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Gas-Phase Generation of 1,1,1,3,3,3-Hexafluoroisopropylidene Anion Radical: Proton Affinity and $\Delta H_f°$ of $(CF_3)_2C^{-}\cdot$ and $(CF_3)_2CH^-$

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Abstract: 1,1,1,3,3,3-Hexafluoroisopropylidene anion radical ($(CF_3)_2C^{-}\cdot$; *m/z* 150) was generated in a flowing afterglow apparatus at 298 K by dissociative electron attachment to the corresponding diazo compound, $(CF_3)_2C{=}N_2$. Using the bracketing method, the proton and H-atom affinities of $(CF_3)_2C^{-}\cdot$ were determined (PA = 365.0 ± 2 kcal mol^{-1}; $DH°((CF_3)_2C^{-}{-}H)$ = 100 ± 3 kcal mol^{-1}) using a series of potential H^+ or H-atom donors, respectively. The carbanion $(CF_3)_2CH^-$ (*m/z* 151) was cleanly produced by H-atom transfer from PH_3 to *m/z* 150 and PA($(CF_3)_2CH^-$) = 364.0 ± 2 kcal mol^{-1} and $\Delta H_f°((CF_3)_2CH^-)$ = −330.1 ± 2 kcal mol^{-1} were determined. From these thermochemical data, $\Delta H_f°((CF_3)_2C^{-}\cdot)$ = −282.2 ± 4 kcal mol^{-1} was calculated. Other thermochemical data available from these results were $\Delta H_f°((CF_3)_2CH\cdot)$ = −280.0 ± 6, $DH°((CF_3)_2CH{-}H)$ = 99.0 ± 6, and EA($(CF_3)_2CH\cdot$) = 50.1 ± 8 kcal mol^{-1}.

Hypovalent ion radicals (HIR) are defined as charged radical species which contain *less* than the number of attached substituents found in the neutral free-radical system normally associated with the central atom of the free radical. Carbene and nitrene anion radicals ($R_2C^{-}\cdot$, $RN^{-}\cdot$) are anionic (HAR) subclasses of carbon- and nitrogen-centered HIR molecules which contain the electron pair of the anion and the spin-unpaired electron of the radical formally on the same nuclear center. The electronic arrangement and coordination unsaturation about the central atom lead to reactions of these species as bases and nucleophiles, and as free radicals.

Studies of the chemistry of HIR species in the condensed phase are plagued by several major problems (questions) including (a) is the HIR species or a precursor anion radical the reactant, and (b) if the HIR molecule is formed, will the reactions with solvent molecules overwhelm the desired reaction of added reactants with the HIR species. We have been able to eliminate both of these problems by generating the HIR species and determining its chemistry in the gas phase. Under these conditions, the HIR is essentially isolated from solvent (helium is the buffer gas) and counterion effects, and we can be certain that the HIR is the reactant in the desired ion–molecule reaction. Other significant advantages in such gas-phase studies are that the kinetics of these *intrinsic* ion–molecule reactions can be measured and the thermochemical properties of the HIR species can be determined.

Our previous studies have dealt with the thermochemical properties and chemistry of two HAR molecules, cyclopentadienylidene anion radical (c-$C_5H_4^{-}\cdot$)[1] and phenylnitrene anion radical ($PhN^{-}\cdot$).[2-4] The smaller proton (PA) and hydrogen-atom affinities (HA) of $PhN^{-}\cdot$ compared to c-$C_5H_4^{-}\cdot$[5] allowed $PhN^{-}\cdot$ to be used to determine (a) competitive nucleophilic 1,2- vs. 1,4-addition mechanisms with acyclic α,β-unsaturated molecules,[3] (b) absolute and relative reactivities for nucleophilic addition reactions with carbonyl groups in various organic structures,[4] and (c) nucleophilic reactivities in competitive S_N2 displacement and carbonyl addition processes.[4]

Our recent gas-phase studies in the area of HAR species have centered on the generation of structurally simpler carbene anion radicals using dissociative electron attachment with the corresponding diazo compounds. In this paper, we report the generation of 1,1,1,3,3,3-hexafluoroisopropylidene anion radical, $(CF_3)_2C^{-}\cdot$, and determination of its PA, HA, and $\Delta H_f°$. The availability of $(CF_3)_2C^{-}\cdot$ also allows for preparation of the corresponding carbanion $(CF_3)_2CH^-$ by various H-atom transfer reactions with $(CF_3)_2C^{-}\cdot$. The PA and $\Delta H_f°$ of the carbanion are reported along with the thermochemical properties of several related molecules.

Experimental Section

The flowing afterglow (FA) apparatus with the modular flow tube design used in these investigations has been previously described.[1,6] Briefly, $(CF_3)_2C^{-}\cdot$ (*m/z* 150) was generated by dissociative electron attachment with $(CF_3)_2C{=}N_2$ in the upstream end of the flow tube. Small concentrations (1 to 5 × 10^{10} molecules cm^{-3}) of the diazo compound were mixed with the helium buffer gas and flowed past the electron gun. N_2 was added to the flow through an inlet port 10 cm downstream of the electron gun to quench (Penning ionization) the He(2^3S) metastable atoms produced at the electron gun. Addition of SF_6 through the neutral inlet port located 45 cm downstream of the electron gun *did not* produce $SF_6^{-}\cdot$, indicating complete electron capture by the diazo compound yielding $(CF_3)_2C^{-}\cdot$ in the upstream end of the flow tube.

With helium as the buffer gas, the standard reaction conditions in the 150 × 7.15 cm i.d. stainless steel flow tube were buffer gas pressure (P_{He}) of 0.5 torr and flow velocity ($\bar{v}$) of 80 m s^{-1} which were maintained by a large, fast pumping system. All kinetic and product branching fraction studies were repeated at P_{He} = 1.0 torr and $\bar{v}$ = 36 m s^{-1} (a) to ensure that $(CF_3)_2C^{-}\cdot$ was in its ground state prior to its reaction with neutrals, and (b) to look for termolecular collisional stabilization of adduct and cluster ions. No P_{He} dependency was observed for the rate constants or product branching fractions from the ion–molecule reactions of $(CF_3)_2C^{-}\cdot$ with neutral substrates given in this study. Therefore, we conclude that $(CF_3)_2C^{-}\cdot$ was cooled to its vibrational ground state in the 45 cm of the flow separating the electron gun and neutral substrate inlet port.

The ion–molecule reaction distance (neutral inlet port to the first sampling nose cone) was 62.5 cm.[6] This distance was held constant, and variable concentrations of the neutral substrate were added. The ion signals of $(CF_3)_2C^{-}\cdot$ (*m/z* 150) and products monitored by a quadrupole mass spectrometer were recorded at each concentration of neutral. Under pseudo-first-order reaction conditions, with the neutral in large excess compared to the ion concentration, the slope of the log $[(CF_3)_2C^{-}\cdot]$ vs. neutral concentration decay plot was readily converted into the bimolecular rate constant for the ion–molecule reaction.[1,6]

The helium (99.99% purity) and nitrogen used in this study were supplied by Knoll Products. The other gases and liquids used (and suppliers) were PH_3, CH_3Cl, and CH_3SH (Matheson); $HCCl_3$, CH_3CN, CH_3OH, $PhNH_2$, CH_3NO_2, $PhCOCH_3$, and $(CH_3)_2CO$ (Fisher); (C-

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(1) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491–6498.

(2) (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 6599–6603. (b) McDonald, R. N.; Chowdhury, A. K. *Ibid.* **1980**, *102*, 5118–5119.

(3) (a) McDonald, R. N.; Chowdhury, A. K. *J. Phys. Chem.* **1982**, *86*, 3641–3645. (b) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.*, **1980**, *102*, 6146–6147.

(4) (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 198–207. (b) McDonald, R. N.; Chowdhury, A. K. *Ibid.* **1981**, *103*, 674–679.

(5) PA($PhN^{-}\cdot$) = 372 ± 2 kcal mol^{-1}, $D°(PhN^{-}{-}H)$ = 91.4 ± 3 kcal mol^{-1}, $\Delta H_f°(PhN^{-}\cdot)$ = 60 ± 2 kcal mol^{-1};[2a] PA(c-$C_5H_4^{-}\cdot$) = 377 ± 2 kcal mol^{-1}, $D°(c\text{-}C_5H_4^{-}{-}H)$ = 103.9 ± 5.2 kcal mol^{-1}, $\Delta H_f°(c\text{-}C_5H_4^{-}\cdot)$ = 70.7 ± 3.2 kcal mol^{-1}.[1]

(6) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 2194–2203.

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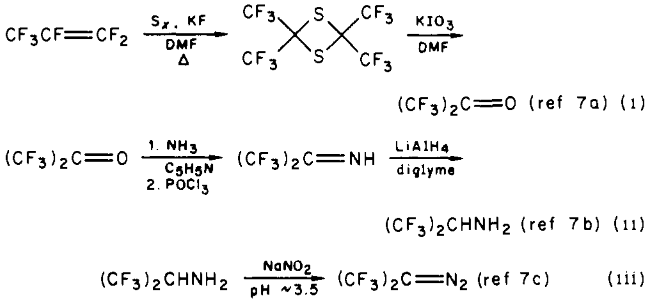
Table I. Summary of Kinetic and Product Data for the Ion–Molecule Reactions of 1,1,1,3,3,3-Hexafluoroisopropylidene Anion Radical ($(CF_3)_2C^{-}\cdot$)

reaction	ion + neutral reactants	products [assumed neutral]	fraction of product ion signal	k_{total},[a] cm^3 molecule^{-1} s^{-1}
1	$(CF_3)_2C^- + (CF_3)_2C{=}N_2 + He$	$\rightarrow (CF_3)_2C{=}N{-}N{=}C(CF_3)_2^{-}\cdot + He$	1.00	$(2.3 \pm 0.2) \times 10^{-26}$ [d]
2a	$(CF_3)_2C^{-}\cdot + CH_3SH$	$\rightarrow (CF_3)_2CH^- [+\cdot SCH_3]$	0.83	$(5.3 \pm 0.5) \times 10^{-10}$
2b		$\rightarrow CH_3S^- [+(CF_3)_2CH\cdot]$	0.11	
2c		$\rightarrow H_2C{=}S^{-}\cdot [+(CF_3)_2CH_2]$	0.06	
3a	$(CF_3)_2C^{-}\cdot + HCCl_3$	$\rightarrow (CF_3)_2CH^- [+\cdot CCl_3]$	0.80	$(2.2 \pm 0.2) \times 10^{-10}$
3b		$\rightarrow Cl_3C^- [+(CF_3)_2CH\cdot]$	0.20	
4a	$(CF_3)_2C^{-}\cdot + CF_3CH_2OH$	$\rightarrow CF_3CH_2O^- [+(CF_3)_2CH\cdot]$	*b*	$(6.3 \pm 0.2) \times 10^{-10}$
4b		$\rightarrow HF_2^- + HF_2^-(HOCH_2CF_3) +$ $CF_3CH_2O^-(HF)(HOCH_2CF_3)_m +$ $CF_3CH_2O^-(HOCH_2CF_3)_n$	*b*	
5a	$(CF_3)_2C^{-}\cdot + C_2H_5CHO$	$\rightarrow (CF_3)_2C{=}C(O^-)H [+\cdot C_2H_5]$	0.60	$(1.2 \pm 0.1) \times 10^{-11}$
5b		$\rightarrow (CF_3)_2CH^- [+C_2H_5CO\cdot]$	0.39	
5c		$\rightarrow (CF_3)_2C{=}C(O^-)CH_3 [+\cdot H]$	0.01	
6a	$(CF_3)_2C^{-}\cdot + CH_3CHO$	$\rightarrow (CF_3)_2C{=}C(O^-)H [+\cdot CH_3]$	0.62	$(4.3 \pm 0.3) \times 10^{-12}$
6b		$\rightarrow (CF_3)_2CH^- [+CH_3CO\cdot]$	0.29	
6c		$\rightarrow (CF_3)_2{=}C(O^-)CH_3 [+\cdot H]$	0.09	
7	$(CF_3)_2C^{-}\cdot + PH_3$	$\rightarrow (CF_3)_2CH^- [+\cdot PH_2]$	1.00	$(3.7 \pm 0.6) \times 10^{-11}$
8	$(CF_3)_2C^{-}\cdot + CH_3CN$	$\rightarrow (CF_3)_2CH^- [+\cdot CH_2CN]$	1.00	$(1.6 \pm 0.2) \times 10^{-11}$
9	$(CF_3)_2C^{-}\cdot + (CH_3)_2C{=}O$	$\rightarrow (CF_3)_2CH^- [+\cdot CH_2C({=}O)CH_3]$	1.00	1.0×10^{-12} [c]
10	$(CF_3)_2C^{-}\cdot + CH_3OH$	→ no reaction		$\leq 10^{-13}$
11	$(CF_3)_2C^{-}\cdot + PhNH_2$	$\rightarrow (CF_3)_2CH^- [+PhNH\cdot]$	1.00	*e*
12	$(CF_3)_2C^{-}\cdot + ((CH_3)_3C)_2CHOH$	→ no reaction		*e*
13	$(CF_3)_2C^{-}\cdot + CH_3Cl$	→ no reaction		$\leq 10^{-13}$

[a] *k*'s are estimated to be accurate to ±25%. Errors are standard deviations from multiple determinations. No P_{He} dependency (0.4 to 1.1 torr) was observed on *k*'s or branching fractions. [b] Anion %'s were variable depending on CF_3CH_2OH concentration added due to cluster-ion formation. [c] Measured at P_{He} = 1.1 torr and $\bar{v}$ = 36 m s^{-1}; single determination. [d] Termolecular rate constant for adduct formation in units of cm^6 molecule^{-2} s^{-1}. [e] The neutral in this experiment was added to the flow as vapor from a reservoir from the liquid; k_{total} cannot be measured.

$F_3)_2CHOH$ and C_2H_5CHO (Eastman); CH_3CHO (Malinkrodt); CF_3CH_2OH (Halocarbon); and $F_2C{=}CFCF_3$ (PCR). $((CH_3)_3C)_2CHOH$ was synthesized by $LiAlH_4$ reduction of the ketone (Fluka). All liquids were dried and distilled and a constant-boiling center-cut was used. Gases were used as received. All reagents were transferred to glass storage bulbs after three freeze–pump–thaw degassing cycles.

Preparation of $(CF_3)_2C{=}N_2$. The sequence of reactions with references used to prepare $(CF_3)_2C{=}N_2$ (bp 13 °C) from $F_2C{=}CFCF_3$ are listed in eq i–iii. The diazo compound was bulb-to-bulb distilled, showed no impurities by 70-eV positive ion mass spectrometry, and could be stored at liquid N_2 temperature for several months without detectable decomposition. *While we encountered no difficulties in handling this diazo compound, precautions (good hoods, ventilation, and explosion shields) should always be taken when working with such chemicals.*



Results

Generation of $(CF_3)_2C^{-}\cdot$. When a mixture of $(CF_3)_2C{=}N_2$ in helium was flowed past the electron gun in the upstream end of the flow tube of the FA, $(CF_3)_2C^{-}\cdot$ (*m/z* 150) was produced by dissociative electron attachment (eq iv). The cross section for

$$(CF_3)_2C{=}N_2 + e^- \rightarrow \underset{m/z\ 150}{(CF_3)_2C^{-}\cdot} + N_2 \qquad \text{(iv)}$$

electron attachment by $(CF_3)_2C{=}N_2$ must be quite large since only small concentrations (1 to 5 × 10^{10} molecules cm^{-3}) were required to attach all of the available electrons in a short distance of the flow (see Experimental Section). This proved to be essential to the present studies since $(CF_3)_2C^{-}\cdot$ undergoes a fast termolecular reaction with $(CF_3)_2C{=}N_2$ yielding the adduct *m/z* 328 considered to be the symmetrical azine anion radical shown in reaction 1, Table I. Formation of this adduct is analogous to the reaction

$$(CF_3)_2C^{-}\cdot + (CF_3)_2C{=}N_2 \xrightarrow{He} \underset{m/z\ 328}{(CF_3)_2C{=}N{-}N{=}C(CF_3)_2^{-}\cdot} \qquad (1)$$

of $c\text{-}C_5H_4^{-}\cdot$ with $c\text{-}C_5H_4N_2$ yielding the corresponding azine anion radical as the major product.[1] Such adduct species are believed formed by addition (condensation) of the carbene anion radical to N_β of the diazo compound. The absence of the product of addition at C_α of the diazo compound and loss of N_2,[1] $(CF_3)_2C{=}C(CF_3)^{-}\cdot$, in this case, possibly means that the perfluoro olefin has a negative electron affinity. Therefore, in the absence of a high efficiency in electron capture by $(CF_3)_2C{=}N_2$, the sole product anion would have been *m/z* 328. In the present experiments, *m/z* 328 was only a very minor ion observed at the low concentrations of $(CF_3)_2C{=}N_2$ employed.

Proton Affinity of $(CF_3)_2C^{-}\cdot$. To determine the PA of $(CF_3)_2C^{-}\cdot$, the reactions of $(CF_3)_2C^{-}\cdot$ with a series of potential H^+-donor molecules of known gas-phase acidity[8] were investigated. H^+ transfer was judged to have occurred by a decrease in the intensity of the *m/z* 150 ion signal intensity and formation of the ion signal corresponding to the mass of the conjugate base of the added H^+-donor (eq v). Thus, the PA($(CF_3)_2C^{-}\cdot$) was tightly bracketed

$$(CF_3)_2C^{-}\cdot + HA \rightarrow A^- + (CF_3)_2CH\cdot \qquad \text{(v)}$$

between the ΔH°_{acid}'s[8] of CF_3CH_2OH and C_2H_5CHO ($\Delta H^\circ_{acid}(HA) = PA(A^-)$) (Table II) giving PA($(CF_3)_2C^{-}\cdot$) = 365.0 ± 2 kcal mol^{-1}.

The use of C_2H_5CHO to establish the thermochemical threshold for PA($(CF_3)_2C^{-}\cdot$) has been questioned by a referee on two grounds: (a) carbonyl-containing carbon acids generally undergo slow H^+-transfer reactions where $\Delta H^\circ \sim 0$ kcal mol^{-1},[9] and (b)

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(7) (a) Anello, L. G.; Van Der Puy, M. *J. Org. Chem.* **1982**, *47*, 377–378. (b) Middleton, W. J.; Krespan, C. G. *Ibid.* **1965**, *30*, 1398–1402. (c) We wish to thank Professor Jerry Mohrig, Carleton College, for the directions given in eq iii.

(8) Bartmess, J. E.; McIver, R. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

(9) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891–7898.

Table II. Data for Bracketing PA($(CF_3)_2C^{-}\cdot$) in H^+-Transfer Reactions with HA Molecules (eq v)

reaction	HA	product ion[a]	H^+ transfer	ΔH°_{acid}(HA),[b] kcal mol^{-1}
2b	CH_3SH	→ CH_3S^- (*m/z* 47)	yes	359.0 ± 2
3b	$HCCl_3$	→ Cl_3C^- (*m/z* 117)	yes	362 ± 6
4a	CF_3CH_2OH	→ $CF_3CH_2O^-$ (*m/z* 99)	yes	364.4 ± 2
5	C_2H_5CHO	$\not\rightarrow$ $CH_3HC{=}C(O^-)H$ (*m/z* 57)	no	365.9 ± 2
6	CH_3CHO	$\not\rightarrow$ $H_2C{=}C(O^-)H$ (*m/z* 43)	no	366.4 ± 2
11	$PhNH_2$	$\not\rightarrow$ $PhNH^-$ (*m/z* 92)	no	367.1 ± 2
12	$((CH_3)_3C)_2CHOH$	$\not\rightarrow$ $((CH_3)_3C)_2CHO^-$ (*m/z* 143)	no	367.3 ± 2

[a] Data given in Table I. [b] Reference 8.

Table III. Data for Bracketing $DH^\circ((CF_3)_2C^{-}\text{-}H)$ in H-Atom Transfer Reactions with HR Molecules (eq vi)

reaction	neutral R–H[a]	H-atom transfer	DH°(R–H),[b] kcal mol^{-1}
7	PH_2–H	yes	83.9 ± 3
2a	CH_3S–H	yes	91.8 ± 2
8	$NCCH_2$–H	yes	92.9 ± 2.5
3a	Cl_3C–H	yes	95.5[c]
9	$CH_3C({=}O)CH_2$–H	yes	98.0 ± 2.6
13	ClH_2C–H	no	101.7[d]
10	CH_3O–H	no	104 ± 1

[a] Data given in Table I. [b] Reference 8. [c] Furuyama, S.; Golden, D. M.; Benson, S. W. *J. Am. Chem. Soc.* **1969**, *91*, 7564–7569. [d] Reference 11.

the absence of the enolate anion may be due to kinetic disfavor since other reaction channels were observed. While we agree with this general criticism, we point out that the total rate constants for the reactions of $(CF_3)_2C^{-}\cdot$ with C_2H_5CHO (reaction 5) and CH_3CHO (reaction 6) are quite small, and we searched for the signals of the two enolate anions (*m/z* 57 and 43, respectively) without success. This was the same result in the reaction of $(CF_3)_2C^{-}\cdot$ with $(CH_3)_2C{=}O$ (reaction 9) where only very slow H-atom transfer was observed with no evidence of H^+ transfer.

To more fully answer this central point of the investigation, we examined the reactions of $(CF_3)_2C^{-}\cdot$ with $PhNH_2$ and $((CH_3)_3C)_2CHOH$. Neither of these neutrals had sufficient vapor pressure to allow us to measure their reaction rate constants in the FA. However, their vapors were added to the flow through inlets attached directly to small reservoirs of the liquid neutral. With $PhNH_2$ (ΔH°_{acid} = 367.1 ± 2 kcal mol^{-1}),[8] H-atom transfer occurred, but not H^+ transfer. With $((CH_3)_3C)_2CHOH$ (ΔH°_{acid} = 367.3 ± 2 kcal mol^{-1}),[8] no reaction was observed.[10] Based on these results (or lack thereof), we believe that the PA($(CF_3)_2C^{-}\cdot$) given above is correct.

In our previous investigations with $c\text{-}C_5H_4^{-}\cdot$ and $PhN^{-}\cdot$, their ΔH_f°'s could be calculated once their PA's were bracketed since the ΔH_f°'s of the radical products, $c\text{-}C_5H_5\cdot$ and $PhNH\cdot$, had been previously determined.[1,2] However, in the present case, the $\Delta H_f^\circ((CF_3)_2CH\cdot$ is unknown and additional results are required to enable $\Delta H_f^\circ((CF_3)_2C^{-}\cdot)$ to be calculated.

Hydrogen-Atom Affinity of $(CF_3)_2C^{-}\cdot$, $DH^\circ((CF_3)_2C^{-}\text{–}H)$. The approach taken to determine the H-atom affinity (HA) of $(CF_3)_2C^{-}\cdot$ was similar to the bracketing of its PA (above), however, using potential H-atom donor molecules of known DH°(R–H)'s (eq vi). The specific reactions from Table I of interest in this connection are listed in Table III.

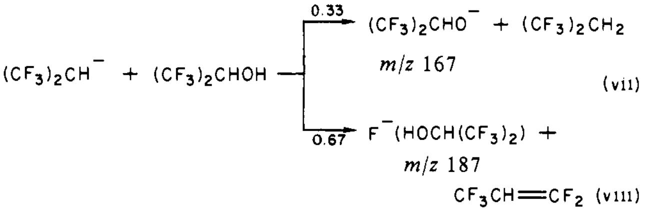
$$\underset{m/z\ 150}{(CF_3)_2C^{-}\cdot} + HR \rightarrow \underset{m/z\ 151}{(CF_3)_2CH^-} + \cdot R \qquad (vi)$$

The major difference in determining the HA and PA of $(CF_3)_2C^{-}\cdot$ (*m/z* 150) is that the signal of the product ion from H-atom transfer adds to the 3.3% (M + 1) ion of the starting anion radical while H^+ transfer generally yields a totally new ion not present in the original negative ion spectrum. This means that as the threshold for H-atom transfer is approached from the positive side, the rate slows and only relatively small changes in the signal at *m/z* 151 occur. This is what was observed with acetone (reaction 9). The reaction with CH_3Cl (reaction 13) was carried out for two purposes, potential H-atom transfer[11] and/or S_N2 displacement; no reaction was observed. From these results, we conclude that $DH^\circ((CF_3)_2C^{-}\text{–}H)$ = 100 ± 2 kcal mol^{-1}.

The absence of H-atom transfer between $(CF_3)_2C^{-}\cdot$ and CH_3OH was surprising since $DH^\circ(HOCH_2\text{–}H)$ = 95.9 kcal mol^{-1};[12] $DH^\circ(CH_3O\text{–}H)$ = 104 ± 1 kcal mol^{-1}.[8] We believe that this is related to the results obtained in the reactions of $c\text{-}C_5H_4^{-}\cdot$ with CH_3OD and C_2H_5OD where exclusive D-atom transfers were observed.[1] Therefore, it appears that the sole interaction between $(CF_3)_2C^{-}\cdot$ and the alcohol in hydrogen-bonded adducts, and probably also in loose orbiting collision complexes, occurs between C_2 of the carbene anion radical and the H–O bond of the alcohol.

Proton Affinity and ΔH_f° of $(CF_3)_2CH^-$. To complete the thermochemical data needed to calculate $\Delta H_f^\circ((CF_3)_2C^{-}\cdot)$, the value for PA($(CF_3)_2CH^-$) was required. Since the carbanion $(CF_3)_2CH^-$ (*m/z* 151) was the exclusive product from the H-atom transfer from PH_3 to $(CF_3)_2C^{-}\cdot$, this was selected as the source of *m/z* 151. Based on the rate constant for reaction 7, Table I, sufficient PH_3 was added via the inlet port 10 cm downstream of the electron gun to the helium flow containing $(CF_3)_2C^{-}\cdot$ to convert it completely to $(CF_3)_2CH^-$ within 10 cm of the flow tube. This allowed for collisions with the buffer gas in the next 35 cm of the tube to cool excited *m/z* 151 ions to their vibrational ground state prior to reaching the inlet port through which potential H^+-donor molecules were added. These data are summarized in Table IV.

There is a problem in the use of alcohols as potential H^+ donors to establish the PA($(CF_3)_2CH^-$) as illustrated in the reaction of $(CF_3)_2CH^-$ with $(CF_3)_2CHOH$ (ΔH°_{acid} = 348.4 ± 2 kcal mol^{-1})[13] (eq vii and viii). In this fast reaction (k_{total} = (4.9 ± 0.4) × 10^{-10}



$$(CF_3)_2CH^- + (CF_3)_2CHOH \xrightarrow{0.33} \underset{m/z\ 167}{(CF_3)_2CHO^-} + (CF_3)_2CH_2 \qquad (vii)$$

$$(CF_3)_2CH^- + (CF_3)_2CHOH \xrightarrow{0.67} \underset{m/z\ 187}{F^-(HOCH(CF_3)_2)} + CF_3CH{=}CF_2 \qquad (viii)$$

cm^3 molecule^{-1} s^{-1}), only one-third occurred by H^+ transfer producing $(CF_3)_2CHO^-$ (*m/z* 167) with the remaining two-thirds yielding $F^-(HOCH(CF_3)_2$ (*m/z* 187), the product of an elimination process. Formation of the related cluster ion $F^-(HOCH_2CF_3)$ (*m/z* 119) was the exclusive product in the fast reaction (k_{total} = (5.2 ± 0.5) × 10^{-10} cm^3 molecule^{-1} s^{-1}) of $(CF_3)_2CH^-$ with CF_3CH_2H. The reaction of $(CF_3)_2CH^-$ with $(CH_3)_3COH$ (ΔH°_{acid} = 373.3 ± 2 kcal mol^{-1})[8] initially produced the disolvate cluster ion $F^-(HOC(CH_3)_3)_2$ as the exclusive product at a slow rate (k_{total} = (9.2 ± 0.6) × 10^{-12} cm^3 molecule^{-1} s^{-1}). Even the less acidic hydroxyl compounds CH_3OH (ΔH°_{acid} = 379.2 ± 2

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(10) With both of these high-boiling neutrals, large signals for their conjugate bases were observed using this inlet from their H^+ transfers to CH_3O^- generated in the upstream end of the flow tube.

(11) See: Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516–1535, for a compilation of bond dissociation energies of various organic molecules.

(12) O'Neal, H. E.; Benson, S. W. In "Free Radicals"; Kochi, J. K.; Ed.; Wiley: New York, 1973; Vol. 2.

(13) From ΔG°_{acid} (($CF_3)_2CHOH$) = 340.8 kcal mol^{-1} (private communication from Professor R. W. Taft) and assuming ΔS°_{acid} ~ 25.5 cal mol^{-1} deg^{-1} at 298 K yields the ΔH°_{acid}.

Table IV. Data for Bracketing PA($(CF_3)_2CH^-$) in H^+-Transfer Reactions with HA Molecules

HA	product ion	H^+ transfer	ΔH°_{acid}(HA),[a] kcal mol^{-1}
$(CF_3)_2CH^- + (CF_3)_2CHOH$	$\rightarrow (CF_3)_2CHO^-$ (m/z 167)	yes[c]	348.4 ± 2[b]
$(CF_3)_2CH^- + CH_3NO_2$	$\rightarrow CH_2NO_2^-$ (m/z 60)	yes	358.7 ± 2
$(CF_3)_2CH^- + CH_3SH$	$\rightarrow CH_3S^-$ (m/z 47)	yes	359.0 ± 2
$(CF_3)_2CH^- + HCCl_3$	$\rightarrow Cl_3C^-$ (m/z 117)	yes	362 ± 6
$(CF_3)_2CH^- + CH_3C({=}O)Ph$	$\rightarrow CH_2{=}C(O^-)Ph$ (m/z 119)	yes	363.2 ± 2
$(CF_3)_2CH^- + CF_3CH_2OH$	$\not\rightarrow CF_3CH_2O^-$ (m/z 99)	no[d]	364.4 ± 2
$(CF_3)_2CH^- + C_2H_5CHO$	$\not\rightarrow CH_3CH{=}C(O^-)H$ (m/z 57)	no	365.9 ± 2
$(CF_3)_2CH^- + CH_3CHO$	$\not\rightarrow H_2C{=}C(O^-)H$ (m/z 43)	no	366.4 ± 2

[a] Reference 8. [b] Reference 13. [c] E1cb elimination with formation of the cluster $F^-(HOCH(CF_3)_2)$ is a major reaction channel. [d] Fast E1cb elimination with formation of the cluster $F^-(HOCH_2CF_3)$ is the exclusive reaction channel.

kcal mol^{-1})[8] and H_2O (ΔH°_{acid} = 390.8 ± 0.4 kcal mol^{-1})[8] yield the clusters $F^-(HOCH_3)_{2,3}$ (m/z 83, 115) and $F^-(H_2O)_{3,4}$ (m/z 73, 91), respectively, in even slower reactions. From these results, we conclude that formation of the cluster ion products of elimination, $F^-(HOR)_x$, result from a separate process involving coordination of ROH on fluorine of the carbanion in a solvent-assisted E1cb elimination mechanism. This and other evidence supporting this mechanism will be the subject of a separate publication.[14]

Since slow H^+ transfer between $(CF_3)_2CH^-$ and CF_3CH_2OH would not be observed because of the fast elimination process yielding the cluster ion $F^-(HOCH_2CF_3)$, this result *cannot* be used to establish the upper limit of the threshold for PA($(CF_3)_2CH^-$). Thus, we must rely on the reactions with carbon-based acids. Here we note that *no* reactions were observed between $(CF_3)_2CH^-$ and C_2H_5CHO or CH_3CHO; no decay of $(CF_3)_2CH^-$ (m/z 151) and no ion product formed. Therefore, $k \le 10^{-13}$ cm^3 molecule^{-1} s^{-1} for these two neutrals. However, a small amount of H^+ transfer was observed between $(CF_3)_2CH^-$ and $CH_3C({=}O)Ph$ (ΔH°_{acid} = 363.2 ± 2 kcal mol^{-1})[8] when vapors of the ketone were swept into the flow from a reservoir of the liquid using argon as the sweep gas. Based on these results, we assign PA($(CF_3)_2CH^-$) = 364 ± 2 kcal mol^{-1}. From eq ix, we calculate $\Delta H_f^\circ((CF_3)_2CH^-)$ =

$$(CF_3)_2CH^- + H^+ \xrightarrow{PA} (CF_3)_2CH_2 \qquad \text{(ix)}$$

−330.1 ± 2 kcal mol^{-1} using $\Delta H_f^\circ(H^+)$ = 367.2 kcal mol^{-1} [15] and $\Delta H_f^\circ((CF_3)_2CH_2)$ = −326.9 kcal mol^{-1}.[16]

$\Delta H_f^\circ((CF_3)_2C^{-}\cdot)$ and Other Thermochemical Properties. The above experimentally derived thermochemical data for $\Delta H_f^\circ((CF_3)_2CH^-)$ and $DH^\circ((CF_3)_2C^-{-}H)$ allow $\Delta H_f^\circ((CF_3)_2C^{-}\cdot)$ = −282.2 ± 4 kcal mol^{-1} to be calculated using the relationship given in eq x.

$$(CF_3)_2CH^- \xrightarrow{DH^\circ} (CF_3)_2C^{-}\cdot + H\cdot \qquad \text{(x)}$$

Using this calculated $\Delta H_f^\circ((CF_3)_2C^{-}\cdot)$ value, a number of additional thermochemical properties of related molecules can be obtained. The relationships and the calculated thermochemical property are given in eq xi–xiii.

$$(CF_3)_2C^{-}\cdot + H^+ \xrightarrow{PA} (CF_3)_2CH\cdot \qquad \text{(xi)}$$

$$\Delta H_f^\circ((CF_3)_2CH\cdot) = \Delta H_f^\circ((CF_3)_2C^{-}\cdot) + \Delta H_f^\circ((H^+) - PA((CF_3)_2C^{-}\cdot) = -280.0 \pm 6 \text{ kcal mol}^{-1}$$

$$(CF_3)_2CH_2 \xrightarrow{DH^\circ} (CF_3)_2CH\cdot + \cdot H \qquad \text{(xii)}$$

$$DH^\circ((CF_3)_2H{-}H) = -\Delta H^\circ_f((CF_3)_2CH_2) + \Delta H^\circ((CF_3)_2CH\cdot) + \Delta H^\circ_f(H\cdot) = 99.0 \pm 6 \text{ kcal mol}^{-1}$$

$$(CF_3)_2CH\cdot + e^- \xrightarrow{EA} (CF_3)_2CH^- \qquad \text{(xiii)}$$

$$EA((CF_3)_2CH\cdot) = \Delta H_f^\circ((CF_3)_2CH\cdot) - \Delta H_f^\circ((CF_3)_2CH^-) = 50.1 \pm 8 \text{ kcal mol}^{-1}$$

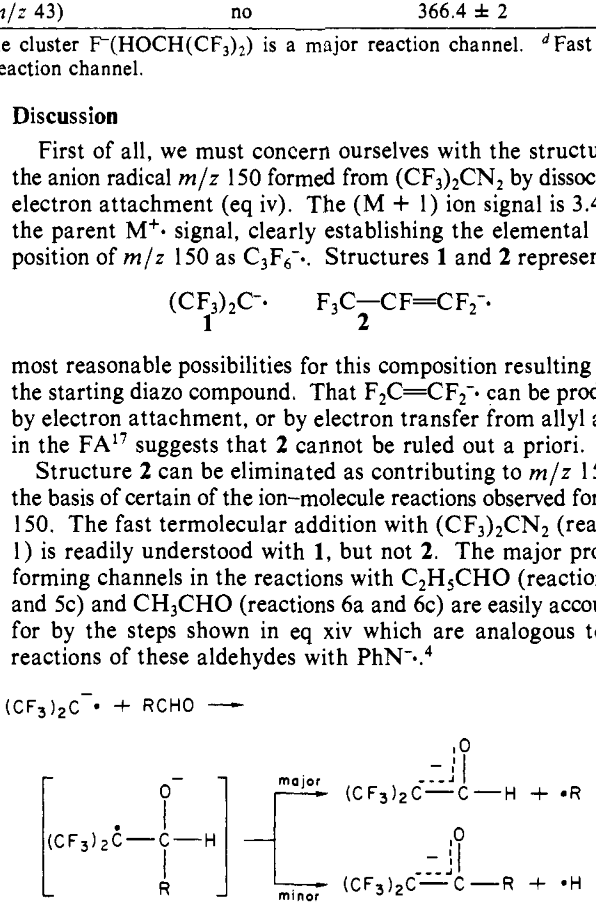
Discussion

First of all, we must concern ourselves with the structure of the anion radical m/z 150 formed from $(CF_3)_2CN_2$ by dissociative electron attachment (eq iv). The (M + 1) ion signal is 3.4% of the parent $M^{+}\cdot$ signal, clearly establishing the elemental composition of m/z 150 as $C_3F_6^{-}\cdot$. Structures **1** and **2** represent the

$$\underset{\mathbf{1}}{(CF_3)_2C^{-}\cdot} \qquad \underset{\mathbf{2}}{F_3C{-}CF{=}CF_2^{-}\cdot}$$

most reasonable possibilities for this composition resulting from the starting diazo compound. That $F_2C{=}CF_2^{-}\cdot$ can be produced by electron attachment, or by electron transfer from allyl anion in the FA[17] suggests that **2** cannot be ruled out a priori.

Structure **2** can be eliminated as contributing to m/z 150 on the basis of certain of the ion–molecule reactions observed for m/z 150. The fast termolecular addition with $(CF_3)_2CN_2$ (reaction 1) is readily understood with **1**, but not **2**. The major product forming channels in the reactions with C_2H_5CHO (reactions 5a and 5c) and CH_3CHO (reactions 6a and 6c) are easily accounted for by the steps shown in eq xiv which are analogous to the reactions of these aldehydes with $PhN^{-}\cdot$.[4]



(xiv)

We have also examined the reaction of m/z 150 with $(CF_3)_2C{=}O$. We previously observed a minor amount of electron transfer in the reaction of $PhN^{-}\cdot$ with $(CF_3)_2C{=}O$ establishing EA($(CF_3)_2C{=}O$) ≥ 33 kcal mol^{-1}.[18] Since it appears highly likely that EA($CF_3CF{=}CF_2$) < 23 kcal mol^{-1}, structure **2** should undergo electron transfer with $(CF_3)_2C{=}O$ yielding the stable ketyl anion radical m/z 166 ($(CF_3)_2CO^{-}\cdot$) while **1** should yield $(CF_3)_2C{=}C(O^-)CF_3$ (m/z 247) by nucleophilic carbonyl addition followed by radical β-fragmentation (shown in eq xiv) with loss of $\cdot CF_3$. The fast reaction (k = (2.9 ± 0.1) × 10^{-10} cm^3 molecule^{-1} s^{-1}) of m/z 150 with $(CF_3)_2C{=}O$ exclusively formed the enolate anion m/z 247. Based on these unique results, we conclude that the structure of the exclusive, primary m/z 150 species formed by dissociative electron attachment with $(CF_3)_2C{=}N_2$ is that of the carbene anion radical **1**.

One of the number of questions about hypovalent anion radicals (HAR) is how the PA of the doublet HAR species would compare with that of the corresponding closed-shell anion (HAR + ·H), e.g., PA($R_2C^{-}\cdot$) vs. PA(R_2CH^-). At a zeroth-order level of approximation, we might expect their PA's to be the same. However, this ignores the fact that the conjugate acid of the $R_2C^{-}\cdot$ species is a radical, $R_2CH\cdot$, while protonation of the R_2CH^- anion yields the neutral R_2CH_2 molecule. Therefore, the absolute ordering

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(14) McDonald, R. N.; McGhee, W. D.; Chowdhury, A. K., unpublished results.

(15) "JANAF Thermochemical Tables", *Natl. Stand. Ref. Data Ser.* (*Natl. Bur. Stand.*), **1971**, No. 37.

(16) Calculated from group additivities: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(17) McDonald, R. N.; Chowdhury, A. K., unpublished results.

(18) EA(PhN) = 33.3 ± 0.8 kcal mol^{-1}: private communication from Professor J. I. Brauman.

Table V. Condensed- and Gas-Phase Acidities of Various Fluorinated Alkanes

	pK_a[a]		$\Delta H°_{acid}$[b]
$H_3C–H$	40	$H_3C–H$	416.6 ± 2
$F_3C–H$	28	$F_3C–H$	375.6 ± 2
$CF_3(CF_2)_5CF_2–H$	27	$CF_3CF_2–H$	372.5 ± 3[b,c]
		$CF_3CFH–H$	372.5 ± 3[b,c]
		$CF_3CH_2–H$	375 ± 3
$(CF_3)_2CF–H$	18	$(CF_3)_2CH–H$	364 ± 2[d]
$(CF_3)_3C–H$	11		

[a] Reference 25. [b] Reference 8. [c] Reference 22. [d] This study.

of the $\Delta H_f°$'s of the starting ions and their products will determine the δPA of $R_2C^{-}\cdot$ and R_2CH^-.

The latter considerations were used to explain why $\delta PA = 21 \pm 4$ kcal mol^{-1} for $c\text{-}C_5H_4^{-}\cdot$ (PA = 377 ± 2 kcal mol^{-1}) and $c\text{-}C_5H_5^-$ (PA = 356.1 ± 2 kcal mol^{-1}).[1] This comes from the combined thermochemical results of $\Delta H_f°(c\text{-}C_5H_5\cdot) - \Delta H_f°(c\text{-}C_5H_4^{-}\cdot) \sim -10$ kcal mol^{-1} and $\Delta H_f°(c\text{-}C_5H_6) - \Delta H_f°(c\text{-}C_5H_5^-) \sim +11$ kcal mol^{-1}.[1] Another way to view this is that protonation of $c\text{-}C_5H_4^{-}\cdot$ yields $c\text{-}C_5H_5\cdot$ with a much stronger C–H bond (by 21 ± 4 kcal mol^{-1}) than the C–H bond formed in $c\text{-}C_5H_6$ ($DH°(c\text{-}C_5H_5\text{-}H) = 81.1 \pm 1.5$ kcal mol^{-1}).[19] Comparing $PhN^{-}\cdot$ (PA = 372 ± 2 kcal mol^{-1})[2] with $PhNH^-$ (PA = 367.1 kcal mol^{-1}),[8] the HAR molecule was only 5 kcal mol^{-1} more basic, which emphasizes the point of similar N–H bond dissociation energies in $PhNH^-$ and $PhNH_2$. The present results of $PA((CF_3)_2C^{-}\cdot) = PA((CF_3)_2CH^-)$ within the error limits mean that $DH°((CF_3)_2CH\text{–}H) = DH°((CF_3)_2C^-\text{–}H)$.

From the outset, the possibility for autofragmentation of $(CF_3)_2CH^-$, formed by H-atom transfer to $(CF_3)_2C^{-}\cdot$ (eq vi), according to eq xv was considered. However, the thermochemical

$$(CF_3)_2CH^- \rightarrow CF_3CH{=}CF_2 + F^- \qquad \text{(xv)}$$

data show that this reaction is strongly endothermic, $\Delta H° = +40.2$ kcal mol^{-1}.[21] This is also the binding enthalpy of F^- to the olefin $CF_3CH{=}CF_2$ at C_1 which compares favorably with the binding enthalpies given for F^- with $CH_2{=}CF_2$ ($\Delta H° = 33$ kcal mol^{-1}), $CHF{=}CF_2$ ($\Delta H° = 35$ kcal mol^{-1}), and $CF_2{=}CF_2$ ($\Delta H° = 44$ kcal mol^{-1}).[22]

By replacing the C–H bonds in CH_3OH sequentially with C–CF_3 bonds, the field effect of β-CF_3 groups on the acidity of the hydroxyl proton show good additivity with $\delta\Delta G°_{acid} \sim 15$ kcal mol^{-1} per CF_3 groups.[23] Such additivity on the acidity of CH_4 by replacing C–H bonds by CF_3 groups is definitely *not* observed. Using $PA(H_3C\text{–}H) = 416.6 \pm 1$ kcal mol^{-1} [8] for comparison, the reported $PA(CF_3CH_2\text{–}H) = 375 \pm 3$ kcal mol^{-1} [8,22] gives $\delta_1 PA_{\alpha\text{-}CF_3} = 41.6$ kcal mol^{-1} for the first α-CF_3 group. The present result of $PA((CF_3)_2CH^-) = 364 \pm 2$ kcal mol^{-1} gives $\delta_2 PA_{\alpha\text{-}CF_3} = 11$ kcal mol^{-1} for the second α-CF_3 group. These data are similar to the kinetic pK_a estimates made for various fluorinated alkanes compared to CH_4 in the condensed phase listed in Table V.[25] Andreades[25] ability to measure H/D exchange with the perfluorinated alkanes required that β-elimination of F^- from the R_f^- carbanion was slow in the exchange medium of $CH_3O^-/DOCH_3$.

Table VI. $\Delta H°_{acid}$'s of Various Substituted Methanes by -CN, $-COCH_3$, and -Ph Groups

compound	$\Delta H°_{acid}$,[a] kcal mol^{-1}	δ_1,[b] kcal mol^{-1}	δ_2,[c] kcal mol^{-1}
CH_4	416.6		
CH_3CN	372.2	44.4	
$CH_2(CN)_2$	328.2		44.0
CH_3COCH_3	368.8	47.8	
$CH_2(COCH_3)_2$	343.7		25.1
CH_3Ph	379.0	37.6	
CH_2Ph_2	364.5		14.5

[a] Reference 8. [b] $\Delta H°_{acid}(CH_4) - \Delta H°_{acid}(CH_3X)$. [c] $\Delta H°_{acid}(CH_3X) - \Delta H°_{acid}(CH_2X_2)$.

Table VII. Thermochemical Data Determined in This Study at 298 K

$PA((CF_3)_2C^{-}\cdot) = 365.0 \pm 2$ kcal mol^{-1}
$\Delta H°_f((CF_3)_2C^{-}\cdot) = -282.2 \pm 4$ kcal mol^{-1}
$PA((CF_3)_2CH^-) = 364.0 \pm 2$ kcal mol^{-1} $= \Delta H°_{acid}((CF_3)_2CH_2)$
$DH°((CF_3)_2C^-\text{-}H) \simeq 100 \pm 2$ kcal mol^{-1}
$\Delta H_f°((CF_3)_2CH^-) = -330.1 \pm 2$ kcal mol^{-1}
$\Delta H_f°((CF_3)_2CH\cdot) = -280.0 \pm 6$ kcal mol^{-1}
$DH°((CF_3)_2CH\text{-}H) = 99.0 \pm 6$ kcal mol^{-1}
$EA((CF_3)_2CH\cdot) = 50.1 \pm 8$ kcal mol^{-1}

This was also the gas-phase result where reaction of $(CF_3)_2CH^-$ with CH_3OH occurred very slowly ($\sim 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) to yield the cluster ion $F^-(HOCH_3)_2$.[14]

The large difference in $\delta_1 PA_{\alpha\text{-}CF_3}$ and $\delta_2 PA_{\alpha\text{-}CF_3}$ does not appear to fit simple models for either the field effect or for fluorine negative hyperconjugation. Since fluorine negative hyperconjugation is a type of resonance substituent effect, the acidifying effects of several groups which can interact with a carbanion center through resonance in the gas phase are listed in Table VI. The field/resonance effect of the linear CN group(s) is additive ($\delta_1 = \delta_2$). However, the sizable changes in δ_1 and δ_2 for the bulkier acetyl and phenyl groups suggest that a coplanar arrangement of the two groups attached to the carbanion carbon is sterically unfavorable. This would result in rotation of the two groups to reduce the nonbonded repulsions and attenuate the resonance stabilization by the separate substituent groups leading to $\delta_2 < \delta_1$. We suggest that this a reasonable explanation for $\delta_1 PA_{\alpha\text{-}CF_3} > \delta_2 PA_{\alpha\text{-}CF_3}$. However, the falloff in δ_2 compared to δ_1 for the CF_3 groups is greater than that observed for acetyl and phenyl substituents. This further suggests that the carbanion carbon in $CF_3CH_2^-$ and $(CF_3)_2CH^-$ may be sp^3 hybridized which would increase the nonbonded interactions of the attached CF_3 groups in the secondary carbanion compared to sp^2 hybridization of C_2.

We hasten to consider two points which relate to the above analysis and suggestions. First, the lower limit of the bracketed $PA((CF_3)_2CH^-)$ was firmly established by the observed H^+ transfer with $PhC({=}O)CH_3$ while the upper limit was set by the absence of H^+ transfer with the carbon acids C_2H_5CHO and CH_3CHO (Table IV). Thus, it is remotely possible that $PA((CF_3)_2CH^-) > 364 \pm 2$ kcal mol^{-1}. This would further reduce $\delta_2 PA_{\alpha\text{-}CF_3}$ and make the falloff (δ_1 vs. δ_2) even more unusual for this system.

The second point is that $PA(CF_3CH_2^-)$ may be low by ≥ 5 kcal mol^{-1}. The result of such an increase in $PA(CF_3CH_2^-)$ would be to decrease $\delta_1 PA_{\alpha\text{-}CF_3}$ and increase $\delta_2 PA_{\alpha\text{-}CF_3}$, bringing them in line with those values listed in Table VI. However, it is not immediately obvious from the reported data[8,22] that this is the case. A reinvestigation of $PA(CF_3CH_2^-)$ appears warranted, especially in light of the ready E1cb elimination reactions we have observed for $(CF_3)_2CH^-$ with ROH molecules.[14]

Summary of Thermochemical Data from This Study. The important thermochemical data determined in the present study at 298 K are summarized in Table VII.

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(19) Calculated using $\Delta H_f°(c\text{-}C_5H_6) = 31.9 \pm 0.3$ kcal mol^{-1} [20a] and $\Delta H_f°(c\text{-}C_5H_5\cdot) = 60.9 \pm 1.2$ kcal mol^{-1}.[20b]

(20) (a) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. (b) Furuyama. S.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.*, **1971**, *3*, 237–248.

(21) (a) $\Delta H_f°(CF_3CH{=}CF_2) = -229.9$ kcal mol^{-1} (calcd).[16] (b) $\Delta H_f°(F^-) = -60.0$ kcal mol^{-1} (Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data*, **1977**, *6*, Suppl. No. 1).

(22) Sullivan, S. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1160–1165.

(23) CH_3OH ($\Delta G°_{acid} = 372.6 \pm 2$ kcal mol^{-1}),[8] CF_3CH_2OH ($\Delta G°_{acid} = 356.8 \pm 2$ kcal mol^{-1}),[8] $(CF_3)_2CHOH$ ($\Delta G°_{acid}$) = 340.8 ± 2 kcal mol^{-1}),[13] and $(CF_3)_3COH$ ($\Delta G°_{acid} = 326.7 \pm 2$ kcal mol^{-1}).[24]

(24) Private communication from Professor R. W. Taft.

(25) Using the kinetic H/D exchange data of Andreades (Andreades, S. *J. Am. Chem. Soc.*, **1964**, *86*, 2003–2010), Cram (Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965; pp 69–71) calculated the pK_a estimates for the R_f–H compounds in Table V.