observed relative rates obtained has not been reported.

Inspection of molecular models based upon the above conformations indicates more ring crowding for the HMX E2 transition state in comparison to the RDX E2 transition state with *N*-nitro functionalities and carbon–hydrogen moieties causing varying degrees of unfavorable steric interactions in the HMX transition state. These steric interactions critically depend upon how the ring was adjusted about the adjacent reacting groups (H–C–N–NO_2).

An interesting correlation exists between the binding constants and the second-order rate constants for both the RDX and HMX hydrolyses (see Table I). The HMX hydrolysis rate becomes very nearly constant at [EHDMABr] $\geq 10^{-3}$ M, while the RDX hydrolysis rate continues to increase up to [EHDMABr] = 10^{-2} M. This phenomenon can best be explained in terms of saturation of the formed micelles at a lower surfactant concentration for HMX as compared to RDX (binding constant for HMX is more than twice that of RDX); hence, HMX can be considered totally bound to the micelles at [EHDMABr] $\approx 10^{-3}$ M, and any further increases in surfactant concentration should have only a negligible effect on the second-order hydrolysis rate. On the other hand, RDX is incompletely bound at [EHDMABr] $\approx 10^{-3}$ M; consequently, further increases in detergent concentration should increase the second-order hydrolysis rate as the remaining unbound RDX from the aqueous phase is incorporated into the micellar phase.

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Registry No.—RDX, 121-82-4; HMX, 2691-41-0; EHDMABr, 124-03-8.

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Reversible Dealkylation of Protonated *tert*-Butylbenzene. Position of the Equilibrium[1]

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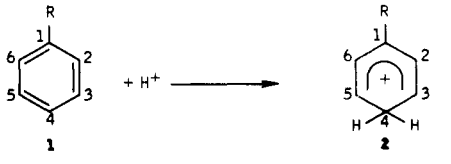
tert-Butylbenzene (**1d**) is protonated in HF–TaF_5, but in contrast with the behavior reported in HF–SbF_5 or FSO_3H–SbF_5, it does not form any significant amount of *tert*-butyl cations (**3**) by dealkylation between −60 and −10 °C. A dealkylation–realkylation equilibrium is established under these conditions, as indicated by partial disproportionation to di- and tri-*tert*-butylbenzene and benzene and by trapping **3** with CO, but the equilibrium is displaced virtually completely toward the alkylated material. Cation **3** prepared from *tert*-butyl chloride is stable in HF–TaF_5 under these conditions. 1,3,5-Tri-*tert*-butylbenzene (**5**) is protonated in HF–TaF_5–SO_2 solutions with very little side reactions. Dealkylation of **1d** in HF–SbF_5 or FSO_3H–SbF_5 is due to complete protonation of the dealkylation product benzene. The HF–TaF_5 system has an acidity which is high enough to stabilize *tert*-butyl cations and protonate monoalkylbenzenes virtually completely, but which is not sufficient to protonate benzene completely.

On dissolving monoalkylbenzenes (for instance **1a–c**) in superacids, the protonated species **2** were evidenced spectroscopically.[2,3]

Treatment of *tert*-butylbenzene (**1d**) under the same conditions (in HF–SbF_5 or FSO_3H–SbF_5 solutions) was found to lead to complete dealkylation, with the formation of the *tert*-butyl cation (**3**).[4] The ion **2d** was observed in 6:1



(1)

1 **2**

a: R=Me; **b**: R=Et; **c**: R=$CHMe_2$; **d**: R=CMe_3

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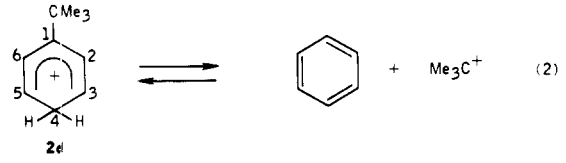
Table I. ^{13}C NMR Spectra of Alkylbenzenes and Their Protonated Forms

compd	solvent[a]	temp, °C	carbon-13 chemical shifts[b] C-1[c]	C-2	C-3	C-4	C-5	C-6	C-α
1a[d]	A	30	137.9	129.1	128.3	125.4			21.4
2a[e]	D	−70	200.9	136.5	178.0	46.4			27.9
1b	A	30	144.3	127.9	128.4	125.7			29.0
1b	B	−10	144.4	127.2	128.2	125.3			28.5
2b[e]	C[f]	−75	204.2	135.6	179.1	47.0			35.6
1d	A	38	151.1	125.2	128.0	125.4			34.7
	B	−10	151.6	125.1	128.1	125.1			34.3
2d[g]	C[f]	−60	210.7	(129)	176.7	44.8			41.0
1,3-$C_6H_4Et_2$	A	38	144.4	128.6	144.4	125.5	127.7	125.5	29.1
	B	−10	144.6	127.9	144.6	124.8	127.1	124.8	28.7
1,3-$C_6H_4Et_2$-4H$^+$	C[f]	−60	199.6	133.7	207.1	48.4	172.8	133.7	34.8,[h] 33.3[i]
1,3,5-$C_6H_3Et_3$	A	38	144.6	125.4					29.0
1,3,5-$C_6H_3Et_3$-H$^+$	C[f]	−60	198.8	130.8	199.9	49.3			35.7,[h] 33.3[i]
5	A	38	150.0	119.5					35.0
5-H$^+$	C[j]	−60	202.0	126.6	206.0	44.7			40.7[k]

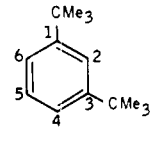
[a] (A) $CDCl_3$, (B) CF_3COOH, (C) HF–TaF_5, (D) HF–SbF_5 (1:1) + 1–2 vol of SO_2ClF. [b] Parts per million from internal ($CDCl_3$) or external Me_4Si (acid solutions). [c] Numbering is as in the formulas. [d] Literature values: δ 137.6 (C-1), 129.1 (C-2), 128.5 (C-3), 125.4 (C-4), and 21.5 (C-α). [M. Bullpitt, W. Kitching, D. Doddrell, and W. Adcock, *J. Org. Chem.*, **41**, 760 (1976)]. [e] Reference 3c. [f] HF/TaF_5/ArH = 30–35:1:0.33. [g] Tentative assignments; based on the observations made with protonated toluene (**2d**) and ethylbenzene (**2b**), the signals for **2d** are broader at −60 °C than the signals for **4-H$^+$** and **5-H$^+$** appearing in the spectrum. By subtracting the spectrum of **5-H$^+$**, the following signals were assigned to **4-H$^+$**: 203.8 (C-1), 212.6 (C-3), and 172.6 (C-5) ppm. [h] Groups bonded to C-1. [i] Groups bonded to C-3 and C-5. [j] HF/TaF_5/ArH = 15:1:0.4, diluted with 1 vol of SO_2. [k] Only one signal for C-α was seen (probably for the groups bonded to C-3 and C-5). The other signal might be coincident with the C-4 CH_2 peak.

FSO_3H–SbF_5 only below −60 °C, under which conditions it was stable enough so that its ^1H NMR spectrum could be recorded.[3a] On warming, it dealkylated completely and apparently irreversibly.[3a,4b,5] 1,3-Di-*tert*-butylbenzene (**4**), 1,3,5-tri-*tert*-butylbenzene (**5**), and other *tert*-butyl-substituted aromatics also dealkylated rapidly and completely to ion **3**. These observations indicated that the dealkylation equilibria (such as eq 2) are fully displaced to the right.

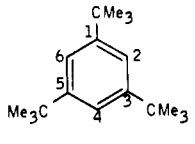


(2)

2d



4



5

By investigating the protonation of **1d** in HF–TaF_5 (30–35:1) superacid solution, we now find that equilibrium 2 is shifted almost completely to the left. It has been shown previously that monoalkylbenzenes are fully protonated in HF–TaF_5 at a TaF_5–ArH ratio of 3:1.[3c] Dissolving *tert*-butylbenzene (**1d**, 0.33 mol) in (30–35:1) HF–TaF_5 resulted in disproportionation with the formation of benzene, *tert*-butylbenzene (**1d**), *m*-di-*tert*-butylbenzene (**4**), and 1,3,5-tri-*tert*-butylbenzene (**5**) as evidenced by GLC analysis of samples which had been quenched in ice–pentane mixtures. This observation indicates that the dealkylation–realkylation process takes place in HF–TaF_5. As a further proof, free *tert*-butyl cations could be trapped on treatment with CO as pivaloyl cations, a portion of which subsequently reacted with benzene to form pivalophenone. Nevertheless, at −60 °C the ^{13}C NMR spectrum of the acid solution did not reveal any significant concentration of the *tert*-butyl cation (**3**). A separate experiment in which *tert*-butyl chloride (0.33 mol) was ionized in HF–TaF_5 (30:1) showed that the *tert*-butyl cation (**3**) is stable in this solution at −15 °C; even warming the sample for a short time at room temperature did not alter its ^{13}C NMR spectrum. This represents the first reported observation of an alkyl cation in the HF–TaF_5 system. Until now, stable solutions of alkyl cations have been obtained in superacids based on SbF_5,[6] $AlCl_3$–HCl (under pressure),[7] $GaBr_3$–SO_2,[8] or $AlBr_3$–SO_2ClF.[9] In the spectrum of **3** (at −15 °C) the signal for the sp^2 carbon atom (δ 335.7)[10] is weak, but the strong methyl signal (δ 46.5)[10] should be discernible even if **3** were in low concentration.[11] In the HF–TaF_5 solution of *tert*-butylbenzene (**1d**) this peak would appear at the downfield end of the relatively weak signal centered at δ 44.8 which was assigned to the ring sp^3 carbon (CH_2) of **2d** and of the protonated disproportionated products **4-H$^+$** and **5-H$^+$**. The methyl signals of the bound *tert*-butyl groups in **2d**, **4-H$^+$**, and **5-H$^+$** appear in the spectrum of this solution as a strong group of peaks between 27.1 and 28.5 ppm.[12]

1,3,5-Tri-*tert*-butylbenzene (**5**), which was dealkylated completely in HF–SbF_5 or FSO_3H–SbF_5 solutions,[4] was also protonated in HF–TaF_5. Since the product, a fluorotantalate salt, is insoluble in HF, the mixture was diluted with SO_2. The ^{13}C NMR spectrum of this solution (at −60 °C) indicated no measurable dealkylation of the cation **5-H$^+$** to the *tert*-butyl cation (**3**). (The chemical shifts of the hydrocarbons and of their protonated forms are given in Table I.)

The spectrum of **5-H$^+$** shows sharp signals at −60 °C and is not complicated by peaks due to disproportionation products. This ensures a maximum detectability of cation **3**; hence, its virtually complete absence is indicated. On the other hand, as it has been found for other monoalkylbenzenes protonated in HF–TaF_5,[3c] the signals for **2d** are broadened at −60 °C by the interconversion of the ortho- and para-protonated isomers. The absence of peaks for the *tert*-butyl cation (**3**) in the ^{13}C NMR spectrum of the solution obtained from *tert*-butylbenzene (**1d**) in HF–TaF_5 is still compatible with the presence of a finite amount of **3** in rapid equilibration with the protonated *tert*-butylbenzene (**2d**). If this were the case, the recorded chemical shift for C-α (Table I) should be intermediate between the values for C$^+$ in **3** (δ 335.7) and for C-α in **2d** in the absence of any contribution from **3**. However, the difference between the chemical shifts for the aliphatic quaternary carbon[12] in the acid solution and in the unprotonated form is about the same for *tert*-butylbenzene as for the pair **5** and

5-H$^+$ and is similar to the protonation shifts observed in all of the other alkylbenzenes investigated (Table I).[13] Therefore, the equilibrium concentration of *tert*-butyl cation in mixture at −60 °C is very small.

On warming, most signals broaden considerably due to intra-[3a,b] and intermolecular[2a,3c] transfer of protons and *tert*-butyl groups. However, the signal for the methyl carbons, while broadened, remained sharp enough to allow the determination of its chemical shift. This did not change (28.0 ± 0.5 ppm) between −60 and −10 °C. An increase in concentration of free *tert*-butyl cations (**3** δCH_3 = 46.5 ppm) with temperature would produce a downfield shift. Therefore, it can be concluded that equilibrium 2 is still displaced to the left, virtually completely, at the highest temperature investigated (−10 °C).

We can rationalize previous reports[4] of the quantitative formation of *tert*-butyl cation (**3**) from protonated *tert*-butylarenes (**2d, 4-H$^+$, 5-H$^+$**). Benzene, produced by dealkylation, is fully protonated in the stronger acids used previously.[1] It is the protonation of benzene, in a subsequent step, which is responsible for the displacement of equilibrium 2 to the right. On the other hand, the true position of the equilibrium could not be determined in a much weaker acid either since under these conditions *tert*-butyl cations would undergo partial deprotonation and be consumed in hydride transfer and oligomerization reactions.[14] The HF–TaF_5 mixture (30–35:1) was perfectly suited for the purpose of this study since its acidity is high enough to stabilize *tert*-butyl cations (**3**) and to fully protonate monoalkylbenzenes,[3c] yet not sufficiently high so as to protonate benzene completely.[1]

Experimental Section

General. The alkylbenzenes employed were A.R. grade commercial materials (Aldrich or Chemical Samples, Co.), the purities of which were tested by GLC and NMR. ^{1}H NMR spectra were recorded at 60 MHz (Varian A-60 instrument); ^{13}C NMR spectra were recorded in the FT mode at 25.2 MHz (Varian XL-100 instrument). TaF_5 (Ozark Mahoning) was sublimed and HF was fractionated before use. HF–SbF_5 (1:1) (Aldrich), used as received, was diluted with SO_2FCl (Aldrich) which had been vacuum distilled. All of the superacid solutions were prepared in a nitrogen drybox in Teflon or Kel-F vessels. The amount of water in these solutions was evaluated from the intensity of the ^{1}H NMR signal of H_3O^+; this was generally very weak or absent.

Preparation and Study of Protonated Aromatic Solutions. The aromatic hydrocarbon, neat or dissolved in Freon-11 and cooled to −78 °C, was added dropwise from a capillary pipet (or in small portions of solid for **5**) to the solution or suspension of SbF_5 or TaF_5 in HF with or without SO_2FCl, cooled at −78 °C, with magnetic stirring. In some cases it was necessary to warm slightly the solution after mixing in order to dissolve the solids. Samples of the acid solution were placed in acid-resistant NMR tubes, and the remainder of the solution was quenched in an ice–pentane mixture, separated, neutralized, dried, and then analyzed by GLC (Carbowax 20 M, 5% on 60–80 mesh Gaschrom Q, 4.5 m × 3 mm o.d. column, at 110 °C). In the case of **5** a new solid (**5-H$^+$** salt) precipitated. Addition of an equal volume of SO_2 dissolved it almost completely at −78 °C. This supernatant solution was used for NMR.

After completion of the NMR studies, the NMR samples were also quenched and analyzed for any further transformation which might have taken place while recording the spectra.

The possibility of alkyl group transfer during quenching has been studied for **5**. This starting material was 98% pure; the probable impurity was *p*-di-*tert*-butylbenzene. The suspension obtained on protonation and the SO_2 solution used for running the spectra both gave, after quenching, a mixture of **1, 4,** and **5** in a 0.5:2.5:97.5 ratio and 99% purity (GLC, after correcting for pentane). The remainder (1%) of the mixture consisted of several minor components. In one experiment, part of the original suspension was quenched in a mixture of ice water and benzene and then was extracted with pentane. The ratio of **1, 4,** and **5** (3:6.5:90.5) in this solution was not much different from that of the sample quenched without adding benzene, while the purity (GLC, after correcting for pentane and benzene) had changed to 95–96% and the remainder (4–5%) consisted again of several minor components in similar quantities.

Acknowledgment. The NMR spectra were run by the Magnetic Resonance Laboratory of the Analytical and Information Division of Exxon Research and Engineering Co. under the supervision of Dr. M. T. Melchior, who is also thanked for helpful discussions.

Registry No.—**1a,** 108-88-3; **1b,** 100-41-4; **1d,** 98-06-6; **2d,** 36348-52-4; **5,** 1460-02-2; **5-H$^+$,** 69855-38-5; 1,3-$C_6H_4Et_2$, 141-93-5; 1,3-$C_6H_4Et_2$-4H$^+$, 56694-18-9; 1,3,5-$C_6H_3Et_3$, 102-25-0; 1,3,5-$C_6H_3Et_3$-H$^+$, 56694-19-0; SbF_5, 7783-70-2; TaF_5, 7783-71-3; HF, 7664-39-3.

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(12) This assignment was checked in the proton-coupled spectrum.
(13) If the chemical shift for C-α in **2d** was the same as that in **1d,** the amount of **3** in rapid equilibration with **2d** could be $(\delta_{measd} - \delta_{1d})/(\delta_3 - \delta_{1d})$ = (41.0 − 34.5)/(335.7 − 34.5) or 2.2%. However, for all the alkylbenzenes investigated (Table I), C-α moves downfield on protonation by 6.5 ± 1 ppm. For **1d** the value is 41.0 − (34.5 ± 0.2) = 6.5 ± 0.2 ppm.
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