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Ion–Neutral Complexes of Protonated Alkylbenzenes: Experimental and Theoretical Studies

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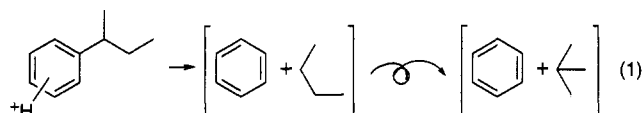
In the gas phase, the unimolecular reactions of metastable protonated alkyl arenes lead to alkyl cation formation with arene loss, protonated arene formation with alkene loss, and benzylic cation formation with alkane elimination. The dissociations are often preceded by an exchange between the hydrogen atoms of the chain and those of the ring, which can be rationalized by an interconversion between [arene alkyl cation] and [protonated arene alkene] ion–neutral complexes. By comparing the reactions of the metastable protonated alkyl arenes and those of their isomeric adducts (arene/alkyl cation) generated in the ion source by ion–molecule reaction, we show that π -complexes [arene alkyl cation] have a significant lifetime. By ab initio calculations, $[\text{C}_6\text{H}_6 \text{ iso-C}_3\text{H}_7^+]$ and $[\text{C}_6\text{H}_7^+ \text{ C}_3\text{H}_6]$ ion–neutral complexes are shown to be energy minima on the potential energy surface. They correspond therefore to stable structures. Two methods, namely, ab initio and semiempirical calculations, are used to calculate the interaction energies of [arene alkyl cation] complexes. The smallest stabilization energy (49 kJ/mol) corresponds to $[\text{C}_6\text{H}_6 \text{ tert-C}_4\text{H}_9^+]$ and the largest (65 kJ/mol) corresponds to $[\text{p-CH}_3\text{C}_6\text{H}_4\text{CH}_3 \text{ iso-C}_3\text{H}_7^+]$. The [protonated arene alkene] complexes are less stabilized (ca. 25 kJ/mol). The calculations also indicate that [arene alkyl cation] complexes have π -structures, but do not correspond to electron donor–acceptor (EDA) systems since, among the components of their interaction energy, the charge exchange term is negligible. Finally, these results are used to propose energy diagrams and fragmentation pathways.

Introduction

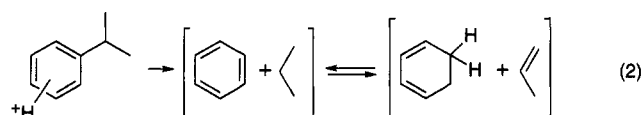
For many years, evidence for the formation of ion–neutral complexes in the gas phase has been searched for, both theoretically and experimentally. Ion–neutral complexes include the concepts of π -complexes, hydrogen-bonded complexes, and ion–dipole complexes.^{1–5} In solution, the intermediacy of π -complexes in electrophilic aromatic substitutions (EAS) was originally proposed by Dewar⁶ and then discussed in many papers.⁷ It was suggested that for the reactions of strong electrophiles the highest transition state corresponds to a π -complex structure, formation of which may be rate determining.⁸ In contrast, other studies conclude that π -complexes are not formed or that their formation is not rate determining.⁹ These π -complexes are described, if they exist as electron donor–acceptor (EDA) systems.⁷

In the gas phase, formation of π -complexes during unimolecular reactions of protonated aromatic compounds was first proposed by Grützmacher et al.¹⁰ Particularly, the formation of such intermediates in the fragmentation of protonated alkylbenzenes^{11–23} has been suggested for three reasons:

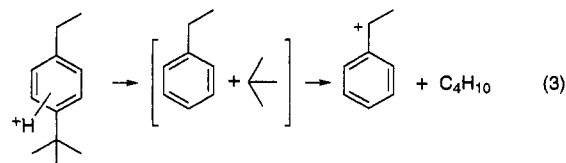
(i) Fragmentation of protonated *n*-alkyl or *sec*-alkylbenzenes yields a *tert*-alkyl cation product. This has been explained^{12,14,17} by the isomerization of the alkyl cation within a [arene alkyl cation] π -complex (eq 1).



(ii) Dissociation of metastable protonated isopropylbenzene is preceded by a H-exchange between the primary hydrogen atoms of the alkyl chain and the phenylic ones, which has been rationalized^{13,16} by the intermediacy of two interconverting ion–neutral complexes (eq 2).



(iii) Metastable protonated *p-tert*-butylethylbenzene eliminates isobutane.¹⁵ A specific hydride abstraction within a [*tert*-C₄H₉⁺ ethylbenzene] π -complex has been proposed to explain the data (eq 3). Similar mechanisms have been described for



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other cases.¹⁸

Whereas these results suggest the intermediacy of π -complexes, there is no definitive evidence to confirm their role as stable intermediates in the reaction pathways, and concerted processes could often account for the data.²³ Furthermore, from

a theoretical point of view, very few calculations have been done on this problem.²²

In this work, both theoretical and experimental studies of the isomerization mechanism of metastable protonated alkylbenzenes are carried out. We show that under chemical ionization conditions metastable protonated alkylbenzenes can isomerize into [arene alkyl cation] complexes, hereafter called " α -complexes", and [protonated arene alkene] complexes, hereafter called " β -complexes". The present study gives experimental evidence for the intermediacy of those α - and β -complexes, whose geometries and energies are calculated. The α -complexes are shown to correspond to π -structures but not to EDA systems. Furthermore, these calculations allow a better understanding of the origin of the stabilization energy in the complexes studied.

Methodology

Experimental Section. The experiments were carried out on a VG/ZAB/2F double-focusing mass spectrometer (B/E geometry). The reactions of low-energy ions were studied by metastable ion kinetic energy spectrometry (MIKE).²⁴ This technique allows for facile isolation of ions generated in the ion source. The unimolecular reactions of these metastable ions are then studied in the field free region. Water was used as the reagent gas to generate H_3O^+ for protonation of alkyl arenes (pressure = 10^{-5} Torr); protonation by CH_5^+ leads to very similar MIKE spectra. The adducts were generated by introducing arene, alkyl halide, and water in the ion source in the ratio 1:1:4 (total pressure = 10^{-4} Torr). Protonation of the alkyl halide leads by simple bond cleavage to the formation of an alkyl cation, which reacts further by addition to the arene.

Typical instrument conditions were 8000 V accelerating voltage, 200 eV ionization energy, and 150 °C ion source temperature.

Collision-induced dissociation (CID) spectra were obtained by introducing helium in the collision cell in the second field free region (FFR) such as to reduce the parent ion by a factor of 0.75.

All unlabeled compounds were available commercially or else synthesized by the Friedel-Crafts method.²⁵ Deuterated alkyl chlorides or iodides were prepared by standard methods.

All synthesized compounds were purified by gas chromatography (column SE30, 3 m), and their purities were checked by ^1H and ^{13}C NMR spectroscopy.

Theoretical Section. 1. *Ab Initio Calculations.* Ab initio calculations were performed on isopropylbenzene and the corresponding α - and β -complexes by using the HONDO 8.1 package.^{26a} Optimized geometries and vibrational frequencies were obtained at the Hartree-Fock level with the 3-21G basis set. Final energetics were computed using the polarized 6-31G** basis (six-component d sets, leading to a total of 200 basis functions). Thus, the computations can be summarized as HF/6-31G**//HF/3-21G.²⁷

Ab initio calculations are useful to establish whether ion-neutral complexes are true minima on the potential energy surfaces (PES) or not. However, they are intractable for a complete exploration of the PES, especially for the larger systems such as *tert*-butylxylene. Furthermore, a reliable account of electron correlation is difficult, whereas it is expected to play a significant role in shaping the potential well of an ion-neutral complex. We have therefore complemented our theoretical study with a completely different strategy.

2. *Simulated Annealing Calculations.* Since it is desirable to explore large portions of the PES, the energy calculation at each point must be rapid. For this purpose, one may take advantage of the fact that within intermolecular complexes the

two partners will to a large extent retain their integrity. We will therefore focus on the *interaction energy* only (with fragments frozen at their equilibrium geometries and wave functions). This can be done by a fit of the electron density (obtained by an ab initio calculation on each molecule or ion), by a superposition of atom- and bond-multipoles. The interaction energy is then calculated through exchange perturbation theory to second order. It is expressed as a sum of electrostatic, polarization, dispersion, charge transfer, exchange repulsion, and exchange dispersion terms which are computed separately.²⁸ This enables the quick calculation of the energy and its first and second derivatives. Efficient determination of extrema on the PES is ensured by a combination of global (simulated annealing)²⁹ and local (quasi Newton)³⁰ methods, and special techniques are used to locate saddle points. A full account of the method has been given elsewhere;²⁸ only selected aspects about each step are given below.

Energy Calculation. The electrostatic term (E_{el}) is expressed as a sum of multipole interactions. The SCF electronic density of each fragment is fit with good accuracy by a sum of a monopole, a dipole, and a quadrupole placed at the location of each atom and of each bond.³¹ A triple- ζ basis is used; geometries are experimental for the neutral species and optimized at the HF/3-21G level for the cations with the GAUSS-IAN 88 program.^{26b}

The polarization term (E_{pol}) is based on the same multipole expansion as above, plus experimental atom- and bond-polarizability increments.

Dispersion terms, included up to C_{10}/r^{10} , are expressed as a sum of atom-atom contributions.

Charge transfer can be included in the method, but is not considered here since ab initio calculations show it to be negligible.

In addition to standard Rayleigh-Schrödinger perturbation theory, *interfragment* antisymmetrization of the wave function leads to a term of exchange repulsion at first order (E_{rep}) and to exchange dispersion and exchange polarization terms at second order. The latter is always negligible and was not included here. The other two terms are computed as sums of atom-atom contributions and must include the variation of the van der Waals radius of each atom with its charge within each molecule. The evaluation of this variation is not obvious, and since our previous article,²² it has been improved.³² This modification has been tested on small systems and allows the reproduction, with an error of 5%, of the structural parameters obtained from spectroscopic constants.³³ Empirical parameters for these terms are obtained in order to reproduce the results of ab initio and symmetry-adapted perturbation calculations. Furthermore, they have been determined in such a way as to be transferable. It is important to note that as in such systems the charge transfer term is negligible, the sum ($E_{\text{el}} + E_{\text{rep}} + E_{\text{pol}}$) obtained by this method is directly comparable to the SCF ab initio interaction energy.

Determination of Extrema. A simulated annealing algorithm is used to locate the portions of the PES corresponding to attractive interactions between the ion and the neutral molecule. Within each portion, a local, gradient-based minimization is performed, and true minima are characterized by a scrutiny of the Hessian eigenvalues.

Saddle points connecting the above determined minima are located by a topological method due to Liotard.³⁴ Given a pair of minima M_1 and M_2 , a starting guess of the saddle point structure SP_1 is made, and an initial path is built as two straight lines $M_1\text{--}\text{SP}_1$ and $\text{SP}_1\text{--}M_2$. The highest energy point on the path is located and shifted along the steepest descent direction

TABLE 1: MIKE Spectra's Branching Ratio of Ions 1–10

		loss of arene		loss of alkene		loss of alkane	
		C ₃ H ₇ ⁺	C ₄ H ₉ ⁺	C ₃ H ₆	C ₄ H ₈	C ₃ H ₈	C ₄ H ₁₀
C ₆ H ₅ -iso-C ₃ H ₇ /H ⁺	1	13		87			
C ₆ H ₅ - <i>tert</i> -C ₄ H ₉ /H ⁺	2		100				
<i>p</i> -CH ₃ C ₆ H ₄ -iso-C ₃ H ₇ /H ⁺	3	2		98			
iso-C ₃ H ₇ - <i>p</i> -xylene/H ⁺	4	1		99			
<i>p</i> -CH ₃ C ₆ H ₄ - <i>tert</i> -C ₄ H ₉ /H ⁺	5		97		3		
<i>p</i> -CH ₃ CH ₂ C ₆ H ₄ - <i>tert</i> -C ₄ H ₉ /H ⁺	6		6		1		93
<i>p</i> - <i>tert</i> -C ₄ H ₉ C ₆ H ₄ -iso-C ₃ H ₇ /H ⁺	7		16		1		83
iso-C ₃ H ₇ C ₆ H ₅ / <i>tert</i> -C ₄ H ₉ ⁺	7'		13				87
2- <i>tert</i> -C ₄ H ₉ - <i>p</i> -xylene/H ⁺	8		17		82		1
<i>p</i> -xylene/ <i>tert</i> -C ₄ H ₉ ⁺	8'		2		8		90
5- <i>tert</i> -C ₄ H ₉ - <i>m</i> -xylene/H ⁺	9		48		2		50
<i>m</i> -xylene/ <i>tert</i> -C ₄ H ₉ ⁺	9'		40		1		59
4- <i>tert</i> -C ₄ H ₉ - <i>o</i> -xylene/H ⁺	10		91		5		4
<i>o</i> -xylene/ <i>tert</i> -C ₄ H ₉ ⁺	10'		94		4		2

TABLE 2: Shifts of the Fragment Ions from the Labeled Metastable Ions 1–10

	<i>tert</i> -C ₄ (H,D) ₉ ⁺ , <i>m/z</i>							loss of C ₄ (H,D) ₁₀ , <i>m/z</i>					loss of C ₄ (H,D) ₈ , <i>m/z</i>							
	57	58	59	62	63	65	66	105	106	110	113	114	107	108	109	110	113	115	116	117
CH ₃ C ₆ H ₄ CH ₃ / <i>tert</i> -C ₄ H ₉ ⁺	100							100					100							
CD ₃ C ₆ D ₄ CD ₃ / <i>tert</i> -C ₄ H ₉ ⁺	88.5	8.5	3								2	98						2.5	12.5	85
CD ₃ C ₆ H ₄ CD ₃ / <i>tert</i> -C ₄ H ₉ ⁺	100									100							100			
CH ₃ C ₆ H ₄ CH ₃ / <i>tert</i> -C ₄ D ₉ ⁺				1.5	15	83.5		97.5	2.5					84.5	13.5	2				

orthogonal to the path. This is based on successive gradient calculations and update of an initial Hessian estimate. The new position of the highest energy point generates a new path, and the procedure is repeated until the gradient at the highest energy point is nearly parallel to the path. The saddle point structure is eventually established by a calculation of the true Hessian.

Results

Experimental Results. The products formed by unimolecular fragmentation of metastable protonated alkylbenzenes in the gas phase^{12–17} are reported in Table 1. Under chemical ionization conditions these ions can lead to three fragmentation reactions (eq 1–3): elimination of arene with alkyl cation formation, elimination of alkene with protonated arene formation, and elimination of alkane with benzylic cation formation. This last fragment ion is observed only when the ring is at least alkyl disubstituted.

Protonated Isopropylbenzene (1). As previously reported,^{13,16} protonated isopropylbenzene (1) and its labeled derivatives lead to two fragment ions, iso-C₃H₇⁺ (13%) and C₆H₇⁺ (87%). Their formation is preceded by an exchange between the primary hydrogen atoms of the chain and the phenylic ones. The hydrogen atom exchange is not statistical, and there is a significant isotope effect for H-transfer. Otherwise, the CID spectra show that the iso-[C₃H₇⁺]/[C₆H₇⁺] ratio value is about 1 and the H atom exchange is smaller than in the MIKE spectra.

Ion 1 and its isomeric adduct 1' formed by reaction of iso-C₃H₇⁺ with benzene lead to the same MIKE spectrum.

Protonated *tert*-Butylbenzene (2). Metastable protonated *tert*-butylbenzene (2) leads to only one fragment ion: *tert*-C₄H₉⁺. No hydrogen atom exchange is observed. The adduct 2' formed by reaction of *tert*-C₄H₉⁺ with benzene has the same behavior.

Protonated *p*-Isopropyltoluene (3) and Isopropyl-*p*-xylene (4). Metastable ions 3 and 4 yield almost exclusively (>98%) protonated arene with propene loss. The same observation can be made on their respective isomeric adducts (toluene/iso-C₃H₇⁺) 3' and (*p*-xylene/iso-C₃H₇⁺) 4'. Labeled reactants indicate that H-exchange prior to dissociation is negligible.

Protonated *p*-*tert*-Butyltoluene (5). This ion, like its isomeric adduct 5' (toluene/*tert*-C₄H₉⁺) leads to *tert*-C₄H₉⁺ for about 97%. There is no H-exchange prior to dissociation.

Protonated *p*-*tert*-Butylethylbenzene (6). Ion 6 leads to *tert*-C₄H₉⁺, *m/z* 57 (6%), to protonated ethylbenzene, *m/z* 107 (1%), and dominantly to the benzylic ion C₆H₅CHCH₃⁺, *m/z* 105 (93%), with isobutane loss. Deuterium labeling shows that one of the secondary benzylic hydrogens is specifically eliminated in the isobutane fragment, while the results for *tert*-C₄H₉C₆H₅-CHDCH₃⁺ show that the kinetic isotope effect, *k_H/k_D*, is about 1.5 for this hydrogen abstraction. The adduct (ethylbenzene/*tert*-C₄H₉⁺) yields the same products in a similar ratio. Reaction of *tert*-C₄D₉⁺ indicates that a small but significant H-exchange precedes the formation of the benzylic ion ([*m/z* 105]/[*m/z* 106] = 6) and the formation of the *tert*-C₄H₉⁺ fragment.

Protonated *p*-*tert*-Butylisopropylbenzene (7). Metastable ion 7 gives two products: *tert*-C₄H₉⁺, *m/z* 57 (16%), and a benzylic ion, *m/z* 119 (83%), with isobutane loss. The adduct 7' (isopropylbenzene/*tert*-C₄H₉⁺) has the same behavior.

Protonated 2-*tert*-Butyl-*p*-xylene (8). Metastable ion 8 yields two main products: *tert*-C₄H₉⁺, *m/z* 57 (17%), and protonated *p*-xylene, *m/z* 107 (82%). The abundance of the *m/z* 105 benzylic ion (isobutane loss) is negligible.

The MIKE spectrum of its isomeric adduct 8' (*p*-xylene/*tert*-C₄H₉⁺) is completely different. The main fragment (90%) corresponds to isobutane loss. The mass shifts of the fragments for labeled adducts are reported in Table 2.

Protonated 5-*tert*-Butyl-*m*-xylene (9). Ion 9 and its isomeric adduct 9' (*m*-xylene/*tert*-C₄H₉⁺) give two abundant products, *m/z* 57 and *m/z* 107 (Table 1). Reaction of (CD₃)₃C⁺ shows that H-exchange occurs prior to dissociation.

Protonated 4-*tert*-Butyl-*o*-xylene (10). The MIKE spectra of ion 10 and of its isomeric adduct 10' are almost identical. H-exchange precedes the dissociation of 10', leading to a *tert*-C₄H₉⁺ dominant product (Table 1).

Reaction of *tert*-C₄H₉⁺ with *p*-*tert*-Butyltoluene (11). This reaction leads to *tert*-C₄H₉⁺ formation, *m/z* 57 (5%), to isobutane loss giving a *m/z* 147 fragment (18%), and to isobutene elimination giving a *m/z* 149 product (77%). When *tert*-¹³CC₃H₉⁺ reacts, half of the *m/z* 57 and *m/z* 149 fragments are respectively shifted to *m/z* 58 and *m/z* 150, while on the other hand the *m/z* 147 remains completely at the same position (Figure 1).

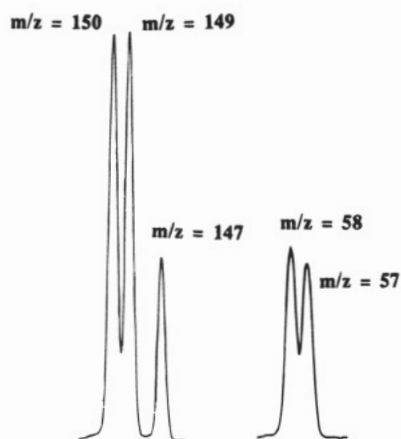


Figure 1. MIKE spectrum of metastable (*p*-*tert*-butyltoluene/*tert*-C₃H₉⁺) adduct ion 11.

TABLE 3: Calculated Total Energies (hartrees) and Zero-Point Vibrational Energies (ZPE, kJ/mol) for Stationary Points on the Potential Surface of Protonated Isopropylbenzene (1) and Its Related Decomposition Products

	$E_{3-21G//3-21G}$	$E_{6-31G**//3-21G}$	ZPE _{3-21G}
1 α -complex	-346.166 598	-348.123 996	543.3
C ₆ H ₆	-229.419 445	-230.713 588	286.4
iso-C ₃ H ₇ ⁺	-116.726 200	-117.392 911	249.8
1 β -complex	-346.154 601	-348.114 185	543.4
C ₆ H ₇ ⁺	-229.722 178	-231.026 734	314.1
C ₃ H ₆	-116.424 009	-117.081 356	226.2
C ₆ H ₆ -iso-C ₃ H ₇ ⁺	-346.186 830	-348.139 304	555.9

TABLE 4: Calculated Total (hartrees) and Relative Energies (kJ/mol) for Structures on the Protonated Isopropylbenzene (1) Potential Surface (C₆H₆ + iso-C₃H₇⁺ Is Used as the Reference for Relative Energies)

	$E_{6-31G**//3-21G}$	ΔE	ΔE with ZPE
1 α -complex	-348.123 996	-46.0	-38.9
1 β -complex	-348.114 185	-20.1	-12.9
C ₆ H ₆ + iso-C ₃ H ₇ ⁺	-348.106 499	0.0	0.0
C ₆ H ₇ ⁺ + C ₃ H ₆	-348.108 090	-4.2	-0.1
C ₆ H ₆ -iso-C ₃ H ₇ ⁺	-348.139 304	-86.2	-66.5

Theoretical Results. Structures and Energies of Complexes.

Theoretical calculations were performed on the α - and β -complexes previously proposed. First, recall that with the semiempirical method the geometry of the complex is optimized with fixed geometries for both partners, which does not take into account the possible formation of a new covalent bond between partners. Consequently, a hydrogen atom transfer in the complexes or an electrophilic addition leading to an arenium ion are forbidden with such calculations. Therefore, we have to confirm that these calculated complexes correspond to true minima on the PES, without a big change in the geometry. We used an ab initio SCF calculation to optimize the structures and calculate the energies of the complexes supposed to be intermediate in the isomerization process of protonated isopropylbenzene. We ran these calculations at the 6-31G**//3-21G level (Tables 3 and 4). Two minima were found²² which were more stable than the final states: one minimum corresponds to the α -complex [C₆H₆ iso-C₃H₇⁺] which has a π -complex structure and a stabilization energy of 46 kJ/mol. The other minimum corresponds to the β -complex [C₆H₇⁺ C₃H₆] with a stabilization energy of 20 kJ/mol. The semiempirical values of stabilization energies and distances are close to the ab initio values (58 and 25 kJ/mol, respectively) (Figures 2 and 3). The differences between the ab initio and semiempirical results can be explained by the two following arguments: (i) in the ab initio

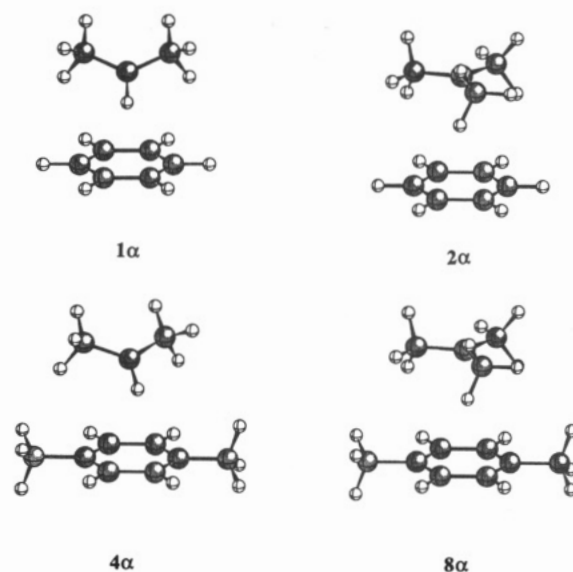


Figure 2. Structures of stationary points of the α -complexes optimized by the semiempirical method.

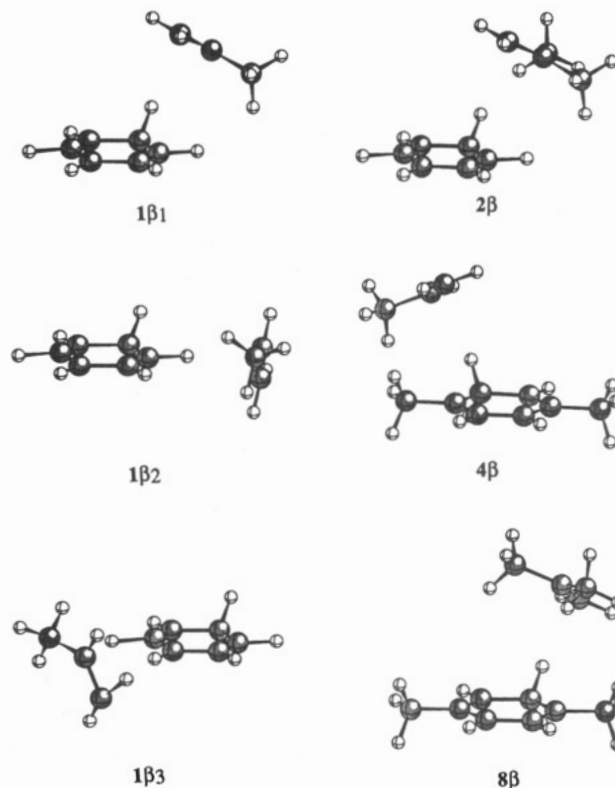


Figure 3. Structures of the most stable stationary points of the β -complexes optimized by the semiempirical method.

SCF calculations, the dispersion term is not taken into account, whereas it is included in the semiempirical method; (ii) the two geometry components are optimized in the ab initio calculations, while they are not in the semiempirical calculations. With the semiempirical method, we have calculated the interaction energy for 1 α with different distances between the plane of the ring and the alkyl cation. It appears that the minimum of E_{SCF} (-41 kJ/mol), the sum ($E_{el} + E_{rep} + E_{pol}$), does not correspond to the minimum of the potential well of the total interaction (E_{tot}) (-58 kJ/mol), which is the sum ($E_{SCF} + E_{disp}$), and corresponds to a longer distance between the middle of the ring and alkyl cation, 3.37 Å instead of 3.14 Å. In the ab initio calculations, without relaxation of the intramolecular degrees of freedom,

TABLE 5: Calculated Interaction Energies for the α - and β -Complexes (kJ/mol) by the Semiempirical Method: $E_{\text{tot}} = E_{\text{el}} + E_{\text{pol}} + E_{\text{disp}} + E_{\text{rep}}$ and $E_{\text{scf}} = E_{\text{el}} + E_{\text{pol}} + E_{\text{rep}}$

	1 α	1 β	2 α	2 β	4 α	4 β	8 α	8 β
E_{el}	-35	-15	-27	-17	-36	-14	-27	-14
E_{pol}	-24	-9	-18	-10	-29	-8	-21	-9
E_{disp}	-21	-13	-21	-15	-25	-14	-25	-18
E_{rep}	+22	+12	+17	+14	+25	+12	+19	+14
E_{tot}	-58	-25	-49	-28	-65	-24	-54	-27
(E_{SCF})	(-37)	(-12)	(-28)	(-13)	(-40)	(-10)	(-29)	(-9)

the SCF interaction energy is equal to -36 kJ/mol and the intermolecular distance is equal to 3.27 Å. These values are in good agreement with the SCF semiempirical values (-41 kJ/mol, 3.37 Å). Therefore, in view of the relatively good agreement between the ab initio and semiempirical methods, all other calculations were carried out using the Claverie method. We calculated the minima on the PES for some of the ion-neutral complexes for which we have described the reactivity: protonated isopropylbenzene (1), protonated *tert*-butylbenzene (2), protonated isopropyl-*p*-xylene (4), and protonated *tert*-butyl-*p*-xylene (8) (Table 5, Figures 2 and 3).

Energy Diagrams. The interaction energies in the complexes may be used to display an energy diagram. The formation enthalpies of protonated alkylbenzenes and dissociation states are taken from the literature.³⁵

Discussion

We will first interpret the experimental results and give experimental evidence for the intermediacy of ion-neutral complexes.

In a second part, we will discuss, using the theoretical results, the energy and the geometry of these ion-neutral complexes. Finally, we will discuss the fragmentation pathways and the energy diagrams.

Intermediacy of Ion-Neutral Complexes: Experimental Evidence. *Existence of β -Complexes [Protonated Arene Alkene].* The H-exchange between the chain and the ring prior to the formation of alkyl cation or protonated arene is observed when the PA (proton affinity) of the arene and the alkene are close to one another ($\Delta\text{PA} < 25$ kJ/mol). This process^{13,16} already described for protonated isopropylbenzene (1) was observed for the adduct-ions 6', 8', 9', and 10' (Table 2). Such an exchange necessarily involves the intermediacy of a β -complex, and its formation results either from a stepwise or from a concerted mechanism (eq 1).

*Existence of α -Complexes [Arene *tert*-C₄H₉⁺].* It has not been possible to demonstrate the intermediacy of α -complexes for systems in which the steric crowding between the two moieties is small. In such a case, it is expected that the ion-molecule reaction leads to the formation of the covalent alkylbenzene structure, even if an ion-neutral complex structure exists on the pathway. This leads to identical MIKE and MIKE-CID spectra in both cases. In order to trap a putative α -complex, we have chosen cases in which isomerization of the complex into the covalent structure involves a high-energy barrier. This is achieved whenever addition of the alkyl cation to the ring is difficult or hindered, as is the case when *tert*-C₄H₉⁺ reacts with xylenes.

While the spectra of 9 and 10 and of their adducts (*o*-xylene or *m*-xylene/*tert*-C₄H₉⁺) are rather similar (Table 1), the spectrum of ion 8 differs completely from that of its adduct 8' (*p*-xylene/*tert*-C₄H₉⁺).

On one hand, the decomposition reaction of the adduct 8' yields C₈H₁₁⁺, *m/z* 107 (isobutene loss), *tert*-C₄H₉⁺, *m/z* 57, and predominantly C₈H₉⁺, *m/z* 105, corresponding to isobutane elimination. This last reaction is not observed with 8 (only 1%).

On the other hand, in the adduct 8', the loss of isobutene and the formation of *tert*-C₄H₉⁺ are preceded by an incomplete H-exchange between the chain and the ring, while isobutane loss is not preceded by a significant H-exchange (Table 2). These data strongly suggest that the adduct 8' corresponds to two non-interconverting structures. One structure is an α -complex which must be the precursor of isobutane loss, while the other has the same behavior as ion 8.

The existence of a barrier between 8 and its α -complex is in agreement with the results of Caccace et al.,²⁰ who have shown by the radiolytic technique that *tert*-C₄H₉⁺ reacts by C-C bond formation with *o*- and *m*-xylene but not with *p*-xylene.

Another way to prove the existence of α -complexes is to perform a reaction between a *tert*-butyl arene and a labeled *tert*-C₄H₉⁺ cation in the ion source. For instance, the reaction of *tert*-¹³CC₃H₉⁺ with *p*-*tert*-butyltoluene clearly shows that the adduct possesses two structures. The first one corresponds to the formation of a covalent C-C bond and leads in the same ratio to *tert*-C₄H₉⁺ and *tert*-¹³CC₃H₉⁺ and in the same ratio also to C₄H₈ and ¹³CC₃H₈ losses.³⁶ On the other hand, a specific elimination of labeled isobutane is observed (Figure 1). We conclude that a noncovalent structure, which may correspond to a weakly bound complex between the arene and the labeled *tert*-butyl cation, intervenes in the reaction. Formed in the ion source, this α -complex survives up to the second field free region, which proves its stability.

These results indicate that an α -complex is formed and has a significant lifetime.

Energy, Geometry, and Nature of α - and β -Complexes. Ab initio and semiempirical calculations confirm that α - and β -complexes correspond to stable structures.

1. α -Complexes. The semiempirical calculations show that four stable α -complexes correspond to an energy minimum with a " π -structure" (Figure 2): 1 α [C₆H₆ iso-C₃H₇⁺], 2 α [C₆H₆ *tert*-C₄H₉⁺], 4 α [*p*-CH₃C₆H₄CH₃ iso-C₃H₇⁺], and 8 α [*p*-CH₃C₆H₄-CH₃ *tert*-C₄H₉⁺]. In these π -structures, the two moieties lie in quasi-parallel planes with the carbonium ion centered above the ring centroid. The smallest stabilization energy value (49 kJ/mol) corresponds to the complex 2 α [C₆H₆ *tert*-C₄H₉⁺], and the largest one (65 kJ/mol) corresponds to the complex 4 α [*p*-CH₃C₆H₄CH₃ iso-C₃H₇⁺]. For these complexes, the stabilization energy increases with the number of methyl substitutions on the arene ring and decreases with the size of the cation. The distance in the optimized geometries between the alkyl cation and the plane of the ring is shorter for the two complexes involving the isopropyl cation (3.140 Å for 1 α and 3.138 Å for 4 α) than for the two complexes involving the *tert*-butyl cation (3.497 Å for 2 α and 3.498 Å for 8 α). These distances are almost the same when the complexes involve either benzene or *p*-xylene. We can assume that there is no hindrance to α -complex formation due to the methyl groups on the ring. In contrast, steric crowding explains the shorter distances between the ring and the alkyl cation in complexes involving the isopropyl group compared to the *tert*-butyl group. The stability of the complexes may be explained by looking at the various interaction energy components.

Components of the Interaction Energy. The total interaction energy (E_{tot}) may be expressed in terms of attractive and repulsive (E_{rep}) components (Table 5). The attractive energy corresponds to the sum of the electrostatic (E_{el}), polarization (E_{pol}), and dispersion energies (E_{disp}). The evolution of the contribution of each term is quite the same if we compare complexes 2α and 1α with complexes 8α and 4α . We can make the same observation if we compare 2α and 8α with 1α and 4α .

We first observe that the number of methyl groups on the cation has a greater influence on the interaction energy than the number of methyl groups on the arene moiety. In fact, only the polarization term increases when we change benzene to *p*-xylene, and from this calculation we can see that indeed *p*-xylene is more polarizable than benzene. It is in qualitative agreement with the experimental values of the polarizability, which are $9.99 \times 10^{-24} \text{ cm}^3$ for benzene^{37a} and $13.70 \times 10^{-24} \text{ cm}^3$ for *p*-xylene.^{37b} Both electrostatic and polarization terms increase when we change *tert*-butyl cation to the isopropyl cation.

If we consider the E_{SCF} and E_{disp} terms, the sum of which leads to the total interaction energy, we can see that E_{SCF} represents the largest contribution to the interaction energy (Table 5). However, the dispersion energy E_{disp} is also very important in these complexes and represents 35%–47% of the interaction energy and 26%–35% of the attractive energy.

2. β -Complexes. The PES present many minima, and different structures have been optimized by the simulated annealing method for the complexes 1β [$\text{C}_6\text{H}_7^+ \text{C}_3\text{H}_6$], 2β [C_6H_7^+ iso- C_4H_8], 4β [$p\text{-CH}_3\text{C}_6\text{H}_5\text{CH}_3^+ \text{C}_3\text{H}_6$], and 8β [$p\text{-CH}_3\text{C}_6\text{H}_5\text{CH}_3^+$ iso- C_4H_8]. In these complexes, one hydrogen of the ring is directed toward the double bond. The most stable form involves a hydrogen of a CH_2 group of the ring (Figure 3).

For β -complexes, stabilization energies and intermolecular distances are smaller than for α -complexes, as found for protonated isopropylbenzene through ab initio calculations (Table 4). If the four most stable minima are compared (Figure 3), the lowest stabilization energy (24 kJ/mol) corresponds to the 4β [$p\text{-CH}_3\text{C}_6\text{H}_5\text{CH}_3^+ \text{C}_3\text{H}_6$] complex and the strongest one (28 kJ/mol) corresponds to the 2β [C_6H_7^+ iso- C_4H_8] complex. The dispersion term accounts for a larger part of the attractive energy for β -complexes than for α -complexes, i.e. 35% in 1β and 2β complexes and 44% in 4β and 8β . Calculated distances are shorter for β -complexes than for corresponding α -complexes. This can be explained by a smaller steric hindrance between the two partners in the β -complexes.

Saddle Points. From the experimental results, we proposed that the isomerization of protonated alkylbenzenes may involve α - or β -complex intermediates, which are the precursors of the observed fragment ions.

Many minima were found for both α -complexes and β -complexes (whether equivalent by symmetry or not). It was interesting to know the requisite energy for the systems to explore these minima. We have then calculated the saddle point energies and their structures in order to describe the energy profile for motions which may occur for the two components in the complexes. These calculations have been done with the chain method (see the Theoretical Section) between the most significant critical points of the PES for complexes 2α , 8α , and 1β .

α -Complexes. The alkyl cation flip in 8α (or 2α) leads to a maximum TS2 (or TS1), in which the plane of the four carbon atoms is nearly perpendicular to the ring's plane (Figure 4), with an activation energy of 12 kJ/mol. In this case we have

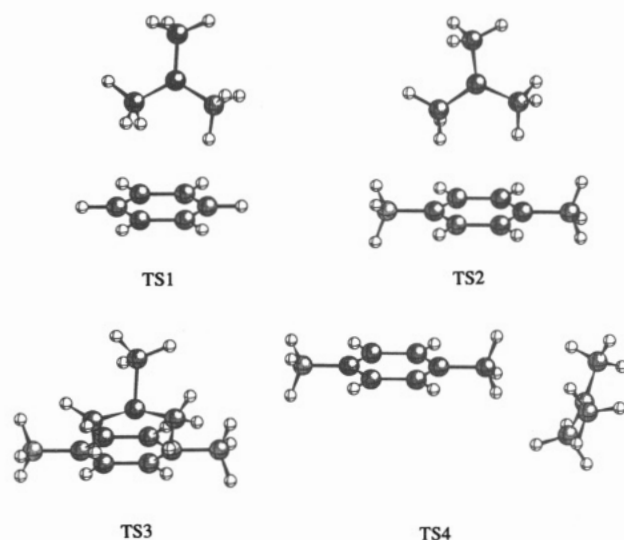


Figure 4. Structures of the saddle points optimized for α -complexes by the chain's method.

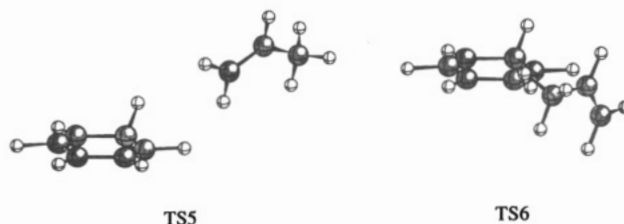


Figure 5. Structures of the saddle points optimized for β -complexes by the chain's method.

also calculated the rotation energy barrier of the *tert*-butyl cation around the axis defined by both the center of the ring and the carbonium. It is only 1 kJ/mol in 8α and less than 0.5 kJ/mol in 2α .

Two saddle points were found for moving the *tert*-butyl cation around the arene, from its initial position to the symmetrical position in the α -complex 8α . The first one, TS3, lies 43 kJ/mol above the stable complex, while the second one, TS4, in which the carbonium center is near the hydrogen of the methyl group of the *p*-xylene, is 41 kJ/mol (Figure 4). The structure of the latter saddle point corresponds to a favorable position for the carbonium ion to induce hydride abstraction from the methyl group.

Here we have three different motions for the same system. The rotation of the carbonium ion around its own axis may be considered as a free rotation. The energy for the *tert*-butyl cation flip in the α -complexes is rather low (13 kJ/mol) and larger for the ring flip which is hindered (42 kJ/mol). Thus, the relative motion between the two partners of the complex is partially hindered.

β -Complexes. From the simulated annealing calculations, many minima were calculated on the PES in which one of the hydrogen atoms of the aromatic ring is directed toward the alkene double bond. First were calculated the saddle points connecting these minima.

Compared to the energy of the corresponding final state, the energies of the saddle points TS5 and TS6 are the following for ion **1** (Figure 5): TS5 (−12 kJ/mol) between $1\beta_1$ (−24 kJ/mol) and $1\beta_2$ (−22 kJ/mol) and TS6 (−18 kJ/mol) between $1\beta_2$ (−22 kJ/mol) and $1\beta_3$ (−23 kJ/mol). Thus, the potential energy barriers connecting the β -complexes lie between 4 and 13 kJ/mol. The saddle point (−9 kJ/mol) corresponding to $1\beta_1$ (−24 kJ/mol) in which propene flips on itself around the axis of the double C–C bond also lies in this energy range.

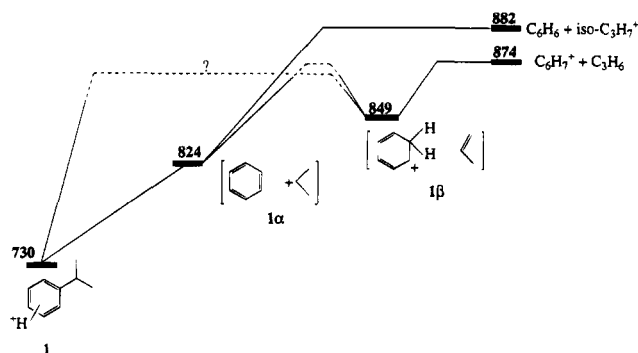


Figure 6. Schematic potential energy diagram for the unimolecular reactions of ion 1. Ion 1 corresponds to a mixture of structures which are protonated on the different carbons of the ring. These structures easily interconvert,^{10d} and only the ipso structure leads to 1α. The formation enthalpy of 1 indicated in the figure corresponds to the most stable structure.

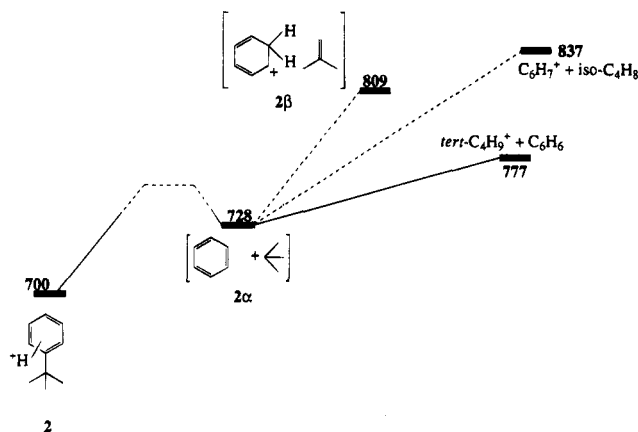


Figure 7. Schematic potential energy diagram for the unimolecular reactions of ion 2. Ion 2 corresponds to a mixture of structures which are protonated on the different carbons of the ring. These structures easily interconvert,^{10d} and only the ipso structure leads to 2α. The formation enthalpy of 2 indicated in the figure corresponds to the most stable structure.

Energy Diagrams and Mechanisms. The energy diagrams were obtained from these results. The reaction pathways will be further discussed.

Protonated Isopropylbenzene (1). The energy diagram of the fragmentation of ion 1 (Figure 6) shows that the heats of formation of the two complexes 1α and 1β lie below that of the first fragmentation state. The sole critical energy for the 1β → 1α transition state was calculated with the AM1 semiempirical method.¹⁶ It was found to be 25 kJ/mol, which means that this transition state lies very near the final state corresponding to C₆H₇⁺ formation. Therefore, both calculation and experiment indicate that H-exchange probably occurs by a stepwise mechanism (1 → 1α → 1β), although the assumption of a straightforward mechanism (1 → 1β) cannot be totally discarded.

Protonated *tert*-Butylbenzene (2). The energy profile for the fragmentation of protonated *tert*-butylbenzene (2) (Figure 7) shows why no hydrogen atom exchange precedes *tert*-butyl cation formation. In fact 2β lies above the only observed decomposition state by 32 kJ/mol, which prevents hydrogen exchange.³⁸ From the energy profile, we can see that the fragmentation of 2 may occur either directly or after the formation of the stable form, 2α.

The decomposition of the metastable ions 1 and 2 shows that the most abundant fragment corresponds to the most stable final state. This is, however, not the case for the decomposition of

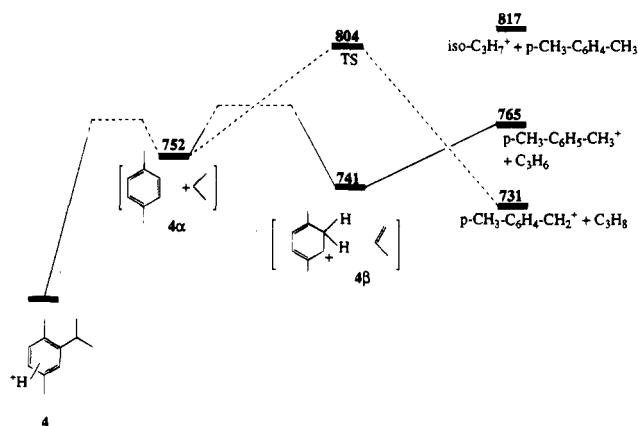


Figure 8. Schematic potential energy diagram for the unimolecular reactions of ion 4.

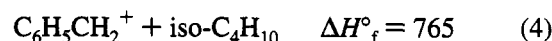
those ions to be discussed below. This indicates that high-energy barriers may exist in these cases.

Protonated *p*-Isopropyltoluene (3) and Isopropyl-*p*-xylene (4). Metastable ions 3 and 4 lead to a single fragmentation: the loss of propene with the formation of a protonated arene. In both cases, thermodynamic data show that the final state corresponding to this fragment lies lower in energy than that for iso-C₃H₇⁺ formation but above that corresponding to the formation of a benzylic cation with propane loss. Therefore, this last reaction implies an energy barrier (Figure 8).

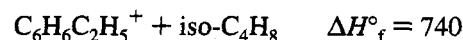
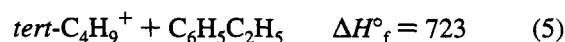
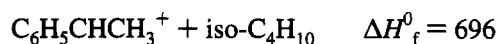
Indeed, in the transition state for hydride abstraction, the isopropyl cation must be near the methyl group of the ring. Calculations for ion 8 show that such structures (TS4, Figure 4) are poorly stabilized. If we assume that this is also the case for ion 4, we can evaluate that the heat of formation of the transition state for hydride abstraction is about 804 kJ/mol and therefore significantly above that for the single decomposition state observed. This explains why this reaction does not occur even though it leads to the most stable final state.

Protonated *p*-*tert*-Butyltoluene (5) and *p*-*tert*-Butylethylbenzene (6). Ion 5 leads only to *tert*-C₄H₉⁺, and ion 6 essentially yields C₆H₅CHCH₃⁺. In both cases, the product ion corresponds to the most stable final state³⁵ (the formation enthalpy of the various possible products are given in eqs 4 and 5).

p-*tert*-C₄H₉C₆H₅CH₃⁺ (5):



p-*tert*-C₄H₉-C₆H₅-CH₂CH₃⁺ (6):



The abundance of the C₆H₅CHCH₃⁺ fragment for ion 6 is particularly interesting and shows that the transition state energy for isobutane elimination lies below the final state corresponding to *tert*-C₄H₉⁺ formation. It is in agreement with the thermodynamic data if we consider that the α-complex can isomerize

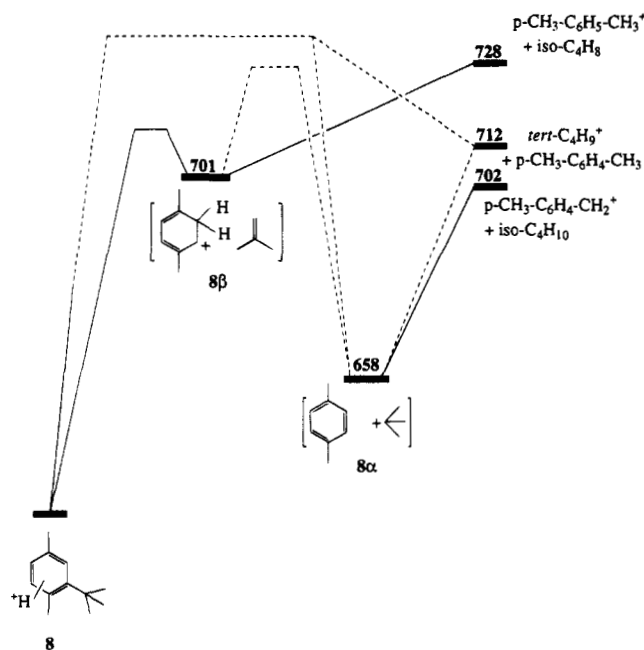


Figure 9. Schematic potential energy diagram for the unimolecular reactions of ion 8.

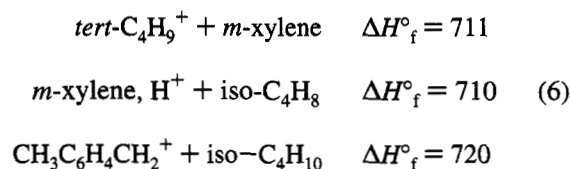
into a transient structure in which the *tert*-butyl cation is near the benzylic hydrogens of the ethylbenzene. The calculations done for ion 8 show that such a structure (TS4, Figure 4) is only 12 kJ/mol lower than the final state corresponding to *tert*-C₄H₉⁺ formation. If we extrapolate this value to the case of ion 6, we can show that the transition state energy for hydride abstraction is about 710 kJ/mol and therefore lies below those of the final states leading to other fragments. Moreover, the isotope effect for hydride abstraction from this structure is rather low (1.5), which confirms that the hydride abstraction step is not associated with an important energy barrier.

Protonated *tert*-Butylxylenes 8, 9, and 10. The metastable ion 8 leads to different branching ratios, depending on whether it is generated by the protonation of *tert*-butyl-*p*-xylene or by the reaction of *tert*-butyl cation with *p*-xylene. Such a difference is not observed for the other isomers involving *o*- and *m*-xylene. This has been explained by the fact that the formation of a C-C covalent bond by reaction in the gas phase of the *tert*-C₄H₉⁺ cation with *p*-xylene implies a strong barrier.²⁰ For this reason, ion 8 leads preferentially to protonated *p*-xylene and less to the *tert*-C₄H₉⁺ fragment even though the latter corresponds to a more stable final state (Figure 9). We can assume that, in this case, the stretching of the C(benzene)-C(butyl) bond is followed by a migration of a primary hydrogen on the ring, leading to a concerted process to the β -complex and then to dissociation. Since there is a barrier to produce *tert*-C₄H₉⁺ by simple cleavage, there is most probably no easy access from 8 to its α -complex and therefore only 1% of isobutane loss is observed.

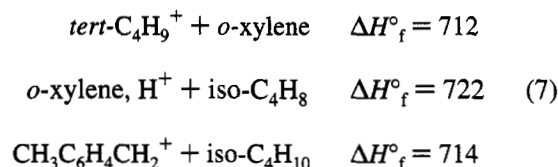
Conversely, the α -complex formed by reaction of *tert*-C₄H₉⁺ with *p*-xylene yields directly the benzylic ion with isobutane loss, which corresponds to the more stable final state.³⁵ Since the transient structure of the α -complex in which the cation is near one methyl group corresponds to an energy of 699 kJ/mol, hydrogen abstraction is almost athermic in this case (Figure 9).

Such phenomena are not observed with the isomeric ions 9 and 10. Ion 9 yields *tert*-C₄H₉⁺ and protonated *m*-xylene, while 10 leads preferentially to *tert*-C₄H₉⁺, in agreement with the formation enthalpies of the various products (eqs 6 and 7).

5-*tert*-butyl-*m*-xylene/H⁺ (9):



4-*tert*-butyl-*o*-xylene/H⁺ (10):



Conclusion

1. From our experiments, we have demonstrated in several examples that α -complexes [arene alkyl cation] have a significant lifetime. Their isomeric β -complexes [protonated arene alkene] are intermediates in the exchange, often observed, between the hydrogen atoms of the chain and those of the ring.

Investigation of the potential energy surfaces was possible for such big systems by the use of semiempirical calculations using the Claverie method associated with a simulated annealing procedure.

For the [arene alkyl cation] complexes, the stabilization energy increases with the number of substituents on the ring and when the size of the cation decreases. The smallest stabilization energy corresponds to [C₆H₆ *tert*-C₄H₉⁺] (49 kJ/mol), and the largest corresponds to [CH₃C₆H₄CH₃ *iso*-C₃H₇⁺] (65 kJ/mol). These complexes have π -structures, but do not correspond to EDA systems.

For the [protonated arene alkene] complexes, the stabilization energy is smaller (about 25 kJ/mol).

As expected, the dispersion energy is a very important component in the interaction energy, both in the α - and β -complexes.

2. The outcome of a unimolecular reaction is, of course, mainly determined by the relative energies of the complexes and of the final states. For instance H-exchange is not observed when the β -complex lies higher in energy than the products formed. However, two kinds of energy barriers can have a determining role on the fragmentation process: (i) the one connecting the protonated alkylbenzene to its α -complex when there is steric crowding between the two moieties in the latter; (ii) the one connecting the protonated alkylbenzene (and/or its α -complex) to the β -complex. Since H-transfer is accompanied by an important geometry change of the system, this process involves a significant energy barrier. For this reason, a strong primary isotope effect is observed for H-transfer, and H-exchange between the chain and the ring, when observed, is always incomplete.

3. This behavior contrasts that of protonated *tert*-butyl alkyl ethers, *tert*-C₄H₉OHCH₃⁺ for instance,³⁹ whose fragmentation involves the intermediacy of an " α -complex" [*tert*-C₄H₉⁺ CH₃-OH] and a " β -complex" [iso-C₄H₈ CH₃OH₂⁺]. In this case, the H-transfer which connects the two complexes occurs with a small geometry change and therefore does not involve an important energy barrier. In such models, H-exchange is rapid and no significant isotope effect is observed for H-transfer.

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