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Reactions of gaseous halocarbonyl cations with aromatic compounds: ionic carbonylation of inert C–H bonds

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Dedicated to Dr. Helmut Schwarz on the occasion of his 60th birthday, and for his most outstanding contribution to gas-phase ion chemistry.

Abstract

The mass-selected halocarbonyl cations FCO^+, $ClCO^+$, and $BrCO^+$ were reacted with benzene, thiophene, pyrrole, and furan and a few of their alkyl derivatives to evaluate the ability of XCO^+ ions to promote C–H bond activation of aromatic compounds (M–H) via gas-phase ionic carbonylation. This novel reaction occurs via electrophilic addition followed by prompt HX elimination, forms the respective acylium ions ($M–CO^+$), and competes with electron abstraction and X^+ transfer. The intrinsic gas-phase reactivity order observed for ionic carbonylation was: $FCO^+ > ClCO^+ > BrCO^+$. The ability of the fluorosulfinyl cation (FSO^+) to promote analogous ionic sulfonylation of aromatic compounds was also tested, but owing to its high recombination energy, FSO^+ acts as a potent oxidizing agent and electron abstraction dominates. A novel, highly efficient and nearly exclusive O-abstraction reaction of FC^+ and SF^+ with N_2O was used to the straightforward preparation of gaseous FCO^+ and SFO^+. B3LYP/6-311G++(d,p) potential energy surface diagrams were elaborate to help rationalize the observed reactivity trends.

Keywords: Pentaquadrupole mass spectrometry; Carbonylation; Halocarbonyl cations; Aromatic C–H bond activation; Acylium ions; Ion–molecule reactions

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1. Introduction

Unreactive molecules can be chemically activated and then converted into useful products by selective functionalization of their inert bonds using a variety of reactions, such as halogenation, oxidation, and carbonylation. The gas phase provides a suitable environment in which to study the intrinsic reactivity of ions with neutral molecules, and to perform fast screening for potential model reactions [1]. In the gas-phase solvent-free diluted mass spectrometric environment [2], many efficient ion–molecule reactions able to functionalize a variety of inert bonds have been described. In particular, Schwarz and his coworkers [3] have studied the gas-phase activation of a variety of intrinsically inert bonds by an extensive series of metal cations and derivatives. To mention a few examples, they have recently reported the hydrolytic activation of C–F bonds by intrinsically unreactive chromium cations [3a], the regio- and diastereoselective C–H bond activation of valeramide and 3-methyl valeramide by bare Fe^+ ions [3b], the P–H bond

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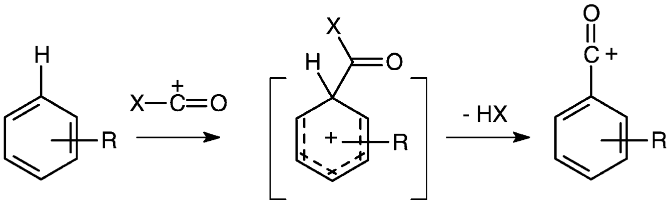


Scheme 1.

activation of phosphane [3c] by Fe^+, Co^+, Ni^+, Ru^+, Rh^+, Pd^+, Os^+, Ir^+, and Pt^+, and C–H bond activation in methane by FeS^+ resulting in methane to methanethiol conversion [3d].

Carbonylation of benzene, the selective functionalization and activation of its inert C–H bond by CO, has been extensively investigated for both experimental and fundamental reasons. Many strategies have been developed to perform benzene carbonylation which includes the Gatterman–Koch formylation, and techniques based on transitional metal catalysts, organometallic reagents, and photochemical and radical processes [4]. Acylium ions ($R–C^+{=}O$) constitute a class of stable, long-lived, versatile, and reactive cations, and a variety of new reactions of gaseous acylium ions of synthetic and analytical importance have been described [5]. We were the first to report [6] an ionic carbonylation reaction of benzene and derivatives with halocarbonyl cations, namely, the gaseous chlorocarbonyl cation $ClCO^+$, a haloacylium ion. This novel ion–molecule reaction results in the selective CO functionalization of an inert C–H bond of benzene and some of its derivatives with the formation of benzoyl cations (Scheme 1, X = Cl). Note that this reaction can also be classified as an ionic *transcarbonylation* reaction because a haloacylium ion is converted into an aryl acylium ion ($XCO^+ \rightarrow ArCO^+$).

More recently, Grandinetti et. al. [7] have used gaseous NF_2^+ to form FCO^+ via ionic fluorination of CO, and found that the fluorocarbonyl cation FCO^+ also promotes ionic carbonylation of the C–H bond in benzene and toluene (Scheme 1, X = F). FCO^+ is readily available in the gas phase, and has also been characterized in a liquid nitrogen cooled negative glow discharge [8], but in solution it appears that FCO^+ cannot be properly stabilized with presently known Lewis acids [9]. For $ClCO^+$, however, a stable $ClCO^+SB_3F_{16}^-$ salt has been recently synthesized [9]. Furthermore, $ClCO^+$, $BrCO^+$, and ICO^+ have been observed in SO_2ClF solutions by ^{13}C NMR spectroscopy, but attempts to observe the lightest FCO^+ failed [10]. It appears therefore that ionic carbonylation in the condensed phase would be more feasible using the heavier halogen analogues (for instance in Lewis acid salt forms), in particular the stable and well-characterized [11] chlorocarbonyl cation $ClCO^+$.

In this work, we have performed gas-phase reactions of the three gaseous halocarbonyl cations, FCO^+, $ClCO^+$, and $BrCO^+$, with benzene, furan, thiophene, and pyrrole (and a few of their alkyl derivatives) to compare the intrinsic abilities of XCO^+ to promote ionic carbonylation of inert C–H aromatic bonds. By analogy with FCO^+, we also formed and tested the ability of the fluorosulfinyl cation FSO^+, an ion expected to be highly electrophilic, to perform unprecedented ionic sulfonylation of inert C–H aromatic bonds.

1.1. Experimental section

The gaseous ions were produced, reacted, and their products analyzed via double stage (MS^2) and triple stage (MS^3) mass spectrometric experiments performed with an Extrel (Pittsburgh, PA, USA) pentaquadrupole ($Q_1q_2Q_3q_4Q_5$) mass spectrometer [12]. The gaseous FCO^+ was obtained via a novel gas-phase O-abstraction reaction [12] of mass-selected FC^+ with N_2O, whereas gaseous $ClCO^+$ and $BrCO^+$

ions were obtained by 70 eV electron ionization of CH_3COCl and CH_3COBr, respectively. SFO^+ was also prepared via O-abstraction of SF^+ from N_2O [14]. In the MS^2 experiments via which ion–molecule reactions were performed, Q_1 was used to mass select the ion of interest, the neutral reagent was added to q_2, and ion–molecule reactions occur at translational energy near 1 eV. Product ion mass spectra were acquired by scanning Q_5, while operating Q_3 in the broad band rf-only mode. The target gas pressure in q_2 caused typical beam attenuation of 50–80%, that is, multiple low-energy collision conditions were used in q_2 to increase reaction yields and to promote collisional quenching of both the reactant and product ions, although lower yields but essentially the same set of products with small variations on relative abundances were always observed at single collision conditions.

For the MS^3 experiments, Q_3 was used to mass select a q_2 product ion of interest either for further 10 eV collision dissociation with argon or reactions with a second neutral molecule at near 1 eV collisions in q_4, while scanning Q_5 for spectral acquisition. The 10 eV CID energies were taken as the voltage difference between the ion source and the collision quadrupole. The indicated pressure in each differentially pumped region was typically 2×10^{-6} (ion source), 8×10^{-6} (q_2), and 8×10^{-5} (q_4) Torr, respectively (1 Torr = 133.3 Pa). Total energies of optimized geometries with no symmetry constraints were calculated at the B3LYP/6-311G++(d,p) level of theory [15] run on Gaussian 98 [16]. Energies, vibrational frequencies, and details of the optimized structures are available from the authors upon request.

2. Results and discussion

2.1. Straightforward preparation of gaseous FCO^+: O-abstraction of FC^+ from N_2O

Although FCO^+ is formed readily upon 70 eV EI of several suitable (but not readily available) neutrals [17], as well by ionic fluorination of CO by $NF_2{}^+$ [7], we have used a novel gas-phase ion–molecule reaction to prepare FCO^+. Using a pentaquadrupole ($Q_1q_2Q_3q_4Q_5$) mass spectrometer [18], FC^+ of m/z 31 was formed upon 70 eV EI of CF_4 and then mass-selected by the first mass-analyzing quadrupole: Q_1. Reactions in q_2 with N_2O under low, near 1 eV energy, and multiple collision conditions afforded nearly exclusively FCO^+ of m/z 47 via a highly efficient O-abstraction reaction (Fig. 1).

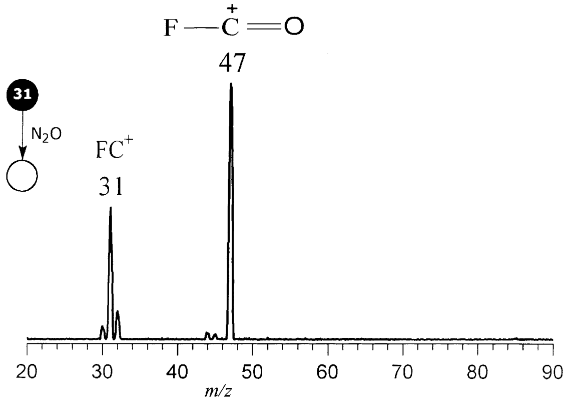


Fig. 1. Product ion mass spectrum for the reaction of mass-selected FC^+ of m/z 31 with N_2O. A novel, highly efficient, and nearly exclusive O-abstraction reaction yields (unequivocally) gaseous FCO^+ of m/z 47.

2.2. Reactions of the three halocarbonyl cations with benzene

The isotopomeric $^{35/37}ClCO^+$ and $^{79/81}BrCO^+$ halocarbonyl cations were prepared via 70 eV EI of acetyl chloride and acetyl bromide, respectively, two of their suitable and readily available neutral precursors. Fig. 2 displays the product ion mass spectra for reaction of the three mass-selected FCO^+, $^{35}ClCO^+$, and $^{79}BrCO^+$ ions with benzene. Actually, a MS^3 experiment was performed for FCO^+ since this ion was prepared “on-line” in q_2 via reactions of Q_1 mass-selected FC^+ ions (Fig. 1), mass-selected by Q_3, and further reacted with benzene in q_4, while scanning Q_5 to acquire the sequential product ion mass spectrum (Fig. 2a). For the three XCO^+ ions, three competitive reactions (Scheme 2) are observed:

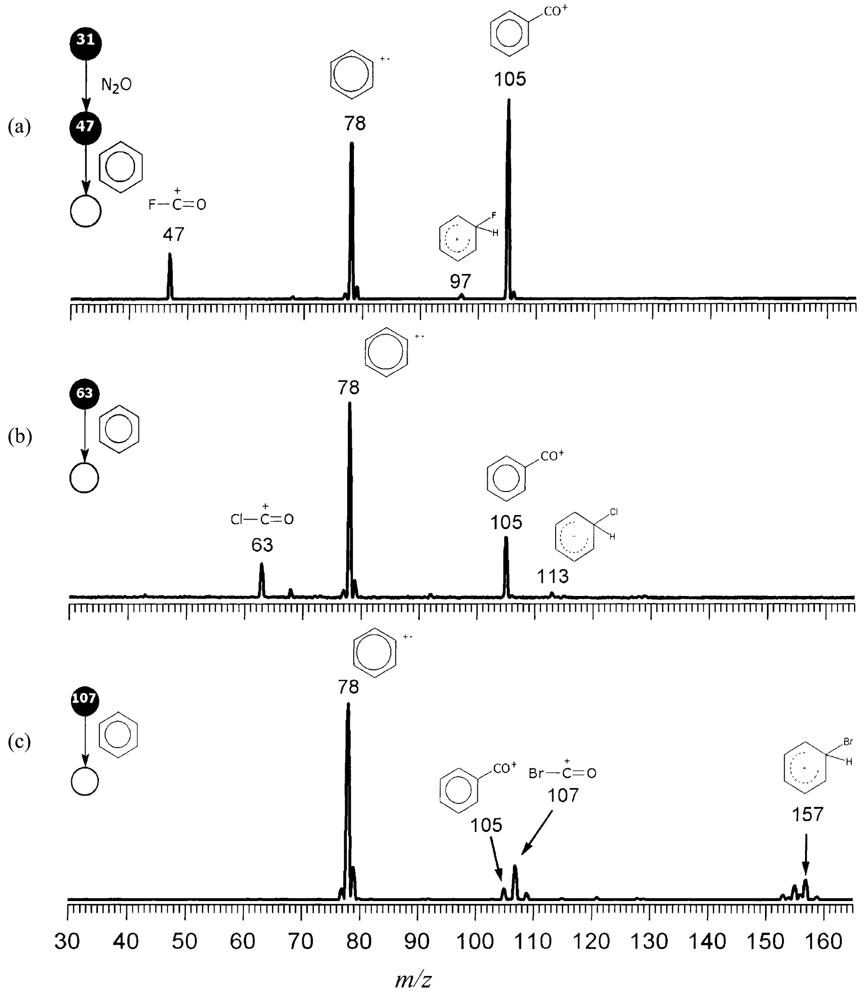
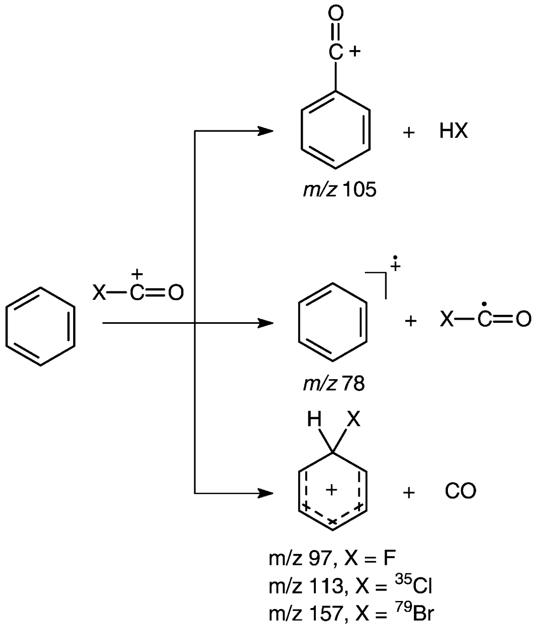


Fig. 2. (a) Sequential product ion mass spectrum for the reaction of mass-selected FCO^+ of *m*/*z* 47 (formed via reactions of FC^+ of *m*/*z* 31 with N_2O, see Fig. 1) with benzene. Product ion mass spectra for the reaction with benzene of mass-selected (b) $ClCO^+$ of *m*/*z* 63 and (c) $BrCO^+$ of *m*/*z* 107.

(i) ionic carbonylation that yields the benzoyl cation ($PhCO^+$) of *m*/*z* 105, (ii) electron abstraction that yields ionized benzene of *m*/*z* 78, and (iii) X^+ transfer that yields the corresponding protonated fluorbenzene of *m*/*z* 97, protonated chlorobenzene of *m*/*z* 113, and protonated bromobenzene of *m*/*z* 157.

For FCO^+ (Fig. 2a), ionic carbonylation occurs to a great extent, and $PhCO^+$ of *m*/*z* 105 is the major ionic reaction product. Electron abstraction (*m*/*z* 78) is the second most favored reaction, whereas F^+ transfer [19] (*m*/*z* 97) is minor. The yield of ionic carbonylation relative to that of electron abstraction (*m*/*z* 105: *m*/*z* 78) decreases from FCO^+ (Fig. 2a) to $ClCO^+$ (Fig. 2b) and then to $BrCO^+$ (Fig. 2c), whereas X^+ transfer occurs to limited extent in all cases. Hence, the ability of XCO^+ ions to promote ionic carbonylation of benzene, as measured relative to the competitive electron abstraction reaction, decreases in the order: $FCO^+ > ClCO^+ > BrCO^+$. To rationalize such a trend in reactivity and the ion's tendency to



Scheme 2.

undergo the competitive electron abstraction reaction, the recombination energies of the three halocarbonyl cations should be compared. The recombination energy of FCO^+ has been experimentally measured: 9.3 ± 0.1 eV [20], which makes electron abstraction from benzene (IE = 9.25 eV) slightly exothermic, but we have been unable to find reliable experimental recombination energies for $ClCO^+$ and $BrCO^+$. Owing, however, to decreasing electronegativity of the halogen atom, recombination energy is likely to decrease from FCO^+ to $ClCO^+$ and then to $BrCO^+$, thus disfavoring electron abstraction and favoring indirectly ionic carbonylation in a reactivity order reverse to that observed experimentally. A theoretical estimation using B3LYP/6-311G++(d,p) calculations gave the following adiabatic recombination energies: FCO^+ (8.47 eV), $ClCO^+$ (7.62 eV), and $BrCO^+$ (7.57 eV), and an IE for benzene of 8.08 eV. As electron abstraction from benzene still occurs for $ClCO^+$ and $BrCO^+$, conversion of translational to internal energy is likely to occur and to drive these endothermic reactions during the low-energy collisions of the ions with benzene. At the same time, however, the decreasing electronegativity of the halogen atom makes the ions less electrophilic from FCO^+ to $ClCO^+$ and then to $BrCO^+$; hence, electrophilic addition that leads to ionic carbonylation of benzene is disfavored.

2.3. Theoretical calculations

To help rationalize the reactivity trends observed in reactions of the three halocarbonyl cations with benzene, theoretical calculations at the B3LYP/6-311G++(d,p) level were performed. Fig. 3 shows a potential energy surface diagram for the reactions of the three halocarbonyl cations with benzene. For FCO^+, electrophilic addition to benzene is predicted to be highly exothermic (−65.1 kcal/mol), whereas further HF loss occurs via a favorable transition state which lies −31.6 kcal/mol in energy below the reactants and yields the final ionic carbonylation products, $PhCO^+$ and HF, in an overall −82.7 kcal/mol exothermic process. For $ClCO^+$ and $BrCO^+$, however, electrophilic addition to benzene is much less exothermic, −33.9 kcal/mol for $ClCO^+$ and −26.9 kcal/mol for $BrCO^+$, whereas further HX loss occurs via TS's which lie in energy *above the reactants* (+10.3 kcal/mol for $ClCO^+$ and +7.5 kcal/mol for $BrCO^+$), although the final ionic carbonylation products are formed in overall exothermic reactions, −54.4 kcal/mol for $ClCO^+$ and −46.5 kcal/mol for $BrCO^+$. The (slightly) endothermic access to TS's is in line therefore with the reduced ionic carbonylation reactivity of $ClCO^+$ and $BrCO^+$, with the dominance of the competitive electron abstraction, even though their recombination energies are lower than FCO^+.

2.4. Reactions of FCO^+ with thiophene, pyrrole, and furan

In electrophilic substitution reactions, which take place predominantly at the 2-position, five-membered heterocycles are much more reactive than benzene, and resemble the most reactive benzene derivatives. Fig. 4 displays the product ion mass spectra for reactions of FCO^+ (the most electrophilic halocarbonyl cation)

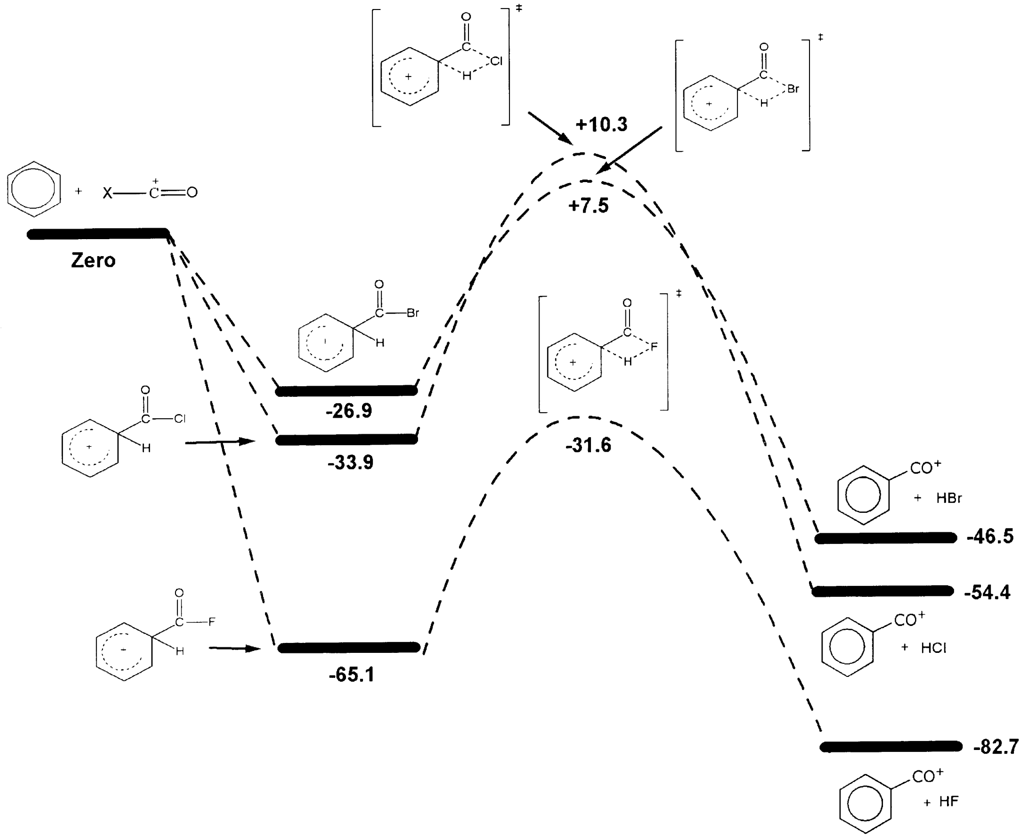


Fig. 3. B3LYP/6-311G++(d,p) potential energy surface diagram for the reactions of the halocarbonyl cations XCO^+ with benzene. Energies are given in kcal/mol. Transition states were characterized by a negative vibrational frequency: TS for FCO^+ ($-1462\,cm^{-1}$), $ClCO^+$ ($-1254\,cm^{-1}$), $BrCO^+$ ($-1195\,cm^{-1}$).

with thiophene (and 2,5-dimethylthiophene), pyrrole, and furan. The three competitive reactions observed for benzene are also observed for the three simplest five-membered heterocycles, but despite the expected higher reactivity in electrophilic ionic carbonylation, electron abstraction is the main reaction in all cases. Electron abstraction yields the respective ionized heterocycles: ionized thiophene of *m*/*z* 84 (Fig. 4a), ionized pyrrole of *m*/*z* 67 (Fig. 4c), and ionized furan of *m*/*z* 68 (Fig. 4d). For thiophene and pyrrole, ionic carbonylation also occurs to a considerable extent forming the respective $M–CO^+$ acylium ions of *m*/*z* 111 and *m*/*z* 94. For furan, ionic carbonylation that yields $M–CO^+$ of *m*/*z* 95 occurs to a rather limited extent. Similar to the reactions with benzene (Fig. 1a) and except for furan, F^+ transfer is in all cases a minor reaction that yields likely protonated 2-fluorothiophene of *m*/*z* 103, 2-fluoropyrrole of *m*/*z* 86, and 3-fluorofuran of *m*/*z* 87. Therefore, for ionic carbonylation with FCO^+, the reactivity order of the aromatic compounds tested is: benzene > thiophene > pyrrole > furan. FCO^+ also transfer F^+ to furan (Fig. 4d) rather efficiently since for the relative reaction yield, one should count not only the intact F^+ transfer product of *m*/*z* 87 but also its ionic fragment of *m*/*z* 59 formed by CO loss [19].

2.5. Alkyl substitution

Two opposing effects are expected on alkyl substitution on aromatic rings. Alkyl substitution results

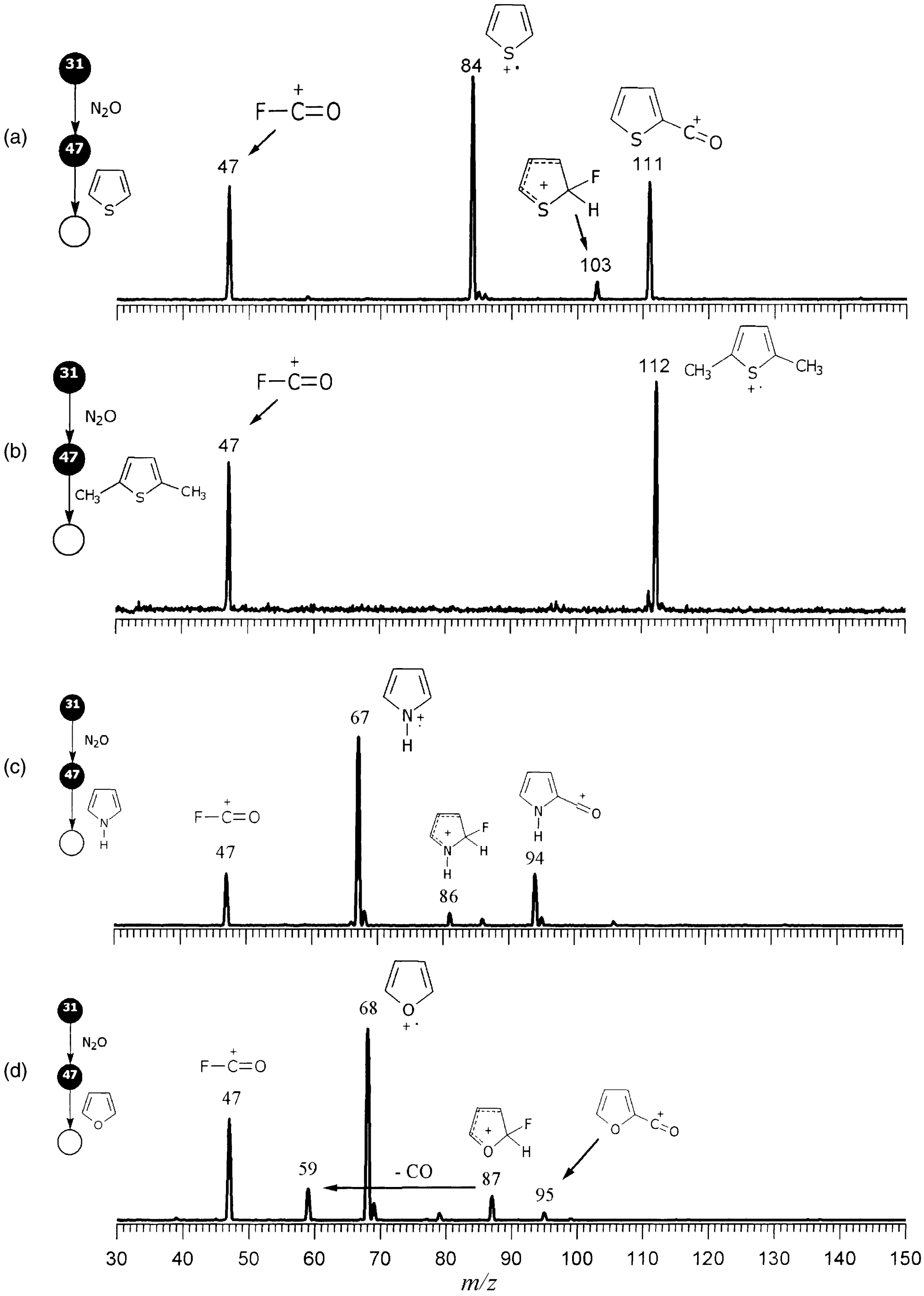


Fig. 4. Sequential product ion mass spectra for the reaction of mass-selected FCO^+ of *m/z* 47 (formed via reactions of FC^+ of *m/z* 31 with N_2O, see Fig. 1) with (a) thiophene, (b) 2,5-dimethylthiophene, (c) pyrrole, and (d) furan.

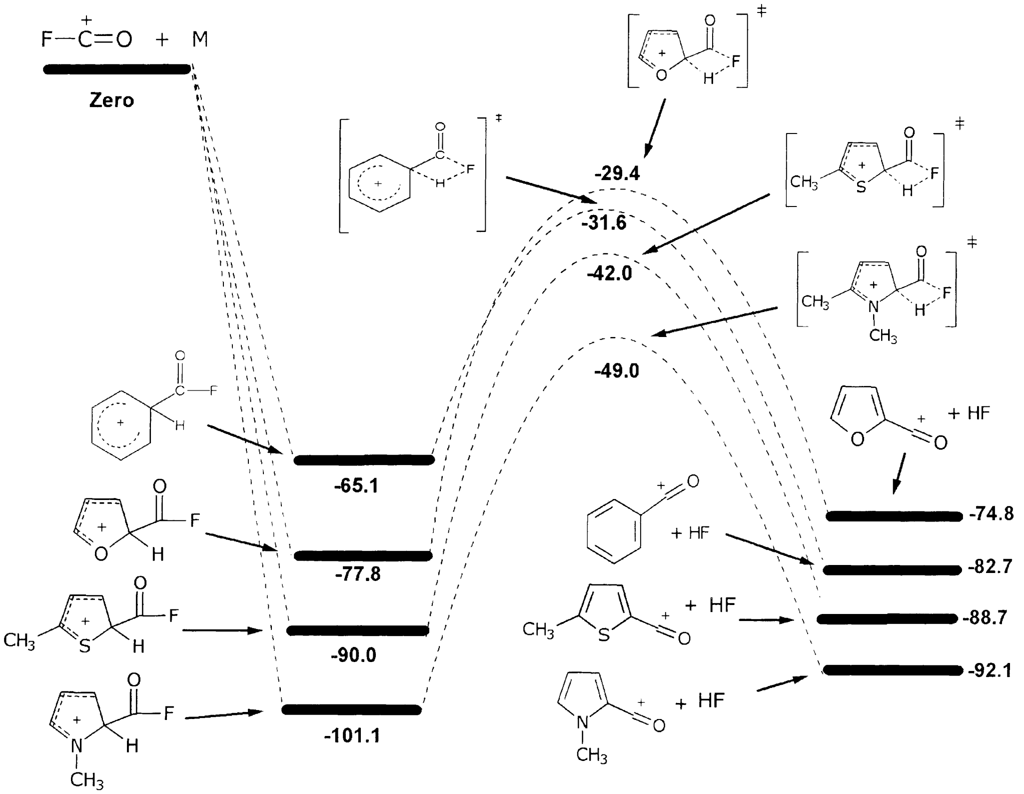
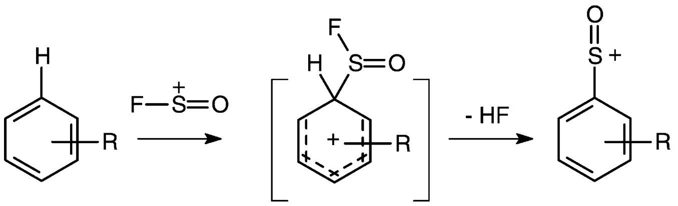


Fig. 5. B3LYP/6-3111G++(d,p) potential energy surface diagram for the reactions of FCO^+ with benzene, furan, 2-methylthiophene, and *N*-methylpyrrole. Energies are given in kcal/mol. Transition states are characterized by one negative vibrational frequency. TS for benzene ($-1462\,cm^{-1}$), furan ($-1616\,cm^{-1}$), 2-methylthiophene ($-1617\,cm^{-1}$), and *N*-methylpyrrole ($-1636\,cm^{-1}$).

both in a higher electron density of the ring π electron cloud, which should favor electrophilic ionic carbonylation, and lower IEs, which should favor the competitive electron abstraction. Overall, alkyl substitution for the five-membered heterocycles favors electron abstraction: for instance, whereas FCO^+ reacts with thiophene (8.87 eV) by ionic carbonylation to a considerable extent (Fig. 3a), it forms only a minor ionic carbonylation product with 2-methylthiophene (8.61 eV) reacting mainly by electron abstraction (spectrum not shown). Furthermore, FCO^+ reacts with 2,5-dimethylthiophene exclusively by electron abstraction (Fig. 4b). *N*-Methylpyrrole is also somewhat less reactivity than



Scheme 3.

pyrrole toward ionic carbonylation (spectrum not shown).

2.6. Theoretical calculations

The diagram of Fig. 5 compares the theoretical predictions for the reaction of FCO^+ with benzene, furan, 2-methylthiophene, and *N*-methylpyrrole. Electrophilic addition of FCO^+ to furan, 2-methylthiophene, and *N*-methylpyrrole are even more exothermic (−77.8, −90.0, and 101.1 kcal/mol, respectively) than that to benzene (−65.1), whereas further HF loss occurs in overall −74.8, −88.7, and −92.1 kcal/mol highly exothermic processes via favorable TS's lying in energy very close or below that of benzene. Therefore, when compared with benzene and when considered separately, ionic carbonylation with FCO^+ for furan, thiophene, and pyrrole are, in theory, equally or even more favorable. But the five-membered ring aromatic compounds, despite these predicitions and their high reactivity in electrophilic substitutions, fail to react efficiently by ionic carbonylation with FCO^+. Such limited reactivity is likely a result of the highly favorable competitive electron abstraction reaction owing to the relatively low IEs of the neutral reactants: benzene (9.25 eV) > furan (8.21 eV), thiophene (8.87 eV) > pyrrole (8.21 eV). Furan (8.88 eV) has the highest IE among the five-membered heterocycles tested here, very close to that of thiophene; hence its very low reactivity toward ionic carbonylation is

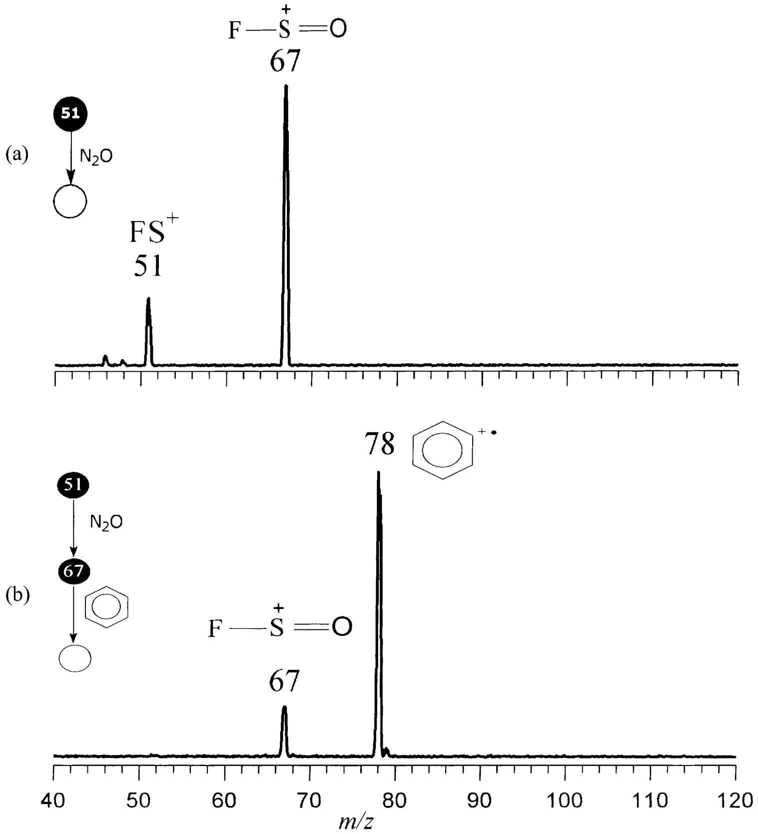


Fig. 6. (a) Product ion mass spectrum for the reaction of mass-selected FS^+ with N_2O. A novel, highly efficient, and practically exclusive O-abstraction reaction forms FSO^+ of *m*/*z* 67. (b) Sequential product ion mass spectrum for reactions of FSO^+ with benzene; the ion acts as a potent oxidizing agent and electron abstraction occurs exclusively yielding ionized benzene of *m*/*z* 78.

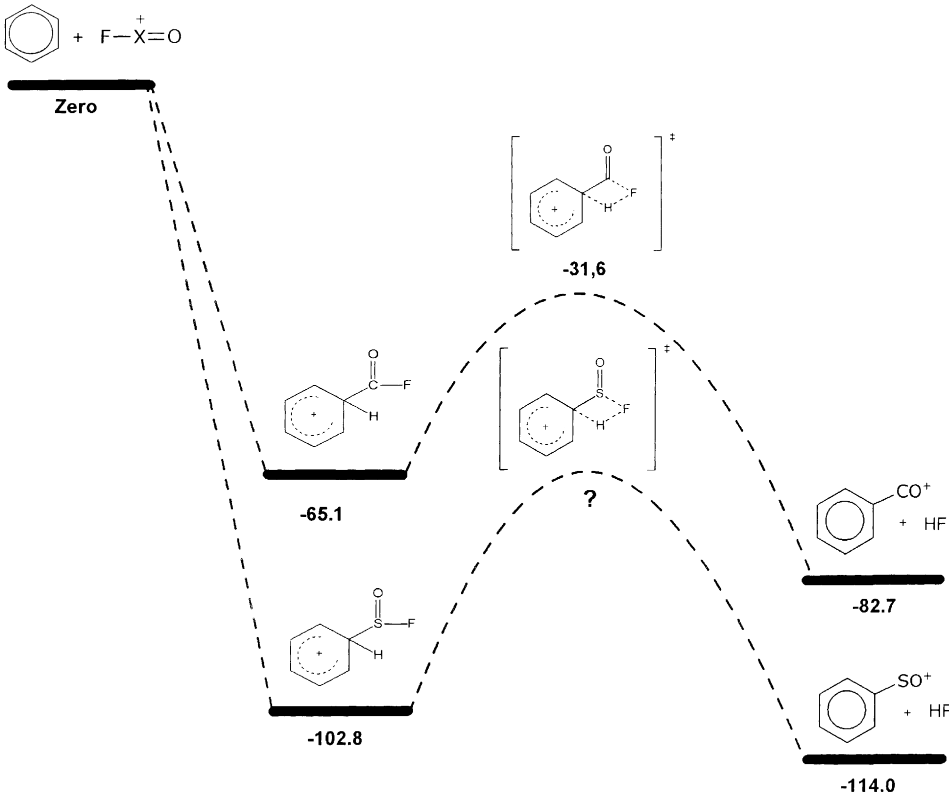


Fig. 7. B3LYP/6-3111G++(d,p) potential energy surface diagram for the reactions of FCO^+ and FSO^+ with benzene. Energies are given in kcal/mol. The TS for HF loss from the FSO^+ addition product to benzene could not be located, and its energy is roughly estimated by analogy with that for FCO^+. The transition state for FCO^+ was characterized by a negative vibrational frequency of $-1462\,cm^{-1}$.

surprising, although its relatively high tendency to react by F^+ transfer (Fig. 4d) may be further suppressing ionic carbonylation.

2.7. FSO^+

In analogy with FCO^+, the highly electrophilic fluorosulfinyl cation FSO^+ could react in principle by electrophilic addition followed by HF loss so as to result in unprecedented ionic sulfonylation of inert C–H bonds of aromatic compounds (Scheme 3). To test therefore this possibility, the fluorosulfonyl cation FSO^+ was prepared also via a novel O-abstraction reaction [13], of FS^+ from N_2O (Fig. 6).

The sequential product ion mass spectrum of Fig. 6b shows, however, that FSO^+ reacts with benzene solely by electron abstraction to form ionized benzene of *m/z* 78. Electron abstraction is also the dominant reaction of FSO^+ with furan, pyrrole, and thiophene (spectra not shown).

2.8. Theoretical calculations: FCO^+ vs. FSO^+

The diagram of Fig. 7 compares the theoretical predictions for reaction of FCO^+ and FSO^+ with benzene. When ionic sulfonylation is considered separately, FSO^+ is predicted to be a highly efficient electrophile (more so than FCO^+) and a potentially effective ionic sulfonylating agent since its electrophilic addition to benzene is considerably more exothermic (−102.8 kcal/mol) than that of FCO^+ (−65.1 kcal/mol), whereas further HF loss is overall highly exothermic by as much as −114.0 kcal/mol (−82.7 kcal/mol for FCO^+). Although at the B3LYP/6-311G++(d,p) level we have been unable to locate the TS for HF loss for FSO^+ sulfonylation, we expect by analogy with FCO^+ that such TS lies in energy considerably below the reactants (Fig. 7). Ionic sulfonylation of FSO^+ with benzene is therefore, by itself, both kinetically and thermodynamically favorable. Ionic sulfonylation is likely suppressed, however, by unfavorable competition with electron abstraction owing to the relatively high recombination energy of FSO^+. Our calculations at the B3LYP/6-311G++(d,p) level indicate the following adiabatic recombination energies: 8.47 eV for FCO^+ and 9.49 eV for FSO^+. The recombination energy of FSO^+ is therefore considerably higher than that of benzene (9.25 eV), furan (8.88 eV), thiophene (8.87 eV), and pyrrole (8.21 eV); hence FSO^+ is a potent oxidizing agent and it is not surprising that electron abstraction dominates.

3. Conclusion

As for the ability to promote C–H bond activation of aromatic compounds (M–H) via ionic (*trans*)*carbonylation*, the intrinsic reactivity order of the three gaseous halocarbonyl cations tested is: $FCO^+ > ClCO^+ > BrCO^+$. In solution, since the quite reactive $ClCO^+$ chlorocarbonyl cation is readily available [9,11], such reaction could be tested to perform similar condensed-phase ionic carbonylation of aromatic compounds. In the gas phase, O-abstraction of FC^+ from N_2O has been demonstrated to be a straightforward reaction for the preparation of the highly electrophilic fluorocarbonyl cation FCO^+, and for its on-line use in the activation of inert C–H bonds of aromatic compounds via gas-phase ionic carbonylation. Although by analogy with FCO^+, the FSO^+ fluorosulfinyl cation is predicted to function as an effective ionic sulfonylation agent, as also pointed out by B3LYP/6-311G++(d,p) calculations, FSO^+ is found to act as a potent oxidizing agent owing to its relatively high recombination energy. Therefore, in reactions of FSO^+ with aromatic compounds, electron abstraction dominates.

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