Gas-Phase Actinide Ion Chemistry: FT-ICR/MS Study of the Reactions of Thorium and Uranium Metal and Oxide Ions with Arenes

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Gas-phase reactions of M^+, M^{2+}, MO^+ (M = Th and U), and UO_2^+ with several arenes (benzene, naphthalene, toluene, mesitylene, hexamethylbenzene, and 1,3,5-tri-*tert*-butylbenzene) have been studied by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS). For M^+ ions C−H and/or C−C bond activation was observed in the primary reactions for all of the arenes studied. MO^+ and UO_2^+ ions yielded the adduct species, with the exceptions of the reactions of MO^+ with hexamethylbenzene and 1,3,5-tri-*tert*-butylbenzene, for which bond activation products also formed. In the M^{2+} reactions charge-transfer products dominated, but formation of doubly charged bond activation products was also observed with all the arenes. Product distributions and reaction rate constants are reported and related to the electronic configurations of the reacting ions, the polarizabilities of the arenes, and the energetics of the different reactions.

Introduction

The reactivity of lanthanide and actinide ions with hydrocarbons and other organic molecules in the gas phase has received considerable attention in recent times, compared with the small number of reports in the last two decades in which the reactivity of d transition-metal ions was extensively studied.[1−6] This recent research involving the f-block ions has been mainly due to efforts of our groups,[7−11] of Schwarz and co-workers,[12−17] and more recently of Gibson,[18,19] expanding previous work from the groups of Beauchamp,[20−23] Freiser,[24−27] Armentrout,[28,29] and Geribaldi.[30−32] Concerning the reactivity of actinide ions with organic molecules in particular, reports to date include ion-beam studies of the reactions of U^+ with CD_4,[20,21] CH_3F, CH_3Cl, and CCl_4,[22] a preliminary Fourier transform ion cyclotron resonance mass spectrometric (FT-ICR/MS) study of the reactivity of U^+ with 1,3,5-tri-*tert*-butylbenzene and 2,4,6-tri-*tert*-butylphenol,[7] and very recent FT-ICR/MS studies of the reactions of U^+ [15] and Th^+ [11] with alkanes and alkenes.

As we continue to probe various aspects of the gas-phase reactivity of lanthanide and actinide ions, we report in this paper an FT-ICR/MS[33−35] study of the reactions of thorium and uranium ions (M^+, M^{2+}, MO^+,

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and UO_2^+) with several arenes (benzene, naphthalene, toluene, mesitylene, hexamethylbenzene, and 1,3,5-tri-*tert*-butylbenzene). While the results of the M^+ reactions expand recent work involving alkanes and alkenes[11,15] and have been reported in preliminary form,[7,9,36] the results corresponding to the oxide ions and to the doubly charged cations constitute the first studies of the reactivity of these ions with organic molecules; U^{2+} ions have been recently used to produce, for the first time in the gas phase, the "bare" uranyl cation UO_2^{2+}, by reaction with O_2 and N_2O.[37]

Experimental Section

The experiments were carried out by use of a Finnigan-FT/MS (Madison, WI) 2001-DT FT-ICR mass spectrometer, equipped with a 3 T superconducting magnet and interfaced with a Spectra-Physics Quanta-Ray GCR-11 Nd:YAG laser operated at the fundamental wavelength (1064 nm). Pure thorium and uranium samples were prepared at the Institute for Transuranium Elements-JRC (Karlsruhe, Germany) by the splat technique[38] and were used to produce the singly or doubly charged metal ions by direct laser desorption/ionization of the metal pieces mounted on the automatic solids probe of the instrument. The metal oxide ions were produced by direct laser desorption/ionization of the oxide layer on the surface of the metal samples or by use of a formation period prior to isolation, in which the oxophilic thorium and uranium ions were oxidized by reaction with background water or oxygen. Isolation of the desired ions was achieved with the SWIFT technique.[39,40]

The organic reagents, obtained commercially, were introduced in the spectrometer through an Andonian Cryogenics Model 120 leak valve, to pressures in the range $5 \times 10^{-8}-5 \times 10^{-7}$ Torr on the "source" side of the dual ion trap of the instrument, as measured by a calibrated ion gauge. Pressure calibration was achieved using the reactions $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$[41] and $CH_3COCH_3^+ + CH_3COCH_3 \rightarrow$ products[42] and included corrections for the different ionization efficiencies of the arenes,[43] with necessary estimates based on experimental or estimated molecular polarizabilities.[44] Uncertainties in this pressure calibration procedure may lead to errors in the absolute rate constants, estimated to be ±50%. The rate constants were determined from the pseudo-first-order decay of the reactant ion relative signal magnitude as a function of time at constant organic reagent pressure and are reported as reaction efficiencies, that is, as fractions of the Langevin, k_L (or average dipole orientation theory, k_{ADO}, in the case of toluene), collisional rates.[45]

Single ions formed by laser desorption/ionization may exhibit a wide distribution of translational and electronic energies.[46] Collisional cooling of the reactant ions was performed for representative reactions, and while no changes, in relation to reactions where no thermalization events were used, were observed in the product distributions or the rate constants for the reactions of the singly and doubly charged metal ions, for the metal oxide ions a few differences were observed in the reaction products formed. The thermalization procedure typically involved a 1 s collisional period with argon introduced into the vacuum chamber through General Valve Corp. Series 9 pulsed solenoid valves to pressures of $\sim 10^{-5}$ Torr.

Due to the oxophilicity of thorium and uranium, reactions of the metal ions and some of its reaction products with residual water and oxygen were observed for long reaction periods; drying of the organic reagents by standard methods[47] prior to use was found to reduce the formation of oxygenated products. In the reactions of M^+ and M^{2+} ions, formation of oxygenated products was taken into account in the kinetics calculations by considering that half of the $MO^{+/2+}$ and $MOH^{+/2+}$ ions formed resulted from the reaction of the bare metal ion with the background; all other products containing both oxygen and a hydrocarbon fragment were considered to result from the reaction of all of the products other than the metal ions.

Results and Discussion

Reactivity of Th^+ and U^+ with Arenes. Table 1 summarizes the primary products and branching ratios obtained in the reactions of Th^+ and U^+ with benzene, benzene-d_6, naphthalene, toluene, mesitylene, hexamethylbenzene, and 1,3,5-tri-*tert*-butylbenzene; in Table 2 we report the corresponding reaction efficiencies, and Table 3 shows the secondary products obtained.

As seen in Table 1, Th^+ and U^+ are reactive with all the arenes studied, inducing dehydrogenations and/or losses of small hydrocarbon fragments, which in some cases result from the cleavage of the aromatic rings.

In the case of benzene, dehydrogenation was the only process observed for both metal ions (apart from a small contribution of the adduct species in the case of U^+), most probably corresponding to the formation of an M^+–benzyne species; Sc^+,[48] Y^+,[48] Nb^+,[49] and Ta^+ [49] also dehydrogenate benzene, as do the lanthanide series ions La^+,[9,19,48] Ce^+,[9,16,19] and Gd^+.[9,19] The formation of M^+–benzyne implies that $D(M^+-C_6H_4) \geq 363$ kJ/mol, using a recently determined value of 446.0 kJ/mol for ΔH°_f-(o-C_6H_4)[50] and other thermochemical data taken from standard sources.[51-53] When benzene-d_6 was used, formation of the adduct ion $MC_6D_6^+$ in significant amounts, in comparison to the reaction with benzene (see Table 1), could be observed in conjunction with the $MC_6D_4^+$ species; moreover, as seen in Table 2, an increase in reaction efficiency was also observed. These

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Table 1. Product Distributions in the Primary Reactions of Th^+ and U^+ with Arenes

arene (L)	product ion and rel abundance (%)			
	Th^+		U^+	
benzene	$Th(L - H_2)^+$	100	UL^+	9
			$U(L - H_2)^+$	91
benzene-d_6	ThL^+	12	UL^+	33
	$Th(L - D_2)^+$	88	$U(L - D_2)^+$	67
naphthalene	$Th(L - H_2)^+$	15	UL^+	36
	$Th(L - C_2H_2)^+$	85	$U(L - H_2)^+$	46
			$U(L - C_2H_2)^+$	18
toluene	$Th(L - H_2)^+$	87	$U(L - H_2)^+$	91
	$Th(L - C_2H_2)^+$	13	$U(L - 2H_2)^+$	9
mesitylene	$Th(L - H_2)^+$	100	$U(L - H_2)^+$	100
hexamethylbenzene	$Th(L - H_2)^+$	25	$U(L - H_2)^+$	54
	$Th(L - 2H_2)^+$	63	$U(L - 2H_2)^+$	38
	$Th(L - C_2H_6)^+$	12	$U(L - 3H_2)^+$	8
1,3,5-tri-*tert*-butylbenzene	ThL^+	2	UL^+	18
	$Th(L - H_2)^+$	6	$U(L - H_2)^+$	3
	$Th(L - 2H_2)^+$	3	$U(L - 2H_2)^+$	3
	$Th(L - CH_4, H_2)^+$	24	$U(L - CH_4)^+$	37
	$Th(L - CH_4, 2H_2)^+$	11	$U(L - CH_4, H_2)^+$	3
	$Th(L - CH_4, 3H_2)^+$	5	$U(L - CH_4, 2H_2)^+$	4
	$Th(L - 2CH_4)^+$	10	$U(L - 2CH_4)^+$	12
	$Th(L - 2CH_4, H_2)^+$	11	$U(L - 2CH_4, H_2)^+$	5
	$Th(L - 2CH_4, 2H_2)^+$	3	$U(L - C_4H_{10})^+$	11
	$Th(L - 3CH_4)^+$	10	$U(L - C_5H_{12}, H_2)^+$	4
	$Th(L - C_4H_{10})^+$	3		
	$Th(L - C_4H_{10}, H_2)^+$	2		
	$Th(L - C_5H_{12}, H_2)^+$	2		
	$Th(L - C_5H_{12}, 2H_2)^+$	8		

Table 2. Efficiencies (k/k_L) of the Reactions of Th^+ and U^+ with Arenes

arene	reacn efficiency (k/k_L)	
	Th^+	U^+
benzene	0.26	0.11
benzene-d_6	0.51	0.27
naphthalene	0.78	0.51
toluene[a]	0.38	0.30
mesitylene	0.94	0.46
hexamethylbenzene	1.01	0.69
1,3,5-tri-*tert*-butylbenzene	2.67	1.15

[a] k/k_{ADO}.

results are in agreement with previous observations of the effect of deuteration,[54] which tends to increase adduct lifetimes due to lower vibrational frequencies in the adduct species. Another noticeable feature of the reactions of Th^+ and U^+ with benzene (and benzene-d_6) is the formation of a species with the formulation $MC_{10}H_8^+$ as a secondary product (see Table 3) in the case of thorium. This species results from the reaction of $ThC_6H_4^+$ with a benzene molecule and is formed in 60% yield together with 40% of $Th(C_6H_4)(C_6H_6)^+$, with an overall efficiency $k/k_L = 0.08$. The formation of $MC_{10}H_8^+$ in conjunction with the adduct species $M(C_6H_4)(C_6H_6)^+$ has been described previously for $CrC_6H_4^+$, [55] and apparently corresponds to the cycloaddition of benzene to benzyne, with subsequent formation of naphthalene and acetylene, a process that is exothermic by 151 kJ/mol.[51] It is interesting to note that for $UC_6H_4^+$ only adduct formation is observed, as in the case of $ScC_6H_4^+$.[48]

In the reactions of Th^+ and U^+ with naphthalene, besides dehydrogenation (and adduct formation in the case of uranium), cleavage of the aromatic rings with elimination of C_2H_2 is observed, leading to $MC_8H_6^+$, species which in the case of thorium is the major primary product formed. For comparison, Ta^+ ions react with benzene with formation of $TaC_6H_4^+$ and $TaC_4H_4^+$;[49] in the case of Th^+ and U^+, the larger polarizability of naphthalene compared to that of benzene (see Table 4) facilitates the opening of the new reaction channel corresponding to elimination of C_2H_2.

In the case of the methyl-substituted arenes toluene, mesitylene, and hexamethylbenzene, single and multiple dehydrogenations are the major reaction pathways observed (Table 1); for Th^+ ions, additional reaction channels where hydrocarbon losses occur could be identified, as in the case of toluene, where elimination of C_2H_2 implies cleavage of the aromatic ring. Again, the greater polarizability of the substituted arenes compared to that of benzene (Table 4) has the effect of adding new channels to the reacting systems; another factor that facilitates the reactivity is the presence of weak C−H bonds in the methyl substituents ($D(C_6H_5\text{-}CH_2{-}H) = 368$ kJ/mol in toluene[52]) compared to the strong aromatic C−H bonds of benzene and naphthalene ($D(C_6H_5{-}H) = 464$ kJ/mol in benzene[52]).

The case of 1,3,5-tri-*tert*-butylbenzene is noteworthy due to the large number of primary products formed in the reactions with both Th^+ and U^+ ions, corresponding mainly to multiple neutral losses (Table 1). The rather large polarizability of 1,3,5-tri-*tert*-butylbenzene (Table 4) and the availability of weak C−C bonds ($D(C_6H_5C(CH_3)_2{-}CH_3) = 308$ kJ/mol in *tert*-butylbenzene[52]), in addition to the presence of aliphatic C−H bonds of moderate strength ($D(C_6H_5C(CH_3)_2CH_2{-}H) \approx 420$ kJ/mol assumed to be equal to $D(i\text{-}C_4H_9\text{-}H)$ in butane[52]) in the *tert*-butyl substituents, are certainly important factors contributing to the multitude of products ob-

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Table 3. Products of the Secondary Reactions of Th^+ and U^+ with Arenes

arene (L)	product ion	
	Th^+	U^+
benzene	$Th(L_2 - H_2)^+$ $Th(L_2 - H_2, C_2H_2)^+$	UL_2^+ $U(L_2 - H_2)^+$
benzene-d_6	ThL_2^+ $Th(L_2 - D_2)^+$ $Th(L_2 - D_2, C_2D_2)^+$	UL_2^+ $U(L_2 - D_2)^+$
naphthalene	$Th(L_2 - H_2)^+$ $Th(L_2 - C_2H_2)^+$	UL_2^+ $U(L_2 - H_2)^+$ $U(L_2 - C_2H_2)^+$
toluene	$Th(L_2 - H_2)^+$ $Th(L_2 - 2H_2)^+$ $Th(L_2 - H_2, C_2H_2)^+$	$U(L_2 - H_2)^+$ $U(L_2 - 2H_2)^+$ $U(L_2 - 3H_2)^+$
mesitylene	$Th(L_2 - H_2)^+$ $Th(L_2 - 2H_2)^+$	$U(L_2 - H_2)^+$ $U(L_2 - 2H_2)^+$
hexamethylbenzene	$Th(L_2 - H_2)^+$ $Th(L_2 - 2H_2)^+$ $Th(L_2 - 3H_2)^+$ $Th(L_2 - H_2, C_2H_6)^+$ $Th(L_2 - 2H_2, C_2H_6)^+$	$U(L_2 - H_2)^+$ $U(L_2 - 2H_2)^+$ $U(L_2 - 3H_2)^+$
1,3,5-tri-*tert*-butylbenzene	ThL_2^+ $Th(L_2 - H_2)^+$ $Th(L_2 - 2H_2)^+$ $Th(L_2 - CH_4, H_2)^+$ $Th(L_2 - CH_4, 2H_2)^+$ $Th(L_2 - CH_4, 3H_2)^+$ $Th(L_2 - 2CH_4)^+$ $Th(L_2 - 2CH_4, H_2)^+$ $Th(L_2 - 2CH_4, 2H_2)^+$ $Th(L_2 - 3CH_4)^+$ $Th(L_2 - C_4H_{10}, H_2)^+$ $Th(L_2 - C_4H_{10}, 2H_2)^+$ $Th(L_2 - C_5H_{12}, H_2)^+$ $Th(L_2 - C_5H_{12}, 2H_2)^+$ $Th(L_2 - C_5H_{12}, 3H_2)^+$ $Th(L_2 - C_6H_{14}, H_2)^+$ $Th(L_2 - C_6H_{14}, 2H_2)^+$	UL_2^+ $U(L_2 - H_2)^+$ $U(L_2 - 2H_2)^+$ $U(L_2 - CH_4)^+$ $U(L_2 - CH_4, H_2)^+$ $U(L_2 - CH_4, 2H_2)^+$ $U(L_2 - 2CH_4)^+$ $U(L_2 - 2CH_4, H_2)^+$ $U(L_2 - C_4H_{10})^+$ $U(L_2 - C_5H_{12})^+$ $U(L_2 - C_5H_{12}, 2H_2)^+$

Table 4. Polarizabilities (α) of the Arenes Studied

arene	α (Å^3)[a]
benzene	10.32
naphthalene	17.48
toluene	12.26
mesitylene	15.38
hexamethylbenzene	20.81
1,3,5-tri-*tert*-butylbenzene	32.45

[a] Experimental or estimated values from ref 44.

served. The reactivity of Th^+ and U^+ ions with this particular arene can be compared with previous results from our laboratories on the reactivity of lanthanide series ions with the same substrate, where multiple neutral losses were also observed, especially for the more reactive lanthanide cations.[8] As seen in Table 2, the experimental rate constants exceed the collisional rate constants for both Th^+ and U^+ reactions, an observation that deserves further comment. Apart from the uncertainties in the pressure calibration procedure indicated in the Experimental Section, an underestimation of the Langevin rate constants is undoubtedly occurring due to the large anisotropic polarizability and the presence of a quadrupole moment in the neutral reagent;[44,56−62] these effects, which are valid for all the arenes studied, become particularly important in the case of the large, highly polarizable, 1,3,5-tri-*tert*-butylbenzene molecule. Relevant to this problem is some very recent work on the limitations of polarization models of ion−molecule collisions.[63,64]

In summary, Th^+ and U^+ ions are able to activate, with high kinetic efficiencies, a variety of arenes. As in the case of alkanes and alkenes,[11,15] Th^+ ions are more reactive than U^+ ions. In terms of both product formation and reaction efficiencies, the reactivity appears to be closely related to the polarizabilities and the energies of the C−H and C−C bonds of the different arenes studied. As discussed in the previous studies of the reactivity of Th^+ and U^+ ions with alkanes and alkenes,[11,15] the electronic configurations of the reacting ions,[65] ground state $6d^27s$ in the case of Th^+ and $5f^37s^2$ in the case of U^+ (with the low-lying configuration $5f^36d7s$ at 0.04 eV), are appropriate to bring about activation of C−H and/or C−C bonds.

Reactivity of ThO^+, UO^+, and UO_2^+ with Arenes. In the reactions of thorium and uranium oxide ions ThO^+, UO^+, and UO_2^+ with benzene, naphthalene, toluene, mesitylene, hexamethylbenzene, and 1,3,5-tri-*tert*-butylbenzene, adduct formation is the main process observed. In the case of hexamethylbenzene and 1,3,5-tri-*tert*-butylbenzene, and as shown in Table 5, dehydrogenation and demethanation channels, respectively, could also be observed for ThO^+ and UO^+. In Table 6 we present the efficiencies k/k_L of the reactions studied. In secondary reactions of the adduct species formed, attachment of a second intact arene molecule was observed in all cases, with kinetic efficiencies 2−6 times lower than the ones determined for the primary reactions. Attachment of an intact arene molecule was also observed in secondary reactions of the activation products formed in the cases of ThO^+ and UO^+ with hexamethylbenzene and 1,3,5-tri-*tert*-butylbenzene.

From these results it is apparent that the presence of the oxo ligands causes a pronounced decrease in the reactivity relative to the metal ions, and only in the case of the more polarizable arenes hexamethylbenzene and 1,3,5-tri-*tert*-butylbenzene, which also contain weak C−H and C−C bonds, respectively, are activation products formed. In a recent study of the ion−molecule reactions of first-row transition-metal oxide cations MO^+ with benzene,[66] Schwarz and co-workers observed that the early-transition-metal oxides ScO^+, TiO^+, and VO^+ exclusively underwent adduct formation. In a comprehensive review of the gas-phase chemistry of transition-metal oxide ions by Schröder and Schwarz,[67] it can be seen that one of the major driving forces in the reactivity

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Table 5. Product Distributions in the Primary Reactions of ThO^+ and UO^+ with Hexamethylbenzene and 1,3,5-Tri-*tert*-butylbenzene

arene (L)	product ion and rel abundances (%)			
	ThO^+		UO^+	
hexamethylbenzene	$ThOL^+$	66	UOL^+	52
	$ThO(L - H_2)^+$	34	$UO(L - H_2)^+$	48
1,3,5-tri-*tert*-butylbenzene	$ThOL^+$	8	UOL^+	17
	$ThO(L - CH_4)^+$	92	$UO(L - CH_4)^+$	83

Table 6. Efficiencies (k/k_L) of the Reactions of ThO^+, UO^+, and UO_2^+ with Arenes

arene	reacn efficiency (k/k_L)		
	ThO^+	UO^+	UO_2^+
benzene	0.05	0.02	0.02
naphthalene	0.40	0.16	0.42
toluene[a]	0.13	0.03	0.10
mesitylene	0.37	0.19	0.45
hexamethylbenzene	1.58	0.48	1.41
1,3,5-tri-*tert*-butylbenzene	2.02	0.82	1.63

[a] k/k_{ADO}.

of these species is the strength of the M^+-O bond. In the case of thorium and uranium, very strong metal ion−oxygen bonds are present ($D(Th^+-O) = 876$ kJ/mol, $D(U^+-O) = 807$ kJ/mol, and $D(UO^+-O) = 764$ kJ/mol),[51,68] in agreement with our observations of adduct formation as the main reaction pathway of these ions with benzene and other arenes.

The dehydrogenation and demethanation processes observed in the reactions of ThO^+ and UO^+ with hexamethylbenzene and 1,3,5-tri-*tert*-butylbenzene raise some questions in relation to their possible mechanisms. Although, at this point, we are not able to provide a description of the electronic structures of these oxide ions, it is rather plausible that the M^+-O bonds can be described as double bonds, leaving, respectively, one and two electrons available for thorium and uranium ions to form new bonds; if in the case of uranium an insertion mechanism can still be envisioned, it is not the case for thorium, for which a multicentered concerted or a "direct" mechanism could be operative. In any case, these reactions have important driving forces in the large amount of energy available in the collision complexes, due to the high polarizability of the arenes, and in the reduced barriers arising from the weakness of the C−H and C−C bonds.

Not unexpectedly, the reaction efficiencies in Table 6 follow the same trend as the polarizabilities of the arenes (Table 4) and, as already observed in the case of the metal ions (see Table 2), the reactions with the larger, more polarizable arenes have efficiencies significantly larger than 1, again showing the limitations of the Langevin model in dealing with these molecules, as discussed at the end of the previous section. Another interesting aspect of the values in Table 6 is their relative magnitude relative to the oxide ions: $UO^+ < UO_2^+ \approx ThO^+$; while the greater efficiency of the ThO^+ reactions compared to those of UO^+ is in keeping with the greater reactivity of Th^+ compared to U^+, the observation that UO_2^+ is more efficient than UO^+ in adduct formation could be a consequence of the presence of two U−O bonds with a larger number of vibrational modes available for the radiative stabilization of the collision complexes.[69]

Reactivity of Th^{2+} and U^{2+} with Arenes. The reactions of the doubly charged cations Th^{2+} and U^{2+} with benzene, benzene-d_6, naphthalene, toluene, mesitylene, hexamethylbenzene, and 1,3,5-tri-*tert*-butylbenzene showed a predominance of charge-transfer channels: $M^{2+} + \text{arene} \rightarrow M^+ + \text{arene}^+$. Formation of doubly charged bond activation products, basically with the same single and multiple eliminations of H_2 and/or small hydrocarbons and the same relative abundances as in the case of the singly charged cations, was also observed with all the arenes. In some cases, hydride or/and methide ion transfer reactions also occurred: $M^{2+} + \text{arene} \rightarrow MH^+ + (\text{arene} - H)^+$ or $M^{2+} + \text{arene} \rightarrow MCH_3^+ + (\text{arene} - CH_3)^+$. In Table 7, the relative importance of the three main reaction channels for the various arenes studied is presented, while in Table 8 we show the corresponding reaction efficiencies.

Tonkyn and Weisshaar first,[4,70] and later Freiser and co-workers,[26,71−73] were able to show that the reactivity of doubly charged early-transition-metal cations with hydrocarbons was not limited to charge exchange, the only reaction pathway expected due to the fact that the second ionization energies of metals are generally higher than the first ionization energies of organic molecules. In those studies, formation of doubly charged bond activation products, as well as H^- or CH_3^- transfer reactions, could be observed along with electron transfer; a simple one-dimensional potential energy curve-crossing model was satisfactorily used by the authors to explain the observed reactivity patterns. In brief, at long range, the reactants, $M^{2+} + RH$ follow attractive ion-induced dipole potential energy curves, whereas the charged products of electron transfer, $M^+ + RH^+$, or hydride transfer, $MH^+ + R^+$, follow repulsive Coulombic potential energy curves. The exothermicities of the reactions determine the curve crossing points and the products observed: for instance, if the crossing distance is too large for the transfer of an electron or a hydride to be possible, M^{2+} ions may survive the crossing points, attain short distances, and be involved in the formation of doubly charged products.

The dominance of charge transfer in the reactions of Th^{2+} and U^{2+} ions is consistent with the second ionization energies of the metals (11.9 eV for both thorium and uranium[68]) being significantly higher than the first ionization energies of the arenes (compiled in Table 9). In Table 10 we present the calculated exothermicities and curve-crossing distances for the electron transfer reactions, as indicated by the model outlined above.

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Table 7. Product Distributions in the Primary Reactions of Th^{2+} and U^{2+} with Arenes

	product ion and rel abundance (%)			
arene (L)	Th^+		U^+	
benzene	Th^+, L^+	80	U^+, L^+	83
	$Th(L - H_2)^{2+}$	20	$U(L - H_2)^{2+}$	17
benzene-d_6	Th^+, L^+	77	U^+, L^+	85
	$Th(L - D_2)^{2+}$	23	$U(L - D_2)^{2+}$	15
naphthalene	Th^+, L^+	80	U^+, L^+	77
	$Th(L - H_2)^{2+}$	12	$U(L - H_2)^{2+}$	23
	$Th(L - C_2H_2)^{2+}$	8		
toluene	Th^+, L^+	67	U^+, L^+	74
	ThH^+, $(L - H)^+$	3	UH^+, $(L - H)^+$	4
	$Th(L - H_2)^{2+}$	16	$U(L - H_2)^{2+}$	17
	$Th(L - 2H_2)^{2+}$	6	$U(L - 2H_2)^{2+}$	5
	$Th(L - C_2H_2)^{2+}$	8		
mesitylene	Th^+, L^+	74	U^+, L^+	76
	ThH^+, $(L - H)^+$	4	UH^+, $(L - H)^+$	5
	$Th(L - H_2)^{2+}$	13	$U(L - H_2)^{2+}$	12
	$Th(L - 2H_2)^{2+}$	6	$U(L - 2H_2)^{2+}$	5
	$Th(L - C_2H_6)^{2+}$	3	$U(L - C_2H_6)^{2+}$	2
hexamethylbenzene	Th^+, L^+	75	U^+, L^+	79
	ThH^+, $(L - H)^+$	4	UH^+, $(L - H)^+$	3
	$ThCH_3^+$, $(L - CH_3)^+$	3	UCH_3^+, $(L - CH_3)^+$	2
	$Th(L - 2H_2)^{2+}$	10	$U(L - 2H_2)^{2+}$	14
	$Th(L - C_2H_6)^{2+}$	8	$U(L - C_2H_6)^{2+}$	2
1,3,5-tri-*tert*-butylbenzene	Th^+, L^+	80	U^+, L^+	81
	ThH^+, $(L - H)^+$	2	UH^+, $(L - H)^+$	2
	$ThCH_3^+$, $(L - CH_3)^+$	6	UCH_3^+, $(L - CH_3)^+$	7
	$Th(L - ...)^{2+}$	12	$U(L - ...)^{2+}$	10

Table 8. Efficiencies (k/k_L) of the Reactions of Th^{2+} and U^{2+} with Arenes

	reaction efficiency (k/k_L)	
arene	Th^{2+}	U^{2+}
benzene	0.66	0.44
benzene-d_6	0.59	0.46
naphthalene	0.90	1.36
toluene[a]	0.51	0.77
mesitylene	0.80	1.39
hexamethylbenzene	0.96	1.38
1,3,5-tri-*tert*-butylbenzene	1.02	0.78

[a] k/k_{ADO}.

Table 9. Ionization Energies (IE) of the Arenes Studied

arene	IE (eV)[a]
benzene	9.24
naphthalene	8.14
toluene	8.82
mesitylene	8.41
hexamethylbenzene	7.85
1,3,5-tri-*tert*-butylbenzene	8.19

[a] Values from ref 51.

Table 10. Calculated Exothermicities and Curve-Crossing Distances for Electron-Transfer Reactions of Th^{2+} or U^{2+} with Arenes

arene	ΔH_{reacn} (eV)[a]	r (Å)
benzene	−2.66	6.0
naphthalene	−3.76	4.9
toluene	−3.08	5.4
mesitylene	−3.49	5.1
hexamethylbenzene	−4.05	4.9
1,3,5-tri-*tert*-butylbenzene	−3.71	5.4

[a] Calculated from values in refs 51 and 68.

The observation of H^- and CH_3^- transfer channels for the substituted arenes (see Table 7) can also be accounted for by the model, although, due to the lack of thermochemical data, exothermicities and curve-crossing points can only be calculated for hydride transfer in the case of U^{2+} with benzene and toluene.[21,51−53,68] For benzene, the exothermicity $-\Delta H = 0.98$ eV and the curve-crossing distance $r = 14.78$ Å can be calculated, while for toluene we obtain $-\Delta H = 3.00$ eV and $r = 5.50$ Å, in agreement with the experimental results, that is, absence of hydride transfer in the case of benzene. For the other arenes, on the basis of known C−H bond dissociation enthalpies,[51−53] we could predict the absence of this reaction channel for naphthalene, as observed experimentally. In what concerns the CH_3^- transfer pathway, we can perform an estimate of the exothermicity and curve-crossing point for the system U^{2+}/toluene, considering that $D(U^+- CH_3)$ is similar to $D(U^+- H)$,[21,51] which leads to $-\Delta H = 1.37$ eV and $r = 10.72$ Å, apparently in accordance with the absence of this transfer channel in the case of toluene. The fact that CH_3^- transfer is observed only for hexamethylbenzene and 1,3,5-tri-*tert*-butylbenzene could arise from the presence of weak $C-CH_3$ bonds in the *tert*-butyl substituents of 1,3,5-tri-*tert*-butylbenzene[52] and from a weakening of $C-CH_3$ bonds in hexamethylbenzene, as compared to toluene. In the case of thorium, a small increase in the strength of the bonds to the singly charged cation, as compared to uranium, is not expected to cause any significant changes in the relative importance of H^- and CH_3^- transfer channels, as observed experimentally.

The formation of an appreciable amount of doubly charged bond activation products (between 10 and 30%, as seen in Table 7) means that, according to the potential energy curve-crossing model, an important fraction of M^{2+} ions surpass the crossing points and reach the potential well that corresponds to the formation of the collision complexes, which can then proceed to the products. The elimination of H_2 and other small neutrals indicates that bond insertion mechanisms

Table 11. Product Distributions in the Reactions of Th^+ and U^+ Formed by Charge Transfer from Th^{2+} and U^{2+} to Arenes

	product ion and rel abundances (%)			
arene (L)	Th^+		U^+	
benzene	$Th(L - H_2)^+$	48	$U(L - H_2)^+$	100
	$Th(L - 2H_2)^+$	10		
	$Th(L - C_2H_2)^+$	5		
	$Th(L - C_2H_4)^+$	24		
	$Th(L - C_4H_4)^+$	5		
benzene-d_6	$Th(L - D_2)^+$	57	$UL+$	9
	$Th(L - 2D_2)^+$	10	$U(L - D_2)^+$	87
	$Th(L - C_2D_2)^+$	5	$U(L - C_2D_4)^+$	4
	$Th(L - C_2D_4)^+$	24		
	$Th(L - C_4D_4)^+$	5		
naphthalene	$Th(L - H_2)^+$	22	UL^+	17
	$Th(L - 2H_2)^+$	30	$U(L - H_2)^+$	66
	$Th(L - C_2H_2)^+$	15	$U(L - C_2H_2)^+$	17
	$Th(L - C_2H_4)^+$	6		
	$Th(L - C_4H_4)^+$	12		
	$Th(L - C_4H_6)^+$	6		
	$Th(L - C_6H_6)^+$	9		
toluene	$Th(L - H_2)^+$	72	$U(L - H_2)^+$	77
	$Th(L - 2H_2)^+$	14	$U(L - 2H_2)^+$	19
	$Th(L - C_6H_4)^+$	14	$U(L - C_2H_4)^+$	4
mesitylene	$Th(L - H_2)^+$	26	$U(L - H_2)^+$	57
	$Th(L - 2H_2)^+$	22	$U(L - 2H_2)^+$	20
	$Th(L - C_2H_6)^+$	52	$U(L - C_2H_4)^+$	6
			$U(L - C_2H_6)^+$	17
hexamethylbenzene	$Th(L - H_2)^+$	5	$U(L - H_2)^+$	25
	$Th(L - 2H_2)^+$	27	$U(L - 2H_2)^+$	39
	$Th(L - 3H_2)^+$	9	$U(L - 3H_2)^+$	19
	$Th(L - C_2H_6)^+$	54	$U(L - C_2H_6)^+$	8
	$Th(L - C_2H_6, H_2)^+$	5	$U(L - C_2H_6, H_2)^+$	8

might be operative. Th^{2+} has two unpaired electrons in its ground-state electron configuration 5f6d and also in the configurations $6d^2$, 5f7s, and 6d7s at 0.008, 0.31, and 0.68 eV, respectively;[65] the ground-state configuration of U^{2+} is $5f^4$, with configurations $5f^36d$, $5f^37s$, and $5f^26d^2$ at 0.03, 0.46, and 2.41 eV, respectively.[65] The inspection of these electronic configurations raises the question of direct f-electron participation in the bonding, particularly in the case of U^{2+}, where the first electronic configuration with two unpaired non-f electrons is at a rather high energy above the ground state and argues in favor of a different bond activation mechanism.

Another important aspect of the electron-transfer reactions of doubly charged cations is the energy deposition in the charged products. Freiser et al. have conducted studies of the kinetic energy release in single charge transfer reactions of group 5 doubly charged cations with benzene, drawing conclusions on the kinetic and internal energy partitioning and showing that the product ions possessed significant kinetic energies.[74,75] In our study, evidence for the excess energy (kinetic and/or internal) deposited in the M^+ ions formed in the electron-transfer process can be obtained by comparing the data in Table 11, which shows product distributions for the reactions with arenes of the Th^+ and U^+ ions that resulted from the primary charge transfer pathways, with the data in Table 1, which contains the product distributions for the reactions with (in principle) thermalized Th^+ and U^+ ions formed by laser desorption/ionization. In almost all of the cases, the M^+ ions formed in the electron transfer reactions give rise to several products that correspond to multiple neutral losses, which is an indication of the existence of excess energy in the reactant ions.

As a final comment on the reactions of doubly charged thorium and uranium cations with arenes, we wish to discuss briefly the kinetic efficiencies presented in Table 8. Due to the predominance of the electron-transfer channels, reaction efficiencies apparently show a greater dependence on the ionization energies (Table 9) than on the polarizabilities of the arenes (Table 4). Whereas in the case of the singly charged ions the reactions necessarily proceed through the formation of encounter complexes, in the case of the doubly charged ions the dominant electron-transfer process most probably proceeds through a long-range mechanism, as discussed above. This difference is also evident in the case of benzene-d_6, for which we found reaction efficiencies similar to those of benzene for both Th^{2+} and U^{2+}, while for Th^+ and U^+ deuteration caused a doubling of the reaction efficiency (see Table 2).

Conclusions

In the present study we were able to contribute with additional data to the barely explored gas-phase chemistry of actinide ions, namely by showing that thorium and uranium monoxide and uranium dioxide cations are fairly unreactive species, due to the strong metal ion–oxygen bonds and that doubly charged thorium and uranium cations have an interesting chemistry, being able to activate aromatic hydrocarbons. The results obtained with the singly charged cations expand previous studies with alkanes and alkenes,[11,15] confirming the high reactivity of these metal ions and the finding that Th^+ is more reactive than U^+.

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As in our previous study of the reactivity of Th^+ with alkanes and alkenes,[11] the results obtained herein allow us to make a few tentative predictions of the reactivity along the actinide series. In what concerns the singly charged cations, the ground-state electronic configurations[65,76] point toward reactivities close to those of Th^+ and U^+ in the first half of the series for Ac^+, Pa^+, Np^+, and Cm^+. The reactivity of the metal oxide ions is more difficult to predict, as there are only $D(M^+{-}O)$ values available for M = Th, U, Np, Pu.[51,68] Recent work on the neutral monoxides[77,78] can give some clues on how $D(M^+{-}O)$ could vary along the actinide series. Concerning the doubly charged cations, two aspects can be considered: there is a small and rather regular increase in the second ionization energy along the series,[68,76] indicating that a small increase in the relative importance of charge transfer (to organic molecules) could occur on moving toward the end of the series; the data available on the electronic configurations of the doubly charged actinide ions are scarce and point to a dominance of $5f^n$ ground states beyond uranium,[65,76] which indicates that activation of hydrocarbons or other organic molecules will probably be difficult to observe. Clearly, experimental work done with protactinium and the transuranium elements would be desirable to try to complete the picture of the actinide series ion chemistry, based until now on thorium and uranium.

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