Cationic Micellar Catalysis of the Aqueous Alkaline Hydrolyses of 1,3,5-Triaza-1,3,5-trinitrocyclohexane and 1,3,5,7-Tetraaza-1,3,5,7-tetranitrocyclooctane[1]

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The kinetics for the aqueous alkaline hydrolyses of 1,3,5-triaza-1,3,5-trinitrocyclohexane (RDX) and 1,3,5,7-tetraaza-1,3,5,7-tetranitrocyclooctane (HMX) in the presence of cationic micelles of ethylhexadecyldimethylammonium bromide (EHDMABr) have been investigated using an LC mode of analysis. Both hydrolyses showed excellent second-order rate constants. Activation parameters were determined for the HMX hydrolysis using the Eyring equation. RDX hydrolysis showed a maximum rate enhancement of 100-fold (at 1×10^{-2} M EHDMABr), while the HMX hydrolysis had a maximum relative rate increase of 27-fold (at 1×10^{-2} M EHDMABr). Conformations of HMX and RDX in the ground state and transition state are used in an attempt to explain the observed rate differences between the RDX and HMX hydrolyses.

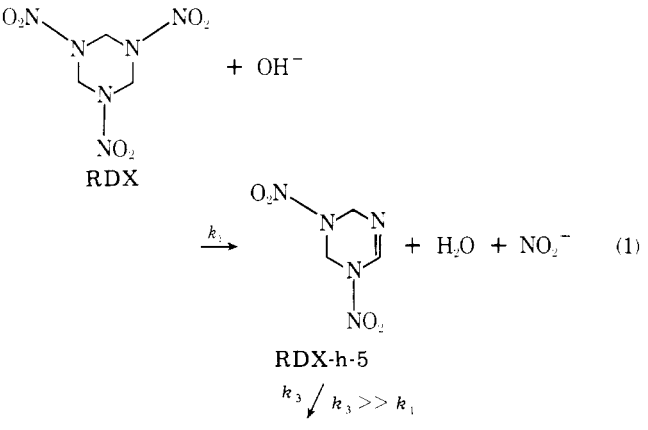
Although studies on the aqueous homogeneous alkaline hydrolyses of 1,3,5-triaza-1,3,5-trinitrocyclohexane (RDX) and 1,3,5,7-tetraaza-1,3,5,7-tetranitrocyclooctane (HMX) have been previously reported,[4-6] no study has considered the possible rate enhancement effects due to the presence of a cationic surfactant system. Therefore, in conjunction with extensive experiments performed in our laboratory on the treatment of munitions wastewater for the removal of 2,4,6-trinitrotoluene (TNT) using various surfactants,[2,3] it was decided to extend such surfactant–explosive experiments to the cyclic polynitramine explosives RDX and HMX.

Results obtained with the aqueous surfactant–TNT systems indicated an initial formation of a TNT addition complex (Janovsky reaction) with a subsequent precipitation from solution of a surfactant–TNT complex salt.[2,3] This rather unexpected finding has led to an effective and simple technique for the removal of TNT from munitions wastewater. While a comparable reaction was not observed for the nonaromatic nitramine explosives RDX and HMX, it was anticipated that a substantial rate enhancement of their alkaline hydrolysis reactions should be observed in a cationic surfactant system due to the "micellar phenomenon". A significant rate enhancement would complement the observed TNT–surfactant reaction in the total removal of nitroexplosives from munitions waste.

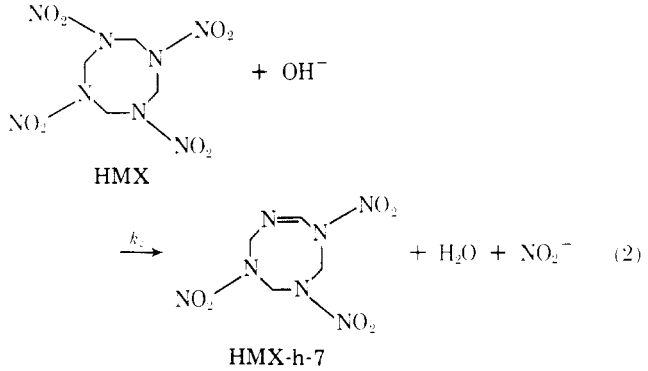
The proposed mechanism for the alkaline hydrolysis of RDX has considered a bimolecular elimination process with the liberation of nitrous acid.[4,5] The first step is considered to be a proton abstraction by base from the relatively acidic methylene hydrogens with a simultaneous elimination of a nitrite group from the adjacent ring nitrogen. This initial mode of attack was apparently demonstrated by Hoffsommer et al.[5] in a study in which they used hexaprotio and hexadeuterio RDX and compared the respective rates of hydrolyses in aqueous alkaline solution. The kinetic isotope effect was shown to be approximately 2.4. This finding thus supported a previous contention that the initial rate-determining step is a proton abstraction by base.[4]

Significantly, they also demonstrated evidence for the existence of 1,3,5-triaza-3,5-dinitrocyclohex-1-ene (RDX-h-5). This is the very product expected from the initial bimolecular elimination. Basically, the proof consisted of a novel way of generating 1,3,5-triaza-3,5-dinitrocyclohex-1-ene using a basic ion exchange resin, gas chromatographic separation of the reactants and products, and finally a mass spectral analysis of the suspected species upon elution from the gas chromatograph.[5]

The evidence thus amassed indicated the initial rate-determining step shown in eq 1 for the aqueous alkaline hydrolysis of RDX.[4,5] Further reaction of the intermediate RDX-h-5 was shown to be 10^5 times faster than that of RDX.[5]



In analogy to the RDX hydrolysis, the HMX hydrolysis presumably follows the same course of elimination with the formation of 1,3,5,7-tetraaza-3,5,7-trinitrocyclooct-1-ene (HMX-h-7). Proof for the existence of this intermediate has not been demonstrated, although second-order rate dependence for the HMX hydrolysis has been previously shown.[6]



The scant amount of work done on the alkaline hydrolysis of HMX as compared with that of RDX is probably due in part to the difficulties involved in analyzing directly for HMX by a convenient and accurate procedure. A direct gas chromatographic method previously used for RDX analyses[5] is impossible for HMX due to its extremely low vapor pressure. A TLC method developed by Glover and Hoffsommer[7] is not very amenable to kinetic study work, and an indirect gas chromatographic analysis for nitrite ions by conversion to nitrobenzene is quite tedious.[8]

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The only convenient alternative to the above methods seemed to be the Griess analysis for nitrite ion,[9,10] a spectrophotometric technique using a diazo coupling reaction between *N,N*-dimethyl-1-naphthylamine and sulfanilamide in the presence of the product nitrite ions to produce a colored azo dye which can be monitored at 520 nm in a UV–vis spectrophotometer. Indeed, this method was used in preliminary studies on the alkaline hydrolysis of RDX in a cationic surfactant system, but shifts in the wavelength of maximum absorption for the azo dye caused by its incorporation into the micellar phase[11] led to difficulties in standardization procedures, and this method was pursued only to the extent of establishing evidence for a cationic micellar catalysis.

Recent progress in high performance liquid chromatography (LC) has led to an extremely accurate and convenient method for nitramine and nitroaromatic explosive determinations.[12,13] With the proper choice of column, mobile phase composition, and flow rate, excellent separations of RDX or HMX from their respective alkaline hydrolysis products can be obtained in rapid fashion with excellent reproducibility. After extensive preliminary experiments, a reverse phase chromatographic system with an integral UV detector system established itself as the most convenient analysis route.

Hence, with the above-mentioned works on RDX and HMX alkaline hydrolyses as a background and utilizing an LC mode of analysis, the micellar catalytic effects due to an aqueous cationic surfactant system on the alkaline hydrolysis reactions of RDX and HMX were investigated.

Experimental Section

Materials. RDX[14] and HMX[15] were synthesized by the methods reported. Both compounds were purified by recrystallization (four times) from aqueous acetone. Each sample was subsequently checked for purity by NMR and IR. Deuterated acetone was used to solubilize RDX and HMX for the NMR spectra using a Varian A-60 spectrometer (60 MHz). RDX had a singlet at δ 6.40 (δ 6.38[16]), and HMX had a singlet at δ 6.40 (δ 6.38[16]). Me_4Si was used as an internal reference for both spectra. IR spectra of RDX and HMX were run on a Perkin-Elmer 457 IR recording spectrophotometer as Nujol mulls and pressed KBr pellets and were compared with the IR spectra of pure samples of RDX and HMX.[17] Melting points of RDX and HMX were 202–203 (203.5 °C[16]) and 280 °C (282 °C[16]), respectively.

Separate LC analyses on prepared aqueous solutions of RDX and HMX gave single peaks on the chromatogram traces under a variety of operating conditions (flow rate and mobile phase composition). A subsequent mixture of the aqueous nitramine solutions gave two well-separated peaks at the respective retention times for RDX and HMX under the prevailing chromatographic conditions (see Analyses section). A differential refractometer detector (Waters Associates, R-401) was used in conjunction with the UV detector (Waters Associates, Model 440) to ensure that no impurities were contained in the respective samples. No impurities were detected using the above LC analysis.

Cationic surfactant ethylhexadecyldimethylammonium bromide (EHDMABr) was obtained from Eastman Co., Rochester, N.Y., in a specially purified grade (>98%). The surfactant was washed extensively with anhydrous ether and then recrystallized twice from hot methanol.[11]

Fisher ACS certified sodium hydroxide pellets were used as a source of hydroxide ions for all RDX and HMX studies.

The methanol used in the mobile phase compositions was a special LC–UV grade obtained from Burdick and Jackson (Muskegon, Mich.), and no further purification was necessary.

Analyses. The critical micelle concentration (cmc) for the cationic surfactant EHDMABr was determined in distilled water solutions using a Cahn RG automatic electrobalance (Cahn Instruments Co., Paramount, Calif.) by a surface tension method (ring pull).[20] Various concentrations of detergent were prepared with distilled water over the range 1×10^{-5} to 6×10^{-2} M, and the surface tension of each solution was subsequently determined. The experimentally determined cmc was 9.5×10^{-4} M, which agreed quite closely with the value for trimethylhexadecylammonium bromide (CTABr, 9.2×10^{-4} M),[11] a very close homologue to EHDMABr (a methylene moiety in the head group being the only difference in molecular structure). A cmc value for EHDMABr has not been reported.

Aliquots of the RDX and HMX alkaline reaction solutions were withdrawn from the reaction vessel and quenched immediately with an appropriate volume of 10 N hydrochloric acid (see Kinetics section for explicit details concerning this procedure). The aliquots were subsequently analyzed for remaining nitramine by LC or visible spectroscopy (Griess method in preliminary studies only).

A Cary 14 recording spectrophotometer (Applied Physics Corp.) was used to determine RDX concentrations based upon the Griess analysis[10] during the preliminary studies. Cells of 1 and 10 cm were employed (depending on the extent of reaction), and a similar quenching procedure was used in the Griess analysis as for the later LC analysis. Calibration curves of RDX concentration vs. absorbance were prepared by hydrolyzing standards of RDX in excess base at an elevated temperature (boiling water bath).[10] As alluded to above, it was necessary to prepare calibration curves at various surfactant concentrations by the above procedure since the λ_{max} of the azo dye changed as the cmc of the surfactant was approached (λ_{max} varied from 520 to 460 nm).[11]

A Waters Associates ALC-GPC-201 liquid chromatograph (LC) was used for all subsequent analyses. For the RDX analysis, a Bondapak C-18 reverse phase column was used with a particle size of 37–50 μm and a 2 mm i.d. × 61 cm length. For the HMX analysis, a Microbondapak C-18 reverse phase column was employed with a particle size of 10 μm and a 4 mm i.d. × 30 cm length. Both columns are essentially a chemically bonded layer of octadecylsilane (Si–C-18) to a solid glass bead support and can be purchased from Waters Associates. Use of these columns with polar mobile phases (i.e., water–methanol mixtures) establishes the reverse phase nature of the separations.

Chromatographic conditions for the RDX analysis were as follows: mobile phase composition, 70% water–30% methanol (isocratic); flow rate, 1 mL/min with a resulting pressure of 1000 psi; UV dectector (254-nm wavelength monitor) set at 0.1 absorbance units full scale (AUFS) sensitivity.

Chromatographic conditions for the HMX analysis consisted of the following: mobile phase composition, 60% water–40% methanol (isocratic); flow rate, 1 mL/min with a pressure of 1250 psi; UV detector (254-nm wavelength monitor) set at 0.02 AUFS.

Since the nitramine peaks were symmetrical, the method of peak height measurement was employed to calculate RDX and HMX concentrations.[18,19] Calibration curves were constructed prior to each kinetic run by injecting prepared standards into the LC under the chromatographic conditions to be used for the subsequent reaction solution separations. Standards were also injected during and at the end of each run to ensure accurate quantitation throughout a given kinetic analysis.

Kinetics. Stock solutions of RDX and HMX were prepared by weighing out 50 mg of RDX and 24 mg of HMX and transferring each to a 2000-mL volumetric flask. The flasks were filled approximately three-fourths full with distilled water, and the resulting heterogeneous solutions were stirred for 8–10 days to effect complete solution. The respective solutions were then filtered through a 0.45-μm millipore filter (Millipore Corp., Bedford, Mass.) and finally filled to volume with 0.45-μm filtered distilled water. This procedure gave a 25 ppm (1.13×10^{-4} M) RDX standard stock solution and a 12 ppm (4.05×10^{-5} M) HMX standard stock solution. Dilutions of these stock standards were made to give 6.25, 12.50, and 18.75 ppm RDX standards and 6 and 9 ppm HMX standards. These standards were then injected into the LC for each RDX or HMX kinetic run, and a calibration curve was thus obtained.

Stock solutions of EHDMABr were prepared in the following concentrations: 2×10^{-2}, 1×10^{-2}, 5×10^{-3}, and 5×10^{-4} M; the latter three were prepared by dilution of the former. Distilled water was used for all surfactant solution preparations, and each was filtered through a 0.45-μm millipore filter.

A typical kinetic run consisted of the following sequence. A 37.5-mL amount of the nitramine main stock (25 ppm RDX or 12 ppm HMX) was pipetted into a three-neck ground glass joint flask of 100-mL capacity fitted with an overhead electric stirrer. The requisite volumes of standard surfactant and base were accurately pipetted into the reaction vessel to give a 50-mL reaction solution volume. Reaction time commenced with the addition of a NaOH solution. A Precision Scientific electronic timer was used to monitor time passage during all experiments. The stock solutions used for any given kinetic run and the vessel containing the reactants were thermostated in a constant temperature bath held to ±0.05 °C for at least 1 h prior to a run.

RDX and HMX concentrations were determined at a specific time by removing 1000-μL aliquots of the reaction mixture with a calibrated 250–1000-μL variable Finnpipette fitted with disposable

Table I. Second-Order Rate Constants for the Alkaline Hydrolyses of RDX and HMX with Ethylhexadecyldimethylammonium Bromide (EHDMABr) at 25 °C

[EHDMABr], M × 10^4	10^3k_2 for RDX[a,b]	10^4k_2 for HMX[a,b]	k_2(RDX)/k_2(HMX)
0	4.0 ± 0.2	3.0 ± 0.3	13.3
0.25	4.0 ± 0.2		
0.50	4.2 ± 0.2	3.0 ± 0.3	14.0
0.75	4.1 ± 0.2		
1.00	4.1 ± 0.2		
2.50	7.2 ± 0.3	4.6 ± 0.3	15.7
5.00	29.3 ± 2	22.8 ± 2	12.9
7.50	57.1 ± 2	36.6 ± 2	15.7
10.0	99.3 ± 2	62.0 ± 2	16.0
20.0	210 ± 20	66.3 ± 2	31.7
40.0	300 ± 20	76.9 ± 2	38.8
60.0	380 ± 20		
80.0	420 ± 20		
100.0	420 ± 20	80.0 ± 2	52.5

[a] In M^{-1} s^{-1}. [b] Error determination limits using standard deviation from the mean.

Table II[a]

	$\Delta G^{\ddagger}$ [b]	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
RDX[c]	20.7	22.6	+8
HMX	22.3	24.5	+7.5

[a] $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ are in kcal mol^{-1}, and $\Delta S^{\ddagger}$ is in cal deg^{-1} mol^{-1}. [b] ln k vs. $1/T$ was plotted from 25, 35, and 45 °C. [c] Values for RDX from ref 5.

polypropylene tips (Variable Volumetrics, Inc., Wilmington, Mass.) and quenching immediately in 10–20 μL (depending on initial hydroxide concentration) of an approximately 10 N hydrochloric acid solution. A 50-μL amount of the quenched sample was then injected into the chromatograph using an LC microsyringe (0–100 μL, variable, Precision Sample Co., Baton Rouge, La.) under the previously described operating conditions.

Neither RDX nor HMX was destroyed in the quenched acidic solution (pH ~1.5). This was demonstrated by periodically removing 50-μL aliquots of a mixture which consisted of 1000 μL of nitramine stock (25 ppm RDX or 12 ppm HMX) and 10 μL of the 10 N HCl solution with the LC microsyringe and injecting them directly into the chromatograph. No peak height changes were noted for either RDX or HMX, nor were there any extraneous peaks in the resulting chromatograms that might indicate acidic breakdown products of the respective nitramines. A similar procedure was carried out with surfactant plus nitramine. No peak height changes were noted.

Since the initial hydroxide ion concentration was introduced in large excess in relation to nitramine (typically 300–1000-fold molar excess in the case of RDX and 800–3000-fold molar excess for HMX), pseudo-first-order kinetics were obeyed.[5]

Results

The second-order rate constants for the alkaline hydrolyses of RDX and HMX are summarized in Tables I and II. Each second-order rate constant at a given surfactant concentration was obtained from at least four different hydroxide ion concentrations. A plot of these resulting pseudo-first-order rate constants vs. initial hydroxide ion concentration was linear. The slope of the plot corresponded to k_2, the second-order rate constant.

Binding constants for the RDX or HMX and micelle interaction were obtained by previously reported methods.[20] The binding constant for the RDX–micelle interaction was found to be 3.9×10^4 M^{-1}, and that for the HMX–micelle interaction was 8.6×10^4 M^{-1}. Thus, HMX would appear to bind to the micelle twice as strongly as does RDX. Intuitively, such a binding constant ratio would seem to be plausible; HMX is very much less soluble than RDX in water, and therefore HMX should have a stronger affinity for the relatively nonpolar micellar phase than RDX. This should result in a higher binding constant for HMX.

Activation parameters ($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) for the HMX hydrolysis were obtained using the transition-state complex formulation (Eyring equation) by plotting ln k vs. $1/T$ over the temperature range 25 to 45 °C. The activation parameters are collected in Table II.

Discussion

Upon examination of the activation parameters (Table II) the entropies of activation are found to be nearly the same, and it may be concluded that the orientations of molecular species involved at the respective transition states are very nearly the same; moreover, since the RDX hydrolysis has been shown to be an E2 process,[5] it would therefore seem quite plausible to conclude that the initial rate-determining step for the HMX hydrolysis also follows an E2 mechanism. The positivity of $\Delta S^{\ddagger}$ for the two hydrolyses can be subsequently interpreted in terms of an increase in randomness of all of the molecular species involved at the transition in comparison to the reactant state. This increase in randomness at the transition state is presumably due to the delocalization of negative charge which results from the combination of the negatively charged hydroxide ion and the neutral nitramine, the randomness thus resulting from a desolvation effect of the water molecules from about the hydroxide ion and the nitramine molecule to a new solvation shell about the nitramine–hydroxide complex at the transition state.

Rate enhancement for both the RDX and HMX alkaline hydrolyses in the cationic surfactant EHDMABr commenced at a detergent concentration between 1×10^{-4} and 2.5×10^{-4} M and increased up to a concentration of 1×10^{-2} M. The maximum rate enhancements attained for RDX and HMX hydrolyses were 100- and 27-fold, respectively (Table I).

Two factors can accommodate the kinetic results obtained for the RDX and HMX alkaline hydrolyses in an aqueous cationic surfactant system: (1) hydrophobic interactions between the nitramine molecules and the micellar phase which result in a greater local concentration for the nitramines at the micellar surface (preferential solubilization at the micelle–aqueous interface), and (2) the electrostatic stabilization of the resulting E2 transition state in the micellar phase relative to the bulk aqueous solution.[11] These two factors result in a faster rate of hydrolysis for either nitramine in the micellar phase relative to that in the bulk aqueous solution, and hence in the observed rate enhancement effect of the cationic surfactant EHDMABr on the hydrolyses of RDX and HMX.

The rate of hydrolysis of RDX was significantly greater than that of HMX both in the presence and absence of the cationic surfactant EHDMABr. Various spectroscopic investigations indicate that RDX exists preferentially in a chair conformation with *N*-nitro groups disposed in equatorial positions.[16,21–23] The NMR spectrum of HMX contains a singlet corresponding to the chemical shift equivalent methylene groups with no indication of an intra-methylene chemical shift difference.[16] This result has been interpreted as indicating a rapid octahydro-1,3,5,7-tetrazocine ring inversion along with a simultaneous inversion of configuration at the ring nitrogen atoms. This conformational interconversion is entirely analogous to the RDX case.[16] Subsequent Raman and infrared spectroscopic studies on HMX indicate a crown-type conformation.[24]

The respective conformations of RDX and HMX are similar to cyclohexyl and cyclooctyl compounds. Experimental results on E2-type eliminations of cycloalkyl tosylates[25] and cycloalkyl bromides[26] have shown that the rates of cyclohexyl derivatives are favored over those of the corresponding cyclooctyl compounds. An explanation on possible causes for the

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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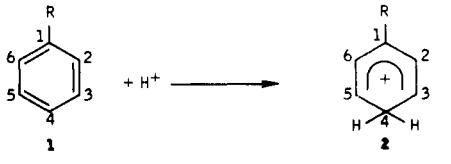
tert-Butylbenzene (**1d**) is protonated in HF–TaF_5, but in contrast with the behavior reported in HF–SbF_5 or FSO_3H–SbF_5, it does not form any significant amount of *tert*-butyl cations (**3**) by dealkylation between −60 and −10 °C. A dealkylation–realkylation equilibrium is established under these 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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