Ionic Fluorination of Carbon Monoxide as a Route to Gas-Phase Carbonylation of Inert C–H and N–H Bonds

Felice Grandinetti,* Federico Pepi, and Andreina Ricci

Abstract: Gaseous FCO^+ ions from the ionization of mixtures of nitrogen trifluoride and carbon monoxide execute selective and efficient CO-functionalization of the C–H bonds of benzene and toluene and of the N–H bond of ammonia. The occurrence of these carbonylation reactions has been unambiguously ascertained by Fourier-transform ion cyclotron resonance (FT-ICR) spectrometry, and the details of the structure and the mechanism of formation of the precursor FCO^+ ions have been investigated. FT-ICR experiments show that these ions, structurally assigned as $F-C-O^+$ by collisionally activated dissociation (CAD) spectrometry, arise from the reaction of $CO^{\cdot+}$ with NF_3 and of NF_2^+ with CO. Combining the latter F^+ transfer with the independently observed fluoride-ion abstraction by FCO^+ from NF_3 results in a catalytic cycle in which gaseous NF_2^+ ions promote the conversion of carbon monoxide into carbonic difluoride, F_2CO, with nitrogen trifluoride as the source of F.

Keywords
carbon monoxide · carbonylations · fluorine compounds · gas-phase chemistry

Introduction

The chemical activation of unreactive molecules and their conversion into useful products is still a challenging problem facing chemists. In particular, selective functionalization of inert C–C, C–H, or N–H bonds with species such as oxygen, carbon monoxide, carbon dioxide, and sulphur dioxide is legitimately regarded as an ultimate goal in the chemical activation of such small gaseous molecules. The high interest in this coupled activation is not focused exclusively on reactions occurring in solution or at interfaces. Rather, the attractive opportunity of investigating intrinsic aspects of reactivity in the absence of the complicating effects of ligands, counterions, solvation, etc., stimulates the design of simple gas-phase model reactions, which can contribute substantially to the comprehension of the fundamental aspects of this chemistry, and, in addition, may provide suggestions for novel reactions in solution. Thus, the coupled activation of molecular oxygen and olefinic C–C and C–H bonds by gaseous transition-metal cations has recently been reported,[1] and the formation of stable adducts of CO_2 with naked cations such as V^+,[2] Mg^+,[3] and Fe^+[4] is regarded with considerable interest with respect to the possible coupled activation of carbon dioxide and hydrocarbons.

One of the general points emerging from our recent investigation of the gas-phase chemistry of simple fluorinated cations such as CF_3^+,[5] SiF_3^+,[6] and NF_2^+[7] by Fourier transform ion cyclotron resonance (FT-ICR) spectrometry[8] is the ability of these ions to undergo efficient HF elimination following addition to various hydrogenated molecules including water, alcohols, amines, and aromatic substrates, with resultant formation of ionic fragments which incorporate the CF_2, SiF_2, or NF moieties. The main limitation to the actual occurrence of such addition–elimination reactions comes from the recombination energy of the fluorinated ion, which has to be low enough to prevent facile electron capture from the nucleophile. Generalization from these findings suggests the possibility of ionic fluorination of a small gaseous molecule, M, as a conceivable route to the functionalization of n-type or p-type nucleophiles, NuH, according to the reaction sequence of Equations (1 a,b).

$$M \xrightarrow{\text{Ionic fluorination}} FM^+ \qquad (1a)$$

$$FM^+ + NuH \longrightarrow Nu{-}M^+ + HF \qquad (1b)$$

Gaseous FM^+ ions ($M = CO, CO_2, SO_2$) could in principle be obtained from the ionization of appropriate neutral precursors; this would permit investigation of reaction (1 b). However, in this paper, we wish to discuss the route to the coupled activation of M and NuH based on the ionic fluorination of M. The details of the coupled activation of carbon monoxide and unreactive molecules such as benzene, toluene, and ammonia, based on the unprecedented gas-phase ionic fluorination of carbon monoxide, are described here. The latter process, conveniently performed under mass spectrometric conditions with nitrogen trifluoride as the source of F, adds to the number of strategies so far developed for promoting the extensively investigated carbonylation reaction.[9]

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Results and Discussion

Ionic fluorination of carbon monoxide—preparation of gaseous FCO^+ ions: Although gaseous FCO^+ ions are detected in abundance from the electron-impact ionization of suitable neutral precursors such as HFCO,[10a] F_2CO,[10b] and ClFCO,[10b] the gas-phase ionic fluorination of carbon monoxide is still unreported. We found that the latter process can be successfully accomplished under mass spectrometric conditions with nitrogen trifluoride as the source of F. Gaseous FCO^+ ions are detected in abundance from the ionization of mixtures of NF_3 and CO introduced into the external source of the FT-ICR (p ca. 10^{-4} mbar) at nominal ratios ranging from approximately 1:1 to approximately 5:1. A representative mass spectrum is shown in Figure 1.

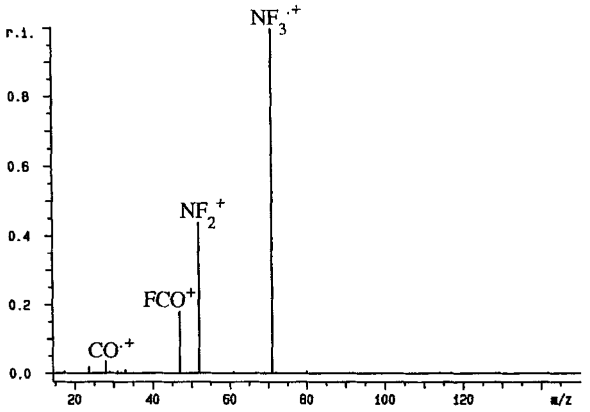


Fig. 1. Mass spectrum (70 eV) of a NF_3/CO gaseous mixture (p ca. 10^{-4} mbar; approximate ratio 5:1).

Besides the $NF_3^{\cdot+}$ ($m/z = 71$), NF_2^+ ($m/z = 52$), and $CO^{\cdot+}$ ($m/z = 28$) ions arising from the ionization of NF_3[11] and CO, only one additional intense peak was detected, at $m/z = 47$, and unambiguously assigned as FCO^+ by exact mass measurements. The relative intensity of this ion was found to be slightly sensitive to the composition of the gaseous mixture, increasing from about 20% to about 30% of the base peak when the NF_3/CO ratio was changed from approximately 5:1 to approximately 1:1.

Structure of the gaseous FCO^+ ions: Before investigating the ionic routes responsible for the formation of the gaseous FCO^+ ions, we addressed the question of their structure.[12] In fact, irrespective of its detailed mechanism (vide infra), the ionic fluorination of carbon monoxide could lead, at least in principle, to a pure $F(CO)^+$ isomer or to a mixture of $F{-}CO^+$ and $F{-}OC^+$. Tentative evidence for the exclusive formation of the fluoroformyl cation, $F{-}CO^+$, comes from the results of ab initio calculations. The structure of the two conceivable $F(CO)^+$ isomers has been optimized at the MP2(FULL)/6-31G* level of theory and an accurate evaluation of their relative stability has been performed by means of the recently developed Gaussian-2 (G2) procedure.[13] Whereas the formal attachment of F^+ to the carbon atom of CO leads to the linear $F{-}C{-}O^+$ isomer (r(C–F) = 1.218 Å, r(C–O) = 1.140 Å), previously investigated[14] by various theoretical methods, the $F{-}O{-}C^+$ isomer possesses a bent structure (r(O–F) = 1.401 Å, r(C–O) = 1.213 Å, $\alpha = 129.2°$), and, at the G2 level of theory, the energy difference with $F{-}CO^+$ is calculated to be as large as 157.1 kcal mol^{-1}.[15] Assuming that the quoted enthalpy of formation of $F(CO)^+$, so far reported as 160 ± 11 kcal mol^{-1} from the adiabatic ionization potential of the $FCO^{\cdot}$ radical[16] and recently reevaluated as 178.1 ± 2.3 kcal mol^{-1} from the energy of formation from F_2CO,[17] refers to the more stable isomer, a *theoretical* enthalpy of formation of 335.2 kcal mol^{-1} is obtained for the $F{-}OC^+$ isomer. The exclusive formation of $F{-}CO^+$ from the ionic fluorination of carbon monoxide is more convincingly supported by structurally diagnostic mass spectrometric experiments. The CAD[18] spectrum of the FCO^+ ions obtained from the ionization of an approximately 3:1 mixture of nitrogen trifluoride and carbon monoxide introduced into the chemical ionization source (p ca. 10^{-1} mbar) of the ZAB-2F spectrometer is shown in Figure 2. Consistent with a $F{-}C{-}O^+$ connectivity, it shows two intense CF^+ ($m/z = 31$; 61.1%) and $CO^{\cdot+}$ ($m/z = 28$; 34.3%) fragments and a much less intense contribution from $C^{\cdot+}$ ($m/z = 12$; 2.3%). In addition, the FCO^{2+} signal ($m/z = 23.5$; 2.3%) arising from charge-stripping is clearly visible. Moreover, an indistinguishable fragmentation pattern (similarity index[19] 13.3) is obtained from model ions, most likely characterized by the $F{-}CO^+$ connectivity, obtained from the electron impact (70 eV) ionization of acetyl fluoride, CH_3COF. The structural equivalence of the two ionic populations is independently supported by their identical reactivity. Irrespective of their formation process, thermalized FCO^+ ions from the external source of the FT-ICR undergo the same reaction sequences (vide infra) when allowed to react with various nucleophiles, introduced in the resonance cell at typical pressures of around 10^{-8}–10^{-7} mbar. Finally, our conclusion that fluoroformyl cations exclusively are formed from the gas-phase ionic fluorination of carbon monoxide is fully consistent with previous results from liquid-nitrogen-cooled discharge experiments of mixtures of F_2 and CO.[14d] The observed ions were assigned as $F{-}CO^+$ by their millimeter-wave spectrum, the details of which have been interpreted with the aid of high-level ab initio calculations.

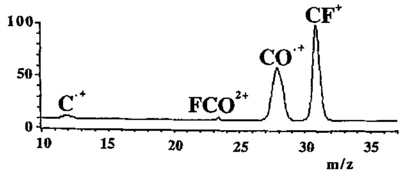


Fig. 2. CAD spectrum of the FCO^+ ions obtained from the ionization of a NF_3/CO gaseous mixture (≈3:1; p ca. 10^{-1} mbar).

Mechanism of formation of the gaseous FCO^+ ions: The detailed ion–molecule reactions responsible for the formation of FCO^+ from the ionization of the NF_3/CO mixtures have been subsequently investigated. In particular, the conceivable precursor ions $CO^{\cdot+}$, $NF_3^{\cdot+}$ and NF_2^+, produced in the external source of the FT-ICR by the electron-impact (70 eV) ionization of carbon monoxide and nitrogen trifluoride, were allowed to react with NF_3 or CO, introduced into the resonance cell at typical pressures of around 10^{-8}–10^{-7} mbar. A representative plot of the time dependence of the abundances of all the ionic species formed from thermalized $CO^{\cdot+}$ ions reacting with NF_3 is shown in Figure 3. The intensity of the $CO^{\cdot+}$ signal decreases exponentially (correlation coefficient 1.0) and, most significantly, FCO^+ is formed, together with $NF_3^{\cdot+}$ and NF_2^+, according to the branching ratio depicted in Scheme 1. From the average of different independent runs, the overall rate constant $k_2 = k_{2a} + k_{2b} + k_{2c}$ is evaluated as 8.0×10^{-10} cm^3 molecule^{-1} s^{-1}, which leads to $k_{2a} = 4.7 \times 10^{-10}$, $k_{2b} = 2.1 \times 10^{-10}$, and $k_{2c} = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. From the collision rate constant of

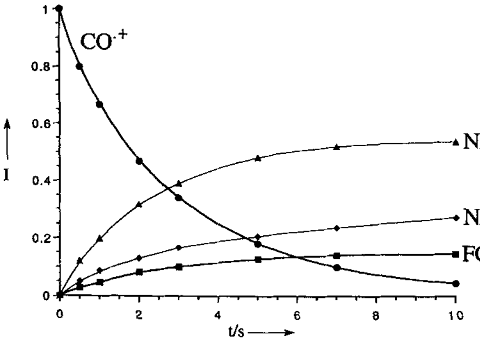
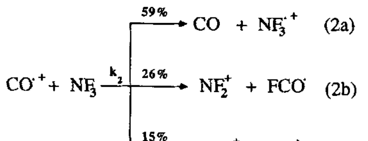


Fig. 3. Time dependence of the relative intensities (I) of the ions observed when thermalized $CO^{\cdot+}$ ions are allowed to react with NF_3 ($p = 1.6 \times 10^{-8}$ mbar).



Scheme 1.

$CO^{\cdot+}$ with NF_3, calculated as 1.01×10^{-9} cm^3 molecule^{-1} s^{-1} by the average dipole orientation (ADO) theory,[20] the efficiency of the overall decay of $CO^{\cdot+}$ is 0.79 from the k_2/k_2(ADO) ratio, which provides a reasonable explanation for the low intensity of the $CO^{\cdot+}$ signal observed in the mass spectrum of Figure 1. In addition, the efficiencies of reactions (2a–c) are evaluated as k_{2a}/k_2(ADO) = 0.47, k_{2b}/k_2(ADO) = 0.21 and k_{2c}/k_2(ADO) = 0.11, respectively. The high efficiency of the electron transfer reaction (2a) is consistent with its exothermicity, evaluated as $\Delta H°(2a) = -24.1$ kcal mol^{-1}.[21] In addition, the recombination energy of CO, 14.0 eV, is higher than the potential of formation of NF_2^+ from NF_3, 13.71 eV,[22] which makes accessible the exothermic fluoride ion abstraction (2b), $\Delta H°(2b) = -27$ kcal mol^{-1}. Although the actual formation of the $FCO^{\cdot}$ radical from (2b) cannot be directly ascertained, the reaction would result as slightly endothermic ($\Delta H°(2b) = +1.9$ kcal mol^{-1}) if formation of $F^{\cdot}$ and CO were assumed, and should not occur to any significant extent under our FT-ICR conditions. The fluorine abstraction reaction (2c) leads to the formation of FCO^+ from the reaction of $CO^{\cdot+}$ with nitrogen trifluoride. Based on the thermochemical data discussed in the previous paragraph, this process results as exothermic ($\Delta H°(2c) = -79.6$ kcal mol^{-1}) only if formation of $F{-}CO^+$ is assumed, which is fully consistent with the conclusions from the structurally diagnostic experiments. The observation of (2c) is of interest if compared with the previously reported reactions of $CO^{\cdot+}$ with other conceivable fluorinating agents, including carbon tetrafluoride and sulphur hexafluoride.[23] The $CO^{\cdot+}$ ion reacted with CF_4 and SF_6 nearly at the collision limit, but only CF_3^+ and SF_5^+, respectively, were observed as the ionic products, although the formation of FCO^+ is energetically possible. The different reactivity of $CO^{\cdot+}$ toward the various fluorine donors probably reflects the difference between the relatively low $F_2N{-}F$ dissociation enthalpy, 58 kcal mol^{-1}, and the high $F_3C{-}F$ and $F_5S{-}F$ dissociation enthalpies, 132 and 92 kcal mol^{-1}, respectively, and suggests the possible use of nitrogen trifluoride as an effective fluorinating agent of gaseous radical cations.

Whereas the $NF_3^{\cdot+}$ ions were found to be unreactive toward carbon monoxide, thermalized NF_2^+ undergo the F^+ transfer reaction of Equation (3) as the only observable ion–molecule reaction when allowed to react with CO introduced into the resonance cell of the FT-ICR at a typical pressure of about 10^{-7} mbar. The formation of the triplet electronic state of the NF radical in Equation (3) is suggested by thermochemical considerations. In fact, large-scale MRD CI ab initio calculations[24] predict the $X^3\Sigma^-$ ground state of NF to be more stable than the $a^1\Delta$ by 31.4 kcal mol^{-1}. Assuming that the quoted enthalpy of formation of NF, 55.5 kcal mol^{-1}, refers to the triplet state, reaction (3) is exothermic ($\Delta H°(3) = -15$ kcal mol^{-1}) only if formation of ^3NF is assumed. The spin-forbidden character of (3) is fully consistent with the significant activation barrier suggested by its experimentally observed efficiency, calculated to be as low as 0.02 from the ratio of the measured rate constant, $k_3 = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and the collision rate constant, k_3(ADO) $= 7.67 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The observation of reaction (3) is of interest. In fact, whereas numerous F^+ transfer reactions in solution have already been reported,[25] and have stimulated the development of a theoretical quantitative scale for the oxidizing strength of simple fluorinating agents,[26] to the best of our knowledge no gas-phase F^+ transfer reactions have been reported to date. Thus, the observation of (3) invites further, independent work aimed at investigating the possible general occurrence of such processes under isolated conditions.

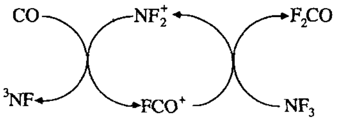
$$NF_2^+ + CO \longrightarrow F{-}CO^+ + {}^3NF \qquad (3)$$

Gas-phase reactivity of FCO^+ with NF_3—the catalytic conversion of carbon monoxide into carbonic difluoride, F_2CO: The FCO^+ ions from the ionization of nitrogen trifluoride and carbon monoxide can in principle undergo further ion–molecule reactions within the precursor gaseous mixture. To investigate the possible occurrence of such processes, thermalized FCO^+ ions from the external source of the FT-ICR were allowed to react with NF_3 or CO introduced separately into the resonance cell at typical pressures of around 10^{-8}–10^{-7} mbar. The fluoride-ion abstraction [Eq. (4)] was the only observed reaction.

$$FCO^+ + NF_3 \longrightarrow NF_2^+ + F_2CO \qquad (4)$$

Whereas the ionic product from reaction (4) can be unequivocally identified, one can only infer the formation of carbonic difluoride and accordingly calculate $\Delta H°(4)$ as -25.1 kcal mol^{-1}. However, the reaction would be strongly endothermic if neutral products other than F_2CO were formed (e.g., $\Delta H°(4) = +101.5$ kcal mol^{-1} if formation of F_2 and CO is assumed) and could not occur under our FT-ICR conditions. The efficiency of reaction (4) is obtained as 0.11 from the ratio of the measured rate constant, $k_4 = 9.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and the collision rate constant, k_4(ADO) $= 8.49 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. In addition, we note here that an efficient fluoride-ion abstraction was also observed when thermalized FCO^+ ions were allowed to react with CH_3COF, which provides independent support for the explanation already provided by Olah and coworkers for the elusive character of FCO^+ in solution.[27] Thus, failure to observe persistent FCO^+ ions when oxalyl fluoride $(FCO)_2$ was treated with SbF_5/SO_2ClF was attributed to their further reaction with $(FCO)_2$, with formation of the highly stable F_2CO.

The combined reactions (3) and (4) promote the catalytic cycle shown in Scheme 2, in which NF_2^+ ions mediate the conversion of carbon monoxide into carbonic difluoride with nitrogen trifluoride as the source of F.



Scheme 2.

A typical example of the time dependence of the ionic abundances observed when thermalized NF_2^+ ions from the external source of the FT-ICR were allowed to react with a mixture of carbon monoxide and nitrogen trifluoride introduced into the resonance cell is shown in Figure 4. The marked deviation from the pseudo-first-order exponential decrease clearly demonstrates the operation of the above catalytic cycle, which causes the NF_2^+ and FCO^+ ions to approach a stationary concentration and their observed ratio (Fig. 5) to reach a constant asymptotic value fully consistent, within experimental uncertainties, with the ratio of the partial pressures of CO and NF_3 and with the independently measured k_3/k_4 ratio. The observation of the above catalytic cycle is of considerable interest, in that it provides the first experimental evidence for the ability of a gaseous *main-group* cation to promote a specific chemical transformation. Since the first report of catalysis in gas-phase positive-ion chemistry,[28] which was concerned with the observation of oxidation cycles involving transition-metal cations and their oxides, numerous examples of chemical reactions mediated by naked,[29] ligated,[30] and even clustered[31] d-block cations have been reported, which adds to the large body of information currently available on gaseous transition-metal ions.[32] By contrast, the catalytic ability of p-block ions has been much less explored, and, to the best of our knowledge, no catalytic cycles involving main-group cations have yet been described. The NF_2^+-mediated fluorination of CO in the net reaction (5)

$$CO + NF_3 \longrightarrow F_2CO + {}^3NF \tag{5}$$

amounts to the catalytic removal of carbon monoxide by a gaseous cation, an alternative to the repeatedly demonstrated oxidation process[28, 32] based on the transition-metal-mediated conversion to carbon dioxide. In addition, reaction (5) is of interest because of the well-recognized role of carbonic difluoride in several atmospheric processes. In the troposphere, it is ultimately produced together with HF from the $CF_3^{\bullet}$ radical from the reaction of various hydrofluorocarbons with OH.[33] In the stratosphere, photolysis of CF_2Cl_2 produces $CF_2Cl^{\bullet}$, which yields F_2CO by reaction with O_2, and, in fact, increasing amounts of F_2CO have been observed in the upper stratosphere.[34]

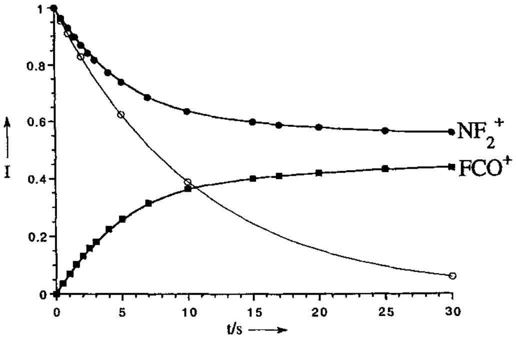


Fig. 4. Time dependence of the relative intensities (I) of the NF_2^+ and FCO^+ signals observed when thermalized NF_2^+ ions are allowed to react with a mixture of NF_3 and CO (1:10). The open circles refer to the decrease of NF_2^+ in the presence of carbon monoxide only.

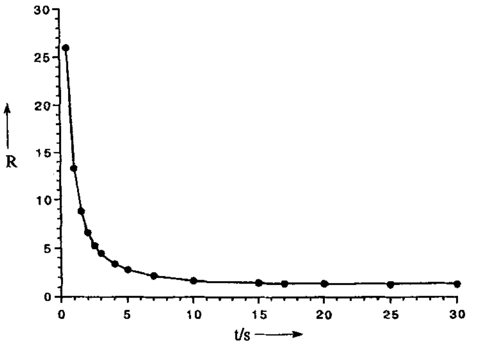


Fig. 5. Time dependence of the ratio (R) of the intensities of the NF_2^+ and FCO^+ signals observed when thermalized NF_2^+ ions are allowed to react with a mixture of NF_3 and CO (1:10).

Gas-phase reactivity of FCO^+ with n-type and p-type nucleophiles—the carbonylation of ammonia and aromatic substrates: The gas-phase chemistry of the FCO^+ ions obtained from the ionic fluorination of carbon monoxide was subsequently investigated with the aim of ascertaining their ability to carbonylate simple hydrogenated molecules. In particular, thermalized FCO^+ ions from the external source of the FT-ICR were allowed to react with several nucleophiles, including hydrogen, water, methanol, ammonia, methane, ethane, benzene, and toluene, introduced into the resonance cell at typical pressures of around 10^{-8}–10^{-7} mbar. In all cases, the elemental composition of the observed ionic products was unambiguously assigned by exact mass measurements, and, if two or more products were detected, the reported branching ratios are the average of at least three independent runs.

The FCO^+ ions were unreactive with H_2, H_2O, and CH_4, but were observed to abstract hydride from CH_3OH, with formation of CH_2OH^+ ions, which eventually transfer a proton to methanol. The enthalpy change of the reaction [Eq. (6)] is

$$FCO^+ + CH_3OH \longrightarrow CH_2OH^+ + HFCO \tag{6}$$

evaluated as $\Delta H^{\circ}(6) = -51.9\,kcal\,mol^{-1}$, and becomes $\Delta H^{\circ}(6) = -53.4\,kcal\,mol^{-1}$ if the equally likely formation of HF and CO as neutral products is assumed. The tendency of the gaseous FCO^+ ions to undergo exothermic H^- abstraction from simple saturated molecules is confirmed by their reaction with C_2H_6. The exclusive formation of the ethyl cation is observed [Equation (7)]; the change in reaction enthalpy changes

$$FCO^+ + C_2H_6 \longrightarrow C_2H_5{}^+ + HFCO \tag{7}$$

from $\Delta H^{\circ}(7) = -32.4\,kcal\,mol^{-1}$ to $-33.8\,kcal\,mol^{-1}$, depending on the assumed neutral product(s).

The reactivity of FCO^+ with NH_3 was subsequently investigated. The time dependence of the ionic abundances observed from isolated FCO^+ is shown in Figure 6. As the most significant result, $H_2N{-}CO^+$ ions were detected, arising from reaction (8), which demonstrates the ionic fluorination of carbon

$$FCO^+ + NH_3 \longrightarrow H_2N{-}CO^+ + HF \tag{8}$$

monoxide as an effective route to the coupled activation of CO and NH_3 in the gas phase. From Figure 6, the intensity of the FCO^+ signal decreases exponentially (correlation coefficient 1.0) according to a rate constant $k_8 = 1.0 \times 10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$, and the efficiency of reaction (8) is evaluated to be as high as 0.59 from the ratio of k_8 and

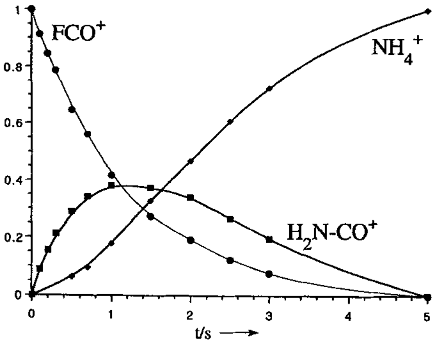


Fig. 6. Time dependence of the relative intensities (I) of the signals observed when thermalized FCO^+ ions are allowed to react with NH_3 ($p = 3.4 \times 10^{-8}$ mbar).

k_8(ADO), 1.69×10^{-9} cm^3 molecule^{-1}s^{-1}. This finding is consistent with the exothermicity of reaction (8), calculated as $\Delta H^\circ(8) = -65.2$ kcal mol^{-1}. From Figure 6, the $H_2N{-}CO^+$ ions from reaction (8) are in turn able to transfer protons to NH_3, and the formation of unreactive NH_4^+ ions is eventually detected at long reaction times. The occurrence of this reaction, unambiguously confirmed by independent isolation experiments with $H_2N{-}CO^+$ ions, is consistent with the difference between the proton affinity of HN–CO, 173 kcal mol^{-1}, and NH_3, 204 kcal mol^{-1}. Because of the low pressure in the FT-ICR cell, no adduct of $H_2N{-}CO^+$ and NH_3 was detected. The formation of such species, which could eventually lead by deprotonation to the formation of $(H_2N)_2CO$, is, however, conceivable under higher pressures of ammonia. The suggestion that the ionic fluorination of carbon monoxide could promote, at least in principle, the conversion of ammonia to urea is of interest, if one thinks of the continuous search for alternative procedures to the commonly employed synthesis based on the reaction of CO_2 with liquid NH_3 at high temperature and pressure.[35] In particular, any practicable route based on the direct use of the easily available raw material CO without preliminary conversion to CO_2, such as the recently proposed one based on a K[Ru^{II}(EDTA-H)(CO)] catalyst,[36] is regarded with considerable interest.

Finally, the possible use of FCO^+ as a reagent in aromatic carbonylation was investigated. The time dependence of the ionic abundances from the reaction of thermalized FCO^+ ions with C_6H_6 is shown in Figure 7. The FCO^+ signal decreases exponentially (correlation coefficient 1.0), and the abundant formation of $C_6H_5{-}CO^+$ ions is detected [Eq. (9a)], together with a minor contribution from the charge transfer reaction (9b); the branching ratio of the two channels is evaluated as 9:1. Thus, the exothermic reaction (9a) amounts to the

$$FCO^+ + C_6H_6 \longrightarrow C_6H_5{-}CO^+ + HF \qquad (9a)$$

$$FCO^+ + C_6H_6 \longrightarrow C_6H_6^{\cdot +} + FCO^{\cdot} \qquad (9b)$$

gas-phase carbonylation of benzene, promoted by the ionic fluorination of carbon monoxide. The selective functionalization of the benzene C–H bonds with CO is a process extensively investigated for both fundamental and practical reasons.[37–42] Some of the procedures employed, such as the Gatterman–Koch formylation,[37] are already textbook examples of electrophilic aromatic substitution,[38] and the number of alternative strategies so far developed is impressive, and only roughly recalled if one mentions the use of transition-metal-based catalysts,[39] organometallic reagents,[40] photochemical,[41] and radical[42] techniques. Reaction (9a) probably occurs by the electrophilic addition of FCO^+ to the aromatic substrate, followed by elimination of a HF molecule from the σ-complex presumed to be formed initially, excited by the exothermicity of its formation process and, in the low-pressure domain of the FT-ICR cell, not stabilized by unreactive collisions with the surrounding molecules. The very high efficiency of this process, calculated as 0.9 from the ratio of the experimental k_{9a}, 1.3×10^{-9} cm^3 molecule^{-1}s^{-1}, and k_9(ADO), 1.4×10^{-9} cm^3 molecule^{-1}s^{-1}, is fully consistent with its enthalpy change, as large as -95 kcal mol^{-1}. In addition, the observation of the minor charge transfer reaction (9b) is compatible with the recently reevaluated recombination energy of FCO^+, 9.3 ± 0.1 eV,[17] but would become endothermic if the previously reported value of 8.76 ± 0.32 eV[16] were adopted (ionization potential of C_6H_6 9.24 eV).

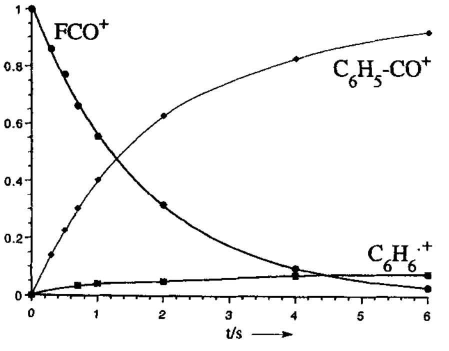


Fig. 7. Time dependence of the relative intensities (I) of the signals observed when thermalized FCO^+ ions are allowed to react with C_6H_6 ($p = 1.8 \times 10^{-8}$ mbar).

Carbonylation is also the most important channel in the reaction of FCO^+ with toluene, together with minor electron capture and hydride transfer reactions. The time dependence of the observed ionic abundances is shown in Figure 8, and the branching ratio of the corresponding ion–molecule reactions is reported in Scheme 3. The decrease in intensity of the FCO^+ signal is exponential (correlation coefficient 1.0) and the overall

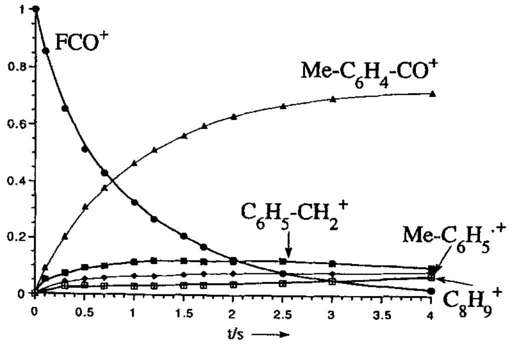
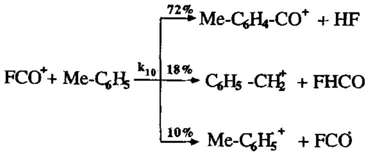


Fig. 8. Time dependence of the relative intensities (I) of the signals observed when thermalized FCO^+ ions are allowed to react with $C_6H_5{-}Me$ ($p = 3.0 \times 10^{-8}$ mbar).



$$FCO^+ + Me{-}C_6H_5 \xrightarrow{k_{10}} \xrightarrow{72\%} Me{-}C_6H_4{-}CO^+ + HF \qquad (10a)$$

$$\xrightarrow{18\%} C_6H_5{-}CH_2^+ + FHCO \qquad (10b)$$

$$\xrightarrow{10\%} Me{-}C_6H_5^{\cdot +} + FCO^{\cdot} \qquad (10c)$$

Scheme 3.

rate constant $k_{10} = k_{10a} + k_{10b} + k_{10c}$ is evaluated as 1.5×10^{-9} cm^{3}molecule^{-1}s^{-1}, which leads to $k_{10a} = 1.1 \times 10^{-9}$, $k_{10b} = 2.7 \times 10^{-10}$, and $k_{10c} = 1.5 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1}. From the collision rate constant of FCO^+ with $C_6H_5{-}CH_3$, calculated as k_{10}(ADO) $= 1.48 \times 10^{-9}$ cm^{3}molecule^{-1}s^{-1}, the efficiency of the carbonylation reaction (10a) is evaluated as k_{10a}/k_{10}(ADO) $= 0.74$, which is comparable, within experimental uncertainties, with the efficiency of the benzene carbonylation reaction (9a). From Figure 8, the slight inflection of the signal of the $C_6H_5{-}CH_2^+$ ions obtained from the exothermic reaction (10b), $\Delta H°(10b) = -65.1$ kcal mol^{-1} if formation of HFCO is assumed, accompanied by the formation of $C_8H_9^+$ ions, comes from the incursion of the secondary process (11), so

$$C_6H_5{-}CH_2^+ + C_6H_5{-}CH_3 \longrightarrow C_8H_9{}^+ + C_6H_6 \tag{11}$$

far reported to occur under the conditions of FT-ICR mass spectrometry and known to involve $C_7H_7^+$ ions of benzyl structure.[43] Lastly, we note here that the gaseous FCO^+ ions were also observed to carbonylate $C_6H_5{-}X$ aromatic substrates, including X = F, Cl, OCH_3, and CN. However, the $X{-}C_6H_4{-}CO^+$ ions (X = F, Cl) do not exceed about 30% of the observed products, and ions from the direct attack of FCO^+ on X and from charge transfer reactions were detected. Thus, although ionic fluorination of carbon monoxide seems a general route to the gas-phase carbonylation of simple aromatics, the selectivity of the process dramatically decreases on passing from benzene and toluene to other substituted arenes. In addition, our findings are consistent with the recent observation of carbonylation products from the reaction of the $ClCO^+$ ions obtained from the electron-impact ionization of CH_3COCl with simple aromatic substrates.[44]

Conclusions

Our investigation of the gas-phase reactivity of the FCO^+ ions obtained from the ionic fluorination of carbon monoxide demonstrates the ability of the C–H bonds of benzene and toluene and of the N–H bond of ammonia to undergo efficient and selective CO-functionalization. The corresponding carbonylated products arise from the electrophilic addition of FCO^+ followed by elimination of a stable HF molecule. Thus, the attachment of F^+ converts the unreactive CO molecule into a strong Lewis acid, which reacts almost exclusively as a C-electrophile because of the peculiar location of the empty p orbital and of the positive charge. Since structural rearrangements are also expected from the binding of F^+ to species such as CO_2 and SO_2 and, in addition, stable FSO_2^+ and FCO_2^+ fragments have been actually detected in the gas phase, our findings encourage the investigation of the ionic fluorination of these small gaseous molecules as a conceivable route to their chemical activation.

Experimental and Theoretical Procedures

The FT-ICR experiments were performed on a Bruker Spectrospin Apex 47e spectrometer equipped with an external ion source [45] and a cylindrical "infinity cell" [46]. The NF_2^+ and FCO^+ ions, produced in the external source, were transferred into the resonance cell, trapped in the field of a 4.7 T superconducting magnet and isolated by "single shots" and broad-band ejection techniques [47]. The ions were subsequently thermalized by unreactive collisions with pulsed-in argon gas and reisolated. The pseudo-first-order rate constants of the reactions investigated were derived from the decay of the precursor-ion signals and converted to absolute rate constants by calibration of the ionization gauge measurement with the tabulated rate constants of suitable ion–molecule processes [48], the estimated error in the absolute rates being ±30%. The CAD spectra were recorded on a VG Micromass ZAB-2F instrument of magnetic/electrostatic (B/E) configuration [49]. Typical operating conditions of the chemical ionization (electron-impact) source were as follows: gas pressure 10^{-1} (10^{-4}) mbar; source temperature 150 (150) °C; emission current 0.5 mA (trap current: 100 μA); repeller voltage ca. 0 (0–5) V; electron energy 50 (70) eV. The FCO^+ ions, accelerated by 8 kV and magnetically mass-selected, were made to collide with helium introduced into the cell of the second field-free region at such a pressure as to reduce the main beam intensity to 70% of its initial value. The fragments arising were detected by varying the deflection voltage of the electrostatic analyzer.

The ab initio calculations were performed with the Gaussian 92 set of programs [50]. The geometries of the investigated species were optimized at the HF/6-31G* and the MP2(FULL)/6-31G* level of theory, and their zero-point vibrational energies, ΔE(ZPE), were obtained by the HF/6-31G* frequencies scaled by 0.893. Approximate QCISD(T)/6-311 + G(3df,2p) energies were calculated at the MP2(FULL)/6-31G* geometries by means of the Gaussian-2(G2) procedure [13]. Briefly, the MP4/6-311G** energy, E_0, is modified with a series of additive corrections defined as follows: $\Delta E(+) = E(\mathrm{MP4/6\text{-}311+G^{**}}) - E_0$, $\Delta E(2df) = E(\mathrm{MP4/6\text{-}311G^{**}(2df)}) - E_0$, $\Delta E(\mathrm{QCI}) = E(\mathrm{QCISD(T)/6\text{-}311G^{**}}) - E_0$ and $\Delta E(\mathrm{HLC}) = (-0.00019\,n_{\mathrm{unpair}} - 0.00614\,n_{\mathrm{pair}})$ hartree, where n_{unpair} and n_{pair} represent the numbers of unpaired valence electrons and valence pairs, respectively. The G1 energy is defined as $E(\mathrm{G1}) = E_0 + \Delta E(+) + \Delta E(2df) + \Delta E(\mathrm{QCI}) + \Delta E(\mathrm{HLC}) + \Delta E(\mathrm{ZPE})$. The further term $\Delta = E(\mathrm{MP2/6\text{-}311+G(3df,2p)}) - E(\mathrm{MP2/6\text{-}311G^{**}(2df)}) - E(\mathrm{MP2/6\text{-}311+G^{**}}) + E(\mathrm{MP2/6\text{-}311G^{**}})$ leads to the G2 energy as $E(\mathrm{G2}) = E(\mathrm{G1}) + \Delta + 0.00114\,n_{\mathrm{pair}}$ hartree.

Acknowledgements: We wish to thank Prof. F. Cacace for his interest in this work, and the Italian Ministero dell' Università e della Ricerca Scientifica e Tecnologica (MURST) and the Consiglio Nazionale delle Ricerche (CNR) for financial support.

Received: October 6, 1995 [F224]

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