J. Am. Chem. Soc. **1983**, *105*, 7267-7271

Nucleophilic Reactions of F_3C^- at sp^2 and sp^3 Carbon in the Gas Phase. Characterization of Carbonyl Addition Adducts

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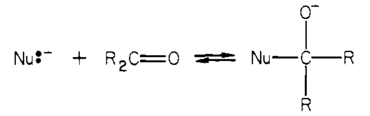
Abstract: The reactions of F_3C^- with CH_3Br and CH_3Cl established the medium kinetic nucleophilicity of F_3C^- on Bohme's reactivity scale for gas-phase S_N2 reactions. The reactions of F_3C^- with $(CH_3)_2C{=}O$ and $CH_3CO_2CH_3$ proceeded by competitive bimolecular H^+ transfer and termolecular carbonyl addition giving the corresponding adduct anions *m/z* 127 and 143, respectively. F_3C^- reacted with the esters $C_6H_5CO_2CH_3$, $CF_3CO_2CH_3$, and $(CH_3O)_2C{=}O$ both by S_N2 displacement forming the corresponding carboxylate anions and by carbonyl addition yielding the adduct anions; with $CF_3CO_2C_2H_5$ and $CF_3CO_2C(CH_3)_3$, the competitive bimolecular reaction channel involved E2 elimination giving $CF_3CO_2^-$. The major reaction channel of F_3C^- with HCO_2CH_3 was the Riveros reaction that produced the series of cluster ions $F_3C^-(HOCH_3)$, $F_3C^-(HOCH_3)_2$, $CH_3O^-(HOCH_3)$, and $CH_3O^-(HOCH_3)_2$, along with a minor amount of carbonyl addition. The fast termolecular reaction of F_3C^- with $(CF_3)_2C{=}O$ exclusively formed the adduct $(CF_3)_3CO^-$ (*m/z* 235) which was characterized as the bound, tetrahedral structure by bracketing its proton affinity. The reaction of F_3C^- with CO_2 giving $CF_3CO_2^-$ was established as a termolecular process when the "apparent" bimolecular rate constant was shown to be P_{He} dependent. These results demonstrate unequivocally that the reactions of gas-phase nucleophiles with the carbonyl group of ketones and esters proceed by addition yielding the corresponding adduct oxyanions which is analogous to the related processes in the condensed phase.

The trifluoromethyl group has been used for years in condensed phase reactions as a "chemically inert" group to destabilize carbonium ions (e.g., $\sigma^+_m = 0.520$ and $\sigma^+_p = 0.612$ are substituent constants for F_3C)[1] and stabilize carbanions. In the gas phase, similar effects of the F_3C group are observed in the acidity (ΔH°_{acid}) of ring substituted phenols[2] and anilines.[3] This effect carries over to the series of alcohols CH_3OH ($\Delta G^\circ_{acid} = 372.6 \pm 2$ kcal mol^{-1}),[3] CF_3CH_2OH ($\Delta G^\circ_{acid} = 356.8 \pm 2$ kcal mol^{-1}),[3] $(CF_3)_2CHOH$ ($\Delta G^\circ_{acid} = 340.8 \pm 2$ kcal mol^{-1}),[4] and $(CF_3)_3COH$ ($\Delta G^\circ_{acid} = 326.7 \pm 2$ kcal mol^{-1})[4] where the CF_3 groups acid strengthening effect is additive ($\delta\Delta G^\circ_{acid} \sim 15$ kcal mol^{-1}).

Our interest in the chemistry of F_3C^- stems from our studies of 1,2- vs. 1,4-addition reactions of nucleophiles with α,β-unsaturated molecules[5] and the observation that F_3C^- served as a good nucleophilic initiator for the anionic oligomerization of $H_2C{=}CHCO_2CH_3$.[6] These factors coupled with our interest in measuring absolute (and relative) reactivities of nucleophilic addition to simple carbonyl-containing molecules[7] suggested that if tetrahedral adducts (**1**) are indeed produced in the gas phase according to eq 1, Nu:$^-$ = F_3C^- should markedly increase the



$$Nu{:}^- + R_2C{=}O \rightleftharpoons Nu{-}\overset{O^-}{\underset{R}{C}}{-}R \qquad \text{(i)}$$

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probability for the direct observation of adducts **1**. This expectation was supported by the observation of the anion *m/z* 197 of the correct mass for the adduct $(CF_3)_2C(O^-)OCH_3$ in the reaction of allyl anion ($C_3H_5^-$) with $CF_3CO_2CH_3$ by the sequence in eq ii–iv.[8] The reasonably large proton affinity of F_3C^- (PA = 375.6 ± 2 kcal mol^{-1})[3a] is only slightly less than that of $C_2H_5O^-$ and indicates that exothermic H^+ transfer from a number of neutral reactants will be a competing reaction channel with addition to the carbonyl group.

$$C_3H_5^- + CF_3CO_2CH_3 \rightarrow [CF_3CO_2^-]^* + CH_3CH_2CH{=}CH_2 \qquad \text{(ii)}$$

$$[CF_3CO_2^-]^* \rightarrow F_3C^- + CO_2 \qquad \text{(iii)}$$

$$F_3C^- + CF_3CO_2CH_3 \xrightarrow{He} \underset{(m/z\ 197)}{(CF_3)_2C(O^-)OCH_3} \qquad \text{(iv)}$$

Bohme et al.[9] reported that stable addition adducts were produced in the gas-phase reactions of H^-, HO^-, and CH_3O^- with $H_2C{=}O$ following third-body collisional stabilization with the buffer gas of the initially formed excited adduct anions. That adducts such as **1** might not be intermediates in reactions of nucleophiles with various derivatives of carboxylic acids gained precedence in the recent report by Kim and Caserio.[10] These latter authors examined the gas-phase acyl transfer from conjugate acids of carboxylic acids and certain derivatives to neutral nucleophiles and concluded that direct displacement (S_N2 type) occurred rather than addition followed by elimination. DeTar[11] has reconsidered the data for several acyl transfer reactions in the condensed phase and suggested that certain of these processes may also proceed by a direct displacement mechanism.[12]

Therefore, it appeared essential to observe and characterize a series of adducts **1** formed in reactions of nucleophilic anions with carbonyl compounds of varying structural types.

Experimental Section

The flowing afterglow (FA) apparatus with a modular flow tube (Figure 1) has been previously described.[6] Briefly, the ion of interest is prepared in the upstream end of a stainless steel flow tube (140 × 7.15 cm i.d.) by electron impact with small concentrations of neutral molecules or by fast ion-molecule reactions using previously generated ions. In

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(11) DeTar, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 7205–7212.

(12) We wish to point out that the gas-phase result reported by Fukuda and McIver (*J. Am. Chem. Soc.*, 1979, *101*, 2498–2499) of CH_3CO_2Ph + $^-OCH_3 \rightarrow CH_3CO_2^-$ [+ CH_3OPh] was in error. The correct product was PhO^- produced by carbonyl addition followed by anionic fragmentation; see: Kleingeld, J. C.; Nibbering, N. M. M.; Grabowski, J. J.; DePuy, C. H.; Fukuda, E. K.; McIver, R. T. *Tetrahedron Lett.* **1982**, *23*, 4755–4758.

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Table I. Summary of Kinetic and Product Data for the Ion-Molecule Reactions of F_3C^-

rxn. no.	ion + neutral reactants	products [assumed neutral]	fraction of product ion signal	$\Delta H°$,[a] kcal mol^{-1}	k_{total},[b] cm^3 $molecule^{-1}$ s^{-1}	k_{ADO},[c] cm^3 $molecule^{-1}$ s^{-1}
1	$F_3C^- + CH_3Br$	$\rightarrow Br^-$ $[+ F_3CCH_3]$	1.00	−62.5	$(2.1 \pm 0.2) \times 10^{-10}$	1.4×10^{-9}
2	$F_3C^- + CH_3Cl$	$\rightarrow Cl^-$ $[+ F_3CCH_3]$	1.00	−54.6	$(5.6 \pm 0.1) \times 10^{-11}$	1.6×10^{-9}
3a	$F_3C^- + (CH_3)_2C{=}O$	$\rightarrow CH_2{=}C(O^-)CH_3$ $[+ HCF_3]$	0.85	−6.8	$(2.5 \pm 0.1) \times 10^{-11}$	2.1×10^{-9}
3b		$\rightarrow (CH_3)_2C(O^-)CF_3$	0.15	−25.1		
4	$F_3C^- + (CF_3)_2C{=}O + He$	$\rightarrow (CF_3)_3CO^- + He$	1.00	−66.9	$(4.5 \pm 0.3) \times 10^{-26}$ [d]	8.1×10^{-26} [d]
5a	$F_3C^- + CH_3CO_2CH_3$	$\rightarrow CH_2{=}C(O^-)OCH_3$ $[+ HCF_3]$	0.72	−4.6	$(5.5 \pm 0.1) \times 10^{-11}$	1.5×10^{-9}
5b		$\rightarrow CH_3(CF_3)C(O^-)OCH_3$	0.28	−10.0		
6a	$F_3C^- + C_6H_5CO_2CH_3$	$\rightarrow C_6H_5(CF_3)C(O^-)OCH_3$	0.77		[e]	
6b		$\rightarrow C_6H_5CO_2^-$ $[+ F_3CCH_3]$	0.23	−57.8		
7a	$F_3C^- + CF_3CO_2CH_3$	$\rightarrow CF_3CO_2^-$ $[+ F_3CCH_3]$	0.67	−70.1	$(1.1 \pm 0.1) \times 10^{-9}$	1.7×10^{-9}
7b		$\rightarrow (CF_3)_2C(O^-)OCH_3$	0.33	−33.7		
8a	$F_3C^- + CF_3CO_2C_2H_5$	$\rightarrow (CF_3)_2C(O^-)OC_2H_5$	0.90	−33.7	$(9.1 \pm 0.1) \times 10^{-10}$	1.8×10^{-9}
8b		$\rightarrow CF_3CO_2^-$ $[+ F_3CC_2H_5]$		−60.0		
8c		$\rightarrow CF_3CO_2^-$ $[+ C_2H_4 + HCF_3]$	0.10	−37.1		
9a	$F_3C^- + CF_3CO_2C(CH_3)_3$	$\rightarrow (CF_3)_2C(O^-)OC(CH_3)_3$	0.92	−33.7	$(8.6 \pm 0.1) \times 10^{-10}$	
9b		$\rightarrow CF_3CO_2^-$ $[+ C_4H_8 + HCF_3]$	0.08	−35.0		
10a	$F_3C^- + (CH_3O)_2C{=}O$	$\rightarrow (CH_3O)_2C(O^-)CF_3$	0.92		$(2.9 \pm 0.3) \times 10^{-11}$	
10b		$\rightarrow CH_3OCO_2^-$ $[+ F_3CCH_3]$	0.08			
11a	$F_3C^- + HCO_2CH_3$	$\rightarrow F_3C^-(HOCH_3) + F_3C^-(HOCH_3)_2 +$ $CH_3O^-(HOCH_3) + CH_3O^-(HOCH_3)_2$	0.96		$(4.2 \pm 0.5) \times 10^{-11}$	1.5×10^{-9}
11b		$\rightarrow CF_3CH(O^-)OCH_3$	0.04			
12	$F_3C^- + CO_2 + He$	$\rightarrow CF_3CO_2^- + He$	1.00	−38.8	1.1 ± 10^{-27} [d]	4.4×10^{-26} [d]

[a] See text and ref 15. [b] Apparent bimolecular k_{total}'s (see Results section for discussion) are estimated to be accurate to ±25%. Errors given are standard deviations from multiple determinations. [c] Calculated collision rate constants using the average dipole orientation theory, ref 16. [d] Termolecular k_{total} in units of cm^6 $molecule^{-2}$ s^{-1} calculated by dividing the "apparent" bimolecular rate constant for decay of F_3C^- by [He]; $[He] = 1.6 \times 10^{16}$ atoms cm^{-3} at 0.5 torr. [e] Not measured.

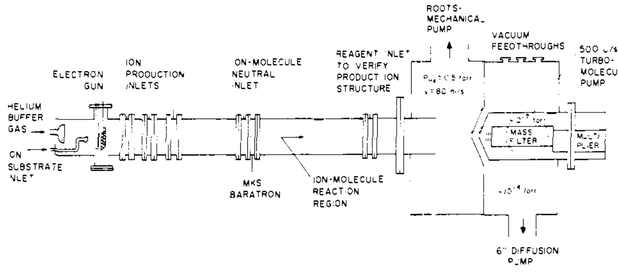

Figure 1. Diagram of the flowing afterglow apparatus.

these experiments, flowing a mixture of H_3N in the buffer gas, helium, over the electron gun yields H_2N^- by dissociative electron attachment (thermal or near-thermalized e^-'s). Addition of HCF_3 to this flow via a port 10 cm downstream of the electron gun yielded vibrationally excited F_3C^- ions by H^+ transfer to H_2N^- ($k = (1.3 \pm 0.2) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}). The vibrationally excited F_3C^- ions were cooled to their vibrational ground state by numerous collisions with the buffer gas ($P_{He} = 0.5$ torr, $\bar{v} = 80$ m s^{-1}) in the next 30 cm of the flow tube prior to reaching the neutral reactant inlet port for addition of the carbonyl-containing substrates. The length of the ion-molecule reaction region was 62.5 cm. The flow was exhausted by means of a large pumping system, but it was sampled into a compartment containing a quadrupole mass spectrometer operating at $\sim 10^{-7}$ torr which monitors the ion composition of the flow.

Kinetic measurements are straightforward and were carried out under pseudo-first-order conditions with the neutral reactant in large excess compared to the ion concentration. The ion-molecular reaction distance was held constant while the concentration of neutral reactant was varied. From the slope of the semilog plot of log $[F_3C^-]$ vs. neutral reactant, the rate constant for the bimolecular ion-molecule reaction was calculated.[13] The estimated error in the rate constants is ±25%. The product ions were also monitored during these experiments which yield the branching fractions reported.

Helium (99.99%; Welders Products) was the buffer gas in these experiments. It was further purified by passage through two traps filled with Davison 4A molecular sieves cooled with liquid N_2 and then warmed to 298 K in a glass coil prior to introduction into the upstream end of the flow tube (Figure 1). Gas and liquid reagents were available from commercial sources (Matheson, PCR, Fisher, Aldrich). The liquid reagents were distilled just prior to use, and a center-cut, constant boiling sample was transferred to a gas storage bulb after three freeze-pump-thaw degassing cycles. The gas reagents were used directly.

Results

The kinetic and product data for the ion-molecule reactions of F_3C^- are summarized in Table I. In all cases, clean pseudo-first-order decay plots of the log ion signal of F_3C^- (m/z 69) vs. concentration of the neutral reactants were observed. The recovery of product ions was always >90% of the decay of the F_3C^- signal. The product channel branching fractions in Table I are the relative product ion signals observed from the mass spectrometer.

In reactions 3 and 5-11 in Table I, the rate constants for decay of the F_3C^- ion signal are listed as bimolecular rate constants. While this is true for the H^+ transfer and S_N2 displacement product channels, observation of the adduct anions requires third-body (termolecular) collisional stabilization of the vibrationally excited adducts by the buffer gas. Since these reactions showed no P_{He} dependence (varied from 0.4 to 1.1 torr) on the "apparent" bimolecular rate constant for decay of F_3C^- or on the branching fraction, saturated termolecularity must be present in the adduct forming product channels even at our lowest buffer gas pressure.

Discussion

Reactions of F_3C^- with CH_3Br and CH_3Cl. For the kinetic nucleophilicity of F_3C^- toward saturated sp^3 carbon to be determined and placed on the reactivity scale of the S_N2 displacement reactions of Bohme et al.,[14a] the reactions of F_3C^- with CH_3Br (reaction 1) and CH_3Cl (reaction 2) were examined. In both of these reasonably exothermic[15] reactions, formation of the corre-

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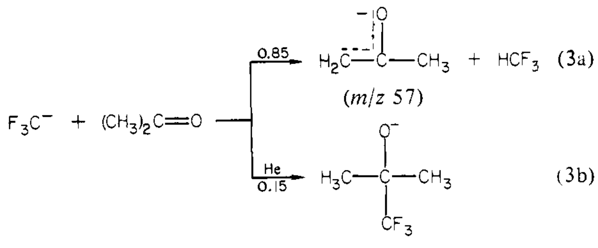
(14) (a) Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. Can. J. Chem. 1976, 54, 1643-1659. (b) See also: Olmstead, W. M.; Brauman, J. I. J. Am. Chem. Soc. 1977, 99, 4219-4228.

(15) The thermochemical data for calculation of $\Delta H°$'s come from standard sources: (a) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. (b) Benson, S. W. "Thermochemical Kinetics"; 2nd ed.; Wiley: New York, 1976. (c) Reference 3a. (d) Calculated $\Delta H_f°$'s for some neutrals were carried out with use of the additivity group tables in ref 15b. (e) $\Delta H_f°(Br^-) = -50.8$ kcal mol^{-1}. (f) $\Delta H_f°(Cl^-) = -54.4$ kcal mol^{-1}. (g) $\Delta H_f°(F_3C^-) = -157.2$ kcal mol^{-1}.[3a]

sponding halide ion was observed. However, the rate constants for both reactions are significantly less than the calculated collision limits, k_{ADO}.[16] This requires that modest barriers separate the collision complexes (F_3C^-/CH_3X) and (X^-/CF_3CH_3) on these double-minimum potential surfaces.[14b,17] Thus, the kinetic nucleophilicity of F_3C^- toward S_N2 displacement with CH_3X molecules must be judged to be *medium*.[14a]

Reactions of F_3C^- with Ketones. The H^+ transfer between F_3C^- and $(CH_3)_2C{=}O$ is exothermic by 6.8 kcal mol^{-1}. Therefore, it was no surprise to find that this was the major product channel in their ion–molecule reaction (eq 3). However, it was gratifying to observe the minor formation of the ion *m/z* 127 which was the sum of the masses of the two reactants. The ion *m/z* 127 was shown not to be the simple hydrogen bonded cluster ion of *m/z* 57 and HCF_3 ($H_2C{=}C(O^-)CH_3{\cdot\cdot}HCF_3$) since the relative intensities of *m/z* 57 and 127 in reaction 3 did not change as a function of varying the [HCF_3] used to generate the F_3C^- anion.



The reaction of F_3C^- with $(CF_3)_2C{=}O$ was examined since only the addition reaction channel was possible. As expected from the reaction exothermicity[18] and the polarizability of this ketone, this fast reaction occurred with the exclusive formation of the adduct anion *m/z* 235. That the rate constant for this reaction was 56% of the termolecular collision limit (k_{ADO})[16] indicated the stability/lifetime of the initially formed excited adduct ($((CF_3)_3CO^-)^*$) and the relative efficiency of collisional stabilization of such excited species in the FA apparatus.

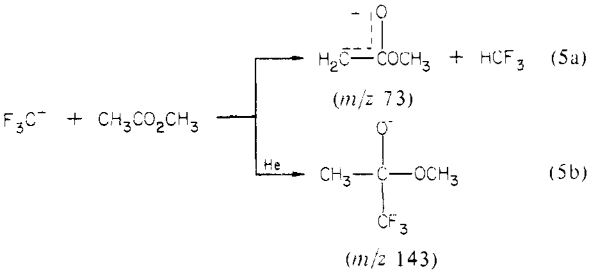
$$F_3C^- + (CF_3)_2C{=}O \xrightarrow{He} \underset{(m/z\ 235)}{(CF_3)_3C{-}O^-} \qquad (4)$$

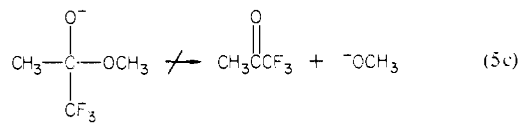
The structures of the adducts *m/z* 127 (eq 3b) and 235 (eq 4), and of the other adducts to be discussed, provide a large density of states in the vibrational and rotational manifold of the adduct. The excess energy of the adduct-forming reaction channel ($\Delta H°$) will be spread over these many states which reduces the probability of sufficient energy concentrating in the stretching vibration of the C–C bond necessary for retro-addition. This increases the lifetime of the excited adduct which allows for collisional deactivation and observation of the adduct anion.

That the above density of states argument cannot be the whole story is seen in the fact that the termolecular addition reactions of H^- and HO^- with $H_2C{=}O$ occurred at about 3% of the collision limit[9] while that of addition of F_3C^- with $(CH_3)_2C{=}O$ was about 0.2% of its collision limit. This suggests that there are also kinetic barriers in these nucleophilic addition processes to carbonyl groups which separate the energy minima of the loose ion–dipole collision complexes and their adducts.

Reactions of F_3C^- with Esters. The reactions of F_3C^- with esters RCO_2R' cannot involve direct nucleophilic displacement to yield $R'O^-$ and $RC({=}O)CF_3$ since such reactions would be strongly endothermic (≥25 kcal mol^{-1}) and would not occur under these gas-phase conditions. However, observation of adduct anions in these reactions would establish that addition to the ester carbonyl group is the lower energy pathway of these two processes.

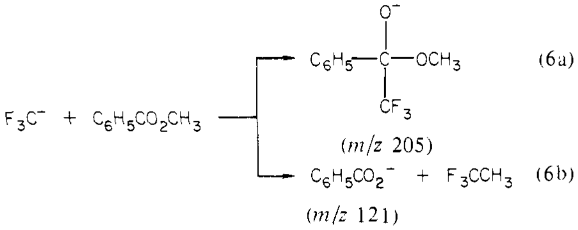
The reaction of F_3C^- with $CH_3CO_2CH_3$ (reaction 5) proceeded with a modest rate constant via two product-forming channels, reaction 5a (78%) involved H^+ transfer ($\Delta H°_{acid}(CH_3CO_2CH_3)$ = 371 kcal mol^{-1})[3] and reaction 5b (28%) yielded the adduct *m/z* 143. The anionic fragmentation of *m/z* 143 shown in eq 5c is strongly endothermic[20] and could not occur since channel 5b was only exothermic by 10 kcal mol^{-1} (Table I). The products of reaction 5c would be expected to undergo H^+ transfer in their loose ion–dipole complex and yield the enolate anion $H_2C{=}C(O^-)CF_3$ (*m/z* 111) and CH_3OH. Anion *m/z* 111 was *not* observed as a product in this reaction. Further, separate studies have shown that enolate anion *m/z* 111 does not form a cluster ion with CH_3OH which eliminates this cluster as a possible structure for the adduct *m/z* 143.





$\Delta H° = +35.3$ kcal mol^{-1}

The reaction of F_3C^- with $C_6H_5CO_2CH_3$ was carried out by adding the vapors of the ester through a special high-boiling inlet connected directly to a reservoir of the liquid ester. Although the rate constant for this reaction could not be measured by using this approach, two product-forming channels were readily observed (eq 6). The major process (77%) involved adduct formation (*m/z* 205) while the minor channel (23%) gave anion *m/z* 121 ($C_6H_5CO_2^-$), the latter presumably formed by S_N2 displacement at methyl C of the ester. Since $C_6H_5CO_2^-$ should be a fairly good anionic leaving group in the S_N2 mechanism and $\Delta H°$ (reaction 6b) = −57.8 kcal mol^{-1}, this result indicates that addition to the carbonyl group of the ester by F_3C^- must be a reaction with a low kinetic barrier separating the initial loose ion–dipole collision complex and the adduct *m/z* 205. The $\Delta H°$ for reaction 6a is considerably *less* than that for reaction 6b. We believe that this failure to follow the product channel of greatest exothermicity demonstrates that closer approach of the anionic nucleophile to the ester group, compared to their separation in the ion–dipole collision complex, is energetically favored along the molecular



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[16] Calculated by using the average dipole orientation theory (ADO): Su, T.; Bowers, M. T. *J. Chem. Phys.*, **1973**, *58*, 3027–3037; *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347–356.

[17] Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993–5999.

[18] $\Delta H_f°((CF_3)_3CO^-)$ = −560.3 kcal mol^{-1} (calcd)[15b,d] using $\Delta H°_{acid}$-$((CF_3)_3COH)$ = 334.3 kcal mol^{-1};[19] $\Delta H_f°((CF_3)_2C{=}O)$ = −336.2 kcal mol^{-1} (calcd)[15b,d] using the group equivalent value of $C(F)_3(CO)$ = −152.4 kcal mol^{-1}.

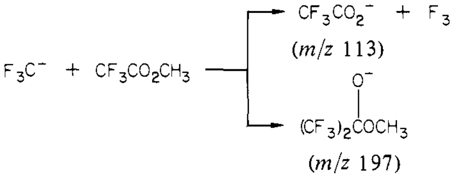
[19] Using $\Delta G°_{acid}((CF_3)_3COH)$ = 326.7 ± 2 kcal mol^{-1} [4] and $\Delta S°_{acid}$-$((CF_3)_3COH)$ = $\Delta S°_{acid}(CF_3CH_2OH)$ = 25.5 cal mol^{-1} deg^{-1}.[3a]

[20] (a) $\Delta H_f°(CH_3(CF_3)C(O^-)OCH_3)$ = −265.2 kcal mol^{-1} (calcd)[15b,d] assuming $\Delta H°_{acid}(CH_3(CF_3)C(OH)OCH_3)$ = 363 kcal mol^{-1}.[20b] (b) $\Delta H°_{acid}$ of the hemiacetal $CF_3CH(OH)OCH_3$ was bracketed between that of $HCCl_3$ ($\Delta H°_{acid}$ = 362 ± 6 kcal mol^{-1})[3] and that of CF_3CH_2OH ($\Delta H°_{acid}$ = 364.4 ± 2 kcal mol^{-1}).[3] We assign the acid strengthening effect of C_α–OCH_3 in hemiacetals and hemiketals to be 1 kcal mol^{-1}.

[21] $\Delta H_f°(C_6H_5(CF_3)C(O^-)OCH_3)$ = −242.4 kcal mol^{-1} (calcd)[15b,d] assuming $\Delta H°_{acid}(C_6H_5(CF_3)C(OH)OCH_3)$ = 353.6 kcal mol^{-1}.[3,20b]

dipole (approximately along the $^{\delta+}C{=}O^{\delta-}$) rather than elsewhere in the molecule.

The reaction of F_3C^- with $CF_3CO_2CH_3$ sets the stage for competitive carbonyl addition and the S_N2 reaction at methyl C with a "super" anionic leaving group.[8,14b] Two product anions, m/z 113 ($CF_3CO_2^-$) and 197 ($(CF_3)_2C(O^-)OCH_3$), were formed in a ratio of 2/1 (reaction 7) in this reaction which occurred on almost every collision. Since the direct displacement of CH_3O^- (+ $(CF_3)_2C{=}O$) from the reactants in reaction 7 is endothermic by 25.7 kcal mol^{-1}, the structure of m/z 197 *cannot* reasonably by represented by the ion–dipole complex ($CH_3O^-/(CF_3)_2CO$).

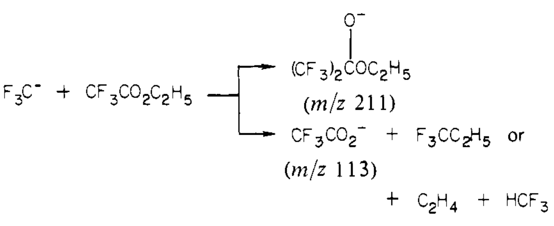


(7a)

(7b)

The fact that reaction channel 7a is exothermic by 70.1 kcal mol^{-1} [22] means that we may be observing only a fraction of the true amount of the S_N2 channel. This is the result of competitive decomposition of some of the vibrationally excited product $CF_3CO_2^-$ ions giving F_3C^- + CO_2 ($\Delta H°$ = +38.8 kcal mol^{-1}) and collisional stabilization by the buffer gas yielding the observed $CF_3CO_2^-$ anions.[8] Therefore, the ratio of reaction channels (7a/7b) = 2 is a lower limit. Since k_{total} is 65% of the calculated collision limit, k_{ADO}, the additional complication of this decomposition pathway means that reaction 7 occurs even closer to the collision limit.

It is known from condensed phase studies of the S_N2 displacement reaction that nucleophilic displacement at C_α of C_2H_5X derivatives is kinetically slower than at methyl C of CH_3X derivatives leading to an average $k_{CH_3}/k_{C_2H_5}$ = 30.[23] This factor appears to carry over to the very fast reaction of F_3C^- with $CF_3CO_2C_2H_5$ (reaction 8) which occurred at 50% of the collision limit. Here we observed that formation of the adduct anion m/z 211 was 90% of the product channels with only 10% leading to production of $CF_3CO_2^-$ (m/z 113). The minor amount of $CF_3CO_2^-$ in reaction 8 may arise by two separate mechanisms, S_N2 nucleophilic displacement at ethyl C_α of the ester (reaction 8b; $\Delta H°$ = −60.0 kcal mol^{-1}) or E2 elimination (reaction 8c; $\Delta H°$ = −37.1 kcal mol^{-1}) since both reactions are exothermic.[24] $CF_3CO_2^-$ is not sufficiently energetic to decompose to F_3C^- and CO_2.



(8a)

(8b)

(8c)

In an attempt to distinguish between the S_N2 (reaction 8b) and E2 (reaction 8c) mechanistic possibilities, the reaction of F_3C^- with $CF_3CO_2C(CH_3)_3$ was examined (reaction 9). Since S_N2 displacement at C_α of the *tert*-butyl is not possible, only elimination reaction 9b could yield $CF_3CO_2^-$. That the k_{total}'s and product channels of reactions 8 and 9 are the same within experimental error lead us to conclude that the reaction channel yielding $CF_3CO_2^-$ in reaction 8 is primarily or exclusively reaction 8c, the E2 elimination pathway.

Thus, $k_{CH_3}/k_{C_2H_5} > 7$ (0.67/0.10) is established in these gas-phase S_N2 reactions which occur at or near the collision limit.[25]

We believe that in each of these reactions, a single loose collision complex $[F_3C^-/CF_3CO_2R]$ is produced which then is partitioned between (a) addition to the ester carbonyl group giving the adduct and (b) attack at the alkyl group (S_N2 for R = CH_3 or E2 for R = C_2H_5) producing $CF_3CO_2^-$. The barriers separating the collision complex and the next stage of the product channels must be small to account for the very fast rates of these reactions. We do not know the degree of enthalpic and/or entropic contributions to the $k_{CH_3}/k_{C_2H_5}$ ratio, but determination of the temperature effects on these and related S_N2 reactions is clearly required.

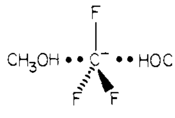
The reaction of F_3C^- with dimethyl carbonate ($(CH_3O)_2C{=}O$, reaction 10) proceeded with a modest rate constant. The major product-forming channel was formation of the adduct m/z 159 along with a minor amount of m/z 75 believed to be the methyl carbonate anion produced by S_N2 displacement at methyl C. These results suggest that a partial list of carboxylate leaving group abilities in S_N2 reactions is $CH_3CO_2^- < CH_3OCO_2^- < C_6H_5CO_2^- < CF_3CO_2^-$. The order of the first and last two carboxylates follow their known PA's.[3a,14b]

The major product channel(s) in the reaction of F_3C^- with HCO_2CH_3 involved formation of a series of cluster ions, m/z 101 ($F_3C^-{\cdot\cdot}HOCH_3$), 133 ($F_3C^-{\cdot\cdot}(HOCH_3)_2$), 63 ($CH_3O^-{\cdot\cdot}HOCH_3$), and 95 ($CH_3O^-{\cdot\cdot}(HOCH_3)_2$), and a minor amount (4%) of the adduct m/z 129 ($CF_3CH(O^-)OCH_3$) (reaction 11). The first-formed cluster ion m/z 101 was readily explained via a Riveros reaction[26] shown in eq 13.[27] Since the rate of the reaction of F_3C^- with HCO_2CH_3 was slow, considerable HCO_2CH_3 (>10^{12} molecules cm^{-3}) was required to decay the signal of F_3C^-. This allows secondary Riveros reactions of [base$^-{\cdot\cdot}$HOCH$_3$] clusters with HCO_2CH_3 to occur.[7] H^+ transfer from CH_3OH to F_3C^- is mildly endothermic (3.6 kcal mol^{-1}).[3a] The similar values of the acid strengths of HCF_3 ($\Delta H°_{acid}$ = 375.6 ± 2 kcal mol^{-1})[3a] and CH_3OH ($\Delta H°_{acid}$ = 379.2 ± 2 kcal mol^{-1})[3a] should produce a reasonably strong hydrogen bonded cluster ion.[28] However, the intensity of the ion signal of m/z 101 was low, went through a maximum at low concentrations of HCO_2CH_3 added to the flow, and decayed rapidly as further HCO_2CH_3 was added yielding the cluster ion m/z 133 (eq 14). The data require that $k_{(14)} > k_{(13)}$.

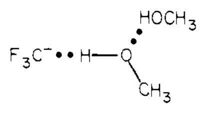
$$\underset{}{F_3C^-} + HCO_2CH_3 \rightarrow \underset{(m/z\ 101)}{F_3C^-{\cdot\cdot}HOCH_3} + CO \qquad (13)$$

$$\underset{(m/z\ 101)}{F_3C^-{\cdot\cdot}HOCH_3} + HCO_2CH_3 \rightarrow \underset{(m/z\ 133)}{F_3C^-{\cdot\cdot}(HOCH_3)_2} + CO \qquad (14)$$

To account for the formation of cluster m/z 63, we suggest that a portion of m/z 133 suffers H^+ transfer yielding m/z 63 and HCF_3. The ratio (m/z 133)/(m/z 63) = 1 was independent of P_{He} from 0.4 to 1.1 torr. Therefore, it appears unlikely that m/z 63 was generated from decomposition of a portion of excited m/z 133 cluster ions since that fraction of m/z 133 decomposing to m/z 63 and HCF_3 should decrease as collisions with the buffer gas increase. It may be that the secondary Riveros reaction of $F_3C^-{\cdot\cdot}HOCH_3$ with HCO_2CH_3 produced two isomeric product cluster ions, the stable symmetrically solvated anion **4**, and the metastable cluster **5**. Cluster **5** might then decompose directly to HCF_3 and $CH_3O^-{\cdot\cdot}HOCH_3$ (m/z 63).[29] The secondary



4



5

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(22) (a) $\Delta H_f°(CF_3CO_2CH_3)$ = −240.7 kcal mol^{-1} (calcd).[15b,d,18] (b) $\Delta H_f°((CF_3)_2C(O^-)OCH_3)$ = −431.6 kcal mol^{-1} (calcd)[15b,d] assuming $\Delta H°_{acid}((CF_3)_2C(OH)OCH_3)$ = 347.4 kcal mol^{-1}.[20b]

(23) Streitwieser, A. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962; pp 11–13.

(24) (a) $\Delta H_f°(CF_3CO_2C_2H_5)$ = −248.9 kcal mol^{-1} (calcd).[15b,d] (b) $\Delta H_f°((CF_3)_2C(O^-)OC_2H_5)$ = −439.8 kcal mol^{-1} (calcd)[15b,d] assuming the same $\Delta H°_{acid}$ of this hemiketal as in ref 22b.

(25) A $k_{CH_3}/k_{C_2H_5}$ = 16 was observed in the reactions of $S^{-\cdot}$ with CF_3CO_2R which also occured at nearly the collision limit.[7]

(26) Faigle, J. F. G.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 2049–2052 and references therein.

(27) $\Delta H°$ = +12.7 kcal mol^{-1} for formation of HCF_3 + CH_3O^- + CO in reaction 13.[15]

(28) (a) Sullivan, S. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1160–1165. (b) Yamdagni, R.; Kebarle, P. *Ibid.* **1971**, *93*, 7139–7143.

Riveros reaction shown in eq 15 was previously established in the FA, $k_{(15)} = (1.2 \pm 0.1) \times 10^{11}$ cm^3 molecule^{-1} s^{-1}.[7]

$$CH_3O^- \cdot\cdot HOCH_3 + HCO_2CH_3 \rightarrow CH_3O^- \cdot\cdot (HOCH_3)_2 + CO \quad (15)$$

Reaction of F_3C^- with CO_2. The reactions of anions (R^-) with CO_2 yielding carboxylate anion products (RCO_2^-) determined in flow systems are listed as termolecular reactions[30] (eq 16) where M is the buffer gas. However, the termolecularity of eq 16 has been established in relatively few examples.

$$R^- + CO_2 + M \rightarrow RCO_2^- + M \quad (16)$$

The reaction of F_3C^- with CO_2 under our standard operating conditions of $P_{He} = 0.5$ torr and $\bar{v} = 80$ m s^{-1} produced exclusively the carboxylate anion m/z 113 with a modest apparent bimolecular rate constant, $k = (1.2 \pm 0.1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Repeating the experiment with the flow exhaust gate valve partially throttled ($P_{He} = 1.1$ torr, $\bar{v} = 36$ m s^{-1}) gave the same product anion, m/z 113, but the apparent bimolecular rate constant doubled, $k = (3.4 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. This change in rate constant as a function of P_{He} is outside of maximum errors and indicates that $(CF_3CO_2^-)^*$ was produced in a distribution of vibrationally excited states which can be stabilized by collisions with third bodies (M) present in the flow (eq 17). Since the

$$F_3C^- + CO_2 \underset{k_E}{\overset{k_{Bi}}{\rightleftharpoons}} (F_3CCO_2^-)^* \xrightarrow{k_M[M]} \underset{(m/z\ 113)}{F_3CCO_2^-} \quad (17)$$

principal third body (M) present in the flow is He, the termolecular rate constant, $k = 1.1 \times 10^{-27}$ cm^6 molecule^{-2} s^{-1}, is calculated for this reaction involving helium in collisional stabilization of the initially produced excited product ion.

Characterization of the Adduct $(CF_3)_3CO^-$ as a Tetrahedral Alkoxide. Brauman et al.[31] reported that $RCOCl_2^-$ species, produced by a Cl^--transfer ion-molecule reaction to neutral RC(=O)Cl, could be minima on the potential surfaces and were "probably best described as a tetrahedral intermediate". Bowie[32] and co-workers have observed small signals attributed to adduct ions formed in the reactions of various anions with anhydrides. Our results of the reactions of $PhN^{-\cdot}$ and $S^{-\cdot}$ with ketones also gave small signals of adduct species, the intensity of which increased with increasing P_{He}.[7] However, the precise structures of these adducts remain ill defined. The most convincing results of addition adduct formation were described by Bohme et al.[9] in the termolecular reactions of H^-, HO^-, and CH_3O^- with $H_2C{=}O$. However, the suggestion that the observed anion products with the mass of the adduct were, in fact, ion-dipole complexes cannot be unequivocally set aside. We, therefore, decided to establish the structure of one of the above adduct ions by determining its proton affinity (PA).

Experiments carried out in the FA are unique among gas-phase methods in that ions can be sequentially produced and reacted by the addition of different reactant gases through inlet ports placed along the length of the flow tube. In the design and construction of our present modular flow tube (Figure 1), an addition port was installed 40 cm downstream of the neutral reactant inlet port. If the ion-molecule reaction of interest was fast (to completely remove precursor ions) and a single (or, at least major) product ion resulted, chemical and/or thermochemical information on this product ion can be obtained to verify its structure from the results of further ion-molecule reactions of this ion with other neutral reagents added via this final port.

Among the present results, the reaction of F_3C^- with $(CF_3)_2C{=}O$ satisfies both requirements of the original ion-molecule reaction. Since $\Delta H^\circ_{acid}((CF_3)_3COH) = PA((CF_3)_3CO^-) = 334.3 \pm 2$ kcal mol^{-1},[18] potential H^+ donors were added through the final port to bracket the PA of the m/z 235 adduct ion. If m/z 235 was the ion-dipole complex $(F_3C^-/(CF_3)_2C{=}O)$, we would expect its PA to be close (or equal) to that of F_3C^- itself.

The three potential H^+ donors of known gas-phase acidity[3a] selected for this study were HCO_2H ($\Delta H^\circ_{acid} = 345.2 \pm 2$ kcal mol^{-1}), HCl ($\Delta H^\circ_{acid} = 333.6 \pm 2$ kcal mol^{-1}), and CF_3CO_2H ($\Delta H^\circ_{acid} = 322.7 \pm 2$ kcal mol^{-1}). The results of adding separately these three acids to the flow containing only the ion m/z 235 produced by eq 4 are shown in eq 18–20. The fact that no reaction

$$m/z\ 235 + HCO_2H \rightarrow \text{no reaction} \quad (18)$$

$$m/z\ 235 + HCl \rightarrow Cl^- + \underset{(m/z\ 271,\ 273)}{(CF_3)_3CO^- \cdot\cdot HCl} \quad (19)$$

$$m/z\ 235 + CF_3CO_2H \rightarrow \underset{(m/z\ 113)}{CF_3CO_2^-} + \underset{(m/z\ 227)}{CF_3CO_2^- \cdot\cdot HO_2CCF_3} + \underset{(m/z\ 349)}{CF_3CO_2^- \cdot\cdot HOC(CF_3)_3} \quad (20)$$

occurred between m/z 235 and HCO_2H establishes the structure of the ion m/z 235 as perfluoro-*tert*-butoxide anion. This is supported by the results from reaction 19 where both products were of similar intensities indicating an equilibrium process between ions and neutrals of similar basicities and acidities, and from reaction 20 where the ions m/z 113 and 227 are the major products and m/z 349 was minor.

Conclusion

We consider that the above data are reasonable and sufficient evidence that each of the adducts produced in reactions 3b, 4, 5b, 6a, 7b, 8a, 9a, 10a, and 11b have the corresponding tetrahedral structures formed by nucleophilic addition of F_3C^- to the carbonyl group of the corresponding neutral reactant. Further, we conclude that this mechanism generally describes the gas-phase reactions of anions with neutral carbonyl-containing molecules and is analogous to that established for related processes in the condensed phase.[33,34]

Acknowledgment. We gratefully acknowledge support of this research from the U.S. Army Research Office and the National Science Foundation (equipment grant) and encouragement from Professor D. W. Setser.

Registry No. F_3C^-, 54128-17-5; CH_3Br, 74-83-9; CH_3Cl, 74-87-3; $(CH_3)_2C{=}O$, 67-64-1; $(CF_3)_2C{=}O$, 684-16-2; $CH_3CO_2CH_3$, 79-20-9; $C_6H_5CO_2CH_3$, 93-58-3; $CF_3CO_2CH_3$, 431-47-0; $CF_3CO_2C_2H_5$, 383-63-1; $CF_3CO_2C(CH_3)_3$, 400-52-2; $(CH_3O)_2C{=}O$, 616-38-6; HCO_2CH_3, 107-31-3; CO_2, 124-38-9.

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(30) Albritton (Albritton, D. L. *At. Data Nucl. Data Tables* **1978**, *22*, 1–101) lists ion-molecule reaction rate constants measured in flow reactors through 1977.

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(33) Bender, M. L. *J. Am. Chem. Soc.* **1951**, *73*, 1626–1629; *Chem. Rev.* **1960**, *60*, 53–113.

(34) For a general discussion and further references, see: March, J. "Advanced Organic Chemistry"; 2nd ed.; McGraw-Hill: New York, 1977; pp 307–311.