trometer used in these studies was provided by NIH Grant GM27551.

Registry No. $[(EtO)_3SiCH_2CH_2PPh_2]Ru(CO)_4$, 80441-14-1; $[(EtO)_3SiCH_2CH_2PPh_2]_3Ru_3(CO)_9$, 80447-60-5; SiO_2, 7631-86-9; $Ru(CO)_4(PPh_2Me)$, 57894-45-8; $[(EtO)_3SiCH_2CH_2PPh_2]Ru(CO)_3PPh_3$, 80441-15-2; $[(EtO)_3SiCH_2CH_2PPh_2]Ru(CO)_3(P(OCH_2)_3CCH_2CH_3)$, 80441-16-3; $Ru_3(CO)_9(PPh_2Me)_3$, 38686-56-5.

Gas-Phase Reactions of Certain Nucleophiles with Alkyl Trifluoroacetates. A New Probe To Distinguish between S_N2 and E2 Mechanisms for Alkyl Derivatives

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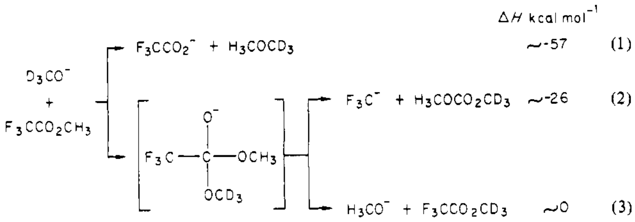
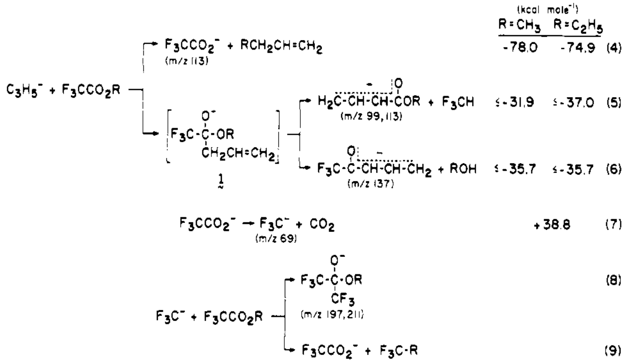
The gas-phase reactions of methyl trifluoroacetate with several nucleophiles appeared to proceed exclusively by the most exoergic reaction channel available, an S_N2 displacement by the nucleophile on the methyl carbon and formation of $CF_3CO_2^-$ (reaction 1).[1,2]



Reactions 2 and 3 illustrate two other potential product-forming channels for the reaction of D_3CO^- with $F_3CCO_2CH_3$; formation of H_3CO^- (reaction 3) was not observed.[1] When this reaction, using H_3CO^-, was repeated in our flowing in afterglow (FA) apparatus (conditions: helium buffer gas, $P_{He} = 0.5$ torr, $\bar{v} = 80$ m s^{-1}, 298 K)[3] to determine the rate constant $[(1.7 \pm 0.2) \pm 10^{-9}$ cm^3 $molecule^{-1}$ $s^{-1}]$, we observed that small amounts of F_3C^- (m/z 69) were produced, going through a maximum (10% of total product signals) in the early stages of the reaction.[4] We wish to report our preliminary results of the related gas-phase reactions of allyl anion with F_3CCO_2R, R = CH_3, C_2H_5, and t-C_4H_9, which establish that (a) *both* displacement on R and carbonyl addition are competitive, product-forming channels, (b) another pathway yielding F_3C^- is the decomposition of excited $F_3CCO_2^-$ formed in highly exoergic nucleophilic displacement processes, and (c) the decomposition of excited $F_3CCO_2^- \rightarrow F_3C^- + CO_2$ (and related decompositions) is useful to distinguish between S_N2 displacement vs. E2 elimination mechanisms in the reactions of C_2H_5X substrates with anions.

To enable us to identify both competitive displacement and addition reaction pathways and to insure that F_3C^- could not reasonably be formed by decomposition of the carbonyl addition adduct, we have used allyl anion[5] ($C_3H_5^-$) as the nucleophile. $C_3H_5^-$ is kinetically a good nucleophile in its reactions with H_3CX compounds,[6] and the anionic decomposition products from the addition adduct **1** (R = CH_3) would be the delocalized enolate anions $H_2C{=}CH{-}CH{=}C({-}O^-)CF_3$ and/or $H_2C{=}CH{-}CH{=}C({-}O^-)OCH_3$ formed by loss of CH_3OH and F_3CH, respectively[7] (discussed below).

The reaction of $C_3H_5^-$ with $F_3CCO_2CH_3$ occurred with essentially every collision, $k = (1.7 \pm 0.1) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}.[9a] The final anion reaction products (addition of 2.4×10^{11} molecules cm^{-3} of ester, $P_{He} = 0.5$ torr, $\bar{v} = 80$ m s^{-1}, 298 K)[3] were $F_3CCO_2^-$ (m/z 113), F_3C^- (m/z 69), $H_2C{=}CHCH{=}C({-}O^-)OCH_3$ (m/z 99), $H_2C{=}CHCH{=}C({-}O^-)CF_3$ (m/z 137), and $(F_3C)_2C({-}O^-)OCH_3$ (m/z 197) in the ratio of 55:23:8:7:7, respectively. From the plot of log ion signal vs. $[F_3CCO_2CH_3]$ added to the flow, it was obvious that the amount of F_3C^- went through an early maximum and then decreased to give the above final results. This was separately shown to be the result of a fast reaction of F_3C^- with $F_3CCO_2CH_3$ [$k = (1.1 \pm 0.1) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}],[9b] giving a 2:1 ratio of $F_3CCO_2^-$ (m/z 113) and the addition adduct $(F_3C)_2C({-}O^-)OCH_3$ (m/z 197). These results lead to the reaction channels formulated in reactions 4–9. That the amount of adduct m/z 197 was only 13% of the signal for m/z 113 from the reaction of $C_3H_5^-$ with $F_3CCO_2CH_3$ while it was 50% of m/z 113 in the reaction of F_3C^- with $F_3CCO_2CH_3$ is consistent with stepwise formation of excited $F_3CCO_2^-$ followed by competitive decomposition (yielding F_3C^- and CO_2) and third-body (He) collisional stabilization.



The reaction of $C_3H_5^-$ with $F_3CCO_2C_2H_5$ was also fast [$k = (1.5 \pm 0.1) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}].[9a] The final ion products were F_3C^- (m/z 69), $H_2C{=}CHCH{=}C({-}O^-)CF_3$ (m/z 137), $F_3CCO_2^-$ (m/z 113), and $(CF_3)_2C({-}O^-)OC_2H_5$ (m/z 211) in a ratio of 32:27:24:17, respectively, under the same conditions given above for the reaction of the methyl ester. (Note the differences in this ratio and that of the methyl ester and the absence of $H_2C{=}CHCH{=}C({-}O^-)OC_2H_5$.[10]) As in the case of the reaction of the methyl ester, the ion signal for F_3C^- (m/z 69) was observed to go through an early maximum. The followup reaction of F_3C^- with $F_3CCO_2C_2H_5$ was separately determined, $k = (9.1 \pm 0.3) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1},[9b] and gave an inverted ratio of 0.1 for the products $F_3CCO_2^-$ (m/z 113) and the adduct $(F_3C)_2C({-}O^-)OC_2H_5$ (m/z 211). While reactions 4 and 6–9 (R = C_2H_5) apply to formation of these products, we must also consider the E2 elimination mechanism (reaction 10) for the formation of $F_3CCO_2^-$ from this ethyl ester.

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[1] Comisarow (Comisarow, M. *Can. J. Chem.* **1977**, *55*, 171) was not explicit in the mechanism by which $CF_3CO_2^-$ was formed.

[2] Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.

[3] McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491.

[4] Formation of small amounts of F_3C^- was observed early in the reaction $H_2N^- + F_3CCO_2H \rightarrow F_3CCO_2^- + NH_3$, $\Delta H = -80$ kcal mol^{-1}, but not in the reaction $F^- + F_3CCO_2CH_3 \rightarrow F_3CCO_2^- + FCH_3$, $\Delta H = -43$ kcal mol^{-1}.

[5] Allyl anion was produced in the upstream end of the flow tube by the reactions (a) $H_2N^- + CH_3CH{=}CH_2$ and (b) $F^- + (H_3C)_3SiCH_2CH{=}CH_2$ (DePuy, C. H.; Bierbaum, V. M.; Flipping, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012.

[6] $C_3H_5^- + CH_3Br \rightarrow Br^- +$ 1-butene, $k = (7.7 \pm 0.3) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}; $C_3H_5^- + CH_3Cl \rightarrow Cl^- +$ 1-butene, $k = (2.9 \pm 0.1) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.

[7] The $\Delta H°_{acid}$'s of the vinylogues $F_3CC({=}O)CH_2CH{=}CH_2$ (≤ 340 kcal mol^{-1}) and $H_2C{=}CHCH_2CO_2CH_3$ (≤ 361 kcal mol^{-1}) are estimated to be ≥ 10 kcal mol^{-1} lower than those of $F_3CC({=}O)CH_3$ (350 kcal mol^{-1}) and $H_3CCO_2CH_3$ (371 kcal mol^{-1}),[8] respectively; $\Delta H°_{acid}(F_3CH) = 376$ kcal mol^{-1} and $\Delta H°_{acid}(H_3COH) = 379$ kcal mol^{-1}.[8] Decomposition of adduct **1** is favored by ≥ 15 kcal mol^{-1} to yield $H_2C{=}CHCH{=}C({-}O^-)OR + HCF_3$ rather than F_3C^- + ester.

[8] Bartness, J. E.; McIver, R. T. "Gas Phase Ion Chemistry"; Bowers, M. T., Ed., Academic Press: New York, 1979; Vol. 2, Chapter 11.

[9] Collision limit rate constants are calculated by the average dipole orientation theory (Su, T.; Bowers, M. T. *J. Chem. Phys.* **1973**, *58*, 3027. *Int. J. Mass. Spectrom. Ion Phys.* **1973**, *12*, 374): (a) $k_{ADO} = 2.1 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} for the reactions of $C_3H_5^-$ with these three esters. (b) $k_{ADO} = 1.8 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} for the reactions of F_3C^- with either ester.

[10] Although both $F_3CCO_2^-$ and $H_2C{=}CH{-}CH{=}C(O^-)OC_2H_5$ are m/z 113, the (M + 1) (m/z 114) ion clearly shows that m/z 113 is only $F_3CCO_2^-$.

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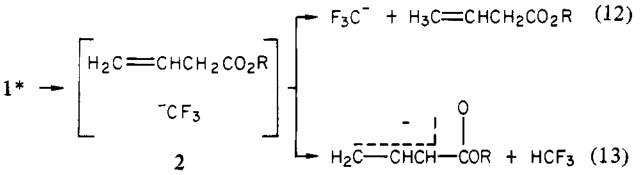
	ΔH, kcal mol^{-1}	
$C_3H_5^- + F_3CCO_2C_2H_5 \rightarrow F_3CCO_2^- + C_2H_4 + C_3H_6$	−52.2	(10)
$C_3H_5^- + F_3CCO_2C(CH_3)_3 \rightarrow F_3CCO_2^- + H_2C{=}C(CH_3)_2 + C_3H_6$	−50.0	(11)

To determine if the exoergicity of reaction 10 would be sufficient to effect the secondary decomposition of $F_3CCO_2^- \rightarrow F_3C^- + CO_2$ observed in the reaction of the ethyl ester, we examined the reaction of $C_3H_5^-$ with the *tert*-butyl ester, $F_3CCO_2C(CH_3)_3$. Here, again, a fast pseudo-first-order decay of $C_3H_5^-$ was observed ($k = (1.3 \pm 0.1) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1})[9a] along with the formation of two product ions, $F_3CCO_2^-$ (*m/z* 113; 18%) and $H_2C{=}CHCH{=}C({-}O^-)CF_3$ (*m/z* 137; 82%). Significantly, *no* ion signals due to F_3C^- or its addition adduct with the ester, $(F_3C)_2C({-}O^-)OC(CH_3)_3$,[11] were observed. These data and the striking similarities between the reactions in (10) and (11) lead to the conclusion that the E2 elimination reaction of $C_3H_5^-$ with $F_3CCO_2C_2H_5$ would *not* yield $F_3CCO_2^-$ with sufficient internal energy to allow it to decompose to produce F_3C^-. Therefore, *the major reaction channel in the reaction of $C_3H_5^-$ with F_3CCO_2R ($R = CH_3$ and C_2H_5) involves nucleophilic displacement of C_α of R, but carbonyl addition by the nucleophile is a competing process.*

The above discussion has assumed that F_3C^- will not be formed by decomposition of the carbonyl addition adducts **1**. Adduct **1** will be produced energetically "hot" and fragment before they are "cooled off" by collisions with the helium buffer gas. Considering the fragmentation channel where the $F_3C{-}C$ bond undergoes heterolysis, a long-lived, ion–neutral collision complex **2** would result.[12] While both exit channels (12) and (13) are overall exoergic (see reactions 5 and 6), proton transfer via exit channel (13) is favored by ≥15 kcal mol^{-1}.[7] This thermochemical argument for fragmentation of **1** by reaction 13 is supported by the observation that F_3C^- was *not* formed in the reaction of $C_3H_5^-$ with $F_3CCO_2C(CH_3)_3$ where carbonyl addition followed by fragmentation of the adduct **1** was the principal reaction channel.



Therefore, we consider the source of the ion F_3C^- in these reactions to be excited $F_3CCO_2^-$.[13] Since the decomposition of $F_3CCO_2^- \rightarrow F_3C^- + CO_2$ (reaction 7) is strongly endoergic (38.8 kcal mol^{-1}), we can expect it to occur only from the more exoergic reactions leading to excited $F_3CCO_2^-$ (reaction 4).[4] Such unimolecular decomposition will compete with stabilization by collisions with the buffer gas (k_s[He]).

The relatively low exoergicity (−57 kcal mol^{-1}) of the S_N2 channel in the reaction of H_3CO^- with $F_3CCO_2CH_3$ (reaction 1) also suggests that F_3C^- will not be formed by this channel. Thus, the observation of F_3C^- as a product of this reaction is believed to arise by the carbonyl addition–anionic fragmentation shown in reaction 2.

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. We thank Tomas Bratt, a summer exchange student from Lunds Institute of Technology, Lund, Sweden, for synthesis of $F_3CCO_2C(CH_3)_3$.

Registry No. H_3CO^-, 8315-60-4; $C_3H_5^-$, 1724-46-5; $F_3CCO_2CH_3$, 431-47-0; $F_3CCO_2^-$, 14477-72-6; F_3C^-, 54128-17-5; $H_2C{=}CHCH{=}C({-}O^-)OCH_2$, 80462-73-3; $H_2C{=}CHCH{=}C({-}O^-)CF_3$, 80462-74-4; $(F_3C)_2C({-}O^-)OCH_3$, 80462-75-5; $F_3CCO_2C_2H_5$, 383-63-1; $(CF_3)_2C({-}O^-)OC_2H_5$, 80462-76-6; $F_3CCO_2C(CH_3)_3$, 400-52-2.

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[11] Formation of the adduct $(F_3C)_2C({-}O^-)OC(CH_3)_3$ is the major reaction channel in the reaction $F_3C^- + F_3CCO_2C(CH_3)_3$. F_3C^- has a considerably lower proton affinity (PA = 375.6 ± 2 kcal mole^{-1})[8] compared to that of $C_3H_5^-$ (PA = 390.8 ± 2 kcal mole^{-1}).[8]

[12] Farneth, W. E.; Brauman, J. I., *J. Am. Chem. Soc.*, **1976**, *98*, 7891.

[13] The decomposition of $F_3CCO_2^-$ has direct solution analogies in the thermal decompositions of $X_3CCO_2^-M^+$ salts and the base cleavages of esters X_3CCO_2R (where R has C_β-H bonds for elimination), producing X_3C^- as sources for $X_2C + X^-$. See: Kirmse, W., "Carbene Chemistry," 2nd. Ed., Academic Press, New York, 1971; pp 137–140.

A Periodonium Trifluoromethanesulfonate. An Isolable 10-I-4 Organoiodine Species

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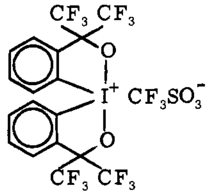
We report the isolation and characterization of a stable pseudotrigonal-bipyramidal (TBP) 10-I-4[1] species with organic ligands,[2a,b] periodonium trifluoromethanesulfonate (triflate) salt **1**.[3] Just as the familiar iodonium ion (an 8-I-2 species) can be viewed as having been derived from an iodinane (a 10-I-3 species) by heterolysis of a bond joining one of the three ligands to iodine, a periodonium ion (a 10-I-4 species) can be viewed as having been derived in this same way from a periodinane[4] (a 12-I-5 species).

$$R_nIX_{5-n} \rightarrow R_nI^+X_{4-n} + X^-$$

The periodonium ion of **1** is isovalent and isostructural with sulfurane **2a**[5] and the phosphoranide anion of **3a**.[6] Earlier studies of **2a**,**b**[5,7] and **3a**,**b**[6,8] provided evidence for the efficacy of the bidentate ligand[5] common to all five structures in stabilizing pseudo-TBP 10-X-4 species which contain hypervalent[9] nonmetals. Sulfuranes **2a**,**b**, in particular, are very stable compounds. In sharp contrast to their acyclic analogues,[10] they are inert toward aqueous acid.[7,11]



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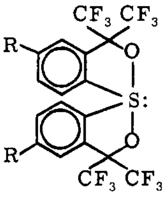
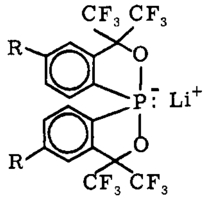


2a R = H
b R = C(CH$_3$)$_3$



3a R = H
b R = CH$_3$

The pictured structure for the periodonium cation **1** is consistent

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[1] Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

[2] (a) The salt $IF_4^+SbF_6^-$ has been made. It is extremely reactive, even toward compounds such as carbon tetrachloride. Its X-ray crystallographic structure shows a distorted TBP geometry for the IF_4^+ cation, with some evidence of bridging to two of the fluorine atoms of the hexafluoroantimonate counteranion. See: Woolf, A. A. *J. Am. Chem. Soc.* **1950**, *72*, 3678. Giber, D. D. *Nucl. Sci. Abstr.* **1973**, *28*, 26892. (b) The periodonium salt $C_6F_5IF_3^+SbF_6^-$ has been observed by ^{19}F NMR spectroscopy in solution in SbF_5 and SO_2Cl_2 at temperatures below −10 °C. The salt decomposes after a few minutes at 40 °C. See: Bardin, V. V.; Furin, G. G.; Yakobson, G. G. *Zh. Org. Khim.* **1980**, *16*, 1256.

[3] Mp 288–291 °C; ^1H NMR (CD_3CN) δ 8.031–8.253 (8 H, complex multiplet); ^{19}F NMR (CD_3CN) δ −72.10 (6 F, q, J_{FF} = 9 Hz), −75.05 (6 F, q, J_{FF} = 9 Hz), −75.04 (3 F, s, CF_3 on $CF_3SO_3^-$); mass spectrum (field desorption) *m/e* 760 ($M^{+\cdot}$), 611 ($M^{+\cdot} - CF_3SO_3$). Anal. ($C_{19}H_8F_{15}IO_5S$) C, H, F, I, S; osmometric *M*, (CH_3CN) 420.

[4] Amey, R. L.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5294.

[5] Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, M. R.; Martin, J. C. *J. Org. Chem.* **1981**, *46*, 1049.

[6] Ross, M. R. Ph.D. Thesis, University of Illinois, 1981.

[7] Martin, J. C.; Perozzi, E. F. *J. Am. Chem. Soc.* **1974**, *96*, 3155.

[8] (a) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *96*, 4618. (b) Granoth, I.; Martin, J. C. *Ibid.* **1979**, *101*, 4623.

[9] Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54.

[10] Arhart, R. J.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 4997.

[11] Michalak, R. S.; Martin, J. C., to be published.

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