Ion-Molecule Reactions in Gaseous CF₄/CO Mixtures. Formation and Reactivity of CF₃CO⁺ Ions

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The reactivity of CF_3CO^+ ions, formed via two different routes, has been studied in the gas phase by the joint use of mass spectrometric and radiolytic techniques, spanning a pressure range from 10^{-8} Torr to ca. 1 atm. The 23 kcal mol⁻¹ exothermic addition of CF_3^+ to CO provides a route to CF_3CO^+ requiring third-body stabilization of the adduct ion. In the 10^{-8} Torr pressure regime of Fourier transform ion cyclotron resonance (FT-ICR) spectrometry, CF_3CO^+ ions from electron ionization (EI) induced fragmentation of trifluoroacetic anhydride yield NuCF₃⁺ products from oxygen-centered nucleophiles (Nu) and XC₆H₄CO⁺ ions from aromatics (C₆H₅X). At ca. 1 atm trifluoroacetylated products are efficiently formed even with strongly deactivated aromatics, showing distinct intra- and intermolecular selectivity features pertaining to the reactant CF₃CO⁺ ions. The reactivity pattern is interpreted according to a kinetic interplay of collisional and chemical events depending on the activation of C₆H₅X toward electrophilic attack.

Introduction

The study of fluorinated carbenium ions is of considerable interest in view of the twofold behavior of fluorine as a substituent. On one hand, it behaves as an electron donor by conjugation to a suitably located positive carbon; on the other, it acts as an electron withdrawer by its powerful inductive effect.¹ Thus, the site and number of fluorine substituents may modulate the electrophilicity of a certain carbenium ion. Exhaustive fluorine substitution gives cationic species unable to behave as Brønsted acids and possibly undergoing isomerization by fluorine shifts, which appear to be elusive and scarcely documented processes.² For these reasons, we have undertaken a study on the formation and the reactivity of fluorinated carbocations in gaseous media. Whereas the gas-phase ion chemistry of CF_3^+ , the simplest perfluorinated alkyl cation, has been extensively studied by mass spectrometric³ and radiolytic techniques,⁴ the species CF_3CO^+ , the next simplest perfluorinated acyl cation after FCO⁺, is practically unknown. We have investigated the gas-phase reactivity of CF₃CO⁺ ions from two different formation routes. The first involves addition of CF_3^+ to CO, an exothermic process which requires collisional stabilization of the excited [CF₃CO⁺]* ion primarily formed, in order to yield persistent adduct ions. To this end, the pressure of the buffer gas required to ensure collisional quenching of the excited $[CF_3CO^+]^*$ ions, thus preventing their back-dissociation, must be of appropriately high value. In this respect, the radiolytic technique⁵ represents a valuable tool for the study of ion-molecule reactions since it allows to operate in medium-pressure ranges, usually inaccessible to mass spectrometric techniques. The second means of producing CF_3CO^+ ions involves EI induced fragmentation following ionization of suitable precursors, such as trifluoroacetic anhydride (TFAA). Since this is a dissociation process, it may be exploited under lowpressure conditions such as those typical of ICR mass spectrometry (ca. 10⁻⁸ Torr), though, even in this case care is required to keep the energy content of the product ion under control. By the joint use of the two techniques, the investigation of the reactivity behavior displayed by CF₃CO⁺ under radiolytic conditions has been integrated with the ICR detection of relevant ion-molecule reaction sequences, thus spanning the wide pressure range from ca. 1 atm to 10^{-8} Torr. The simultaneous presence of CF₃⁺ and

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 CF_3CO^+ ions in the selected gaseous mixtures leads to ionic products from both ions, revealing also novel reactions of the CF_3^+ species. Finally, it is worth mentioning that the reactivity behavior of CF_3^+ and CF_3CO^+ ions with simple molecules bears relevance in the context of possible degradation pathways of fluorinated hydrocarbons under the action of ionizing radiation.

Experimental Part

Materials. CF₄, CO, C₂H₄, NO, O₂, and C₃H₈ were 99.9% pure gases from Matheson Gas Products or Union Carbide. Aldrich Chemical Co. and Fluorochem Ltd. supplied most of the products used as reactants or gas chromatographic standards, except the major number of ring substituted α, α, α -trifluoroacetophenones. These products, required for the isomeric identification of trifluoroacetylation products of aromatic substrates, were synthesized from the reaction of TFAA with the Grignard reagent of the corresponding aromatic precursor XC₆H₄Y (Y = Cl or Br). This procedure gave high yields of single, specifically substituted α, α, α -trifluoroacetophenones, XC₆H₄COCF₃, even in the presence of highly electron-withdrawing X substituents, *e.g.*, X = CF₃. The products were characterized by their NMR and EI mass spectra.

Mass Spectrometric Experiments. Chemical ionization (CI) mass spectra were recorded on a Hewlett Packard Model 5892A quadrupole instrument, equipped with a CI ion source operated at 80 °C.

The FT-ICR experiments were performed with a Bruker Spectrospin Apex TM47e spectrometer equipped with a cylindrical (60-mm length and 60-mm diameter) "infinity" cell and a pulsed magnetic valve. After selection of CF₃CO⁺ ions by broad-band ejection of all other ions present in the cell, argon was admitted by the pulsed valve up to the pressure of ca. 1×10^{-5} Torr. After a suitable pumping time, those CF₃CO⁺ ions surviving fragmentation and thermalized by unreactive collisions with argon were isolated by soft ejection shots, and mass spectra were acquired after various reaction times.

Radiolytic Experiments. Gaseous samples were prepared in 135-mL Pyrex vessels according to standard vacuum procedures. Irradiations were carried out in a 220 Gammacell, Nuclear Canada Ltd., at 40 °C, at a dose rate of 5×10^3 Gy h⁻¹, to a total dose of 10^4 Gy.

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	system composition (Torr)			product pattern $(G_{+M} \times 10^2)^a$					
entry	bulk gas	PhX	additives	XC ₆ H ₄ COCF ₃	XC ₆ H ₄ CF ₃	XC ₆ H₄COF	XC ₆ H ₄ COC ₂ H ₄ F	XC ₆ H ₄ CF ₂ C ₂ H ₄ F	
1	CO, 600 CF4, 100	X = H, 3.3	$C_2H_4, 10$ $O_2, 10$	1.37	1.73	0.40	0.22	0.37	
2	CO, 600 CF ₄ , 100	X = H, 2.3	C ₂ H ₄ , 10 O ₂ , 10 NH ₃ , 10	0.024	0.038	0.036	0.025	0.032	
3	CF4, 680	X = H, 0.96	C_2H_4 , 10 O_2 , 10		2.03	2.77	1.39	1.24	
4	CF₄, 690	X = H, 2.7	H ₂ ¹⁸ O, 5.9		0.064	0.17			
5	CO, 540 CF ₄ , 130	X = Me, 0.92	C_2H_4 , 10 O_2 , 10	1.04	0.66	0.35		0.46	
6	CO, 540 CF ₄ , 120	X = Me, 1.5	NO, 25	1.04	0.30				

TABLE 1: Gas-Phase Reaction of CF_3CO^+ (CF_3^+) with Benzene and Toluene

^a G_{+M} given in μ mol J⁻¹. Standard deviation of data ca. 10%.

The radiolytic products mixtures were recovered from the irradiated vessels by an appropriate amount of extractant solution (internal standard in ethyl acetate) under airtight conditions. After several freeze-thaw cycles ensuring complete washing of the vessels' inner walls, the resulting solutions were analyzed by GC and GC/MS, using a Hewlett Packard Model 5700A gas chromatograph with a flame ionization detector and a HP 5890A gas chromatograph in line with a HP 5970B mass selective detector. The following capillary columns allowed satisfactory separations of the radiolytic product mixtures, with the exception of *m*- and *p*-Cl-C₆H₄COCF₃, which could not be resolved: (i) a 60-m-long, 0.25-mm-i.d. fused silica column coated with a 0.25- μ m film of 20% diphenyl/80% dimethylpolysiloxane (SPB-20 column from Supelco Co.); (ii) a 30-m-long, 0.20-mm-i.d. poly-(ethylene glycol) (Supelcowax 10) bonded-phase column (0.25- μ m film thickness) from Supelco Co.; (iii) a 50-m-long, 0.2mm-i.d. fused silica capillary column, coated with a 0.5-µm crosslinked methylsilicone film (Pona column from Hewlett Packard).

The identity of isomers formed from the trifluoroacetylation of aromatic substrates, C_6H_5X , was established by comparison of their retention times and mass spectra with those of authentic samples under the same operating conditions. The radiochemical yield, G_{+M} , giving the micromoles of product formed per unit absorbed energy (J) was derived using the internal standard (4-(α, α, α -trifluoromethyl)benzaldehyde) calibration method.⁶

Photolysis Experiments. The reaction cell, a glass cylinder 10 cm in length and 5 cm in diameter, equipped with two quartz windows, was connected to a vacuum line, evacuated, and filled with the required gaseous components. The light source was a 150-W medium-pressure mercury arc. After 15-min irradiation, the cell contents were recovered and analyzed as described for the radiolytic product mixtures.

Results

Radiolytic Reactions. The radiolytic products formed in gaseous CF_4/CO mixtures in the presence of benzene or toluene and selected additives are reported in Table 1. The composition of the gaseous systems reflects the quest to trace the ionic origin of the observed products and the effect of additives. All products formally result from aromatic substitution of a ring hydrogen atom by the groups CF_3CO , CF_3 , CFO, $C_2H_4FCF_2$, and C_2H_4 -FCO. The product of major interest, $XC_6H_4COCF_3$ (X = H, CH_3), is formed in the bulk CF_4/CO (ca. 6:1) gaseous mixture, the presence of CO being essential for its formation.

The use of either C_2H_4/O_2 or NO as scavenger of possible radical routes to trifluoroacetylation products does not affect the yield of $CH_3C_6H_4COCF_3$ (cf. entries 5 and 6).

The yield of the trifluoroacetylation products drops instead significantly upon addition of NH_3 , an efficient ion interceptor, under otherwise identical conditions (cf. entries 1 and 2). The formation of XC_6H_4COF closely parallels that of $XC_6H_4CF_3$, both decreasing in the presence of NH_3 . Both products derive

from CF₄, not requiring the presence of CO. The oxygen atom of benzoyl fluoride recovered from experiment 4, run in the presence of H₂¹⁸O, consists of 80% ¹⁸O isotope, thus excluding its formation from unlabeled O_2 as a major pathway. The ionic pathway leading to PhCOF has been further verified by generating its probable ionic precursor in an independent way. In a gaseous mixture of $C_{3}H_{8}/O_{2}/H_{2}^{18}O/CF_{3}Ph$ (690/10/3.1/2.6 Torr, respectively) benzoyl fluoride is formed with 0.009 μ mol J⁻¹ radiochemical yield and 57% 18O content. Finally, the headings XC₆H₄CF₂C₂H₄F and XC₆H₄COC₂H₄F include two isomers each, differing for the position of F in the fluoroethyl group, whose formation is bound to the presence of C_2H_4 . Table 2 illustrates the trifluoroacetylation of mixtures of competing arenes of widely different activation toward electrophilic attack, ranging from mesitylene to α, α, α -trifluorotoluene. Rate constant ratios from the standard equation for competing reactions, *i.e.*, k_X/k_H = $([XC_6H_4COCF_3]/[C_6H_5COCF_3]) \times ([C_6H_6]/[C_6H_5X])$, are reported for each couple PhX/C_6H_6 . The relative reactivities measured by $k_{\rm X}/k_{\rm H}$ increase from the lowest walue, ca. 0.3, of PhCF₃ to reach the leveling limit of 1 common to benzene, toluene, and mesitylene. An "abnormally" high value (ca. 1.2) is observed for a deactivated substrate, PhOCF₃. k_X/k_H values do not typically change much on using a different radical scavenger system (NO instead of C_2H_4/O_2) and in the presence of a strong base (piperidine) ensuring fast deprotonation of primary arenium ions. The same trend characterizes the isomeric distribution of $XC_6H_4COCF_3$, with the exception of $X = CH_3$ where the presence of the base has a positive effect on the relative amount of the ortho isomer. For the same substrate, a 2-fold decrease of the total pressure of the gaseous system brings about an increase of the fraction of meta isomer, which is barely above experimental error. The 2p/m selectivity is slightly above unity (ca. 1.3) in the case of toluene and slightly below 1 (ca. 0.7) in the case of PhCF₃. The highest positional selectivity is displayed in the trifluoroacetylation of PhF $(2p/m \simeq 5)$ and especially PhOCF₃ $(2p/m \simeq 13).$

The trifluoroacetylation of p-CH₃C₆H₄D yields additional information concerning the deuterium content of the isomeric products formed, namely, 95% (in the ortho isomer), 92% (meta), and 71% (para).

The reaction of n-type nucleophiles, such as alcohols and amines, has also been investigated in the standard $CF_4/CO/C_2H_4/O_2$ mixture. The reaction of piperidine (1.7 Torr) yields a significant trifluoroacetylation product (c-C₅H₁₀NCOCF₃, $G_{+M} = 0.023$ µmol J⁻¹) together with (c-C₅H₁₀N)₂CO ($G_{+M} = 0.118$ µmol J⁻¹) and c-C₅H₁₀NCOC₂H₄F ($G_{+M} = 0.016$ µmol J⁻¹).

Mass Spectrometric Results. Chemical ionization mass spectrometric experiments have been run in a CF_4/CO (1:4) mixture at the total pressure of ca. 1 Torr. CF_3^+ is by far the predominant ionic species while the sought CF_3CO^+ ion represents approximately 1% of the total ion intensity. In the FT-ICR cell the formation of CF_3CO^+ has been obtained from EI ionization of

TABLE 2: Inter- and Intramolecular Selectivities for the Gas-Phase Reaction of CF₃CO⁺ with Aromatic Substrates

	system composition (Te	orr)			isomeric composition of products			
bulk gas	aromatic	additives	Х	$k_{\rm X}/k_{\rm H}$	$XC_6H_4COCF_3(o, m, p)$	2p/m		
CO, 580	<i>p</i> -MeC ₆ H ₄ D, 1.6 C ₆ H ₆ , 1.6	C ₂ H ₄ , 10 O ₂ , 10	Me	1.05	21:48:31	1.3		
CO, 530 CF ₄ , 100	C_7H_8 , 1.5 C_6H_6 , 1.4	C ₂ H ₄ , 10 O ₂ , 10 piperidine, 0.6	Me	1.14	46:33:21	1.3		
CO, 230 CF ₄ , 50	C7H8, 0.8 C6H6, 0.7	C ₂ H ₄ , 5 O ₂ , 5	Me	0.94	16:55:29	1.1		
CO, 510 CF4, 100	mesitylene, 1.6 C ₆ H ₆ , 1.7	C ₂ H ₄ , 10 O ₂ , 10		1.01				
CO, 620 CF ₄ , 100	PhOCF ₃ , 1.8 C ₆ H ₆ , 1.8	C ₂ H ₄ , 10 O ₂ , 10	OCF ₃	1.27	67:4:29	15		
CO, 540 CF ₄ , 110	PhOCF ₃ , 1.5 C ₆ H ₆ , 1.5	NO, 25 piperidine, 0.6	OCF ₃	1.20	60:6:34	11		
CO, 530 CF ₄ , 100	PhCF ₃ , 1.8 C ₆ H ₆ , 1.8	C ₂ H ₄ , 10 O ₂ , 10	CF ₃	0.37	5:70:25	0.7		
CO, 570 CF ₄ , 100	PhCF ₃ , 2.0 C ₆ H ₆ , 1.9	NO, 20 piperidine, 0.7	CF ₃	0.34	9:66:25	0.8		
CO, 545 CF4, 100	PhCl, 1.0 C ₆ H ₆ , 1.2	C ₂ H ₄ , 10 O ₂ , 10	Cl	0.61	61(<i>o</i> + <i>m</i>):39(<i>p</i>)			
CO, 580 CF4, 110	PhCl, 1.1 C ₆ H ₆ , 1.1	NO, 22 piperidine, 0.55	Cl	0.89	53(<i>o</i> + <i>m</i>):47(<i>p</i>)			
CO, 540 CF ₄ , 100	PhF, 1.2 C ₆ H ₆ , 1.3	C ₂ H ₄ , 10 O ₂ , 10	F	1.2	30:20:50	5.0		
CO, 590 CF4, 100	PhF, 1.8 CeHe, 1.8	NO, 20 piperidine, 0.66	F	1.0	36:19:45	4.7		

TFAA followed by fragmentation. The CF₃CO⁺ ions thus produced, endowed with excess internal and translational energy, are prone to dissociate to CF₃⁺ and CO and to undergo chargetransfer processes, *e.g.*, with benzene. Dissociation of highly excited CF₃CO⁺ ions and thermalization of the remaining ones were achieved by admitting argon into the cell by means of a pulsed valve. The collisionally quenched CF₃CO⁺ ions exhibited a clean kinetic behavior upon reaction with n- and π -nucleophiles. Whereas reaction with H₂O, a representative n-base, occurs by CF₃⁺ transfer, benzene yields exclusively a carbonylation product. The ion-molecule reactions initiated by CF₃CO⁺ ions thermalized by collisions with Ar in a TFAA/C₆H₆/H₂O mixture are illustrated by the time dependence of ion intensities shown in Figure 1 and are suggested to occur as described in eqs 1-3.The

$$CF_{3}CO^{+} + C_{6}H_{6} \longrightarrow [C_{6}H_{6}COCF_{3}^{+}]^{*} \longrightarrow C_{6}H_{5}CO^{+} + CF_{3}H \quad (1)$$

$$m/z \ 97 \qquad m/z \ 105$$

$$CF_{3}CO^{+} + H_{2}O \xrightarrow{-\infty} CF_{3}OH_{2}^{+} \xrightarrow{+TFAA} TFAAH^{+}$$

$$m/z \ 87 \qquad m/z \ 211$$

$$+C_{6}H_{6} -CF_{3}OH \qquad +C_{6}H_{6} -TFAA \qquad (2)$$

$$C_{6}H_{7}^{+} \qquad C_{6}H_{7}^{+}$$

$$m/z \ 79$$

$$CF_{2}CO^{+} + TFAA \xrightarrow{-\infty} TFAACE_{2}^{+1} \xrightarrow{-\infty} CF_{2}C(OCE_{2})^{+} \qquad (3)$$

$$CF_3CO^+ + TFAA \xrightarrow{-\infty} [TFAACF_3^+] \xrightarrow{-\infty} CF_3C(OCF_3)_2^+$$
 (3)
m/z 251

loss of a ring hydrogen atom necessarily involved in the framentation of the CF₃CO⁺ adduct with benzene is observed as well in the reaction of labeled toluene (eq 4) leading exclusively to ions at m/z 122, which retain the three deuterium atoms of the methyl group.

$$CF_{3}CO^{+} + CD_{3}C_{6}H_{5} \rightarrow$$

$$[CD_{3}C_{6}H_{5}COCF_{3}^{+}]^{*} \rightarrow CD_{3}C_{6}H_{4}CO^{+} + CF_{3}H (4)$$

Thus, at variance with oxygen-centered nucleophiles, aromatic



Figure 1. Time dependence of normalized intensities of major ions $(\Box, m/z 79; \blacklozenge, m/z 87; \Box, m/z 97; \diamondsuit, m/z 105; \Box, m/z 115; \Box, m/z 211; \diamondsuit, m/z 251)$ observed after isolation of CF₃CO⁺ ions (m/z 97) in a TFAA/C₆H₆/H₂O (1:1.3:0.2) mixture at 1.3×10^{-8} Torr.

 π -bases appear to react with CF₃CO⁺ preferably by addition to the carbonyl carbon rather than by CF₃⁺ transfer.

Photolytic Experiments. Photolytic experiments have been performed as a blank to examine radical pathways triggered by CF_3 radicals produced from photolytic cleavage of CF_3I . No α, α, α -trifluoroacetophenone was formed in a CO atmosphere (600 Torr) containing C_6H_6 (10 Torr), O_2 (10 Torr), and 30 Torr of CF_3I . CF_3 radicals led rather to PhOCF₃ and $CF_3OC_6H_4$ -OH, probably involving interaction with O_2 and excluding at the same time a conceivable radical route to trifluoroacetophenones via CF_3CO° radical intermediates.

Discussion

The CF₃CO⁺ Ion. The trifluoroacetyl cation is known in the gas phase only as fragment in the EI mass spectra of compounds such as $(CF_3)_2CO$, trifluoroacetic acid, and its derivatives.

Extremely scant information is available on its thermodynamic properties, including its enthalpy of formation. The binding energy of CF₃⁺ to CO has been estimated by LCAO MO SCF computations⁷ with STO 4.31 G optimized geometries, which gave $\Delta H_5^{\circ} \simeq -70$ kcal mol⁻¹.

$$CF_3^+ + CO \rightarrow CF_3CO^+$$
 (5)

Such a value may be compared with the report, in the same paper, of the binding energy of CH_3^+ to CO, $\Delta H_6^\circ \simeq -79$ kcal mol⁻¹, a value in line with several other determinations based both on experiment and theory.⁸

$$CH_{3}^{+} + CO \rightarrow CH_{3}CO^{+}$$
 (6)

Based on the following considerations, the large negative ΔH_5° value does not seem consistent with ΔH_6° : (i) the three fluorine atoms directly bonded to the cationic center stabilize CF₃⁺ with respect to CH₃⁺ by conjugative interaction, e.g., the fluoride and hydride ion affinities decrease in the order CH₃⁺ > CF₃⁺;^{3e} (ii) the α -CF₃ group in CF₃CO⁺ is highly destabilizing relative to CH₃CO⁺ by inductive electron withdrawal. Both effects, stabilization of the reactant ion and destabilization of the product ion, should concur in making reaction 5 markedly less favorable thermodynamically with respect to reaction 6. These expectations are confirmed by a newly evaluated value of $\Delta H_5^{\circ} = -23$ kcal mol⁻¹, obtained in this work from higher level MP2/6-311G**//HF/6-31G* calculations, which allows one to derive ΔH_f° (CF₃-CO⁺) = 46 kcal mol⁻¹ from the known ΔH_f° values for CF₃⁺ and CO.⁹

Reaction 5 may also represent a way of forming CF_3CO^+ ions in view of the nucleophilic reactivity of CO toward carbenium ions, well documented in solution and in the gas phase, and of the ready availability of CF_3^+ ions in the gas phase. The EI ionization of CF_4 is a highly efficient method for obtaining a CF_3^+ ion population. In fact, the CF_4^{++} molecular ion is unstable and dissociates rapidly to $CF_3^+ + F$. The minor CF_2^+ fragment ion reacts with CF_4 to form $CF_3^{+,3d.e}$ which ultimately represents the only ionic species in the CI mass spectrum.

On admitting CO into the CI ion source, the fraction of primary ionization involving CO will produce CF_3^+ once again¹⁰ via the reaction

$$CO^{*+} + CF_4 \rightarrow CF_3^+ + [F\dot{C}O]$$
(7)

Finally, CF_3^+ should quantitatively turn into CF_3CO^+ according to reaction 5, for which the equilibrium constant of $K = 2 \times 10^{13}$ at 298 K can be calculated, using $\Delta H_5^\circ = -23$ kcal mol⁻¹ and assuming $\Delta S_5^\circ = -20$ cal K⁻¹ mol⁻¹, *i.e.*, the same value found for the association of Na⁺ with CO.¹¹ In contrast with thermodynamic predictions, in the CI mass spectrum of a CF₄/ CO 1:4 mixture at 1 Torr, CF₃CO⁺ represents only about 1% of the CF₃⁺ ion intensity. The probable reason for this apparent discrepancy lies in the fact that the kinetic progress of the reaction requires third-body stabilization of the adduct ion, initially excited by the exothermicity of its formation process, which favors backdissociation to the reactants (eq 8).

$$CF_3^+ + CO \stackrel{(a)}{\underset{(b)}{\rightleftharpoons}} [CF_3CO^+] * \stackrel{(c)}{\underset{-M^*}{\rightarrow}} CF_3CO^+$$
(8)

At the pressure of 1 Torr, the rate of the bimolecular step (c) is too low to compete with back-dissociation (b). On increasing the pressure, the concentration of M ($M = CF_4$, CO) may reach the point to ensure collisional quenching of all [CF_3CO^+]* species, thus making the (a) step irreversible. An experimental check to this prediction was obtained by use of the radiolytic technique, which allows operating in moderately high-pressure regimes with consequent increased frequency of ion-molecule collisions. To this end, the generation of CF_3CO^+ ions by γ -radiolysis of CO/ CF_4 5:1 mixtures was investigated (where ionization leads to CF_3^+ ions via processes which parallel those occurring in CI/MS). At the pressure of 1 atm, efficient formation of CF_3CO^+ was confirmed by the recovery of trifluoroacetylation products, leading support to increased efficiency of collisional thermalization (c), though this finding does not exclude residual back-dissociation (b).

On the other hand, since reaction 8 does not lead to detectable CF₃CO⁺ ions at $P \leq 1$ Torr, the EI-induced fragmentation of TFAA was exploited to obtain CF₃CO⁺ in the low-pressure conditions (ca. 10⁻⁸ Torr) of ICR mass spectrometric experiments.

Radiolytic Reactions. Ionic vs Radical Pathways. A counterpart to the many advantages of the radiolytic technique applied to the study of ion-molecule reactions is represented by the simultaneous occurrence of radical pathways initiated by radical species formed concurrently with charged species. In particular, the γ -radiolysis of CF₄ is a source of CF₃ radicals, electrophilic species whose fate may not be much different from that of CF₃⁺ ions. It is conceivable that CF₃ may react with CO, forming CF_3CO^{\bullet} which may further yield trifluoroacetylated products, thus obscuring the truly ionic reactivity pattern. Scant information is available on $CF_3CO^{.12}$ Though its very stability has been questioned, we have taken measures preventing its formation. Accordingly, the intermediate CF3* radical has been intercepted by two scavenger systems: (i) NO, which reacts with CF₃[•] forming stable CF₃NO with negligible activation energy;¹³ (ii) O_2/C_2H_4 , in view of the known efficiency of the reaction of CF₃[•] with O₂.^{13a} The expected evolution of the intermediate CF_3O_2 radical is by CF₃[•] transfer to C₂H₄, forming a C-centered radical finally trapped by O₂. The use of NO is particularly appropriate since NO is unreactive toward CF_3^+ and therefore does not interfere with ionic reaction sequences.^{3d} The same cannot be said of C_2H_4 , as discussed in a following section. Significantly, the use of either scavenger system does not affect the trifluoroacetylation product pattern, though it may somewhat influence their absolute yields.

The possible incursion of radical pathways to trifluoroacetylated products was further checked by purposely favoring the formation of CF_3CO^{\bullet} , via reactions 9a and 9b, in a gaseous mixture of CF_3I and CO.

$$CF_3I \xrightarrow{h\nu} CF_3^{\bullet} + I^{\bullet}$$
 (9a)

$$CF_3^* + CO \rightarrow CF_3CO^*$$
 (9b)

In the presence of O_2 , the reaction with benzene, a representative aromatic substrate, leads exclusively to oxidized trifluoromethylation products, ruling out the possibility that CF₃CO[•] radicals, even if formed as stable species, play a role in the formation of trifluoroacetylated products.

CF₃CO⁺ Reaction with n-Type Nucleophiles. The radiolytic trifluoromethylation of n-type nucleophiles is a further evidence of CF₃CO⁺ initiated reaction, showing that a population of thermalized CF₃CO⁺ ions is attained under radiolytic conditions. The formation of c-C₅H₁₀NCOCF₃ (NuCOCF₃) as neutral end product from the reaction with piperidine (c-C₅H₁₀NH = NuH) is strongly indicative of a cationic reaction sequence (eqs 10a-10c). In fact, radicals (e.g., CF₃⁺) are known to react with amines by hydrogen abstraction rather than by addition.¹⁴ The electro-

$$CF_3CO^+ + NuH \longrightarrow CF_3CONuH^+$$
 (10a)

$$CF_3CONuH^+ \xrightarrow{\sim} H^+ CF_3 = C \underbrace{(+)}_{Nu}^{OH}$$
 (10b)

 $CF_3CONuH^+/CF_3C(OH)Nu^+ + NuH \longrightarrow CF_3CONu + NuH_2^+$ (10c)

philic attack of CF_3CO^+ is directed instead to the lone pair electrons on nitrogen, yielding an ammonium ion susceptible of undergoing a hydrogen shift (10b). The deprotonation step by a second NuH molecule (10c) should be thermodynamically favorable, based on data for NuH = MeOH,⁹ and explained by the pronounced electron-withdrawing effect of the CF₃ group.

The reaction of $c-C_5H_{10}NH$ gives, besides the trifluoroacetylation product, high yields of $(c-C_5H_{10}N)_2CO$, deriving from addition of CF₃⁺ to piperidine in the presence of unavoidable traces of adventitious water.¹⁵ The question then rises whether CF₃CO⁺ ions may react by CF₃⁺ transfer or else if a residual population of CF₃⁺ ions coexists with CF₃CO⁺ despite the high exothermicity of the addition of CF₃⁺ to CO. Support to the first hypothesis comes from the reaction of CF₃CO⁺ with H₂O, leading to CF₃OH₂⁺ (eq 2) in ICR experiments. However, at their low pressure (ca. 10⁻⁸ Torr), addition reactions are highly unlikely, and the observed ionic products may simply reflect the most favorable dissociative exit channel rather than an intrinsic reactivity at the CF₃ group.

$$CF_{3}CO^{+} + H_{2}O \rightleftharpoons [CF_{3}COOH_{2}^{+}]^{*} \rightarrow CF_{3}OH_{2}^{+} + CO$$
(11)

The second hypothesis, which we favor, is supported by the reactivity behavior of π -type nucleophiles.

CF₃CO⁺ Reaction with π -Type Nucleophiles. Under radiolytic conditions, CF₃CO⁺ ions form aromatic substitution products, whose ionic origin is ensured both by the careful control of possible radical contributions and by the marked decrease of their yields resulting from addition of NH₃, a powerful ion interceptor, to the gaseous systems. Under ICR conditions, the carbonylation reaction (1) observed with benzene and toluene suggests that the electrophilic attack involves exclusively the carbonyl carbon and proceeds by loss of CF_3H (eq 1), since collisional quenching of excited intermediates is highly inefficient at 10⁻⁸ Torr. The CF₃⁺ transfer reaction observed with H2O, a n-type nucleophile, does not occur with aromatic substrates. This makes the CF_3CO^+ ion behave in a unique fashion as trifluoroacetylating agent toward aromatics, with no other interfering reaction. In general, the reactivity behavior emerging from radiolytic experiments conforms to that expected for a strongly electrophilic species, reacting even with highly deactivated substrates, such as PhCF₃, and displaying an intramolecular selectivity consistent with its electrophilic character. The reaction with PhX, X = ortho/paradirecting group, favors the para with respect to the meta position by a factor increasing from X = Me to $X = OCF_3$, which parallels the deactivating effect of X (2p/m = 1.3 (X = Me); 5 (X = F);13 (X = OCF₃)). The CF₃ group is less deactivating at the meta than at the para position (2p/m = 0.8), in agreement with corresponding σ^+ values.

On the basis of intermolecular reactivity data shown in Table 2, the selected aromatic substrates may be grouped into two sets. The first one includes mesitylene, toluene, and benzene, all showing relative reactivities close to unity, unaffected by changes of radical scavenger, system pressure, or presence of base. In this respect, CF₃CO⁺ does not differ from other strong electrophiles such as $C_2H_5^+$ and i- $C_3H_7^{+.16}$ However, a departure from unit relative reactivities is observed on going to deactivated substrates, reaching the lowest value for PhCF₃ ($k(CF_3)/k(H) \approx 0.35$). In the series of relative reactivities, PhOCF₃ shows an abnormally high value $(k(OCF_3)/k(H) \simeq 1.2)$, despite its deactivation toward electrophilic attack. From such data one cannot expect any correlation between the observed intermolecular reactivities and parameters which measure the electronic effect of substituents on the aromatic ring, such as Brown's σ^+ values. The efficiency of the aromatic trifluoroacetylation reaction under study is not determined (at least not solely) by the rate of formation of the σ -complex intermediate or by its stability. Within the general scheme of electrophilic aromatic substitution reactions in the gas phase, the

SCHEME 1



formation of the σ -complex is preceded by the encounter of CF₃- CO^+ and C_6H_5X to form the collision complex [$CF_3CO^+ \cdot C_6H_5X$] (Scheme 1). The overall rate of reaction depends from the values of the rate constants of individual steps. In the hypothesis of neglecting the k_{-1} rate constant, in view of the high exothermicity of the CF_3CO^+ addition to the aromatic substrate, the observed rate constant obeys the relationship $k_{obs} = k_c k_1 / (k_{-c} + k_1)$. Thus, if the aromatic substrate is not deactivated by the presence of an electron-withdrawing group, formation of the σ -complex is fast with respect to back-dissociation of the collision complex $(k_1 > k_2)$ k_{-c}); the reaction rate is determined by the collision frequency, $k_{obs} = k_c$, which is approximately equal for mesitylene, toluene, and benzene, according to their calculated¹⁷ k_c values, which are as follows: mesitylene, 1.3; toluene, 1.2; benzene, 1.1; PhF, 2.4; PhCl, 2.5; PhCF₃, 4.0; PhOCF₃, 3.4 (all data in molecule⁻¹ cm³ $s^{-1} \times 10^9$). This explains the observed leveling of relative reactivity for these three substrates. As the aromatic ring is progressively deactivated, an increasing fraction of collision complexes undergoes back-dissociation (k_{-c}) rather than evolve to σ -complex (k_1) . The two constants become comparable, and relative reactivities depend on several factors. In general, the reactivity of a given substrate reflects the operation of two factors, namely, its collision constant and the height of the barrier to σ -complex formation, which in turn depends on its electronic activation. The significantly different dipole moments of the various aromatics justify the relatively large differences in the collisional rate constants reported above. The high reactivity of PhOCF₃, electronically deactivated with respect to benzene can be explained by the weight of its higher k_c value on the overall rate constants k_{obs} .

Finally, within the framework of Scheme 1, it is to be emphasized that the primary σ -complex may undergo H shifts $(k_3 \text{ and following steps})$ before being deprotonated by a base. This is suggested by the fact that the reaction of CF₃CO⁺ with toluene selectively deuterated in the para position leads to ortho-, meta-, and para-trifluoroacetylated products showing variable deuterium contents ($95 \pm 2\%$, $92 \pm 2\%$, and $71 \pm 2\%$, respectively), which deviate from those expected in the hypothesis of no hydrogen migration from the primary σ -complex (100%, 100%, and 0%). It is significant that some depletion in deuterium content is observed in the ortho product as well, where the substitution site is more remote from the deuterated position. It also appears that intraannular hydrogen shifts compete favorably with a conceivable H migration to the carbonyl oxygen (k_2) , whose product would be undistinguishable from that obtained in the absence of any shifts.

 CF_3^+ -Initiated Reactions. There are two reasons to discuss data concerning the gas-phase reactivity of CF_3^+ ions under radiolytic conditions in the present context. The first one is related to the process of formation of CF_3CO^+ in the pressure range of the radiolytic systems, and the second one reflects the intrinsic interest of previously unreported reactions. It is apparent from Table 1 that trifluoroacetophenones are not the only products arising from the ratiolytic reactions, being accompanied by $XC_6H_4CF_3$ and XC_6H_4CFO , besides $XC_6H_4COC_2H_4F$ and $XC_6H_4CF_2C_2H_4F$ in those systems containing ethylene. In our view, not only $XC_6H_4CF_3$ but also XC_6H_4CFO originates from radiolytically formed CF3⁺ ions, the former one by the previously reported electrophilic substitution.^{4b} The XC₆H₄CFO product may arise from an addition-elimination process, through the intermediacy of a difluorobenzyl cation (eq 12) which undergoes a second addition-elimination step reacting with adventitious water, prior to final deprotonation. An alternative route to the same reactive intermediate is represented by the protonation of PhCF₃, followed by HF elimination under CI/MS conditions. The same occurs in the radiolytic systems where the intermediate difluorobeenzyl cation, formed by HF elimination from PhCF₃ protonated by radiolytically formed $i-C_3H_7^+$ ions, is trapped by $H_2^{18}O$, leading to 57% ¹⁸O-enriched PhCFO. (Incidentally, the incomplete labeling is suggestive of the presence of adventitious H₂¹⁶O).



Isomeric XC₆H₄COC₂H₄F and XC₆H₄CF₂C₂H₄F products, formed in the presence of ethylene, are likely to arise from the addition of CF₃⁺ to C₂H₄, via a reaction sequence involving migration of a fluorine atom.¹⁸ Their ionic origin is consistent with the decrease of their yields in the presence of NH₃ and by the absence of any fluorine rearrangement in the reported reaction of CF₃ radicals with C_2H_4 .¹⁹

The isolation of products deriving from reactions of CF_3^+ , which cannot be ascribed to CF₃⁺ transfer from CF₃CO⁺ to aromatic compounds on the basis of ICR evidence, suggests that the reactant ion population be composed of comparable fractions of CF_3^+ and CF₃CO⁺ ions, despite the thermodynamic trend to the formation of predominant CF₃CO⁺ ions. This probably reflects the kinetic rather than thermodynamic control of the reactions occurring even in the medium-pressure regime of radiolytic systems, where CF_3^+ ions are not completely converted into CF_3CO^+ owing to the fact that third-body stabilization is still inadequate (eq 8). However, it should be pointed out that those CF_3CO^+ ions stabilized by unreactive collisions with the bulk gas, inhibiting their back-dissociation, may reach thermal equilibrium with the environment, prior to reactive encounter with a substrate molecule. This results from the typically low substrate concentration (ca. 4 mol %) within the bulk CF_4/CO gaseous mixture.

Conclusions

CF₃CO⁺ ion has been generated in the gas phase, and its reactivity has been examined in gaseous media at widely different pressures, thus providing the first data on the behavior of this fluorinated cation. CF₃CO⁺ may be obtained from the EI ionization of TFAA in the low-pressure cell of an ICR spectrometer operating at 10⁻⁸ Torr. This technique has allowed us to gain useful information about its ion-molecule reaction sequences with few representative nucleophiles. ICR studies are not suited to detect possible addition processes which require efficient third-body stabilization of excited adducts, nor subtle reactivity differences which are leveled off in the electrostatic activation regime prevailing at 10-8 Torr. To this end, the radiolytic technique, operating in the pressure range of ca. 1 atm, was exploited, which enabled us to establish relative inter- and intramolecular reactivities within a series of aromatic compounds based on the nature and the yields of isomeric neutral products from competition experiments. Radiolytic experiments were typically run under conditions where initially excited intermediates approach thermal equilibrium with the gaseous environment. This opened a route to CF₃CO⁺ involving the exothermic and entropically unfavorable addition to CF_3^+ to CO. Under these conditions, CF₃CO⁺ reacts with the n-type and π -type nucleophilic centers yielding the corresponding trifluoroacetylation products. The reaction with aromatics shows reactivity trends consistent with the known multistep pathway of gas-phase aromatic substitution reactions by gaseous cations, with relative reactivities governed by the interplay of collisional frequency and barriers to the formation of σ -complex intermediates. With respect to the extremely mild CH₃CO⁺ ion, unable to react with benzene and toluene under typical radiolytic conditions,²⁰ CF₃CO⁺ is reactive toward strongly deactivated substrates such as PhCF₃, greatly enlarging the span of gaseous acylation reactions. Such reactivity difference reflects a markedly different thermodynamic drive for the electrophilic aromatic addition step (eq 13). The

$$CY_{3}CO^{+} + C_{6}H_{6} \longrightarrow (13)$$

addition of CF_3CO^+ to benzene (Y = F) may be estimated exothermic by 44 kcal mol⁻¹ to be compared with the 12 kcal mol⁻¹ exothermicity of the corresponding reaction by CH₃CO⁺ (Y = H)²¹ The information on the reactivity behavior of CF₃-CO⁺ is particularly significant since it refers to a species unambiguously reacting by an exclusive addition path to aromatic compounds, i.e., exhibiting a straightforward Lewis acid character, without interfering proton transfer or group transfer (e.g, CF₃) reactions.

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