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Formation and structural discrimination of stable halophenylium ions in the gas phase

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Abstract

Fourier-transform ion cyclotron resonance mass spectrometry has been used to identify and characterize the three isomers of X-phenylium ions (X = Cl, Br), through their reactivity features towards CH_3Y (Y = Cl, Br). Pure *ortho*-, *meta*-, and *para*-X-phenylium ions (X = Cl, Br) have been independently generated in the source of the instrument by CF_3^+-induced F^- abstraction from the corresponding X-fluorobenzenes. Isomeric X-phenylium ions (X = Cl, Br) attack the Y atom and the C–H bonds of CH_3Y yielding excited adducts which undergo extensive fragmentation by releasing a hydrogen halide molecule, a methyl halide, a halogen atom, or a methyl radical. Competition among these fragmentation pathways depends upon the nature of X and Y and the specific X-phenylium isomer. (Int J Mass Spectrom 195/196 (2000) 21–31) © 2000 Elsevier Science B.V.

Keywords: Addition/elimination; Arylium ions; Gas-phase chemistry; Ion-molecule reactions; Methyl halides

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1. Introduction

The structural and electronic properties of arylium ions have intrigued chemists ever since their suggestion as elusive intermediates in the decomposition of arenediazonium salts [1]. In singlet arylium ions **1** (Chart 1), indeed, the vacant orbital and the aromatic π system are orthogonal and therefore unable to interact directly. The general tendency of vacant orbitals in carbocations to acquire the maximum degree of *p* character is contrasted in **1** by the loss of aromaticity and the increase in ring strain so that the formally empty orbital in **1** retains some s character. A considerable flattening of the $C–C^+–C$ angle and some ring distortion from planarity is generally observed in **1** as a response of the strong request of charge dispersal from the vacant sp^2-type orbital over the σ and π framework. In the extreme, a π electron may jump from the ring of **1** to the empty sp^2-type orbital yielding the triplet configuration **2** [2].

A considerable theoretical effort has been devoted in recent years to the assessment of the structure and the multiplicity of the electronic ground state of arylium ions. The most elaborate studies concern the prototype phenylium ion **1** (X = H) and place its singlet $^1A_1$ state more stable than the $^3B_1$ state by 4.9–24.6 kcal mol^{-1} [3–6], in agreement with the available experimental evidence [7]. Similar stability

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Dedicated to the memory of Robert R. Squires, a good friend and stimulating scientist.

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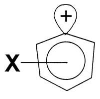

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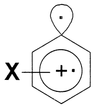

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orders justify the chemical behavior of substituted **1** (X = NO_2, CN, Cl, Br, OH, OCH_3, and CH_3), generated in the liquid as well as in the dense gas phase (5–760 Torr; $T = 25\,°C$) by spontaneous tritium decay of the relevant multitritiated arenes [8,9]. The decay-formed isomeric **1** (X = CN, Cl, Br) retain their original structure for at least 10^{-8}–10^{-9} s, whereas those bearing electron releasing substituents (X = OH, OCH_3, and CH_3) tend to interconvert intramolecularly by 1,2-ring hydrogen transfers, much like the unsubstituted phenylium ion [7].

The ambiguity on the actual structure of $XC_6H_4^+$ ions, generated by conventional unimolecular and bimolecular processes in the low-pressure source of a mass spectrometer [10–13], coupled with their possible structural rearrangements [14], long precluded systematic investigation on the reactivity properties of **1** as a function of the nature and the position of the X substituent. A first attempt to fill up this gap was performed by generating isomeric **1** (X = OH) in the source of a Fourier transform ion cyclotron resonance (FT-ICR) instrument through CF_3^+-induced defluorination of the corresponding fluorophenols [Eq. (1)] and by measuring their different Brønsted acidity toward ammonia [15]. Now, the investigation is extended to isomeric **1** (X = Cl, Br) by measuring their gas-phase reactivity towards CH_3Y (Y = Cl, Br). The results will demonstrate that, despite their much longer lifetimes under low-pressure FT-ICR conditions (several seconds at $\sim 10^{-8}$ Torr), thermalized *ortho*, *meta*, and *para* **1** (X = Cl, Br) retain their original structure and can be readily titred in the gas phase looking at their different reaction patterns towards the selected substrates.

$$CF_3^+ + FC_6H_4X \rightarrow CF_4 + XC_6H_4^+ \tag{1}$$

2. Computational and experimental methodology

Ab initio calculations have been performed with the GAUSSIAN 94 set of programs [16] installed on a Pentium-PRO/S machine (Linux version). The 6-31G(d) [17] basis set was employed to optimize the geometries of the species in the isodesmic reaction 2 (X = Cl) at the B3LYP level of theory [18]. Their total energies have been refined by single-point calculations at the B3LYP level of theory using the more extended 6-311++G(3df,2p) basis sets [19]. The zero-point energies and the thermal corrections (298.15 K) of the four species of Eq. (2) (X = Cl) have been calculated using the B3LYP/6-31G(d) harmonic frequencies and moments of inertia using standard statistical mechanics formulas [20]. The B3LYP/6-311++G(3df,2p)//B3LYP/6-31G(d) enthalpy change at 298.15 K of Eq. 2 (X = Cl) has been combined with the experimental enthalpies of formation of C_6H_6, ClC_6H_5, and $C_6H_5^+$ to derive the enthalpy of formation of *para*-$ClC_6H_4^+$.

$$para\text{-}XC_6H_4^+ + C_6H_6 \rightarrow XC_6H_5 + C_6H_5^+ \tag{2}$$

The reactivity of gaseous isomeric **1** (X = Cl, Br) towards CH_3Y (Y = Cl, Br) was measured by FT-ICR kinetic experiments, using an Extrel FTMS 2001 mass spectrometer, equipped with a dual cell and an Odyssey Data Station. A CF_4 mixture, containing ~10%–15% of a fluorohalobenzene isomer FC_6H_4X (X = Cl, Br), was introduced into the source of the instrument at 300 K and a total pressure of $\sim 1 \times 10^{-6}$ Torr and ionized with 70 eV electrons. Trifluoromethylium ion, CF_3^+, the most abundant ion formed in the plasma, readily abstracts a fluoride ion from FC_6H_4X (X = Cl, Br) yielding predominantly the corresponding $XC_6H_4^+$ isomer [Eq. (1)]. This was injected into the analyzer of the instrument, containing $2.3–3.3 \times 10^{-8}$ Torr of CH_3Y (Y = Cl, Br), and thermalized by collisions with argon pulsed into the analyzer through a magnetic valve. The thermalized $XC_6H_4^+$ (X = ^{35}Cl, ^{79}Br) reactant was subsequently isolated by notch-ejection pulses [21] and allowed to react with CH_3Y [Y = **Cl** (natural $^{35}Cl/^{37}Cl$ mixture), **Br** (natural $^{79}Br/^{81}Br$ mixture)]. The $\ln[XC_6H_4^+]$ vs.

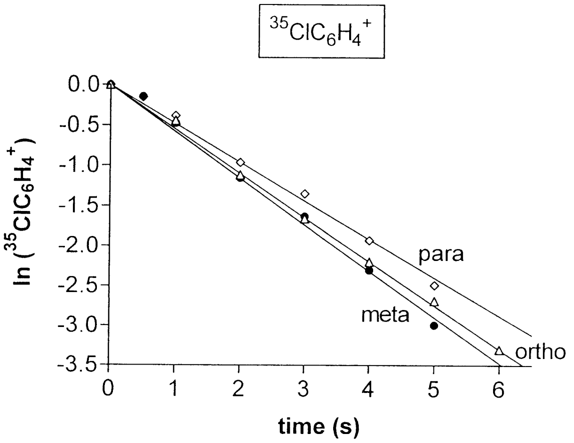


Fig. 1. Decay curves of isomeric $^{35}ClC_6H_4^+$ in gaseous CH_3**Cl** (2.7–3.2 × 10^{-8} Torr).

delay time was found to be linear, as required for thermally equilibrated reactants (Fig. 1).

A similar procedure has been adopted to test the reactivity towards CH_3**Cl** of isomeric $C_7H_7^+$ ions, generated in the FT-ICR source by: (1) 70 eV electron impact on benzyl chloride; (2) 70 eV electron impact on *meta*-chlorotoluene; (3) CF_3^+ attack on benzyl chloride; and (4) CF_3^+ attack on isomeric chlorotoluenes.

3. Results

Fig. 2(a)–2(c) illustrate the time dependence of the stationary concentration of the ionic products from the gas-phase attack of *ortho*-$^{35}ClC_6H_4^+$ on CH_3**Cl**, present in the FT-ICR analyzer at 3.2 × 10^{-8} Torr. The plots concerning the attack on CH_3**Cl** by *meta*- and *para*-$^{35}ClC_6H_4^+$ are reported in Figs. 3(a)–3(c) and 4(a)–4(c), respectively. The kinetic curves of Figs. 2–4 obey the general reaction network given in Scheme 1 leading to several addition-elimination products. Analysis of the curves of the [$^{35}ClC_7H_6^+$] and [$^{37}ClC_7H_6^+$] products [Figs. 2(a), 3(a), and 4(a)] reveals that only a fraction of these ions is reactive towards CH_3**Cl** (k_7 and k_8 in Scheme 1), while the remainder is inert towards the same molecule (k_5 and k_6 in Scheme 1). It should be noted that the ^{37}Cl-to-

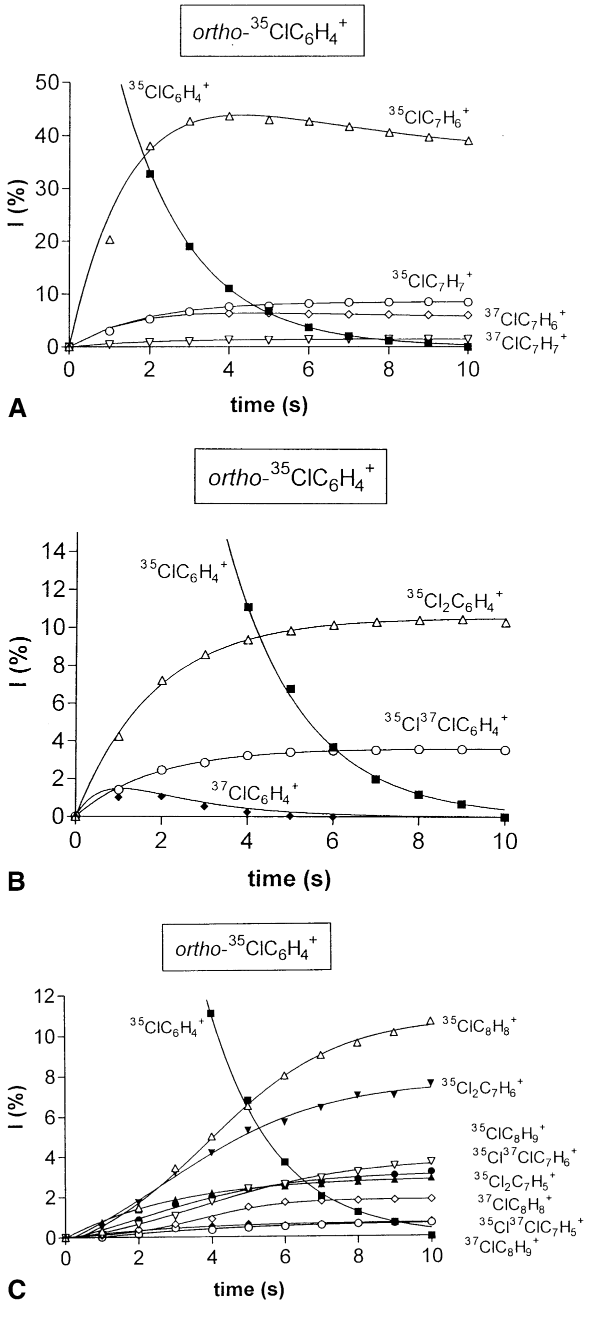


Fig. 2. (a)–(c) Time dependence of the relative abundance of the ionic products from the gas-phase attack of *ortho*-$^{35}ClC_6H_4^+$ on CH_3**Cl** (3.2 × 10^{-8} Torr). For the sake of clarity, the time dependence of the least abundant [$^{37}ClC_7H_5{}^{35}Cl^+$]; *m/z* 163 and [$^{37}ClC_7H_6{}^{37}Cl^{+\cdot}$]; *m/z* 164 fragments is not reported. The solid lines describe the theoretical time dependence of the relative yields of products from the reaction network of Scheme 1 using the rate constants reported in Table 1.

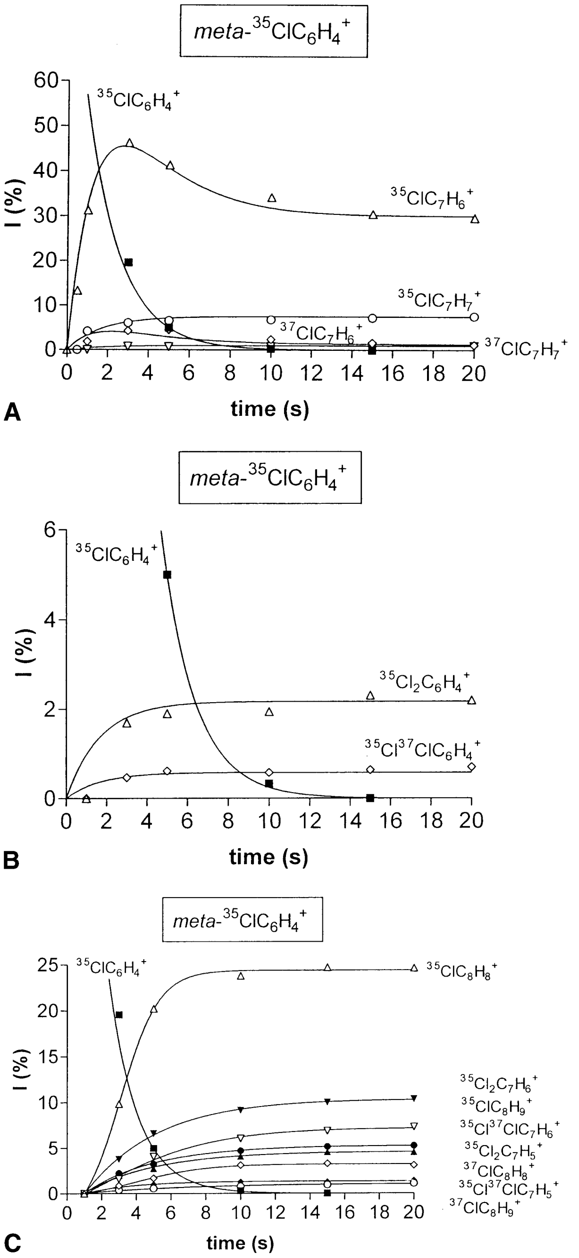


Fig. 3. (a)–(c) Time dependence of the relative abundance of the ionic products from the gas-phase attack of *meta*-$^{35}ClC_6H_4^+$ on CH_3**Cl** (3.1×10^{-8} Torr) (see Fig. 2 caption).

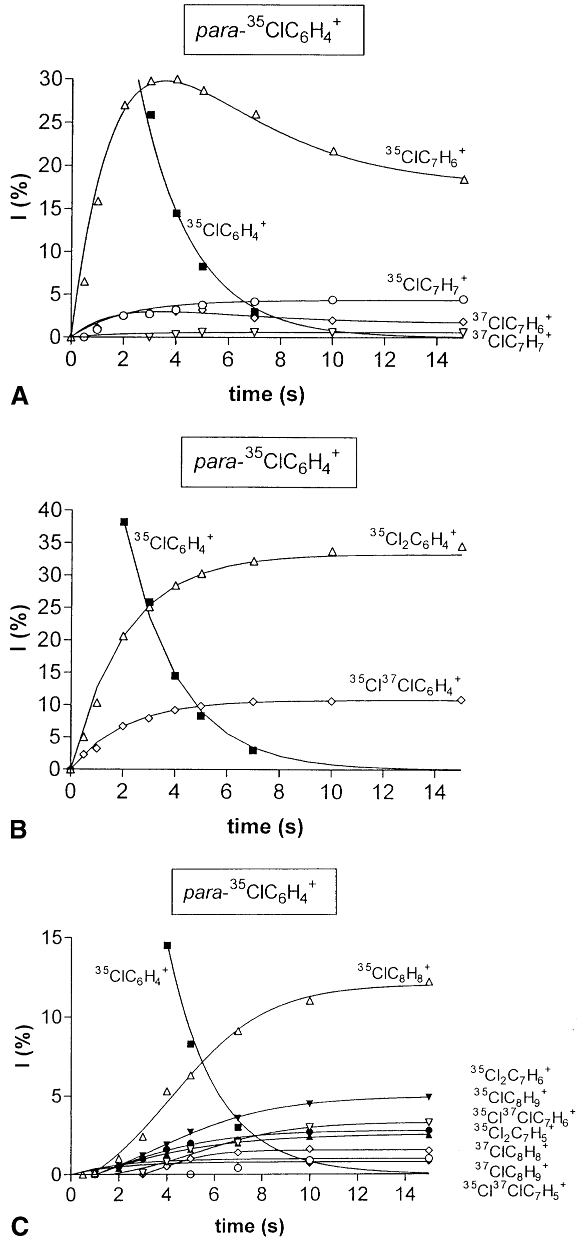
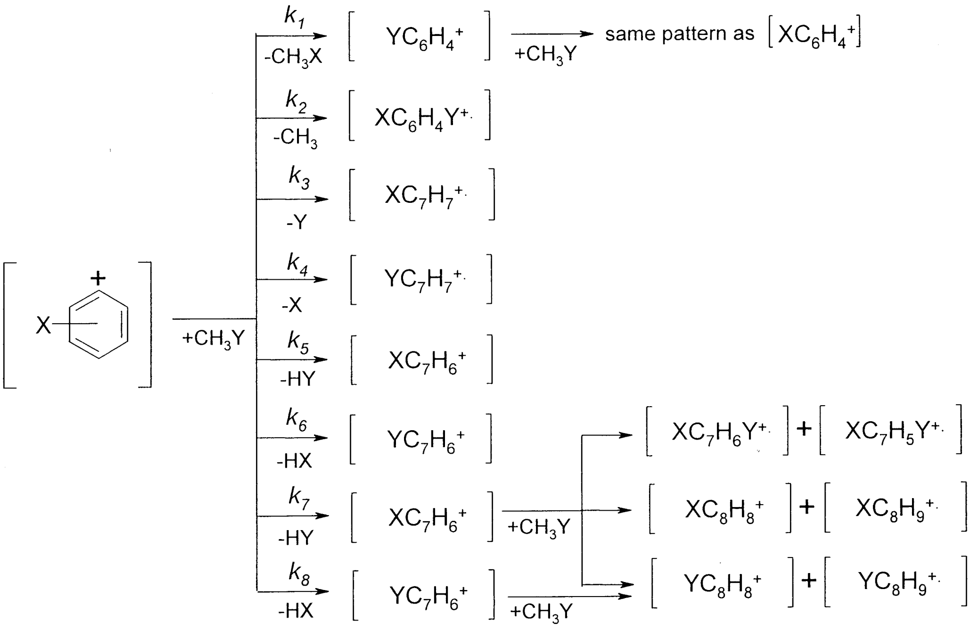


Fig. 4. (a)–(c) Time dependence of the relative abundance of the ionic products from the gas-phase attack of *para*-$^{35}ClC_6H_4^+$ on CH_3**Cl** (2.7×10^{-8} Torr) (see Fig. 2 caption).

^{35}Cl halogen exchange yielding [$^{37}ClC_6H_4^+$] from [$^{35}ClC_6H_4^+$] (k_1 in Scheme 1), is open only to *ortho*-$^{35}ClC_6H_4^+$ [Fig. 2(b)], while it seems precluded to the *meta* and *para* isomers [Figs. 3(b) and 4(b)].

The $^{35}ClC_6H_4^+$/CH_3**Br**, $^{79}BrC_6H_4^+$/CH_3**Cl**, and $^{79}BrC_6H_4^+$/CH_3**Br** exhibit much simpler kinetic patterns. Again, the halogen exchange k_1 is accessible only to the *ortho*-$^{35}ClC_6H_4^+$/CH_3**Br** and *ortho*-



Scheme 1.

$^{79}BrC_6H_4^+/CH_3\mathbf{Br}$. The same process is not observed from the *ortho*-$^{79}BrC_6H_4^+/CH_3\mathbf{Cl}$ pair.

Best fitting treatment of the experimental results of Figs. 2–4 provides an estimate of the rate constants of Scheme 1 for the $^{35}ClC_6H_4^+/CH_3\mathbf{Cl}$ systems, whose values are reported in Table 1 together with the relevant reaction efficiencies. The kinetic parameters of the $^{35}ClC_6H_4^+/CH_3\mathbf{Br}$, $^{79}BrC_6H_4^+/CH_3\mathbf{Cl}$, and $^{79}BrC_6H_4^+/CH_3\mathbf{Br}$ reactions are obtained in the same way and are reported in Table 1 as well.

Analysis of Table 1 reveals that the fraction of reactive collisions between isomeric $XC_6H_4^+$ ($X = {}^{35}Cl, {}^{79}Br$) ions and CH_3Y ($Y = \mathbf{Cl}, \mathbf{Br}$) ranges from 19 to 57% (Σ in Table 1), thus suggesting that a significant fraction of the encounters back dissociate to the reactants. Competition among the reaction pathways of Scheme 1 depends on the nature of X and Y and on the structure of the $XC_6H_4^+$ reactant.

Ancillary experiments on the reactivity of isomeric $C_7H_7^+$ ions towards $CH_3\mathbf{Cl}$, present in the analyzer at 3–4 $\times 10^{-8}$ Torr, lead to the following results: (1) the $C_7H_7^+$ ions generated from 70 eV electron impact on benzyl chloride and *meta*-chlorotoluene and by CF_3^+ attack on benzyl chloride appear absolutely inert towards $CH_3\mathbf{Cl}$ even after 20 s reaction time; (2) the $C_7H_7^+$ ions formed by CF_3^+ attack on isomeric chlorotoluenes appear reactive towards $CH_3\mathbf{Cl}$ yielding predominantly $C_8H_9^+$. No significant formation of $C_8H_{10}^+$ and $\mathbf{Cl}C_7H_7^{+\cdot}$ is observed. At longer reaction times, the $C_8H_9^+$ product further reacts with $CH_3\mathbf{Cl}$ yielding $C_9H_{11}^+$. According to previous assignments [22–24], the benzyl and the tropylium ion structures can be associated to the unreactive $C_7H_7^+$ ions from routes (1) while reactive $C_7H_7^+$ from route (2) can be identified as isomeric tolylium ions.

4. Discussion

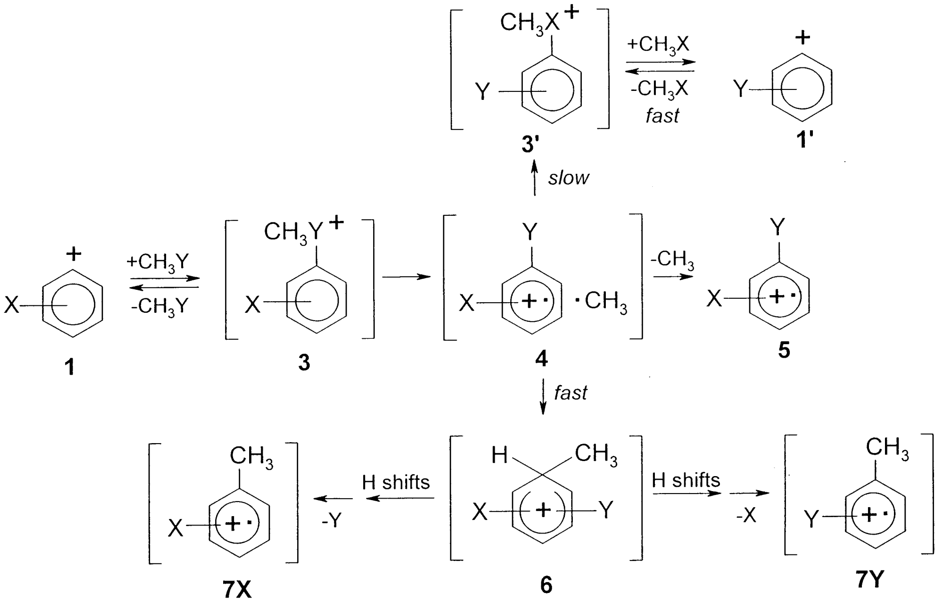
According to the relevant thermochemistry [25–29], reaction (1) is exothermic by less than 21 ($X = Cl$) and 22 kcal mol^{-1} ($X = Br$). This modest exothermicity imparts to the $XC_6H_4^+$ products an internal energy excess which is absolutely insufficient for their unimolecular ring opening or isomerization. Indeed, the energetically most stable open isomers of $XC_6H_4^+$

Table 1
Rate constants ($k_n \times 10^{10}$ cm^3 molecule^{-1} s^{-1}) and efficiencies (eff = k_{obs}/k_{coll}) for the gas-phase attack of isomeric halophenylium ions $XC_6H_4^+$ on methyl halides CH_3Y

n =	1	2	3	4	5	6	7	8	Σ
X = *ortho*-^{35}Cl;	Y = **Cl**								
k_n	0.37	0.72	0.19	0.41	1.03	1.12	0.83	0.76	5.43
eff	0.02	0.04	0.01	0.03	0.06	0.07	0.05	0.04	0.32
X = *meta*-^{35}Cl;	Y = **Cl**								
k_n	—	0.25	0.25	0.25	1.57	0.33	2.43	2.44	7.52
eff	—	0.01	0.01	0.01	0.09	0.02	0.14	0.14	0.42
X = *para*-^{35}Cl;	Y = **Cl**								
k_n	—	2.42	0.14	0.14	0.70	0.37	1.30	0.83	5.90
eff	—	0.14	0.01	0.01	0.04	0.02	0.06	0.04	0.32
X = *ortho*-^{35}Cl;	Y = **Br**								
k_n	1.23	0.28	4.85	—	0.23	—	—	—	6.59
eff	0.08	0.02	0.33	—	0.02	—	—	—	0.45
X = *meta*-^{35}Cl;	Y = **Br**								
k_n	—	0.05	4.27	—	0.49	—	—	—	4.81
eff	—	0.00_3	0.29	—	0.04	—	—	—	0.33
X = *para*-^{35}Cl;	Y = **Br**								
k_n	—	1.00	3.55	—	0.25	—	—	—	4.80
eff	—	0.07	0.24	—	0.02	—	—	—	0.33
X = *ortho*-^{79}Br;	Y = **Cl**								
k_n	—	0.27	—	3.55	0.23	0.15	—	—	4.20
eff	—	0.02	—	0.21	0.01	0.01	—	—	0.25
X = *meta*-^{79}Br;	Y = **Cl**								
k_n	—	—	—	2.56	0.72	—	—	—	3.28
eff	—	—	—	0.15	0.04	—	—	—	0.19
X = *para*-^{79}Br;	Y = **Cl**								
k_n	—	1.98	—	2.09	0.31	—	—	—	4.38
eff	—	0.12	—	0.12	0.02	—	—	—	0.26
X = *ortho*-^{79}Br;	Y = **Br**								
k_n	0.67	0.37	2.85	3.50	0.19	0.23	—	—	7.81
eff	0.04	0.03	0.21	0.26	0.01	0.02	—	—	0.57
X = *meta*-^{79}Br;	Y = **Br**								
k_n	—	—	2.30	2.25	0.60	—	—	—	5.15
eff	—	—	0.17	0.17	0.04	—	—	—	0.38
X = *para*-^{79}Br;	Y = **Br**								
k_n	—	1.46	1.51	1.65	0.19	—	—	—	4.81
eff	—	0.11	0.11	0.12	0.01	—	—	—	0.35

are lying at least 15 kcal mol^{-1} higher in energy than the corresponding singlet arylium structures and their formation involves activation barriers exceeding 60 kcal mol^{-1} [30]. Similarly, unimolecular 1,2 hydrogen shifts within $XC_6H_4^+$ arylium ions are prevented by their substantial activation energy ranging around 30 kcal mol^{-1} [31]. These statements are confirmed by the product patterns and the reaction kinetics of Table 1 which reflect the operation of $XC_6H_4^+$ ions retaining the original closed structure of their FC_6H_4X precursors [8,15].

Analysis of Table 1 reveals that isomeric chloro- and bromophenylium ions can be readily discriminated in the gas phase under FT-ICR conditions on the grounds of their different reactivity towards CH_3Y (Y = **Cl**, **Br**). *Ortho*-chloro- and *ortho*-bromo-phenylium ions can be differentiated from their *meta* and *para* isomers due to their exclusive ability to undergo halogen exchange with CH_3Y (Y = **Cl**, **Br**) (k_1). Among isomeric $XC_6H_4^+$ (X = ^{35}Cl, ^{79}Br), the *para* form displays the highest tendency to accept Y from CH_3Y (Y = **Cl**, **Br**) (k_2) and the *meta* one that of



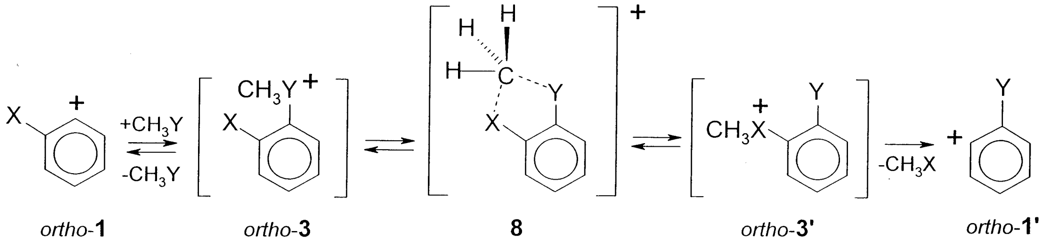
Scheme 2.

abstracting a CH_2 moiety from the same substrates (k_5–k_8).

Obviously, this different behavior must be ascribed to the effect of the X substituent on the selectivity of $XC_6H_4^+$ towards CH_3Y and the stability of the ensuing addition intermediates. As pointed out in related papers, arylium ions are voracious electrophiles, reactive towards hydrogen, nitrogen, carbon monoxide, and most organic molecules [7–13,15,32–35]. They display a carbeniumlike and a carbenelike reactivity by attacking preferentially the lone pairs of *n* and π bases and by inserting selectively into the σ_{C-H} bonds of alkanes. This latter appears to be a two-stage process consisting of the transfer of a hydride to the arylium ion followed by intracomplex addition of the resulting alkyl cation to the formed arene moiety [13,35]. At 10–760 torr of pressure, alkyl halides react with arylium ion to give primarily the corresponding halobenzene, together with benzyl halide, isomeric halotoluenes, and toluene in relative yields increasing by decreasing the pressure [8,36]. Even more fragmentation is seen when the reactions between phenylium ion and methyl halides are carried out at the much lower pressures typical of ICR experiments [32].

The product pattern of Scheme 1 is fully consistent with this picture. Attack of isomeric $XC_6H_4^+$ (X = ^{35}Cl, ^{79}Br) ions on the *n* center of CH_3Y (Y = **Cl**, **Br**) yields predominantly the corresponding [$XC_6H_4YCH_3^+$] onium ion (**3** in Scheme 2). Ions **3**, excited by the exothermicity of their formation process [$-\Delta H°$ (kcal mol^{-1}) = 45–51 kcal mol^{-1}] [37], tend to dissipate their excess energy by back dissociating to reactants. Another way to dispose their excess energy is by homolytic C–Y bond cleavage to yield the CH_3 radical and the [$XC_6H_4Y^{+\cdot}$] moiety [**3** → **5** in Scheme 2; $\Delta H°$ (kcal mol^{-1}) = 43–49]. Competition between the **3** → **1** back dissociation and the **3** → **5** fragmentation accounts for the limited overall efficiency Σ of Table 1. The efficiency of the latter process (k_2 in Scheme 1) turns out to be influenced by the stability of the [$XC_6H_4Y^{+\cdot}$] fragment which increases in the order *meta* < *ortho* < *para*.

The formation of **7X** and **7Y** from isomeric $XC_6H_4^+$ (k_3 and k_4 in Scheme 1) and especially the comparable loss of the X and Y atoms observed in the

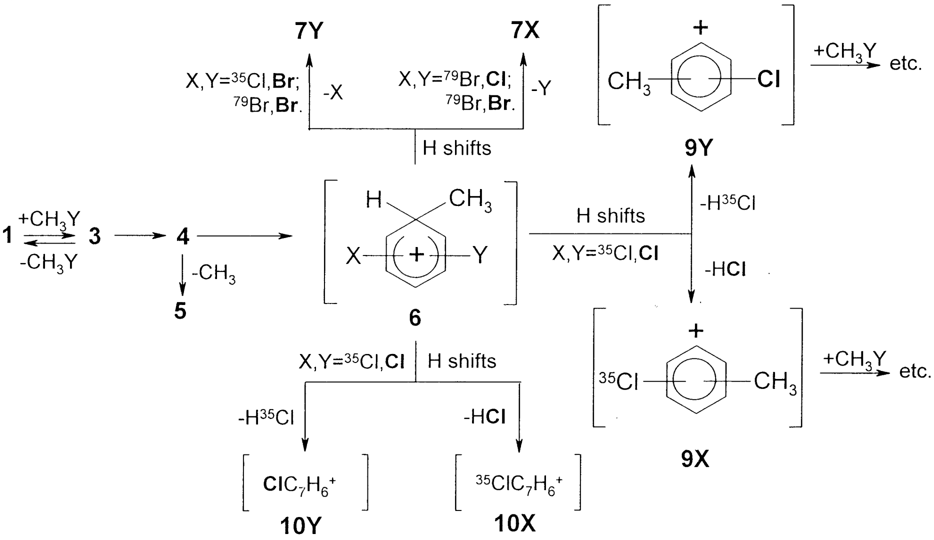


Scheme 3.

X/Y = ^{35}Cl/**Cl** and X/Y = ^{79}Br/**Br** systems (Table 1) are best accounted for by the intermediacy of a long-lived complex **4** in the **3** → **5** dissociation mechanism of Scheme 2. Any alternative mechanism, including that involving the insertion of the $XC_6H_4^+$ ions into the C–Y bond of CH_3Y, followed by loss of a halogen atom, appears rather inadequate to explain the experimental evidence. Indeed, in contrast with the experimental evidence (Table 1), the hypothetical insertion reaction would produce an excited *ipso*-methylated intermediate, wherein extrusion of the geminal Y atom would be much favored over that of the far removed X atom, especially when X = Y. The experimental results are instead much better accommodated by intracomplex recombination in the long-lived complex **4** to give the arenium ion **6** (Scheme 2). Obviously, the exothermic **4** → **6** recombination takes place at the $[XC_6H_4Y^{+\cdot}]$ ring centers which are symmetrically arranged when X = Y (i.e. X/Y = ^{35}Cl/**Cl** and X/Y = ^{79}Br/**Br**). In this case, the X and Y atoms appear as fully interchangeable in the corresponding arenium intermediates **6** and, thus, they can be released with equal efficiency. In this respect, the exclusive loss of bromine when X ≠ Y (i.e. X/Y = ^{35}Cl/**Br** and X/Y = ^{79}Br/**Cl**) responds to the asymmetric spin distribution in the corresponding $[XC_6H_4Y^{+\cdot}]$ moieties and to the more pronounced tendency of bromine vs. chlorine atoms to be eliminated as such from excited halogenoarenium ions [27]. The lack of any observable $[YC_6H_4^+]$ fragments from the attack of *meta* and *para* chloro- and bromophenylium ions on CH_3Y (Y = **Cl**, **Br**) (k_1) is due to the predominance of the exothermic **3** → **4** → **6** process over the competing quasithermoneutral recombination **3** → **4** → **3′**.

The formation of the $[YC_6H_4^+]$ fragments detected in the *ortho*-$^{35}ClC_6H_4^+/CH_3Y$ (Y = **Cl**, **Br**) and *ortho*-$^{79}BrC_6H_4^+/CH_3$**Br** systems must then proceed through a different route. It is tempting to explain this observation as due to the closeness of the two halogens in the onium intermediate *ortho*-**3** of Scheme 3 which may favor direct slightly exothermic or thermoneutral Y-to-X methyl cation transfer via complex **8**, prior to release of the methyl halide.

As pointed out in related investigations [24,27], excited bromoarenium intermediates tend to eliminate more efficiently the halogen atom rather than the hydrogen halide molecule, whereas the reverse is true for excited chloroarenium ions. This tendency is further confirmed by the results of Table 1. Release of hydrogen chloride from excited $^{35}ClC_6H_4^+/CH_3$**Cl** adducts gives rise to two families of $[^{35}ClC_7H_6^+]$ and [**Cl**$C_7H_6^+$] products. The combined yield of these products depends on the structure of the parent $^{35}ClC_6H_4^+$ ion and increases in the order *ortho* ≅ *para* < *meta*. If analyzed in connection to the comparatively low **4** → **5** fragmentation observed in [*meta*-$^{35}ClC_6H_4$**Cl**CH_3^+] (k_2 in Table 1), these findings conform to the competition pattern depicted in Scheme 4, where the intracomplex **4** → **6** recombination and, thus, the subsequent hydrogen chloride loss prevail more in the *meta* isomer than in the *ortho* and *para* ones. A similar mechanism is precluded to the $XC_6H_4^+/CH_3Y$ (X, Y = ^{35}Cl, **Br**; ^{79}Br, **Cl**; ^{79}Br, **Br**) systems, owing to the marked preference of the arenium intermediates of Scheme 4 to release a

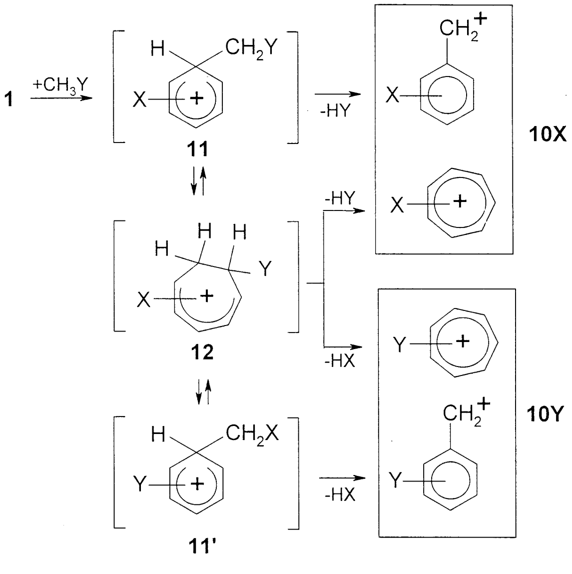


Scheme 4.

bromine atom, rather than a hydrogen halide molecule (k_3–k_4 in Table 1).

A fraction of [$^{35}ClC_7H_6^+$] and [**Cl**$C_7H_6^+$] products is reactive towards CH_3**Cl** and behaves like the parent $^{35}ClC_6H_4^+$ ion (k_7–k_8 in Scheme 1). The remainder is completely inert towards CH_3**Cl** (k_5–k_6 in Scheme 1). The inertness towards CH_3**Cl** of the $C_7H_7^+$ ions, obtained from electron impact on benzyl chloride and on *meta*-chlorotoluene and from CF_3^+ attack on benzyl chloride, points to the unreactive portion of the [$^{35}ClC_7H_6^+$] and [**Cl**$C_7H_6^+$] products (**10X** and **10Y** in Scheme 4) as the corresponding chlorobenzyl and/or chlorotropylium ion structures. Besides, the distinct reactivity towards CH_3**Cl** of the $C_7H_7^+$ ions, arising from CF_3^+ attack on isomeric chlorotoluenes, supports the chlorotolylium ion structures **9X** and **9Y** as the reactive fraction of the [$^{35}ClC_7H_6^+$] and [**Cl**$C_7H_6^+$] products (Scheme 4).

Unreactive **10X** and **10Y** ions are thought to arise from insertion of their parent $XC_6H_4^+$ into the C–H bonds of CH_3Y (**1** → **11** in Scheme 5), followed by 1,2-elimination of a hydrogen halide molecule. Their inertness towards CH_3Y rules out direct HX elimination in **11** to give the corresponding $YCH_2C_6H_4^+$ arylium ion. Moreover, the fact that the **10X** vs. **10Y** distribution is highly sensitive to the structure of the $XC_6H_4^+$ precursor excludes that the **1** → **11** insertion proceeds by a two-stage mechanism involving the preliminary hydride transfer from CH_3Y followed by intracomplex addition of the ensuing CH_2Y^+ to XC_6H_5. Rather, these observations suggest the occurrence of consecutive ring enlargements and contractions in the insertion complex **11** prior to elimination



Scheme 5.

of the hydrogen halide molecule (**11** ↔ **12** ↔ **11′** in Scheme 5).

5. Conclusions

The results of the present study demonstrate that stable halophenylium ions **1** (X = ^{35}Cl, ^{79}Br) can be generated in the source of a FT-ICR spectrometer and their structure easily identified on the grounds of their reactivity towards methyl chloride and bromide (CH_3Y). Isomeric **1** (X = ^{35}Cl, ^{79}Br) exhibit features similar to those of the unsubstituted phenylium ion **1** (X = H) by attacking selectively the Y atom and the C–H bonds of CH_3Y. The relevant intermediates release most of their excess energy by eliminating neutral fragments, including a hydrogen halide, a methyl halide, a halogen atom, or a methyl radical. The relative extent of these competing eliminations depends on both the specific halogens present in the reactants and the structure of the addition intermediates.

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change of Eq. (2) (-7.7 kcal mol^{-1}) and by using the experimental heats of formation of C_6H_6 ($H_f^0 = 19.82 \pm 0.12$ kcal mol^{-1}), ClC_6H_5 ($H_f^0 = 13.01$ kcal mol^{-1}), and $C_6H_5^+$ [26]. This coincidence corroborates the validity of the abovementioned linear correlation. From this, the H_f^0 of **1** (X = Br) can be estimated as large as 279 kcal mol^{-1}. Previous theoretical and experimental evidence [8,28,29] suggests that the H_f^0's of *meta*-substituted **1** (X = Cl, Br) do not diverge much from those of the corresponding *para* isomers, while they are generally several kilocalories per mol lower than those of the *ortho* forms.

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[37] The proton affinities (PA) at the halogen atoms of XC_6H_4Y are taken as equal to those of the corresponding C_6H_5X and C_6H_5Y. These, in turn, are evaluated from the PA of the relevant methyl halides, corrected by ~10 kcal mol^{-1} for the stabilizing effect of the aromatic group. The methyl cation affinities at the halogen atoms of XC_6H_4Y are calculated by lowering the corresponding PA values by the average value of 97 kcal mol^{-1}; cfr. (a) T.B. McMahon, T. Heinis, G. Nicol, J.K. Hovey, P. Kebarle, J. Am. Chem. Soc. 110 (1988) 7591; (b) Z.B. Maksìc, M. Eckert-Maksìc, A. Knezevic, J. Phys. Chem. 102 (1988) 2981). According to the estimated heats of formation of onium intermediates **3**, the enthalpies of reaction **1** → **3** of Scheme 2 are calculated to range from ~ -45 to ~ -51 kcal mol^{-1}. The exothermicity of the unimolecular isomerization **3** → **6** of Scheme 2 is estimated as exceeding 11 kcal mol^{-1} (cfr. Z.B. Maksic, M. Eckert-Maksìc, A. Knezevic, J. Phys. Chem. 102 (1988) 2981). Unimolecular dissociation **3** → **5** of Scheme 2 is endothermic by more than 43 kcal mol^{-1}.