevant for the correlation of acidity with catalytic activity in hydrocarbon conversions. A calibration of acidity using a carbon base as an indicator would be preferable for such a purpose.

Protonated benzene is actually a mixture of chemically identical positional isomers (automers;[18] **2**, eq 1), the interconversion of which is fast above −100 °C. Consequently, the ^{13}C NMR spectrum of **2** at −78 °C exhibits one averaged signal.[4a,b] On the other hand, in view of the low basicity of benzene, the chemical shift for **1** can be obtained by dissolving benzene in the Brønsted acid component of the superacid. In fact, we found that the ^{13}C chemical shift of **1** is not much influenced by solvent (Table I, entries 1, 2, 10, and 17). Therefore, the value for the solution in another solvent, with similar properties, can be employed without much error if benzene is not soluble in the Brønsted acid investigated. The degree of protonation in a given solution can be determined from the observed chemical shift. The latter is the weighted average of the shifts for **1** and **2** (which differ by ca. 16 ppm), provided the temperature is such that the protonation–deprotonation equilibrium is fast.



1 2 (1)

Previous literature data indicated that benzene is largely protonated in a sizable excess of 1:1 $HF-SbF_5$.[4a,b] From the published NMR spectra [4a,b,10] one could not, however, rule out the existence of small amounts (up to 10%) of **1** in equilibrium with **2**. In order to check this possibility, we investigated the protonation of benzene in a 30:1 $HF-SbF_5$ solution,[1] which on the basis of the literature should be a weaker acid than the 1:1 mixture.[19] Moreover, we increased at the same time the concentration of the base, benzene, to an SbF_5 to benzene ratio of 2.86:1 (1:0.35).[20]

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(10) Olah, G. A.; Staral, J. S.; Asencio, G.; Liang, G.; Forsyth, D. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6299.

(11) (a) The priority of Pfeiffer and Wizinger in proposing the mechanism of electrophilic aromatic substitution reactions and the structure of the intermediates has been pointed out in: Olah, G. A. *Acc. Chem. Res.* **1971**, *4*, 240. (b) Pfeiffer, P.; Wizinger, R. *Justus Liebigs Ann. Chem.* **1928**, *461*, 132. (c) See also: Meerwein, H. *Angew. Chem.* **1925**, *38*, 816. (b) These species are most often named Wheland intermediates, after: Wheland, G. W. *J. Am. Chem. Soc.* **1942**, *64*, 900.

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(13) (a) Hammett, L. P. "Physical Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1970; pp 263–313. (b) Ibid., p 278.

(14) Gillespie, R. J.; Peel, T. E. *Adv. Phys. Org. Chem.* **1971**, *9*, 1. Gillespie, R. J.; Peel, T. E. *J. Am. Chem. Soc.* **1973**, *95*, 5173.

(15) (a) Sommer, J.; Schwartz, S.; Rimmelin, P.; Canivet, P. *J. Am. Chem. Soc.* **1978**, *100*, 2576. (b) Sommer, J.; Rimmelin, P.; Drakenberg, J. *Ibid.* **1976**, *98*, 2671.

(16) As a referee pointed out, there is no reason in principle why Hammett measurements are limited to low concentrations of Lewis acid. It is only practical considerations, like the difficulty of finding bases that are sufficiently weak to measure the very high acidities generated by the addition of high concentrations of SbF_5 or like the low solubility of TaF_5, that have so far limited the use of the Hammett method to low Lewis acid concentrations.

(17) (a) Bouwer, D. M.; van Doorn, J. A. *Recl. Trav. Chim. Pays-Bas* **1973**, *91*, 895. (b) Brouwer, D. M.; van Doorn, J. A. *Ibid.* **1970**, *89*, 553.

(18) Balaban, A. T.; Fărcaşiu, D. *J. Am. Chem. Soc.* **1967**, *89*, 1958.

(19) For oxygen bases. ref 17a gives the 1:1 solution as 500 times stronger than a 9:1 solution. On the other hand, from ref 15a the 30:1 solution should be weaker than a 25:1 solution by a factor of 2 or more.

(20) This ratio was not given in ref 4a,b, but it probably was 5:1 or higher: Schlosberg, R. H., personal communication.

The chemical shift for this solution differed by less than 1 ppm from the literature value obtained in 1:1 HF–SbF$_5$[4a,b] (Table I, entries 3 and 4). This difference is smaller than the combined uncertainties of the two measurements, especially when one takes into account the differences in temperature and solvent.[21] Even if the difference were real, consideration of the characteristics of a titration curve clearly indicates that the chemical shift of benzene in 1:1 HF–SbF$_5$ can be taken as the limiting value for the totally protonated material, 2 (rapidly equilibrating mixture of automers). It is more probable, however, that even in the 30:1:0.35 ratio mixture,[22] benzene is practically completely protonated in HF–SbF$_5$.

The HF–TaF$_5$ mixture is a catalyst for various hydrocarbon conversions of practical importance.[23,24] At variance with SbF$_5$, tantalum pentafluoride is stable in a reducing environment. The HF–TaF$_5$ solution has also been used for mechanistic studies on carbocation reactions.[7a,b,25] The Hammett indicator method of acidity measurements could be applied only to very dilute solutions of TaF$_5$ in HF.[26] For the 0.6% (167:1)[22] solution, a H_0 value of −18.85 has been found,[27] which compares with a value of −19.95 for HF–SbF$_5$.[27]

To compare it with HF–SbF$_5$, we investigated first the protonation of benzene in HF–TaF$_5$ at the 30:1:0.33 ratio.[1] The chemical shifts measured between 0 and 30 °C (table I, entry 5) indicate a degree of protonation of about 55%. This finding was substantiated by results from studies of conversion of alkane–cycloalkane mixtures containing 2–5% of benzene. The distribution of benzene between the hydrocarbon and fluorotantalic acid phases is consistent with about half-protonation in the acid.[28] On the other hand, benzene is completely extracted under the same conditions in fluoroantimonic acid.[28]

Previously we reported that *tert*-butyl chloride is fully ionized in HF–TaF$_5$ at a 30:1:0.33 ratio.[7b] It follows then that benzene protonation requires a stronger acidity than what is needed to sustain tertiary alkyl cations in solution.

From the basicity difference between benzene and toluene[12] one predicts that in a 30:1:0.33 mixture of HF–TaF$_5$–monoalkylbenzene, the latter is over 99.8% protonated, in agreement with the experimental findings. This peculiarity of HF–TaF$_5$ (virtually complete protonation of alkylbenzenes but only partial protonation of benzene) has helped to determine the position of the alkylation–dealkylation equilibrium for protonated tertiary alkylbenzenes.[7b] The parallel use of two superacids of different strength, HF–SbF$_5$, and HF–TaF$_5$, to study the mechanism of interconversion of ortho- and para-protonated monoalkylbenzenes has also been reported.[7a]

Decreasing the TaF$_5$/benzene ratio reduces the degree of protonation, as expected. Thus, in a 28:1 HF–TaF$_5$ solution, only 41% of benzene is protonated at a TaF$_5$/benzene ratio of 1.7 (Table I, entry 9).

Our initial studies on HF–TaF$_5$[1] were limited to the 30:1 mixture since TaF$_5$ crystallized from more concentrated solutions at 0 °C. We discovered, however, that solutions of benzene in nonoxidizing superacids are stable at 30 °C, so we could expand the scope of our work. An approximately 4:1 acid could under these conditions be investigated up to a 2.5:1 TaF$_5$/benzene ratio. For the 2.5:1 to 1.7:1 range, the degree of benzene protonation indicates that 4:1 HF–TaF$_5$ (Table I, entries 5–7) is 3–4 times stronger than 30:1 HF–TaF$_5$ (Table I, entries 8 and 9).

The importance of aluminum bromide as a catalyst for carbocationic reactions needs no introduction. It is also well-known that catalytic activity for hydrocarbon conversions requires at least traces of a protonic acid cocatalyst like hydrogen bromide.[29] Yet, there are no acidity data on the HBr–AlBr$_3$ systems, or for that matter on pure, anhydrous HBr. Experimental difficulties due to the physical properties of HBr[30] may serve as an explanation, together with the apparently very low solubility of aluminum bromide.[31] Qualitative evidence, obtained by IR spectroscopy, for at least partial protonation of benzene by HBr–AlBr$_3$ has been published.[32]

For our investigation, dry[25] benzene was mixed with various amounts of purified aluminum bromide in an NMR tube, with external cooling under nitrogen in a drybox. In the absence of any traces of HBr, no color developed on mixing benzene with AlBr$_3$.[33] Measured amounts of hydrogen bromide were introduced into the tube by distillation. The tube was then sealed and warmed at room temperature until the solids dissolved. A brilliant yellow to light brown lower layer and an almost colorless upper layer resulted in all cases. From the volume of the upper layer measured at 0 °C it was estimated that the lower layer contained 3.5–4.0 mol of hydrogen bromide for each mole of aluminum bromide. This was not a function of the excess of HBr (size of the upper layer, Table I, fourth column), but it appeared to decrease somewhat with the increase in the aluminum bromide to benzene ratio.[34] Upon slow cooling, square transparent crystals separated from the lower layer between −5 and −10 °C, in most cases. Thus, as expected,[30c] hydrogen bromide is a poor solvent for carbocations. The lower layer is actually a molten salt, most probably $C_6H_7^+ \cdot Al_2Br_7^-$, which can contain an excess of aluminum bromide[35] or of benzene, depending upon the quantities used. Only a few molecules of HBr are taken into the lower layer, to solvate the anion.[30d]

Each sample was analyzed by carbon-13 NMR, at least at one temperature between −5 and +5 °C. Representative

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[21] SO$_2$FCl was used as solvent in ref 4a–c.

[22] All the reactant ratios throughout the paper are in moles.

[23] This was first proposed for the separation of xylenes from benzene and toluene: Lien, A. P.; McCauley, D. A. U.S. Patent 2 683 764, 1954.

[24] (a) Isomerization of aliphatics: Siskin, M.; Porcelli, J. J. U.S. Patent 3 948 761, 1976; 4 064 189, 1977. McCauley, D. A.; Nevitt, T. D. *Ibid.* 4 214 116, 1980. Siskin, M.; Chludzinski, G. R.; Hulme, R.; Porcelli, J. J.; Tyler, W. E., III. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 379. (b) Hydrogenation of aromatics: Siskin, M.; Wristers, J. U.S. Patent 3 888 937, 1975. Siskin, M. *J. Am. Chem. Soc.* **1974**, *96*, 3641. Wristers, *j. Ibid.* **1977**, *99*, 5051. (c) J. Siskin, M.; Wristers, J.; Porcelli, J. J. U.S. Patent 3 901 790, 1975. (d) Alkylation of alkanes: Siskin, M. *J. Am. Chem. Soc.* **1976**, *98*, 5413. Siskin, M.; Mayer, I. U.S. Patent 4 094 924, 1978. Siskin, M.; Mayer, I. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 191.

[25] Fărcaşiu, D.; Siskin, M.; Rhodes, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 7671.

[26] At saturation point, the HF/TaF$_5$ ratio is 108.6 at 19 °C and 161.1 at 0 °C: Hulme, R., personal communication.

[27] Gillespie, R. J.; Liang, J., personal communication.

[28] Chludzinski, G. R., personal communication.

[29] Pines, H.; Wacker, R. C. *J. Am. Chem. Soc.* **1946**, *68*, 1642.

[30] (a) Mp −86.86, bp −66.72 °C: Giauque, W. F.; Wiebe, R. *J. Am. Chem. Soc.* **1928**, *50*, 2198. (b) P_{vap} = 1.3–1.5 MPa at 0 °C: Drodzovski, E.; Pietrzak, J. *Bull, Int. Acad. Sci. Cracovie* **1913** (A), 219. (c) Dielectric constant 6.29 at −80 °C and 3.82 at 24.7 °C: Schaefer, O. C.; Schlunt, H. *J. Phys. Chem.* **1909**, *13*, 671. (d) See also: Peach, M. E.; Waddington, T. C. "Non-Aqueous Solvent Systems"; Waddington, T. C., ed.; Academic Press: London, 1965; Chapter 3.

[31] Waddington, T. C.; White, J. A. *J. Chem. Soc.* **1963**, 2701.

[32] Perkampus, H.-H.; Baumgarten, E. *Angew. Chem., Int. Ed. Engl.*, **1964**, *3*, 776, and references therein.

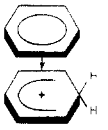
[33] Brown, H. C.; Pearsall, H. W. *J. Am. Chem. Soc.* **1952**, *74*, 191.

[34] For AlBr$_3$/benzene ratios smaller than 1.8 or larger than 3.0, the HBr in the lower layer was larger than 4.0 and smaller than 3.5 mol/mol of AlBr$_3$, respectively. However, in view of the indirect method of measurement, we cannot assign too much significance to differences of 15–20% in the estimated numbers. It has to be stressed that the presence of the upper layer is not necessary in order to obtain the HBr solution of 2 bromoaluminate. We preferred to have at least a very small upper layer, so that evaporation of HBr would not change the composition of solution (lower layer) when NMR spectra were run at two or three temperatures.

[35] It is conceivable that $Al_3Br_{10}^-$ anions might be formed in that case.

chemical shifts are given in Table I (entries 11–17). These chemical shifts are quite similar to those determined for $HF-SbF_5$ solutions. Even more important, the values obtained do not change for variations of the aluminum bromide to benzene ratio between 3 and 2. In fact, all the spectra which we ran for $AlBr_3$–benzene ratios ≥2.0 gave chemical shifts in the 144.6 ± 0.5-ppm range. We conclude from these data that benzene is fully protonated in $HBr-AlBr_3$ mixtures if more than 2 mol of aluminum bromide are present per mole of benzene. Free benzene (**1**) is present in equilibrium with its protonated form (**2**) for mixtures containing less than 2 mol of aluminum bromide per mole of benzene.

A potential problem existed in the presence of two layers in the $HBr-AlBr_3$–benzene mixtures. It is conceivable that the upper layer would extract unprotonated benzene (**1**), thus increasing the degree of protonation measured for the lower layer. This seemed improbable, since the solubility of **1** normally increases in the presence of the protonated material **2**. Thus, only 4 g of **1** can be dissolved in 100 g HF at 30 °C,[36] while the solutions in entries 5–7 of Table I contain about 12, 15, and 24 g of benzene in its unprotonated form (**1**) per 100 g of HF, respectively. It is possible that a charge-transfer complex (**3**) or a hydrogen bonded dimeric ion (**4**) is present in these solutions.



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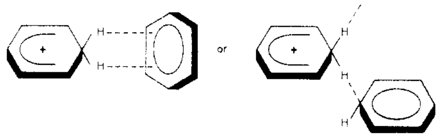

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On the other hand, hexane is soluble up to a concentration of 2 M in a 1 M solution of *tert*-hexyl cations or methylcyclopentyl cations,[25] although hexane has no π-electron system to act as a donor like in **3** or **4**. In any event, benzene should be extracted from the HBr layer into the benzenium bromoaluminate solution, rather than the other way around. Nevertheless, we checked the possible partition of **1** between the two layers by varying the volume of the upper (HBr) layer. We found the same degree of protonation (^{13}C NMR chemical shift) for a 1 mL of **2** bromoaluminate solution in the presence of 0.085 or 3.45 mL of upper layer at a 3:1 $AlBr_3$ to benzene ratio or in the presence of 0.2 or 1.5 mL of upper layer at a 2:1 $AlBr_3$ to benzene ratio. In another experiment, we prepared a sample in which a small amount of **2** bromoaluminate solution ($AlBr_3$ to benzene ratio 3) was made as a drop at the bottom of an NMR tube and covered with 1 mL of HBr. No signal for **1** was seen in the ^{13}C NMR spectrum of this sample; instead, the signal for **2** (fully protonated) was recorded. Therefore, if any organic material is dissolved into the upper layer, it is present there as **2** bromoaluminate rather than as **1**.

In aluminum bromide catalyzed reactions, the actual catalyst is normally a liquid film at the surface of the solid or a sludge. For best results, the sludge is sometimes preformed by the reaction of aluminum bromide with a haloalkane[37] or with a branched alkane *and* hydrogen bromide.[38] These steps generate carbocations, in the first case by ionization and in the second case by protonolysis of carbon–carbon bonds, similar to those described for $HF-SbF_5$,[39] and $HF-TaF_5$.[25] The composition of the sludge has been analyzed at least in one case as 83.9% $AlBr_3$, 6.49% HBr, and 9.53% hydrocarbon material.[38c] On the assumption that the latter consists of hexyl cations,[40] the molar composition of the sludge is 1 $(R^+\cdot Al_2Br_7^-)$:0.8-$(AlBr_3)$:0.7(HBr). This is very close to the composition of our lower layer, except for the smaller amount of hydrogen bromide in the isomerization catalyst. This is easy to rationalize, since the isomerizations were run at atmospheric pressure. The presence of HBr is essential, however; it is known that in order to maintain the catalytic activity in batch operations, HBr gas has to be introduced periodically. Therefore, the acidities which we measured for our $HBr-AlBr_3$ solutions are representative for the actual aluminum bromide catalyst, activated with HBr, and perhaps even for the water-activated catalysts.[41]

Aluminum halides have been considered for a long time to represent the typical "strong" Lewis acid catalysts, being placed at the "strongest" end of the list in any classification.[42] In more recent years, the studies of carbocations in superacids have employed, with very few exceptions, Lewis acid fluorides in HF or FSO_3H as the ionizing medium.[3-7,43] In a recent review, a classification of superacids is proposed.[44] The list of Lewis superacids includes such halides as SbF_5, AsF_5, TaF_5, NbF_5, and BiF_5, but aluminum bromide is not even mentioned. The list of conjugate Brønsted-Lewis superacids includes $HF-TaF_5$, $HF-NbF_5$,[45] and $HF-BiF_5$ but again not $HBr-AlBr_3$.[44] The opinion that $HBr-AlBr_3$ does not possess superacidic strength appears to have spread. Thus, another review has noted that multiple-step rearrangements of polycyclic hydrocarbons, like the conversion of tetrahydrodicyclopentadiene to adamantane, can be achieved both with catalysts based on aluminum halides (especially sludges) and with superacids like fluoroantimonic acid.[46] We find now that aluminum bromide is definitely a catalyst of the superacid class. As the data of Table I show for the 4:1 acids, $HBr-AlBr_3$ is much stronger than $HF-TaF_5$.

A direct comparison of $HBr-AlBr_3$ and $HF-SbF_5$ at the same HX/MX_n/benzene ratios could not be undertaken. Attempts at protonating **1** at SbF_5 to **1** ratios of 1.7 or 2.1 and HF to SbF_5 ratios of 4–8 gave each time a white to tan solid mass, below 0 °C, which did not dissolve in SO_2FCl and became black above 0 °C. On quenching, it was found that **1** had polymerized while Sb^V was partially reduced to Sb^{III}. One could presume that this behavior would indicate incomplete protonation, since samples of *m*-dialkylbenzenes in $HF-SbF_5$ (HF/SbF_5 ratio <1) were reasonably stable even at 95 °C.[47]

We prefer not to speculate upon this matter but to state only that both $HBr-AlBr_3$ and $HF-SbF_5$ are much stronger superacids than $HF-TaF_5$.

The evaluation of superacid strength from the degree of benzene protonation by ^{13}C NMR spectroscopy has been successful for the systems discussed here, and we can expect that the approach can be extended to other super-

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(36) Hulme, R., personal communication.

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(39) Review: Brouwer, D. M.; Hogeveen, H. *Prog. Phys. Org. Chem.* **1972**, *9*, 179.

(40) The sludge in ref 38c was generated by the protonolysis of dimethylhexanes.

(41) (a) Nenitzescu, C. D.; Cantuniari, I. P. *Chem. Ber.* **1933**, *66*, 1097. (b) Achard, R. French Patent 1 431 816, 1966.

(42) See for instance: Balaban, A. T.; Nenitzescu, C. D. N. *J. Chem. Soc.* **1961**, 3553.

(43) See footnotes 6–9 in ref 7b.

(44) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Science* **1979**, *206*, 13.

(45) At concentrations up to 0.4% in Lewis acid, $HF-NbF_5$ is weaker than $HF-TaF_5$;[27] studies of more concentrated $HF-NbF_5$ solutions are in progress in our laboratory.

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(47) Fărcaşiu, D.; Melchior, M. T.; Kastrup, R. V., unpublished results.

acids. Our procedure differs from the classical approach,[13,14] in which the base (indicator) is used in a very small concentration. Benzene is used in our experiments in large, essentially stoichiometric concentrations. On the other hand, this very feature makes our method applicable to the compositions actually existing in the superacid catalysts and, as such, more relevant for potential correlation with the catalytic activity in hydrocarbon conversions.

Experimental Section

General Methods. Aluminum bromide (MC&B, 99%) was melted with pellets (3 mm) of pure aluminum metal[48] and sublimed inside a drybox. It was stored there in Teflon FEP bottles with Teflon caps. Hydrogen bromide (Matheson, 99.8%) was taken from a 1-lb metal cylinder (lecture bottle). The sources and handling of other materials were given in previous papers.[7b,25] A Vacuum/atmospheres Co. drybox was used. ^{13}C NMR spectra were recorded in the FT mode at 25.2 MHz (Varian XL-100 instrument).

Protonation of Benzene in $HBr-AlBr_3$. All the glassware was dried at 120 °C overnight and then transferred quickly to the drybox. Aluminum bromide (5 mmol) was weighed in a calibrated (8 mm o.d., 5.5 mm i.d.) Pyrex tube with a ground joint and Teflon stopper inside the drybox. Benzene (1.55–3.2 mmol) was added from a syringe with a long needle to the $AlBr_3$ at the bottom of the tube, cooled in liquid nitrogen. The amount of benzene was checked by weighing the tube after the addition. In order to avoid static electricity buildup, which would disturb the weighing operation, the tube was handled inside the drybox with aluminum foil connected to the ground. The stopper was then replaced with a vacuum-type stopcock, and the tube was taken out of the drybox and attached to the vacuum line which had been evacuated overnight with the hydrogen bromide cylinder attached. Hydrogen bromide was admitted into the vacuum line through a fritted glass disk in order to retain any solid particles coming from the metal cylinder or valve. It was condensed into a graduated centrifuge tube attached to the vacuum line and cooled in liquid nitrogen. The volume of HBr was measured at −80 °C (CH_2Cl_2–liquid N_2 bath),[49a] and then it was distilled slowly from the measuring tube maintained at −80 °C into the NMR tube submerged entirely in liquid nitrogen. At intervals the liquid nitrogen level was lowered slowly, the HBr frozen at the top of the tube was allowed to melt and flow down the wall to the bottom. This ensured that any $AlBr_3$ which might have adhered to the walls of the tube was washed down to the botton. When the desired volume of HBr (20–50 mmol) was introduced into the NMR tube, the latter was sealed with a torch and then warmed slowly to room temperature until the solids dissolved. This step served also to check the quality of the tube and seal. It was done with the tube behind a shield in a hood. After the NMR spectra were run, the tube was thermostated at 0 °C, the height of the upper layer was measured, and the volume was calculated. It was assumed that the upper layer consists of pure HBr.[49b] The quantity of HBr in the lower layer was determined by difference. The total quantity of HBr in each sample was checked by weighing the sealed tube at the end. The values measured by weight and by the volume distilled from the measuring tube differed by less than 7%.

Protonation of Benzene in $HF-TaF_5$ and $HF-SbF_5$. The samples in 30:1 acids were prepared in Teflon bottles and transferred to the NMR tubes as described previously.[7b] It was noticed, however, for the 4.9:1:(1/2.1) sample that at the temperature at which all solids disappeared, some HF was lost through evaporation during the transfer from the bottle to the NMR tube. Therefore, the other samples at low $HF-TaF_5$ ratios were prepared directly in the NMR tube. The TaF_5 was weighed first, the tube was cooled, and HF was added with a Teflon pipet. The excess of HF, if any, was allowed to evaporate at 20 °C until the weight was right. The tube was cooled again, benzene (preweighed in a vial) was added through a Teflon syringe needle directly to the lower part of the NMR tube, and the weight of the tube was measured again. If necessary, a few crystals of TaF_5 were added at the end to adjust the TaF_5/benzene ratio. In all cases the mixture became homogeneous at or slightly above room temperature; for the 2.5:1 TaF_5/benzene mixture, the tube had to be swirled at 26–30 °C for about 15 min.

Registry No. 1, 71-43-2; HF, 7664-39-3; HBr, 10035-10-6; SbF_5, 7783-70-2; TaF_5, 7783-71-3; $AlBr_3$, 7727-15-3.

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Synthesis and Acidity of Crown Ethers with Pendant Carboxylic Acid Groups[1]

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Ten crown ethers with pendant carboxylic acid groups are synthesized from corresponding hydroxy crown ethers. Within this series of crown ether carboxylic acids there is systematic variation of the following: (a) the crown ether cavity size, while holding the pendant carboxylic acid group constant, (b) the length of the linkage which joins the carboxylic acid group to a common polyether ring, and (c) the lipophilicity, while keeping the polyether ring and linkage which joins the carboxylic acid and polyether ring portions invariant. Dissociation constants of the crown ether carboxylic acids in water are determined.

Recently we reported the facile synthesis of hydroxy dibenzo crown ethers **1a–d** by the reaction of epichlorohydrin with diphenols in alkaline aqueous media.[2] The hydroxyl group "handles" of these functionalized crown ethers provide convenient sites for further structural elaboration.

For the study of ionizable crown ethers as agents for the solvent extraction of metal ions[3-6] or their active transport

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