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International Journal of Mass Spectrometry 267 (2007) 81–88

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Transfer of F^+ versus fluoronium metathesis
Competing reactivities of the gaseous fluoroformyl cation

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Received 11 October 2006; received in revised form 26 January 2007; accepted 20 February 2007
Available online 23 February 2007

Abstract

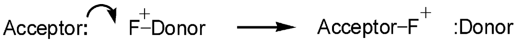
Reactions of unsaturated hydrocarbons with fluoroformyl cation (CFO^+) and of ketene and diketene with CFO^+ and CF_3^+ have been studied in a Flowing Afterglow-Selected Ion Flow Tube (FA-SIFT) in helium at room temperature. Net F^+ transfer from CFO^+ to the neutral reactants, which is observed in the majority of cases studied, can be explained in terms of formation of a covalent adduct followed by expulsion of CO. Other product ions include the products of net metathesis, $>C{=}C< + CFO^+ \rightarrow >C{=}C{=}O + {}^+F{=}C<$, which are observed in nearly half of the hydrocarbons investigated. Reaction of cyclopentadiene with CFO^+ produces *inter alia* two isomeric $C_5H_5^+$ ions, neither of which appears to have the same reactivity, as does the $C_5H_5^+$ ion produced by reaction of propargyl cation ($C_3H_3^+$) with acetylene. Given that the number of plausible $C_5H_5^+$ structures is not very great, one of the ions derived from cyclopentadiene is inferred to have the structure of the cyclopentadienyl cation. The reaction of CFO^+ with ketene gives F^+ transfer, yielding $FCH_2C{\equiv}O^+$, as the major product channel. By contrast, the reaction of CFO^+ with diketene gives no observable F^+ transfer. All observed products can be rationalized as coming from initial adduct ions.

Keywords: Ion–molecule reaction; Halonium metathesis; Cyclopentadienylium; Ketene; Trifluoromethyl cation

1. Introduction

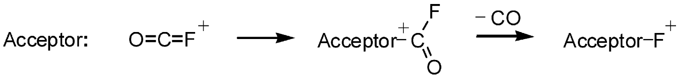
Ionized fluorine, F^+, is among the strongest Lewis acids known to chemistry. In theory, F^+ should attach exothermically to every neutral in its electronic ground state except for helium and neon [1]. In practice, isolated F^+ reacts predominantly by charge transfer [2], because of the high ionization energy of the fluorine atom (17.42 eV) [3].

Reagents that transfer an F^+ equivalent to anions have found a useful role in synthetic chemistry [4]. F^+ donation to neutrals, producing fluorinated cations, requires more vigorous electrophiles. Noble gas adducts (such as KrF^+) [5], adducts of inorganic diatomics (such as FN_2^+) [6], and coordinatively saturated perfluoro cations (such as BrF_6^+) [7] have the power to do this. In the gas phase XeF^+ passes F^+ to gaseous molecules in competition with Xe^+ transfer [8]. The F^+ adduct of acetylene subsequently acts as a Brønsted acid, except where proton transfer is endothermic (as in the reaction with ethylene), in which case it transfers F^+ [9].



(1)

The conventional view of F^+ transfer is represented by Eq. (1) [1]. A lone pair on the acceptor displaces the donor via an interchange mechanism. This paper describes the chemistry of the fluoroformyl cation, CFO^+, as an F^+ donor in competition with other reactions. The nature of this competition suggests the possibility that CFO^+ transfers F^+ via other pathways, such as ion–molecule association followed by expulsion of CO, as Eq. (2) represents. Additional alternatives can also be envisaged, as will be discussed below.



(2)

Fluoroformyl cation has proved elusive in condensed phases, where initial evidence for its observation has been reinterpreted [10]. But CFO^+ is a well-characterized species in the gas phase,

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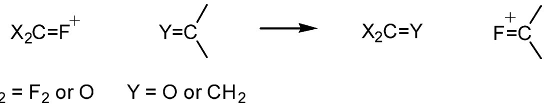
1387-3806/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.ijms.2007.02.019

where its structure confirms that it is isoelectronic with carbon dioxide [11]. Needless to say, the carbon of fluoroformyl cation exhibits strong Lewis acidity.



(3)

Fluoroformyl cation undergoes fluoronium metathesis [12,13], a reaction long known for gaseous perfluorinated alkyl cations [14–21]. Eq. (3) depicts this metathesis reaction schematically, where transposition of F^+ for oxygen or a methylene group takes place via a 4-membered cyclic transition state. The results presented below, demonstrating that fluoronium metathesis and F^+ transfer compete with one another, raise the question of whether both reactions stem from a common intermediate.

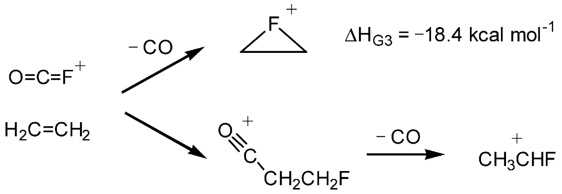
2. Experimental

Ion–molecule reactions were examined using a Flowing Afterglow-Selected Ion Flow Tube (FA-SIFT) apparatus, which has been elsewhere described [22]. The carrier gas was helium at a flow tube pressure of 0.46 Torr, and all reactions were studied at room temperature. Reported relative ion abundances >4% of the total product ionization are rounded to the nearest 5%. Reaction rate constants were extracted from observed ion abundances using published procedures [23]. CFO^+ ions (*m*/*z* 47) were generated by plasma discharge through gaseous oxalyl fluoride (FCOCOF, Oakwood Products, Inc.) in the ion source of the SIFT. Ketene was produced by pyrolysis of diketene and stored in a glass bulb at liquid nitrogen temperature when not in use. G3 calculations were performed using the GAUSSIAN03 program suite.

3. Results

Product ion distributions and rate constants for reaction of CFO^+ with various un-saturated hydrocarbons are summarized in Table 1. CFO^+ was not observed to react at all with carbon monoxide (rate constant $k < 2.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}). The extent of clustering with hydrocarbons was barely detectable, ≤2% of the ion–molecule reaction products (except for styrene). In the case of acetylene, F^+ donation dominates, forming $C_2H_2F^+$ (*m*/*z* 45), which exceeds simple adduct formation (*m*/*z* 73) by approximately 50:1. Some loss of HF from the adduct ion (*m*/*z* 53) is also seen, but only about four times as abundant as the adduct ion itself. The $C_2H_2F^+$ ion reacts with a second acetylene molecule with HF loss to give $C_4H_3^+$ (*m*/*z* 51), which then clusters with up to two more acetylene molecules.

The rate constant for CFO^+ with acetylene may be compared with that of CF_3^+ with acetylene, which proceeds entirely by adduct formation and obeys second-order kinetics with a rate constant of 5.5×10^{-10} cm^3 molecule^{-1} s^{-1} (slightly slower than reported from a previous SIFT study at 300 K (which was performed at a different carrier gas pressure) [20], but in agreement with the value from a low-energy ion beam experiment [21]). F^+ donation also dominates the reaction of CFO^+ with ethylene. Because the ion–molecule reaction product from C_2H_4 has the same nominal mass as CFO^+ itself, deuterated ethylene was examined, as Table 1 summarizes. Two stable isomers of the resulting ion have been demonstrated experimentally [24]: the 1-fluoroethyl cation and the bridged fluoriranium ion (which is 28 kcal mol^{-1} less stable [24–29] and which rearranges to the more favorable structure when collisionally activated [29]). The interchange mechanism symbolized by Eq. (1) above would predict initial formation of the latter structure, as the upper pathway in Eq. (4) represents. Alternatively, CFO^+ could add to the double bond with concomitant transfer of fluorine, as the lower pathway depicts. Subsequent loss of CO with a simultaneous 1,2-hydrogen shift would produce the more stable isomer. In contrast to ethylene, heavier alkenes yield product ions from metathesis in competition with F donation.



(4)

The thermochemistry of ion–molecule reactions can be gauged using G3 theory. The net reaction of CFO^+ with ethylene to give $CH_3CH{=}F^+$ (corresponding to the lower pathway in Eq. (4)) is calculated to be exothermic by −46.8 kcal mol^{-1}. The empirical ΔH has a large uncertainty, owing to variations in the reported heat of formation of gaseous CFO^+, for which the experimental values range from 160 ± 11 kcal mol^{-1} [30] to 178 ± 2 kcal mol^{-1} [31]. Given that the heat of formation of $CH_3CH{=}F^+$ (based on the reported heat of formation and proton affinity of vinyl fluoride [3]) is 159 kcal mol^{-1}, the thermochemistry predicted by the G3 calculation would correspond to a value of 167 kcal mol^{-1} for $\Delta_f H(CFO^+)$. As summarized for the upper pathway in Eq. (4), G3 theory predicts a substantially smaller exothermicity for the simple F^+ transfer that produces the bridged fluoriranium ion.

The reactions of other hydrocarbons with the fluoroformyl cation are treated below. In addition to the ion-–molecule chemistry of CFO^+ with unsaturated hydrocarbons, the reactions of ketene and diketene are also reported and compared with those of CF_3^+.

3.1. Propene and 2-methyl-1-butene

The major product from higher homologues of ethylene is net hydride transfer to give $[M - 1]^+$ ions or fragments resulting therefrom. In the case of propene, the F^+ adduct ion is observed at *m*/*z* 61. Previous studies of this ion suggest that it corresponds to the $(CH_3)_2CF^+$ isomer, regardless of the structure that may have been initially formed [16,17].

Propene is well known to undergo metathesis with CF_3^+ to give CH_3CHF^+, *m*/*z* 47 [22]. Our experiments give the same rate constant and product distribution for that reactant ion as

Table 1
Product ion distributions in ion–molecule reactions of CFO^+ with selected unsaturated hydrocarbons at 300 K

Hydrocarbon	MF^+	$[M-1]^+$	$(M+CFO^+)$–HF	Metathesis (*m/z*)	*k*
HC≡CH	90%		10%		9.8×10^{-10}
$D_2C{=}CD_2$	≥95%				0.7×10^{-9}
$H_2C{=}C{=}CH_2$	85%	15%	2%		1.1×10^{-9}
$CH_3CH{=}CH_2$	25%	70%	1%	[a]	1.1×10^{-9}
$HC{\equiv}CCH{=}CH_2$	60%	35%	5%	3% (*m/z* 57)	1.1×10^{-9}
$H_2C{=}CHCH{=}CH_2$	25%	25%	≤1%	50% (*m/z* 59)	1.4×10^{-9}
$H_2C{=}C(CH_3)C_2H_5$		50%		15% (*m/z* 75)[b]	0.7×10^{-9}
cyclopentadiene	80%	20%	2%	[c]	1.3×10^{-9}
$C_6H_5CH{=}CH_2$[d]			40%	10% (*m/z* 109)	1.8×10^{-9}
cis-3-hexene[d]		25%		5% (*m/z* 61)	1.6×10^{-9}
1-hexene[d]		25%			1.4×10^{-9}

Second-order rate coefficient *k* in units of $cm^3\ molecule^{-1}\ s^{-1}$. Products for which no entry is given were not detected at all. Fractional abundances >4% are rounded off to the nearest 5%.

[a] Same nominal mass as the reactant ion.

[b] The next most abundant ion, *m/z* 55, has nearly the same abundance and probably arises via loss of HF from this metathesis ion (*cf.* [15]).

[c] The mass of a metathesis ion for a cyclic alkene would be the same as that of the $MCFO^+$ ion.

[d] For other major products, see text.

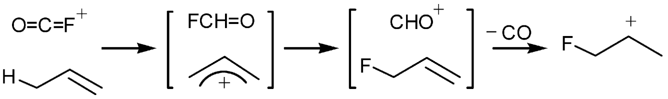
has previously been reported in the SIFT [20]. With CFO^+, the metathesis product (CH_3CHF^+), has the same nominal mass as the reactant ion, so its abundance could not be measured. However, the decay of *m/z* 47 does not deviate measurably from a single exponential, suggesting that formation of an isobaric ion cannot exceed 10% of the products. Fluoronium metathesis of an unsymmetrical alkene can, in principle, give two different metathesis ions. For propene, the lighter metathesis ion would correspond to CH_2F^+, but this product ion was not observed.

Metathesis does take place between CFO^+ and 2-methyl-1-butene to form $CH_3CH_2CFCH_3{}^+$ (*m/z* 75). It is worth noting that this ion has not been detected from the reaction of $CF_3{}^+$ with 2-butanone, because HF is expelled too rapidly to give *m/z* 55 [15]. Under the present conditions, *m/z* 75 and *m/z* 55 are formed to equal extents. No F^+ donation to the 1,1-disubstituted alkene is observed (nor in the hexenes described below), arguably because HF loss to form allylic cations is facile, accounting for the most abundant product.

3.2. cis-3-Hexene and 1-hexene

3-Hexene is the shortest symmetrically 1,2-disubstituted alkene for which the metathesis ions would not have the same nominal mass as CFO^+. A small amount of metathesis ion is seen. The principal product ion from *cis*-3-hexene, though, corresponds to loss of neutral ethylene from the $[M-1]^+$ ion, *m/z* 55 (approximately 55% of the product ion abundance). $[M-1]^+$ ions could come from F^+ donation followed by HF loss, but other mechanisms can also account for such products.

1-Hexene, by contrast, yields no detectable metathesis ion. The major product, *m/z* 55 (approximately 40% of the ion abundance) probably arises from the same series of reactions as in the case of *cis*-3-hexene. The next most abundant ion, *m/z* 69 (25%) is not observed from *cis*-3-hexene. This difference between the isomeric hexenes suggests that *m/z* 69 may result from addition of CFO^+ followed by loss of HF and propene (not necessarily in that order) to give $CH_2{=}CHCH_2CO^+$ or $CH_3CH{=}CHCO^+$.



(5)

One alternative to Eqs. (1) or (2) supposes that $[M-1]^+$ ions form prior to F^+ transfer, via hydride abstraction by CFO^+. A fraction of the product ions might persist in ion-neutral complexes with the neutral product, formyl fluoride, as Eq. (5) illustrates for an arbitrary alkene. Successive fluoride and proton transfer to the resulting allylic cation would lead to β-monofluoro cations, which are known to rearrange rapidly [16].

3.3. Allene

As Table 1 summarizes, allene reacts with CFO^+ to give a roughly 6:1 mixture of F^+ donation and $[M-1]^+$. The $[M-1]^+$ ion (*m/z* 39) reacts further, implying that it has predominantly (if not exclusively) the propargylic $HC{\equiv}CCH_2{}^+$ structure, rather than the more stable, unreactive cyclopropenium structure. No metathesis ion ($H_2C{=}CF^+$, *m/z* 45, the same structure as has been inferred for the F^+ adduct of acetylene [9]) is seen.

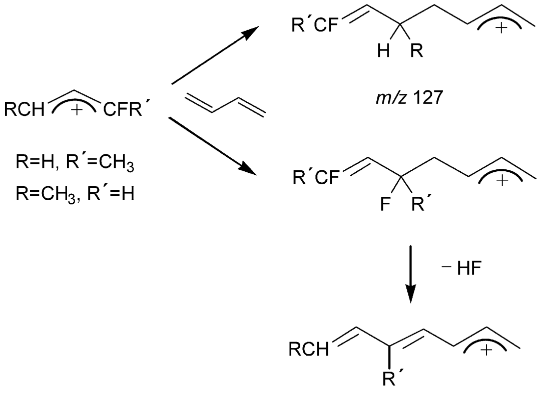
The F^+ adduct of allene (*m/z* 59) also reacts further, adding another molecule of allene (*m/z* 99), but the principal product comes from HF loss from this second adduct (*m/z* 79). The *m/z* 59 ion disappears with a rate coefficient of $5\times10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$, giving a *m/z* 79:*m/z* 99 ratio of 4:1. If electrophilic addition to allene takes place at the center, sp-hybridized carbon, then the adduct ions will enjoy allylic stabilization. Monofluoroallylic ions are known to rearrange in the gas phase [12], however, so the structure of the *m/z* 59 ion remains to be ascertained.

3.4. Vinylacetylene and 1,3-butadiene

Both of these conjugated systems exhibit competition among F^+ donation, metathesis, and net hydride abstraction. The metathesis of vinylacetylene gives a fluorinated propargylic ion, $HC{\equiv}CCHF^+$ (*m*/*z* 57) as a minor product. Of the products listed in Table 1, the $[M-1]^+$ ion (*m*/*z* 51) reacts fastest with the parent neutral. The $HC{\equiv}CCHF^+$ ion reacts nearly as rapidly, while the ion from F^+ donation (*m*/*z* 71) reacts much more slowly.

In contrast to vinylacetylene, half of the ions from reaction of 1,3-butadiene with CFO^+ come from metathesis: $CH_2{=}CHCHF^+$ (*m*/*z* 59). Comparison with the reaction of 1,3-butadiene with CF_3^+ helps interpret the subsequent chemistry of the ion–molecule reaction products. CF_3^+ reacts with butadiene with a rate coefficient of 1.1×10^{-9} cm^3 molecule^{-1} s^{-1} to yield the *m*/*z* 59 metathesis ion as approximately 80% of the ions, with virtually all of the remainder corresponding to loss of HF from the CF_3^+ adduct (*m*/*z* 103). The *m*/*z* 59 ion then goes on to react with another molecule of butadiene to give the further adduct (*m*/*z* 113) and the adduct minus HF (*m*/*z* 93) in nearly equal proportions. The same products are observed from the subsequent reaction of the *m*/*z* 59 from CFO^+ and butadiene.

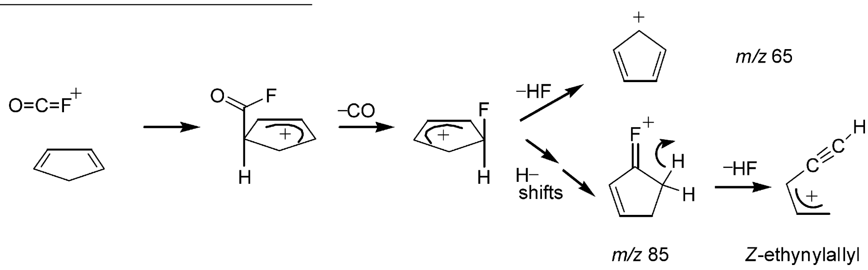
F^+ transfer from CFO^+ to butadiene gives *m*/*z* 73, which reacts with another molecule of butadiene to give a second adduct (*m*/*z* 127). The $[M-1]^+$ from butadiene also adds to a molecule of butadiene (*m*/*z* 107) at roughly the same rate. A variety of constitutional isomers can be envisaged for the *m*/*z* 73 ion. DFT calculations predict that the pair of fluoroallylic cations drawn to the left in Eq. (6) represent the most stable ones [12]. If, indeed, the F^+ adduct of butadiene possesses either of these structures (or a mixture of the two), the stability of the *m*/*z* 127 adduct of a second butadiene molecule suggests that the fluorinated end of the *m*/*z* 71 is not adding to the butadiene terminus. Otherwise, one would expect prompt loss of HF to generate a cation with extended conjugation, as the lower reaction in Eq. (6) depicts.



(6)

3.5. Cyclopentadiene

Little or no adduct ion is seen from reaction of cyclopentadiene with CFO^+. The net result of metathesis with CFO^+ is to sever a double bond, attaching CO to one sp^2 center and F^+ to the other. Metathesis with cyclopentadiene therefore yields $O{=}C{=}CHCH_2CH{=}CHCHF^+$, an isomer of the adduct; hence, an upper bound of 1:50 can be placed on the ratio of metathesis to F^+ donation. F^+ donation leads to the dominant product ion, *m*/*z* 85. Because hydrogen transpositions occur rapidly within cyclic cations, we infer that this $C_5H_6F^+$ has the same structure as the ion produced by metathesis of 2-cyclopentenone with CF_3^+ [13], drawn in the lower pathway of Eq. (7). DFT calculations predict that ion to correspond to the minimum energy for that formula [13].

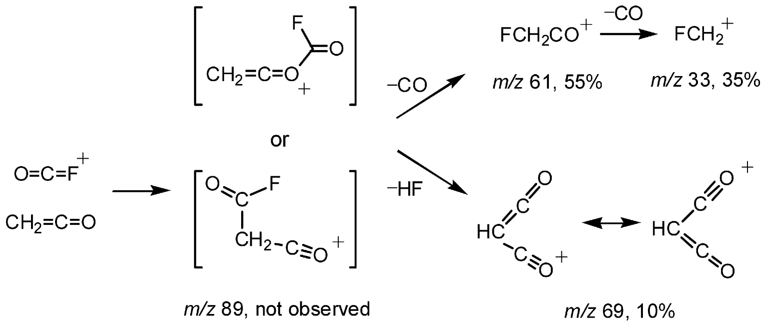


(7)

The $[M-1]^+$ ion from cyclopentadiene, *m*/*z* 65, can arise from $C_5H_6F^+$ via either of two pathways for HF expulsion, as Eq. (7) depicts. A 1,2-elimination would give the cyclopentadienyl cation, as the upper pathway represents. Alternatively, hydrogen shift can lead to the fluoroallylic *m*/*z* 85 ion drawn in Eq. (7) (the global minimum on the $C_5H_6F^+$ potential energy surface [13]), which can then eliminate HF with ring opening to give the *Z*-ethynylallyl cation.

In a separate series of experiments, $C_5H_6F^+$ was generated using CF_4 plus 2-cyclopentenone [13] in the afterglow source and injected into the SIFT. Collisions with the flow gas cause some of the ions to lose HF. The 7.9:1 mixture of $C_5H_6F^+$ and $C_5H_5^+$ was then reacted with allene in the SIFT. The former ion reacts slowly ($k < 10^{-12}$ cm^3 molecule^{-1} s^{-1}), while the latter displayed biexponential decay, producing an adduct of $C_5H_5^+$ with allene, $C_8H_9^+$ (*m*/*z* 105). Approximately 55% of the $C_5H_5^+$ reacted with a rate coefficient of 6×10^{-10} cm^3 molecule^{-1} s^{-1}, while the remaining 45% reacted more slowly by a factor of 100. The $C_5H_6F^+$ ion also reacts with allene to give some adduct ion ($C_8H_{10}F^+$, *m*/*z* 125), as well as fragments from loss of C_2H_2 ($C_6H_8F^+$, *m*/*z* 99) or C_2H_4 ($C_6H_6F^+$, *m*/*z* 97), in approximately a 15:25:60 ratio.

In another series of experiments, 2-cyclopentenone was reacted with CFO^+ in the afterglow source, and the resulting $C_5H_5^+$ ion injected into the SIFT. Some $HC{\equiv}CCH_2^+$ was formed by collision, which is then observed to cluster rapidly with up to five molecules of acetylene, consistent with previous reports [32–34]. The $HC{\equiv}CCH_2^+$ ion also clusters with benzene, as do its adducts with one or two molecules of acetylene. In order to examine $C_5H_5^+$ formed from the 5-membered ring, the mixture of $C_3H_3^+$ and $C_5H_5^+$ (approximately a 4:6



(8)

ratio) was reacted with C_2D_2, so as to permit differentiation of the injected $C_5H_5^+$ from $C_5H_3D_2^+$ formed by addition of $C_3H_3^+$. The $C_5H_5^+$ reacted very slowly, with a rate coefficient <2 × 10^{-12} cm^3 molecule^{-1} s^{-1}.

These experiments suggest there are at least three $C_5H_5^+$ isomers: the adduct of $C_3H_3^+$ with acetylene (which reacts rapidly with acetylene) and two other isomers produced by HF elimination from $C_5H_6F^+$ (neither of which appears to react with acetylene, but one of which reacts rapidly with allene). It is tempting to infer that the two latter isomers are those illustrated in Eq. (7), *viz.* cyclopentadienyl cation and ethynylallyl cation. G3 calculations predict singlet cyclopentadienyl cation to be 8.6 kcal mol^{-1} more stable than the most stable ethynylallyl cation. G3 calculations place the triplet state of cyclopentadienyl cation 5.6 kcal mol^{-1} lower than the singlet, although it is not easy to see how the triplet could be produced via Eq. (7). The lowest energy $C_5H_5^+$ structure is vinylcyclopropenyl cation, which G3 calculations predict to be 0.3 kcal mol^{-1} more stable than triplet cyclopentadienyl cation.

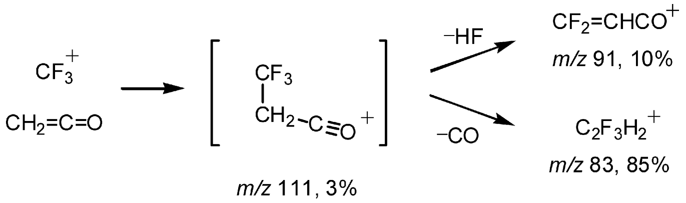
3.6. Styrene

Styrene exhibits a small amount of adduct ion (*m*/z 151, approximately 4% of the ion–molecule reaction products), as well as some metathesis product ($C_6H_5CHF^+$, *m*/*z* 109). The major product corresponds to loss of two molecules of acetylene from the F^+ adduct (*m*/*z* 71, approximately 50% of the ionic products from CFO^+). This *m*/*z* 71 ion may have the same structure as the F^+ adduct of vinylacetylene. In any event, the vapor pressure of styrene was too low to examine the subsequent reactions of its ionic products with the parent neutral.

3.7. Ketene

Ketene can react by metathesis at either the methylene end or the carbonyl. Metathesis at the carbonyl would produce $CH_2{=}CF^+$ (*m*/*z* 45), which is not observed. Metathesis at the methylene end would yield a CFO^+ ion containing the carbon and oxygen from ketene, a degenerate, thermoneutral reaction that cannot be detected without isotopic labelling. Since the disappearance of *m*/*z* 47 in the presence of ketene occurs more slowly than the reactions in Table 1, $k = 7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, it seems possible that the degenerate reaction might be taking place to some extent. However, as noted below, very little (if any) *m*/*z* 47 is produced by the reaction of CF_3^+ with ketene.

Eq. (8) illustrates the reactions observed between CFO^+ and ketene. No simple adduct ion (*m*/*z* 89) is detected, but protonated carbon suboxide (*m*/*z* 69) is seen, which corresponds to loss of HF from the CFO^+ adduct. More than half the product comes from F^+ transfer (CH_2FCO^+, *m*/*z* 61), while the remainder (CH_2F^+, *m*/*z* 33) can be explained as coming from loss of CO from the F^+ adduct. The CH_2FCO^+ reacts with ketene to form, *inter alia*, the adduct (*m*/z 103). Further reaction of CH_2F^+ with ketene would be expected to produce $C_2H_4F^+$, which is isobaric with the *m*/*z* 47 reactant ion. Thus, it is possible that the measured rate constant given above has a systematic error due to production of *m*/*z* 47 in competition with the disappearance of CFO^+.

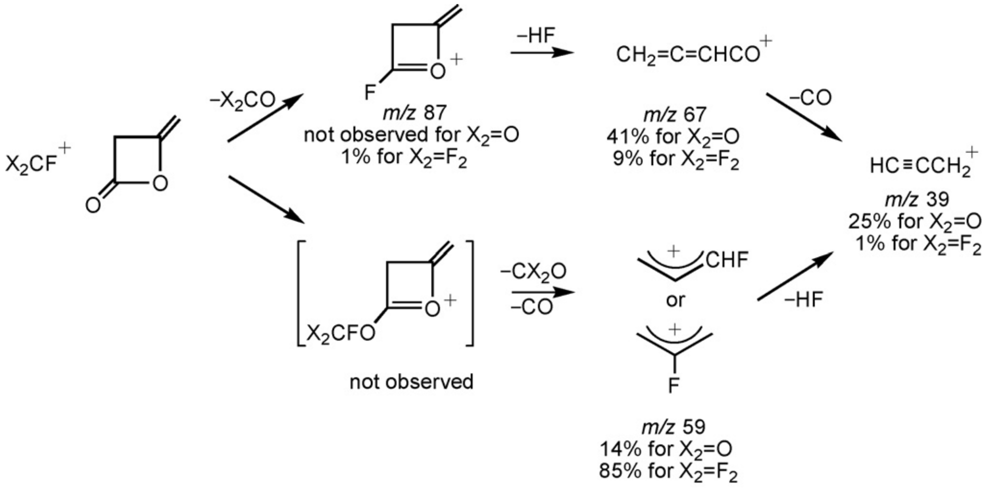


(9)

Comparison with the reaction of CF_3^+ and ketene is instructive. The rate constant is nearly the same as for CFO^+ with, but here only a small amount of the simple adduct, $CF_3CH_2CO^+$ (*m*/*z* 111) is formed, as Eq. (9) portrays. The major product ion, *m*/*z* 83, corresponds to the loss of CO from this adduct. As predicted theoretically [35], the nascent $CF_3CH_2^+$ must rearrange via unimolecular fluorine shift, since *m*/*z* 83 reacts very rapidly with ketene via proton transfer to form acetyl cation, CH_3CO^+ (*m*/*z* 43). Loss of HF from $CF_3CH_2CO^+$ (*m*/*z* 91) constitutes the remainder of the product ions. No metathesis of F^+ for O can be detected, and the level of metathesis of F^+ for CH_2 (*m*/*z* 47) constitutes ≤0.25% of the product.

3.8. Diketene

CFO^+ reacts with diketene close to the collision limit, with a rate coefficient $k = 2.7 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. No adduct or metathesis ions are seen. Nevertheless, the two predominant products can be accounted for by intermediacy of the ion from fluoronium metathesis of the carbonyl oxygen, followed by loss of HF, as illustrated in Scheme 1. The CFO^+ adduct of a carbonyl is the precursor to metathesis, but that ion (*m*/*z* 131) is not detected. However, fluoroallyl ions (*m*/*z* 59) are seen, whose formation can be rationalized in terms of the alternative decomposition pathway drawn at the bottom of Scheme 1.



Scheme 1.

The hypothesis that metathesis takes place finds confirmation in the reaction of diketene with CF_3^+, which goes with a rate coefficient $k = 3.4 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. Here a small amount of F^+-for-O metathesis product is detected (*m/z* 87), in addition the $C_4H_3O^+$ ion from its loss of HF (*m/z* 67). Apparently the $C_4H_3O^+$ is not produced with as much internal energy as the ion from CFO^+, since much less $C_3H_3^+$ is observed. The major ion (*m/z* 59) comes from expulsion of CF_2O and CO from the CF_3^+ adduct of the carbonyl. Expulsion of HF from this ion could provide an alternative pathway to the propargyl ion, as Scheme 1 summarizes.

4. Discussion

In solution, F^+ donation takes place as Eq. (1) represents [1]. It is hard to imagine any alternative pathway by which a noble gas adduct or a coordinatively saturated perfluoro cation might transfer F^+, except via nucleophilic attack at fluorine. The fluoroformyl cation, by contrast, is coordinatively unsaturated, and it can donate F^+ by first forming a covalent adduct at carbon, as Eq. (2) represents. The upper part of Eq. (7) above illustrates that pathway for cyclopentadiene. This hypothesis offers a new mechanism for F^+ donation.

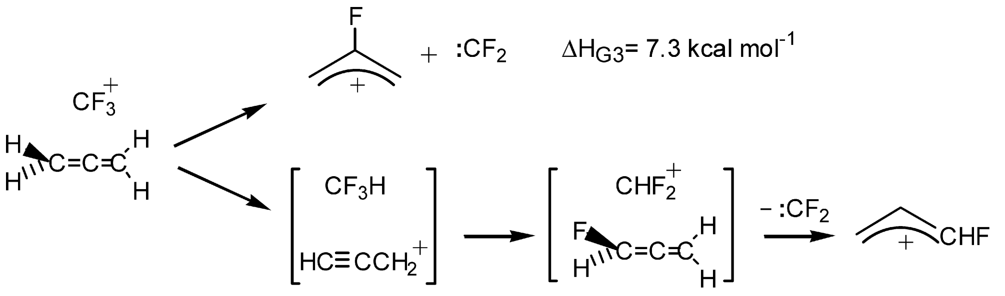
$$O=C=F^+ + N_2 \xrightarrow{\Delta H_{G3}=91\,\text{kcal mol}^{-1}} F=N=N^+ + CO \qquad (10)$$

The experimental evidence for this mechanism is buttressed by G3 calculations. First of all, carbon monoxide binds F^+ much more tightly than does molecular nitrogen. The G3 endothermicity of the transfer from CO to N_2 (shown in Eq (10)), predicts the F^+ affinity of CO to be ≥230 kcal mol^{-1}. In other words, the two isoelectronic, linear triatomic ions in Eq (10) should have different chemical properties. FN_2^+ donates F^+ to atomic xenon[9] and fluorinates methane in solution [36], while CFO^+ ought to be completely inert towards those acceptors.

$$O=C=F^+ + CH_3CO^+ \xrightarrow{\Delta H_{G3}=59\,\text{kcal mol}^{-1}} O=CFCO^+ + CH_3^+ \qquad (11)$$

CFO^+ is a strong electrophile. G3 calculations on the hypothetical transfer of carbon monoxide between two cations shown in Eq. (11) predict a heat of formation of $O{=}CFCO^+$ that implies the attachment of CFO^+ to carbon monoxide should be exothermic by 19 kcal mol^{-1}. Failure to observe clustering of CFO^+ with CO under our SIFT conditions therefore suggests that, if adduct ions form between CFO^+ and other neutrals, they must then undergo unimolecular rearrangement in order for ion–molecule reaction products to be seen.

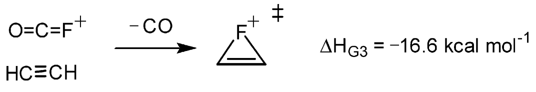
Not long ago, Tsuji et al. reported that gaseous CF_3^+ donates F^+ to allene [37]. They proposed that this reaction takes place via formation of an adduct ion, followed by expulsion of difluorocarbene. In part, their rationale derived from the fact that the major competing reaction is loss of HF from the CF_3^+ adduct ion. Since difluorocarbene is a high energy species, net F^+ transfer from CF_3^+ to a neutral molecule requires a very good acceptor.



(12)

Thermochemical arguments support the contention that CF_3^+ does not donate F^+ via the mechanism of Eq. (1). If that were the case, then transfer would have to occur either to one of the terminal carbons (forming a vinyl cation) or else to the center carbon (forming the more stable allylic cation). The latter transfer is depicted in the upper pathway in Eq. (12). G3 calculations predict this reaction, which produces the 2-fluoroallyl cation, to be significantly endothermic, as summarized for that pathway.

In order for CF_3^+ to donate F^+ to allene exothermically, the lowest energy structures must be formed (1-fluoroallyl cations, as depicted in the lower pathway of Eq. (12)). This reaction necessitates hydrogen rearrangement, either by means of a covalent adduct (as proposed by Tsuji et al. [37]) or via a succession of ion-neutral complexes, as the lower pathway of Eq. (12) represents. While the available experimental data do not differentiate between these alternative mechanisms, the fact that CF_3^+ is also reported to donate F^+ to propyne [37] is consistent with the same sequence of ion-neutral complexes as is drawn above for the reaction of allene.

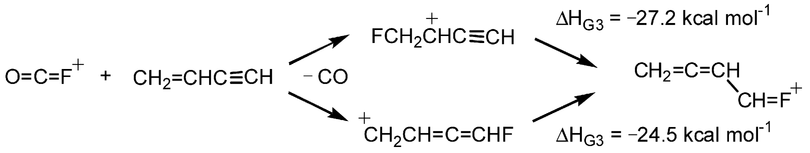


(13)

CFO^+ releases carbon monoxide when it transfers F^+. From a thermochemical standpoint, it can therefore react with a much greater variety of acceptors than can CF_3^+. For instance, as Eq. (13) summarizes, formation of the bridged fluorirenium ion from acetylene is calculated to be exothermic, even though that bridged ion represents a transition state ($CH_2{=}C{=}F^+$ being the only stable isomer). If formed, the bridged ion must rearrange to the stable isomer, which is more stable by 40 kcal mol^{-1}, according to G3 calculations.

Three mechanisms can therefore be envisaged for F^+ transfer from CFO^+: interchange (Eq. (1)), adduct formation followed by rearrangement (Eq. (2)), and hydride abstraction followed by a sequence of ion-neutral complexes (as exemplified by Eq. (5)). The experimental evidence for Eq. (2) comes from the competition between F^+ transfer and metathesis in the C_4 hydrocarbons summarized in Table 1. For reactants with fewer carbons, F^+ transfer takes place, but no metathesis is seen. For reactants with ≥ 5 carbons, metathesis is observed, but no F^+ transfer. We ascribe the failure to detect F^+ transfer to these heavier reactants to the instability of the adducts with respect to unimolecular elimination of HF.

Vinylacetylene is the lightest hydrocarbon for which we observe metathesis in competition with F^+ transfer. If one assumes that rearrangement cannot occur concertedly with the interchange mechanism of Eq. (1), then F^+ must be donated to one end or the other, as represented in Eq. (14). Uggerud [38] has performed calculations showing that the lowest energy constitutional isomer on the $C_4H_4F^+$ potential energy surface corresponds to a fluorinated carbocation conjugated with an allenyl group, drawn to the right in Eq. (14). This ion (in its more favored *E*-geometry) could conceivably be formed by exothermic hydrogen shifts following F^+ transfer, as Eq. (14) portrays.



(14)

Alternatively, hydride abstraction mechanism followed by interconverting ion-neutral complexes (as exemplified by Eq. (5)) is also possible, given that $[M-1]^+$ ions are prominent ion-molecule reaction products. However, the occurrence of metathesis suggests a more economical option, namely that a single adduct ion accounts for all of the observed product ions.

The hydride abstraction mechanism pathway can be ruled out in at least one case. Thermochemical estimates show that this mechanism cannot be operating in the case of ketene, since the $[M-1]^+$ ion, HC_2O^+, has a very high heat of formation [39]. HC_2O^+ is calculated to exist as a ground state triplet [40], and G3 calculations gauge the triplet-singlet gap to be 20.3 kcal. G3 theory predicts the endothermicity of hydride abstraction from ketene by CFO^+ to be 39.3 kcal mol^{-1}, so great that it is hard to imagine that the energy liberated by a noncovalent ion–molecule association could be large enough to overcome the thermochemical barrier. The predominance of transfer to ketene must therefore be ascribed to interchange or decomposition of an adduct ion (or both). Since, as Eq. (8) summarizes, a covalent adduct is a necessary precursor to protonated carbon suboxide, F^+ transfer via an intermediate adduct ion represents a plausible mechanism.

5. Conclusions

Transfer of F^+ via a covalent adduct ion, Eq. (2), accounts for the diversity of products seen when the fluoroformyl cation reacts with a variety of unsaturated molecules. This mechanism posits a common intermediate, the adduct with CFO^+, for two competing pathways, fluoronium metathesis versus F^+ transfer. Both of these reaction pathways are observed, for instance, when CFO^+ reacts with vinylacetylene or 1,3-butadiene. CFO^+ adduct ions with unsaturated hydrocarbons cannot, in many cases, be observed to any great extent under the reaction conditions (except in the case of styrene), because their formation is highly exothermic and they have low barriers for expulsion of HF, CO, or ketene. The hypothesis of an intermediate adduct ion unifies a large number of otherwise disparate experimental data.

Acknowledgement

This work was supported by NSF grant CHE0306515. P.F.W. acknowledges the award of a Marsden Postdoctoral Fellowship.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2007.02.019.

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