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The ion/molecule reactions of CCl_3^+ with acetophenones

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Dedicated to Professor John R. Eyler for his seminal contributions to gas-phase ion chemistry and ion spectroscopy, and for his long-standing collaboration with our group.

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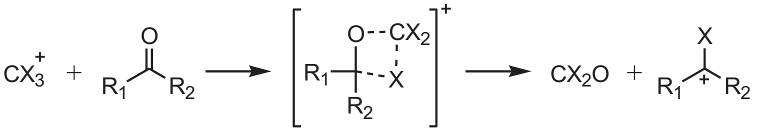
ABSTRACT

The gas-phase ion/molecule of CCl_3^+ with acetophenone studied by FT-ICR techniques reveals three main reaction channels: (a) formation of $PhC^+(Cl)Me$ through the well known halonium metathesis reaction analogous to what is observed for CF_3^+; (b) elimination of HCl containing a ring hydrogen to yield $C_9H_7Cl_2O^+$ ions; (c) formation of $PhCCl_2^+$ by elimination of CH_2CO and HCl, or CH_3COCl. The nature of the $C_9H_7Cl_2O^+$ ions formed in the second reaction was the subject of further experiments and theoretical studies. IRMPD of the $C_9H_7Cl_2O^+$ ions reveals two processes both of which violate the even-electron rule resulting from loss of a chlorine atom or a methyl group. The combined results of the IRMPD processes and the fact that ~57% of the $C_9H_7Cl_2O^+$ ions undergo further reaction with neutral acetophenone allow us to conclude that at least two isomeric species are formed in reaction b. Theoretical calculations and additional experiments with 3′-fluoroacetophenone are consistent with an isobenzofuran structure for the most abundant isomer of $C_9H_7Cl_2O^+$. The observed behavior is quite distinct from that observed for the reactions of CF_3^+ with different acetophenones.

1. Introduction

The reactivity of gas-phase trihalomethyl cations, CX_3^+ (X = F, Cl) has been the subject of considerable interest for several decades. These ions are known to react readily with a number of bases by an electrophilic addition-elimination mechanism [1], to be of potential use as reagents for chemical ionization [2] and etching of silicon surfaces [3], and to undergo gas-phase halonium metathesis reactions with simple ketones and aldehydes [4–8] to yield haloalkyl cations (see Eq. (1)).



(1)

Similar reactions with aromatic ketones bring up the question as to whether initial addition of CX_3^+ to the aromatic ring followed by HX elimination can become competitive with (1). This question is particularly relevant because of the observation that halomethyl cations can promote reactions even with non-activated simple aromatic systems [9].

An early study of the reaction of CF_3^+ with acetophenone, PhCOMe, in an ion beam apparatus lead to the observation of the adduct ion $CF_3^+(PhCOMe)$ almost as the exclusive product [10]. Semi-empirical calculations were used to propose that the adduct resulting from addition at oxygen was substantially more favorable than addition at a ring position. Experiments carried out by FTICR techniques [11–13] show $CF_3^+(PhCOMe)$, $PhC^+(F)Me$ and $C_8H_7^+$ as primary product ions, where $C_8H_7^+$, identified as $PhC^+{=}CH_2$, originates from HF elimination of $PhC^+(F)Me$ produced in the highly exothermic reaction (1). The fact that the $C_8H_8F^+$ gas-phase ions observed in these reactions correspond to $PhC^+(F)Me$ has been unequivocally demonstrated by IRMPD vibrational spectroscopy using a free electron laser [14].

During our studies of the thermal dissociation of the molecular ions of a number of substituted acetophenones generated by different ionization methods [15] we initially explored the reaction of halomethyl cations with acetophenones. Interestingly enough, the

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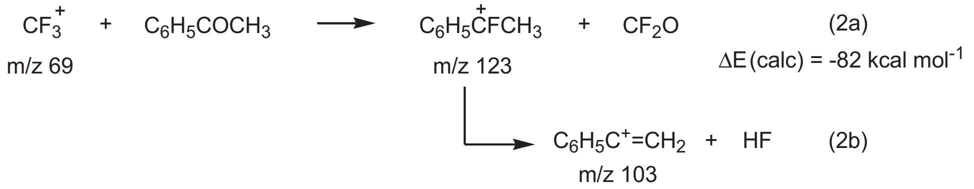
reaction of CCl_3^+ with acetophenone, and some of the substituted acetophenones, proved to give rise to a much richer chemistry than the corresponding reactions with CF_3^+ and suggest that in some cases attack at the ring positions may be competitive with attack at the carbonyl oxygen. This manuscript describes an FTICR study of these reactions coupled with some theoretical calculations to understand the mechanisms of these reactions.

2. Experimental

Experiments were carried out in our FT-ICR spectrometer interfaced to an IonSpec Omega Fourier Transform Data System that has been described in previous reports from these laboratories [15–18]. This spectrometer operates with a water cooled 9″ electromagnet that is normally set at 1.0 T, and contains a ~15.6 cm^3 cubic cell with center holes drilled on both transmitter plates to allow for laser light to go through the cell. The vacuum chamber housing the ICR cell is provided with two opposing ZnSe windows that act as entry and exit ports for infrared laser radiation.



$$\underset{m/z\ 69}{CF_3^+} + C_6H_5COCH_3 \longrightarrow \underset{m/z\ 123}{C_6H_5\overset{+}{C}FCH_3} + CF_2O \qquad (2a) \qquad \Delta E\,(calc) = -82\ kcal\ mol^{-1}$$

$$\underset{m/z\ 123}{C_6H_5\overset{+}{C}FCH_3} \longrightarrow \underset{m/z\ 103}{C_6H_5C^+{=}CH_2} + HF \qquad (2b)$$

CCl_3^+ ions were generated by electron ionization at 15 eV of CCl_4 at nominal pressures $\sim 5 \times 10^{-8}$ Torr. $C^{35}Cl_3^+$ ions (*m/z* 117) were isolated 500 ms after the ionization pulse. Ion/molecule reactions were studied at variable partial pressures, ranging from 0.8 to 20×10^{-8} Torr, of acetophenone, or substituted acetophenones. Secondary reactions were studied by selective isolation of the primary reaction products and their reactivity was followed as a function of trapping time.

Structural features of selected ion/molecule product ions were investigated by IRMPD experiments using a tunable CO_2 laser (LaserTech Group; model LTG250 626G) coupled to a piezoelectric aligner (PZT Aligner/Translator, Burleigh Instruments, model LPZ1000 PZ-80). The laser was operated at 10.46 μm and the output power maintained at 9 W.

Theoretical calculations at the DFT level were carried out with the GAUSSIAN03 suite of programs [19]. Structures were initially optimized at the B3LYP/6-31+G(d,p) level of theory and vibrational frequencies calculated at this level of theory to establish whether structures corresponded to stable species or transition states. Results quoted for ΔE include corrections for zero-point energies (ZPE) calculated without any scaling factors for the vibrational frequencies. In several cases, the final energies were also calculated at the B3LYP/6-311+G(d,p) level. Differences ranging from 0.5 to less than 2 kcal mol^{-1} were obtained for the thermochemistry of the reactions calculated with the two basis sets and were not considered significant for our discussion. Transition states were further characterized by IRC calculations to establish the connection between different stationary states.

All reagents were obtained commercially and subject to several freeze-pump-thaw cycles before sample introduction.

3. Results and discussion

3.1. Ion/molecule reactions of CF_3^+ and CCl_3^+ with acetophenone

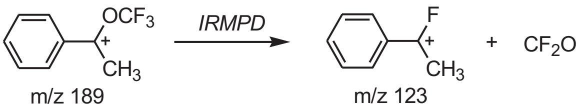
As discussed in Section 1, CF_3^+ has been shown to react with acetophenone [11,12,14] in a manner similar to that of aliphatic ketones. This is illustrated in reaction (2a) where PhC$^+$(F)Me, *m/z* 123, is formed as the main reaction product under our experimental conditions.

$$\underset{m/z\ \ 69}{CF_3^+} + C_6H_5COCH_3 \rightarrow \underset{m/z\ \ 189}{CF_3^+(C_6H_5COCH_3)} \quad \Delta E(\text{calc}) = -85\ \text{kcal mol}^{-1} \qquad (3)$$

Protonated phenylacetylene, *m/z* 103, is also observed as a reaction product (2b) and it can be safely assumed that it originates by loss of HF from activated PhC$^+$(F)Me formed in the highly exothermic reaction (2a). The relationship between these two ions was confirmed by IRMPD experiments on isolated PhC$^+$(F)Me ions. The adduct ion (reaction (3)) amounts to less than 10% of the product ions at short reaction times.

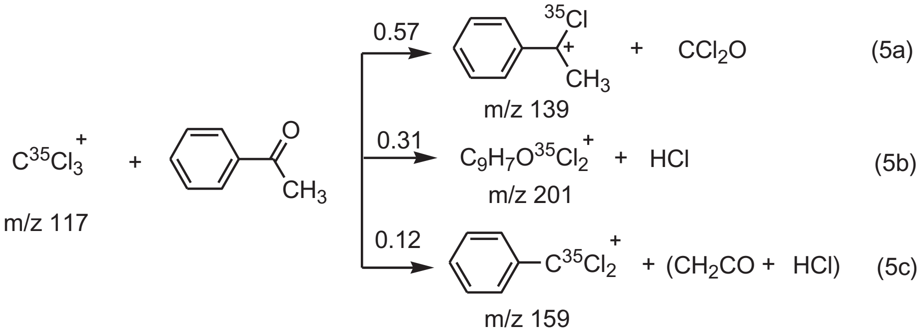
Both PhC$^+$(F)Me and $PhCCH_2^+$ undergo fast proton transfer to neutral acetophenone to yield protonated acetophenone, (PhCOMe)H$^+$ *m/z* 121, which eventually becomes the most abundant ionic species at reaction times longer than 600 ms.

IRMPD experiments on the adduct ion, *m/z* 189, reveal exclusive dissociation to the PhC$^+$(F)Me cation. This strongly suggests that CF_3^+(PhCOMe) corresponds to the carbonyl adduct ion as shown in reaction (4) in agreement with the recent characterization of the vibrational frequency of the C=O–CF_3 stretch of an analog gas-phase adduct ion of an aromatic ketone [20].



(4)

Unlike CF_3^+, a much richer reactivity pattern is observed for the gas-phase CCl_3^+ reaction with acetophenone. Three distinct channels have been observed in our experiments and these are shown below along with the relative product distribution measured at short reaction times.



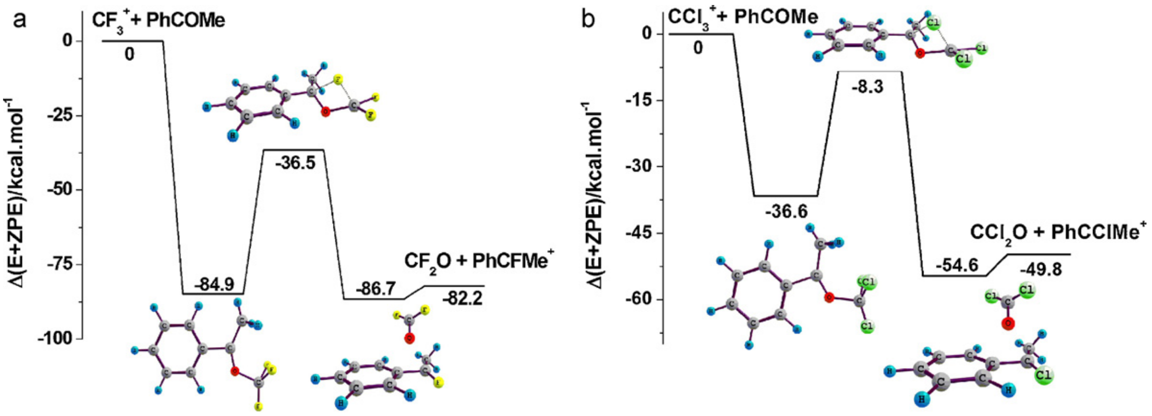


Fig. 1. (a) Energy profile for the reaction of CF_3^+ and acetophenone leading to the formation of $PhC^+(F)Me$ and CF_2O calculated at the B3LYP/6-31+G(d,p) level. (b) Energy profile for the reaction of CCl_3^+ and acetophenone leading to the formation of $PhC^+(Cl)Me$ and CCl_2O calculated at the B3LYP/6-31+G(d,p) level.

$PhC^+(Cl)Me$ ions undergo further reaction by facile proton transfer to neutral acetophenone to yield protonated acetophenone, $PhC^+(OH)Me$ (*m/z* 121), analogous to the behavior observed for $PhC^+(F)Me$ ions.

Some noticeable differences are observed between the reactions of acetophenone with CF_3^+ and CCl_3^+:

(i) the reaction of acetophenone with CCl_3^+ proceeds considerably slower than with CF_3^+;
(ii) while the halonium metathesis leading to $PhC^+(Cl)Me$ is still the main product, reactions (5b) and (5c) suggest that other mechanisms become important with CCl_3^+;
(iii) only minor amounts of the adduct ion $C^{35}Cl_3^+(PhCOMe)$, *m/z* 237, and of $PhC^+{=}CH_2$, *m/z* 103, formed from energy rich $PhC^+(Cl)Me$ ions by HCl elimination, are detected in the reaction with CCl_3^+.

Additional experiments with partially deuterated acetophenones provide some useful insight on the mechanism of the reactions and the likely structure of the product ions. For example, reaction of CF_3^+ with $PhCOCD_3$ yields $C_8H_5D_3F^+$ ions, *m/z* 126, as the main product of reaction (2a). However, reaction (2b) and IRMPD of the *m/z* 126 ion, occur by elimination of both HF and DF in agreement with previous findings that showed extensive randomization between the methyl and ring hydrogens [12,16]. A similar behavior is observed in experiments between CF_3^+ and C_6D_5COMe.

By comparison, experiments with $C^{35}Cl_3^+$ and $PhCOCD_3$ reveal that:

(a) reaction (5b) proceeds exclusively by elimination of HCl to yield *m/z* 204 ions, $C_9H_4D_3O^{35}Cl_2^+$;
(b) reaction (5c) proceeds exclusively by elimination of CD_2CO and DCl (or CD_3COCl) to yield $C_7H_5{}^{35}Cl_2^+$ ions (*m/z* 159).

Similarly, reaction with C_6D_5COMe yields exclusively $C_9H_3D_4O^{35}Cl_2^+$ ions (*m/z* 205) by loss of DCl and $C_7D_5{}^{35}Cl_2^+$ ions (*m/z* 164) by loss of CH_2CO and HCl (or CH_3COCl). Thus we can conclude that reaction (5b) proceeds by loss of a ring hydrogen while reaction (5c) proceeds by loss of all three methyl hydrogens. For these reactions, no randomization is observed between methyl and ring hydrogens.

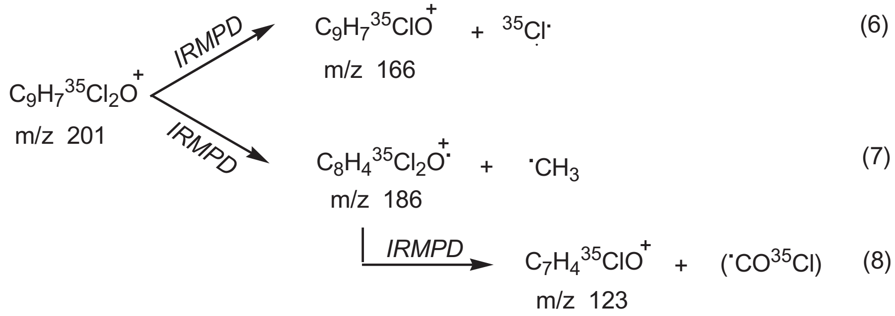
3.2. The PhC⁺(X)Me (X = F, Cl) product ions

While reactions (2a) and (5a) are similar to reactions previously reported for ketones, the calculated energy profiles shown in Fig. 1 reveal some differences. These reactions are highly exothermic for both CF_3^+ and CCl_3^+ but the transition state for the CCl_3^+ reaction is estimated to be 8.3 kcal mol^{-1} below the reactants as opposed to 36.5 kcal mol^{-1} below the reactants for CF_3^+. This difference may well account for the fact that the reaction of CCl_3^+ is slower and that other reaction channels become competitive.

3.3. The C₉H₇Cl₂O⁺ product ions

The results obtained with the partially deuterated acetophenones suggest that reaction (5b) proceeds by elimination of HCl containing a hydrogen atom originally at a ring position and suggests a mechanism involving a ring attack by CCl_3^+. Yet, additional experiments provide strong evidence that more than one isomeric species is formed in reaction (5b).

Dissociation of selected $C_9H_7Cl_2O^+$ ions by IRMPD reveals surprisingly two dissociation channels, (6) and (7), *both of which violate the even electron rule* [21].



The $C_8H_4Cl_2O^{+\bullet}$ ions formed in (7) undergo a secondary IRMPD process by loss of $^\bullet COCl$, or CO and $Cl^\bullet$, as shown in (8).

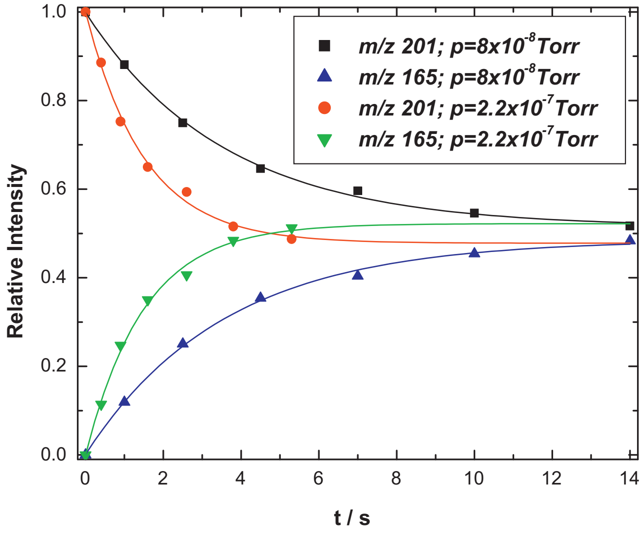


Fig. 2. Kinetics, at two different pressures of acetophenone, of the subsequent reaction of $C_9H_7{}^{35}Cl_2O^+$ (*m/z* 201) ions that leads to $C_9H_6{}^{35}ClO^+$ (*m/z* 165) and HCl. The fact that less than 60% of the ion population undergoes this reaction is noticeable at long reaction times.

Similar IRMPD experiments with the product ions $C_9H_4D_3O^{35}Cl_2{}^+$ (*m/z* 204), from reaction (5b) with $PhCOCD_3$, yield loss of $^\bullet CD_3$ in reaction (7), while the product ions $C_9H_3D_4O^{35}Cl_2{}^+$ ions (*m/z* 205) from reaction (5b) with C_6D_5COMe undergo loss of $^\bullet CH_3$ through reaction (7). Thus, *no scrambling occurs in the activation process* responsible for the dissociation channel shown in (7).

A second interesting observation is the fact that (57 ± 4)% of the $C_9H_7Cl_2O^+$ ions, formed in reaction (5b), slowly undergo further loss of HCl in the presence of acetophenone, as shown in (9).

$$\underset{m/z\ \ 201}{C_9H_7^{35}Cl_2O^+} \xrightarrow{PhCOMe} \underset{m/z\ \ 1656}{C_9H_6^{35}ClO^+} + H^{35}Cl \qquad (9)$$

This feature is illustrated in Fig. 2 for two different pressures of acetophenone. Fig. 2 clearly suggests that this second HCl elimination is pressure dependent but the percentage of reactive $C_9H_7Cl_2O^+$ ions remains constant within our experimental error. The fact that $C_9H_4D_3O^{35}Cl_2{}^+$ ions, formed from the reaction with $PhCOCD_3$ eliminate DCl exclusively, while $C_9H_3D_4O^{35}Cl_2{}^+$ ions, formed from the reaction C_6D_5COMe, eliminate HCl exclusively in the analogous reactions (9) is consistent with loss of a hydrogen atom originally attached to the methyl group. Reaction (9) is unaffected by addition of krypton, nitrogen or benzene to the reaction cell but is accelerated by addition of substrates such as acetone and ethyl acetate without changing the percentage of reactive $C_9H_7Cl_2O^+$ ions. The fact that reaction (9) is not promoted by IRMPD but catalyzed by substrates in a certain range of proton affinities suggests a mechanism involving a proton shuttle between the ion and the neutral. A more elaborate description of the mechanism of this reaction is presently under investigation.

Further IRMPD experiments performed on the unreactive $C_9H_7{}^{35}Cl_2O^+$ ions, isolated after completion of reaction (9), result in the exclusive formation of $C_8H_4{}^{35}Cl_2O^+$ (*m/z* 186) by loss of a methyl group (reaction (7)), followed by sequential loss of CO and ^{35}Cl, or $CO^{35}Cl$, to yield $C_7H_4{}^{35}ClO^+$, *m/z* 123 (reaction (8)).

The combined set of observations is strongly indicative that reaction (5b) yields an isomeric mixture of $C_9H_7Cl_2O^+$ ions. Several potential structures can be proposed for the $C_9H_7Cl_2O^+$ ions and compared with the experimental evidence. These are displayed in Fig. 3 along with the calculated exothermicities for reaction (5b) leading to each one of the putative isomers.

The *ortho* isomer, analogous to **1c** and **1d**, has not been included in Fig. 3 because optimization of this structure leads to isomer **1b**. Isomers **1a** and **1b** appear attractive from the IRMPD evidence and our calculations show that they can interconvert through a reasonably high barrier as illustrated in Scheme 1. Yet, this barrier is located below the energy of the reactants and above the energy of the products of reaction (5b) leading to **1a** and **1b**. Thus, it is presumably possible that both isomers could be formed through a common mechanism.

Structure **1e** is unlikely to be formed in these reactions because it would result from elimination of HCl containing a methyl hydrogen in disagreement with the data obtained for the partially deuterated acetophenones.

Isomers **1c** and **1d** can be generated by $CCl_3{}^+$ attack at the corresponding ring position. Table 1 lists the calculated relative energies for initial adduct formation and the transition state for HCl elimination. From our calculations we can conclude that attack at the *meta* and *para* position would be preferred although the subsequent transition states leading to the final products are estimated to be slightly above the energy of the reactants. It is possible that isomer **1b** could be formed from attack of $CCl_3{}^+$ at the *ortho* position but we have been unsuccessful in characterizing this pathway in our calculations.

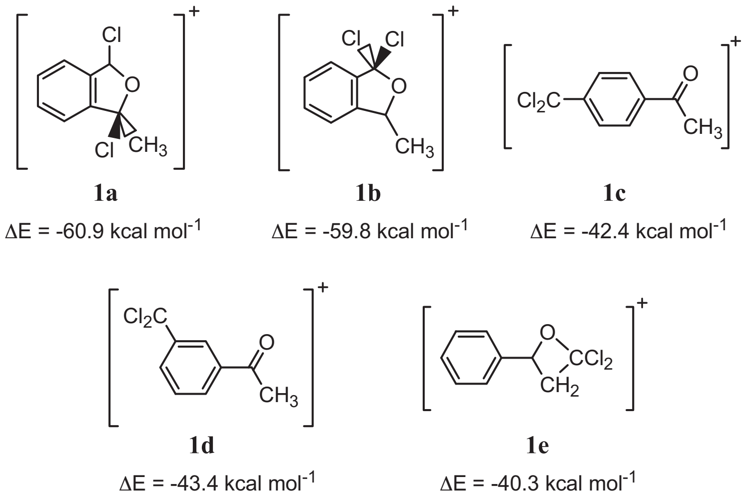
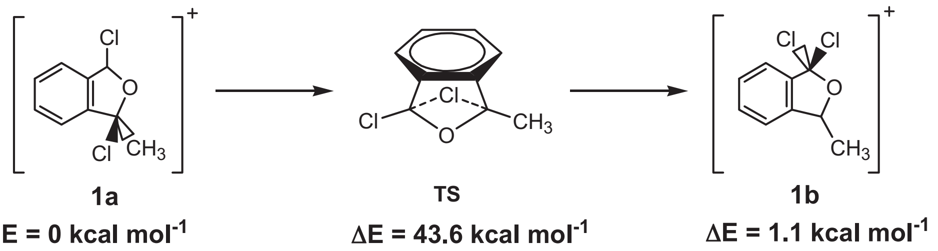
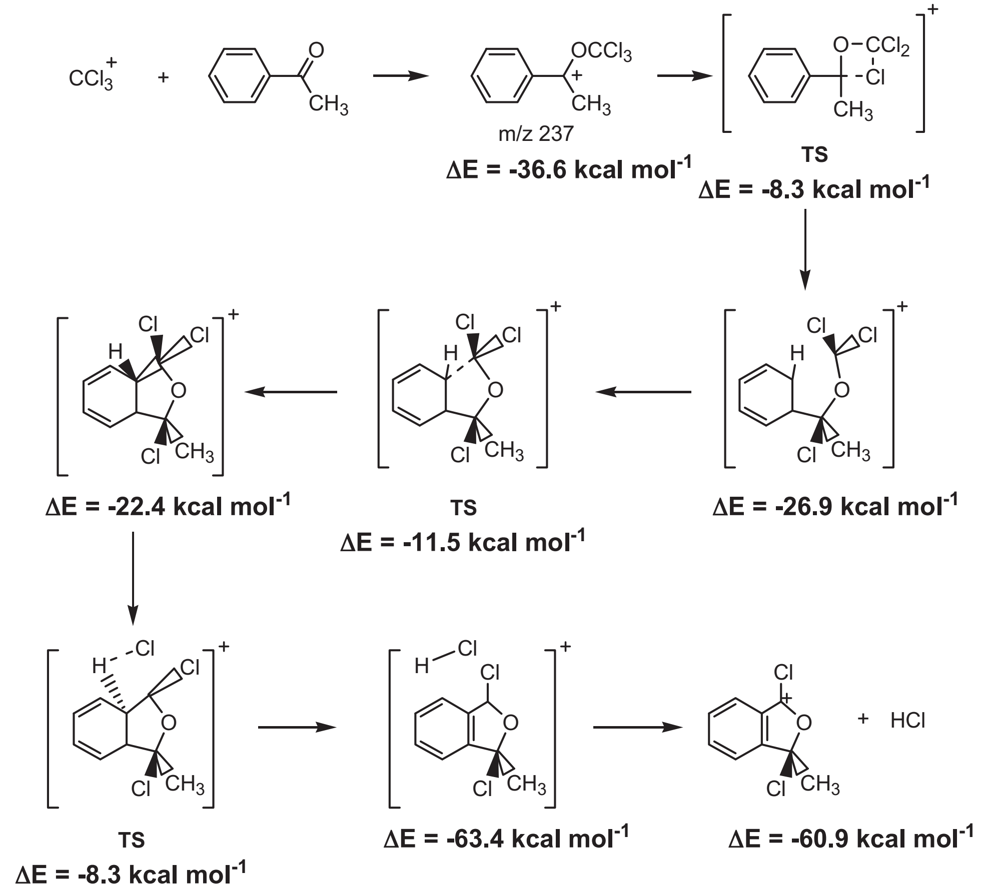


Fig. 3. Possible isomeric species for the product ion of reaction (5b) between $CCl_3{}^+$ and acetophenone and exothermicities calculated at the B3LYP/6-31+G(d,p) level for reaction leading to each isomer.

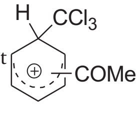
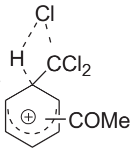


Scheme 1. Mechanism and energetics calculated at the B3LYP/6-31+G(d,p) for the interconversion of isomers **1a** and **1b**.



Scheme 2. A mechanistic pathway for the formation of ion **1a** with relative energies calculated at the B3LYP/6-31+G(d,p) level.

Table 1
Calculated energetics at the B3LYP/6-31+G(d,p) level for the reaction of CCl_3^+ and acetophenone leading to addition of CCl_2^+ at different ring positions. Energies are calculated relative to the energy of the reactants.

	Adduct 	Transition state 	Products
para	−16.2	3.3	−42.3
meta	−16.4	2.1	−43.2
ortho	−13.2	8.5	[a]

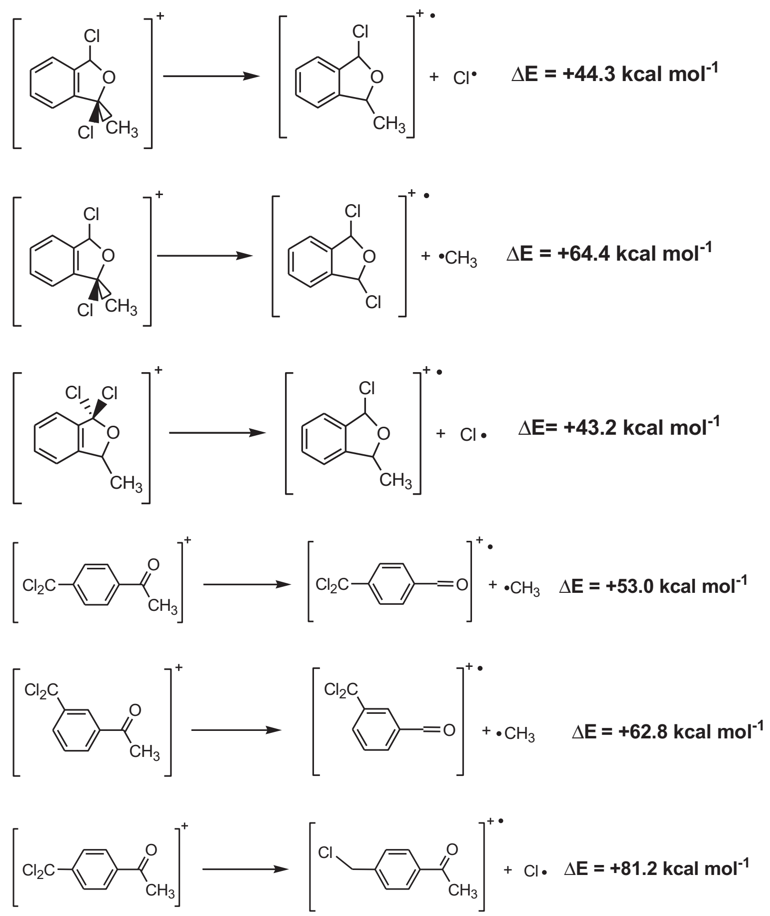
[a] The product ion with CCl_2 in the *ortho* position to the COMe group could not be found because this structure rearranges to structure **1b**. However, the connection between the transition state and **1b** was not characterized by IRC calculations.

Interestingly enough, a mechanistic route for the formation of **1a** was found from the initial CCl_3^+/acetophenone carbonyl adduct as shown in Scheme 2. This mechanism is compatible with the experimental data provided that the scrambling of hydrogens between the methyl group and the aromatic ring occurs only after activation of the $PhC^+(Cl)Me$ ion as suggested by the data on the unimolecular decomposition of $PhC^+(F)Me$ ions [12].

Table 2 lists the calculated energetics for loss of a chlorine atom or a methyl group in the IRMPD experiments for the different isomeric species, **1a**–**1d**. The estimated dissociation energies lead us to some important conclusions:

(i) Loss of a chlorine atom for either isomer **1a** or **1b** is substantially lower in energy than the corresponding loss of a methyl group. These results would make it unlikely that methyl loss could be competitive against chlorine atom loss in an IRMPD

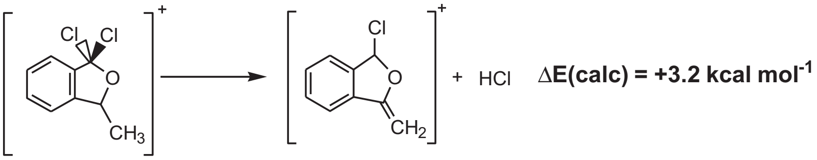
Table 2
Calculated dissociation energies for different isomeric $C_9H_7Cl_2O^+$ ions at the B3LYP/6-31+G(d,p) level for possible IRMPD processes.



process of a relatively simple ion such as the system in consideration. In either case, the dissociation process leads to the formation of the molecular ion of a substituted isobenzofuran. This may account for the violation of the even electron rule in the IRMPD process. There is some evidence that isobenzofurans are characterized by low ionization energies [22] and isobenzofurans typically exhibit the molecular ion as the base peaks in their mass spectra [23,24].

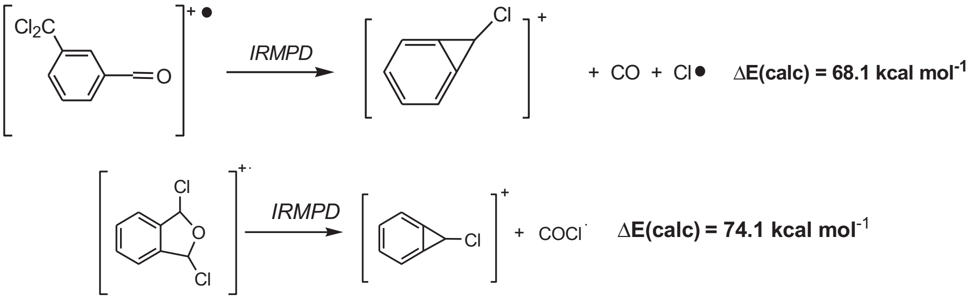
(ii) By comparison, loss of a methyl group is energetically much more favorable than loss of a chlorine atom for isomers **1c** and **1d**. For these isomers, loss of a chlorine atom would not be expected to be competitive with methyl loss in the IRMPD process for these isomers.

Based on the experimental observations and our theoretical calculations it is possible to propose that the most abundant $C_9H_7Cl_2O^+$ isomer formed in reaction (5b) is either **1a** or **1b**. This is consistent with the IRMPD process resulting in loss of a chlorine atom and the subsequent reaction that leads to the second elimination of HCl. As shown below, **1b** can be viewed as a protonated 1-methylene-3,3-dichloroisobenzofuran, or substituted phthalan, that could undergo HCl elimination through a proton shuttle mechanism. Our calculations at the B3LYP/6-311+G(d,p) level predict the proton affinity of the phthalan to be 213.2 kcal mol^{-1} for protonation at the methylene group at 298 K and 209.5 kcal mol^{-1} for protonation at chlorine leading to HCl elimination.



A tentative identification of the second isomer as either **1c** or **1d** is consistent with the IRMPD process for loss of a methyl radical even though the mechanistic pathway for formation of either **1c** or **1d** is estimated to be slightly unfavorable under our experimental conditions. Theoretical calculations for possible routes for the sequential IRMPD process of the *unreactive* $C_9H_7Cl_2O^+$ isomer (reaction (9)) also show that loss of CO and Cl from **1d** is estimated to be somewhat lower in energy than loss of COCl from **1b** in reaction (8).

These findings support the idea that **1c** or **1d** are likely candidates for the unreactive $C_9H_7Cl_2O^+$ isomer.

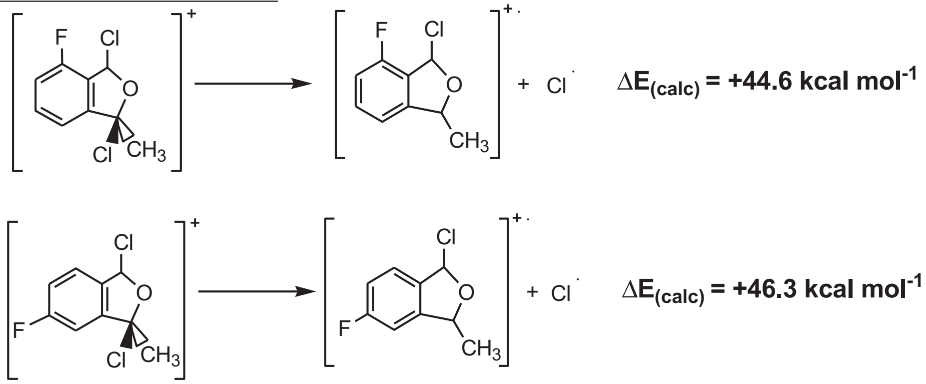


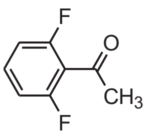
3.4. The $PhCCl_2^+$ product ion of reaction (5c)

The mechanism of reaction (5c) was not thoroughly investigated and preliminary studies show that this reaction can become important in some substituted acetophenones. One possibility is that this reaction proceeds by an *ipso* attack of CCl_3^+ on acetophenone. Initial calculations reveal that attack of CCl_3^+ at the *ipso* position results in a very stable complex that is best described as the association of an acetyl cation with thrichlorotoluene, i.e., $MeCO^+(PhCCl_3)$. However, we have yet to explore all possible pathways for this minor reaction for acetophenone.

3.5. Ion/molecule reactions of CCl_3^+ with substituted acetophenones

The reactions of CCl_3^+ with a number of substituted acetophenones were also studied with the intent of collecting additional information regarding the nature of the products of reactions similar to (5b). 2′,6′-Difluoroacetophenone (**2**), 4′-tert-butyl, 2′,6′-dimethylacetophenone (**3**), and α,α,α-trifluoroacetophenone (**4**) displayed no reactions similar to (5b).





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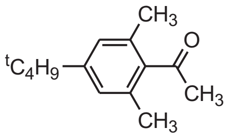
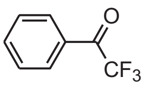
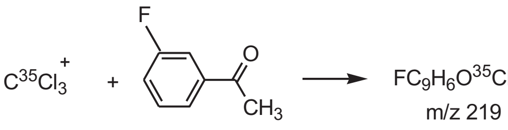


3



4

By comparison, 3′-fluoroacetophenone was observed to react preferentially through reaction (10) over the corresponding halonium metathesis reaction.



(10)

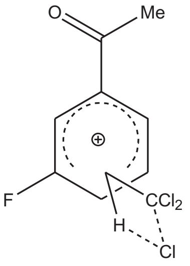
The product ion of reaction (10), $FC_9H_6OCl_2^+$, also undergoes slow loss of a second molecule of HCl in the presence of its neutral precursor similar to reaction (9). However, unlike the case of acetophenone, there is no indication of an unreactive population of $FC_9H_6OCl_2^+$ ions toward reaction (10). The $FC_9H_6OCl_2^+$ ions exhibit a single IRMPD channel as shown in (11).

$$\underset{m/z\ 219}{\mathrm{FC_9H_6^{35}Cl_2O^+}} \xrightarrow{\mathrm{IRMPD}} \underset{m/z\ 184}{\mathrm{FC_9H_6^{35}ClO^+}} + {}^{35}\mathrm{ClH} \qquad (11)$$

Fig. 4 lists some of the possible structures for the $FC_9H_6OCl_2^+$ ions, analogous to those considered in Fig. 3, along with the calculated exothermicities for reaction (10) for formation of the different isomers. Several different possibilities can be considered for these ions and it is interesting to notice that isomer **5g** with the CCl_2 substituent *ortho* to the –COMe moiety is now calculated to be stable in the open form.

The IRMPD process (11) is again consistent with an ion displaying an isobenzofuran structure. As in the previous case, loss of a methyl group is calculated to be a considerably higher energy process and is not observed in the IRMPD of $FC_9H_6OCl_2^+$.

Table 3
Relative energies of the transition states of the reaction between CCl_3^+ and 3′-fluoroacetophenone leading to addition of CCl_2^+ at different ring positions. Relative energies calculated at the B3LYP/6-311+G(d,p) level with respect to the energy of the reactants.

	TS at 2′	TS at 4′	TS at 5′	TS at 6′
	16.2	9.8	9.0	10.9

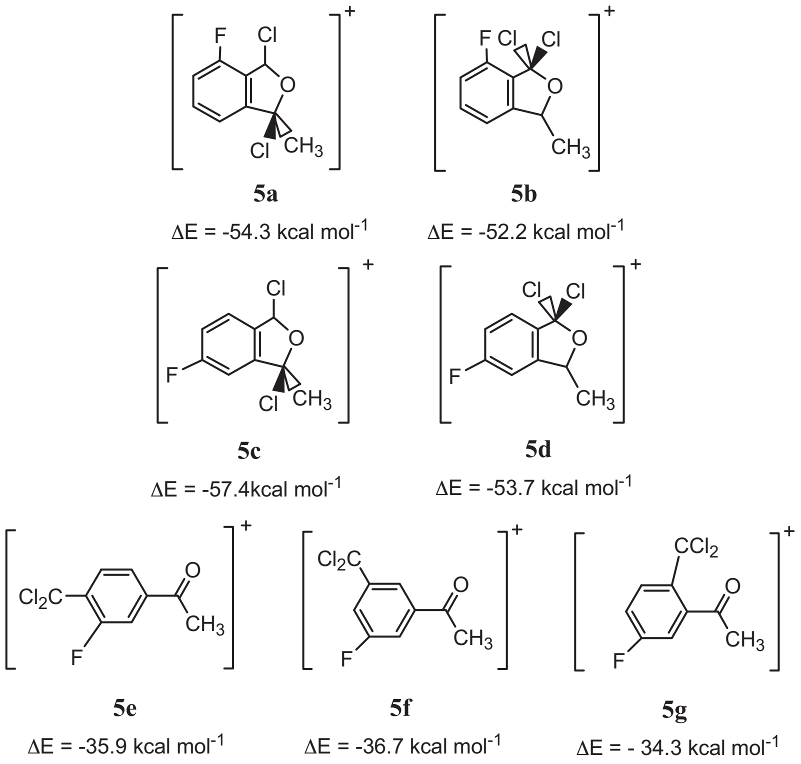


Fig. 4. Possible isomeric species for the product ion of reaction (11) between CCl_3^+ and 3′-fluoroacetophenone and exothermicities calculated at the B3LYP/6-31+G(d,p) level for reaction leading to each isomer.

The behavior of the $FC_9H_6OCl_2^+$ ions generated in reaction (11) is consistent with the formation of one isomer, or of isomers displaying the isobenzofuran skeleton. The reaction products originating from attack of CCl_3^+ at a ring position leading to isomers **5e**–**5g** are predicted to be less favorable than in the case for acetophenone and Table 3 lists the calculated energies for the transition states of these reactions. These higher transition states can explain the fact that these isomers are not formed under our experimental conditions.

4. Conclusions

The reaction of CCl_3^+ with acetophenone reveals some very distinct and interesting features when compared with the reaction of CF_3^+ with the same substrate. The most dramatic difference is the ability of CCl_3^+ to promote a reaction that proceeds by elimination of HCl with the hydrogen coming from the aromatic ring and resulting in the formation of a mixture of isomeric $C_9H_7Cl_2O^+$ ions. The appearance of additional channels in the reaction with CCl_3^+ is attributed to the fact that the energy profile for the main reaction leading to halonium metathesis and formation of $PhC^+(X)Me$ is much less favorable for CCl_3^+ than for CF_3^+.

The combination of IRMPD processes that proceed through violation of the even-electron rule, the secondary reactivity of a fraction of the population of $C_9H_7Cl_2O^+$ ions and theoretical calculations allow us to conclude that at least the most abundant isomer has an isobenzofuran skeleton. Similar arguments suggest that the second isomer corresponds to an ion with the CCl_2 group attached to a ring position. It is hoped that additional experiments involving the characterization of these unique isomers by infrared spectroscopy can elucidate unequivocally the structure of these ions.

Acknowledgments

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References

[1] F. Grandinetti, G. Occhiuzzi, M.E. Crestoni, S. Fornarini, M. Speranza, Int. J. Mass Spectrom. 127 (1993) 123–135.
[2] C. Dehon, J. Lemaire, M. Heninger, A. Chaput, H. Mestdagh, Int. J. Mass Spectrom. 299 (2010) 113–119.
[3] C.F. Abrams, D.B. Graves, Thin Solid Films 374 (2000) 150–156.
[4] J.R. Eyler, P. Ausloos, S.G. Lias, J. Am. Chem. Soc. 96 (1974) 3673–3675.
[5] P. Ausloos, S.G. Lias, J.R. Eyler, Int. J. Mass Spectrom. Ion Processes 18 (1975) 261–271.
[6] V. Nguyen, P.S. Mayer, T.H. Morton, J. Org. Chem. 65 (2000) 8032–8040.
[7] P.S. Mayer, D. Leblanc, T.H. Morton, J. Am. Chem. Soc. 124 (2002) 14185–14194.
[8] D. Leblanc, J. Kong, P.S. Mayer, T.H. Morton, Int. J. Mass Spectrom. 222 (2003) 451–463.
[9] A.E.P.M. Sorrilha, L.S. Santos, F.C. Gozzo, R. Sparrapan, R. Augusti, M.N. Eberlin, J. Phys. Chem. A 108 (2004) 7009–7020.
[10] M. Tsuji, M. Aizawa, Y. Nishimura, Bull. Chem. Soc. Jpn. 69 (1996) 1055–1063.
[11] T. Giroldo, Doctoral thesis, University of São Paulo, São Paulo, Brazil, 2007.
[12] J. Oomens, E. Kraka, M.K. Nguyen, T.H. Morton, J. Phys. Chem. A 112 (2008) 10774–10783.
[13] J. Oomens, T.H. Morton, Angew. Chem. Int. Ed. 112 (2008) 2106–2108.
[14] J. Oomens, T.H. Morton, Eur. J. Mass Spectrom. 16 (2010) 313–319.
[15] T. Giroldo, J.M. Riveros, J. Phys. Chem. A 106 (2002) 9930–9938.
[16] M. Sena, J.M. Riveros, Chem. Eur. J. 6 (2000) 785–793.
[17] E.E. Fileti, P.R.P. Moraes, L. Domingues, J.M. Riveros, J. Mass Spectrom. 42 (2007) 1310–1318.
[18] L.A. Xavier, T.V. Malaspina, N.H. Morgon, J.J. Menegon, J.M. Riveros, Int. J. Mass Spectrom. (2010), doi:10.1016/j.ijms.2010.11.019.
[19] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A.

Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision D.01, Gaussian, Inc., Wallingford, CT, 2004.

[20] J. Oomens, T.H. Morton, Org. Lett. 13 (2011) 2176–2179.

[21] M. Karni, A. Mandelbaum, Org. Mass Spectrom. 15 (1980) 53–64.

[22] J.S. Dewar, A.J. Harget, N. Trinajstic, S.D. Worley, Tetrahedron 26 (1970) 4505–4516.

[23] J.P. Denhez, M. Ricard, M. Corval, Org. Mass Spectrom. 11 (1976) 258–265.

[24] P.W. Dibble, R. Rodrigo, Org. Mass Spectrom. 23 (1988) 743–750.