were observed do we see a hint of the carbene anion radical possibly functioning as a free radical.

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Registry No. $Ph_2C^{\bullet-}$, 62268-73-9; HC_2H, 74-86-2; n-$C_3H_7C_2H$, 627-19-0; CH_3C_2H, 74-99-7; $(CH_3)_2CHOH$, 67-63-0; C_2H_5OH, 64-17-5; CH_3OH, 67-56-1; $C_6H_5CH(CH_3)_2$, 98-82-8; $C_6H_5CH_3$, 108-88-3; p-$CH_3C_6H_4CH_3$, 106-42-3; $CH_3CH{=}CH_2$, 115-07-1; H_2O, 7732-18-5; CH_3Br, 74-83-9; CH_3Cl, 74-87-3; C_2H_5Br, 74-96-4; C_2H_5Cl, 75-00-3; CH_3CHO, 75-07-0; C_2H_5CHO, 123-38-6; $(CH_3)_3CCHO$, 630-19-3; CH_3COCH_3, 67-64-1; CF_3COCH_3, 421-50-1; $CH_3COCOCH_3$, 431-03-8; $CH_3CO_2CH_3$, 79-20-9; HCO_2CH_3, 107-31-3; $CF_3CO_2CH_3$, 431-47-0; $CF_3CO_2C_2H_5$, 383-63-1; $CF_3COSC_2H_5$, 383-64-2; $CH_3COCO_2CH_3$, 600-22-6; CO_2, 124-38-9; CO_5, 463-58-1; CS_2, 75-15-0; O_2, 7782-44-7.

ROH Molecule Assisted Elimination of F^- from $(CF_3)_2CH^-$ and $(CF_3)_2CD^-$ in Gas-Phase E1cb-Type Reactions

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Abstract: The gas-phase reactions of the carbanion $(CF_3)_2CH^-$ with the following series of ROH molecules, $(CF_3)_2CHOH$, CF_3CH_2OH, $(CH_3)_3COH$, CH_3OH, and H_2O, are described. In each case, formation of ROH assisted E1cb elimination cluster ion $F^-(HOR)_x$ ($x \geq 1$) was the major or exclusive reaction channel. The reactions of $(CF_3)_2CD^-$ with these ROH molecules were also examined to observe if D/H exchange occurred in the carbanion–HOR collisions and if deuterium was incorporated into the cluster ion of ROH assisted E1cb elimination. The results from the reactions of $(CF_3)_2CH^-$ and $(CF_3)_2CD^-$ with $(CH_3)_3COH$ [(i) the primary product ion was $F^-(HOC(CH_3)_3)_2$; (ii) extensive D/H exchange was observed in $(CF_3)_2CD^-$, but no deuterium was observed in the fluoride cluster ion product; and (iii) D/H exchange and elimination occurred with the same rate constants] led to the proposal that coordination of $(CH_3)_3COH$ occurred at two separate sites in the carbanion, C_2 for D/H exchange and fluorine of a CF_3 group for the ROH assisted E1cb elimination. The results from the collision limited reactions of $(CF_3)_2CHOH$ and CF_3CH_2OH are consistent with this mechanistic proposal. The reactions of the carbanions with CH_3OH and H_2O were too slow to allow for detailed analysis.

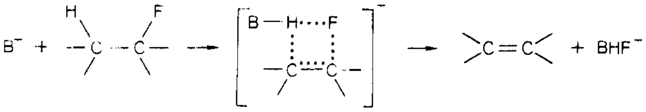
In our reported studies of the generation and thermochemistry of the carbene anion radical $(CF_3)_2C^{\bullet-}$ and the corresponding carbanion $(CF_3)_2CH^-$, the proton affinity of $(CF_3)_2CH^-$ (PA = 364 ± 2 kcal mol^{-1} = $\Delta H^\circ_{acid}((CF_3)_2CH_2)$) was determined with the bracketing method.[1] However, in several reactions of $(CF_3)_2CH^-$ with ROH molecules the primary reaction involved major or exclusive formation of $F^-(HOR)_x$ ($x \geq 1$) cluster ions with the value of x varying with $\Delta H^\circ_{acid}(ROH)$. For example, the fast reaction of $(CF_3)_2CH^-$ with $(CF_3)_2CHOH$ produced a large amount of the cluster ion $(FH)^-OCH(CF_3)_2$[2] along with the product of exothermic H^+ transfer $(CF_3)_2CHO^-$ (eq 1). The related reaction of $(CF_3)_2CH^-$ with $(CH_3)_3COH$ gave initially only the cluster ion $F^-(HOC(CH_3)_3)_2$ as the observed product in a slower reaction.

$$\underset{m/z\ 151}{(CF_3)_2CH^-} + HOCH(CF_3)_2 \rightarrow$$

$$\underset{m/z\ 187}{(FH)^-OCH(CF_3)_2} + CF_3CH{=}CF_2 \quad (1a)$$

$$\rightarrow \underset{m/z\ 167}{(CF_3)_2CHO^-} + (CF_3)_2CH_2 \quad (1b)$$

Studies of gas-phase base (B^-) induced elimination reactions of fluoroethanes,[5] fluoroethenes,[6] and certain β-fluoro alcohols[7,8] usually involve formation of free F^- and FHB^- cluster ions, conjugate bases of the neutral reactants, and other product anions depending on the base and neutral reactant used. A simplified mechanistic assumption for the reactions of the fluoroethanes with B^- would be that F^- would result from an anti-E2 elimination while the cluster ions FHB^- were formed by a syn-E2 or E1cb mechanism.[9] The collision complex (fluoroethyl anion/HB) would be an intermediate in the E1cb process (eq 2).



(2)

The structures of negative ions formed by deprotonating partially fluorinated alkanes and alkenes other than those of the corresponding carbanions have been approached theoretically. Bach et al.[10] showed that the 4-31G geometry optimization of

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[1] McDonald, R. N.; Chowdhury, A. K.; McGhee, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 4112–4116. $\Delta H_f^\circ((CF_3)_2CH^-) = -330.1 \pm 2$ kcal mol^{-1}.

[2] For cluster ions produced where $\Delta H^\circ_{acid}(HF) < \Delta H^\circ_{acid}(ROH)$, the low energy structure will be $(FH)^-OR$, while for the cluster ions where $\Delta H^\circ_{acid}(HF) > \Delta H^\circ_{acid}(ROH)$ the low energy structure is $F^-(HOR)$;[3] $\Delta H^\circ_{acid}(HF) = 371.5 \pm 2$ kcal mol^{-1}.[4a]

[3] Larsen, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 2944–2950.

[4] (a) Bartmess, J. E.; McIver, R. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2, Chapter 11. (b) Moylan and Brauman (Moylan, C. R.; Brauman, J. I. *J. Phys. Chem.* **1984**, *88*, 3175–3176) suggested a small adjustment be made in the ΔH°_{acid} of the alcohols based on their new data.

[5] (a) Sullivan, S. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1160–1165. (b) Ridge, D. P.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 3595–3602.

[6] Sullivan, S. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 5017–5022.

[7] Dawson, J. H. J.; Jennings, K. R. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *25*, 47–53.

[8] Clair, R. L.; McMahon, T. B. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 21–36.

[9] (a) Saunders, W. H.; Cockerill, A. F. *Mechanisms of Elimination Reactions*; Wiley: New York, 1973. (b) Also, see: March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; Chapter 17.

[10] Bach, R. D.; Badger, R. C.; Lang, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2845–2848.

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anti-$CH_2FCH_2^-$ led to a steady increase in the C–F bond length without evidence of a barrier. Schleyer and Kos[11] reported that this carbanion was not bound with respect to F^- and C_2H_4. However, these latter authors found that the minimum energy structure on the $C_2H_4F^-$ potential energy surface was the hydrogen bonded structure $CH_2{=}CH{-}H{\cdot\cdot}F^-$ with an essentially linear $C{-}H{\cdot\cdot}F^-$ bond and an association energy of 9.1 kcal mol^{-1}. Schleyer and Kos also noted that the *cis*- and *trans*-2-fluorovinyl anions were unstable relative to dissociation to C_2H_2 and F^- by 13.7 and 10.3 kcal mol^{-1}, respectively, while the $HC_2{-}H{\cdot\cdot}F^-$ hydrogen-bonded complex was "20.1 kcal mol^{-1} more stable than the separated fragments".[11]

Roy and McMahon[12] reinvestigated the above negative ions using the 4-31G basis set and arrived at similar conclusions. In addition, these authors examined the anions produced by deprotonation of 2-fluoropropene and acetyl fluoride. For $C_3H_4F^-$, the hydrogen-bonded allene$\cdot\cdot F^-$ structure was 8.8 kcal mol^{-1} more stable than that of the 2-fluoroallyl anion (4-31+G basis set), while for $C_2H_2FO^-$ "both *ab initio* calculation and gas phase reactivity results support an enolate structure as the most stable".[12] Some experimental gas-phase data were cited to support their conclusion that $C_2HF_4^-$ was a hydrogen-bonded structure while $C_2F_5^-$ was the sp^3 carbanion.

A closer structural relationship to the present anion $(CF_3)_2CH^-$ was reported by Pross et al.[13] and Schleyer and Kos[11] in ab initio studies of $CF_3CH_2^-$. Dissociation of $CF_3CH_2^-$ to $F_2C{=}CH_2$ and F^- is endothermic by 11.6 kcal mol^{-1} (3-21+G basis set[11]), and the carbanion has a significantly shortened C–C bond and the negative hyperconjugatively interacting C–F bond (anticoplanar to the carbanion lone pair) is elongated relative to the bond lengths in CF_3CH_3.

For the presentation of the Results section, we will assume that the structure of the starting negative ion is that of the carbanion $(CF_3)_2CH^-$. We will deal with this question in the Discussion section. Since our results of the reactions of $(CF_3)_2CH^-$ with ROH yielding cluster ions $FHOR^-$ appeared to be related to the E1cb elimination mechanism,[9,13] we decided to investigate these cluster ion forming reactions using $(CF_3)_2CH^-$ and $(CF_3)_2CD^-$ with several ROH molecules. The results with $(CF_3)_2CD^-$ should allow for observation of D/H exchange occurring in the collisions with ROH and, potentially, to allow for decisions to be made on certain factors in the elimination mechanism.

Experimental Section

The flowing afterglow (FA) used in these studies has been previously described.[1,14] Briefly, the carbene anion radical $(CF_3)_2C^{\cdot-}$ (*m/z* 150) was generated from $(CF_3)_2C{=}N_2$ mixed in the fast helium buffer gas flow by dissociative electron attachment with thermal or near thermal energy electrons in the upstream end of the flow tube. The concentration of $(CF_3)_2C{=}N_2$ added was controlled (needle valve) so that all available electrons were captured within 15 cm from the electron gun. This was established by the absence of a signal for $SF_6^{\cdot-}$ when SF_6 was added to the flow at this point. To produce $(CF_3)_2CH^-$ (*m/z* 151), PH_3 or CH_3CN was added via the inlet port located 15-cm downstream of the electron gun and the exclusive reaction of H atom transfer occurred (for both neutrals, $k_{total} = 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}).[1] To generate $(CF_3)_2CD^-$ (*m/z* 152), CD_3CN (MSD Isotopes, 99.7 atom % D) was added via this inlet port and exclusive D atom transfer occurred. The initially formed, vibrationally excited carbanions were cooled to their vibrational ground states by numerous collisions with the fast flowing helium buffer gas in the next 35 cm of the flow tube. At this point the ROH molecules were added via an inlet port and the ion–molecule reaction occurred in the final 65 cm of the flow tube.

The standard conditions in the 150 × 7.15 cm i.d. stainless steel flow tube were the buffer gas pressure (P_{He}) of 0.5 Torr and flow velocity ($\bar{v}$) of 80 m s^{-1} at 298 K which were maintained by a large fast pumping system. The flow was sampled through orifices in two nose cones into a differentially pumped compartment ($P \approx 10^{-7}$ Torr) containing a quadrupole mass filter and electron multiplier which continuously monitor the ion composition of the flow.

Table I. Kinetic Data for the Reactions of $(CF_3)_2CH^-$ and $(CF_3)_2CD^-$ with ROH Molecules

ROH	K_{total}[a]	k_{LAN}[b]	ΔH°_{acid}-(ROH)[c]
$(CF_3)_2CH^- + (CF_3)_2CHOH$	4.9×10^{-10}	7.0×10^{-10}	348.4[e]
$(CF_3)_2CD^- + (CF_3)_2CHOH$	5.1×10^{-10}		
$(CF_3)_2CH^- + CF_3CH_2OH$	5.2×10^{-10}	6.8×10^{-10}	364.4
$(CF_3)_2CD^- + CF_3CH_2OH$	4.8×10^{-10}		
$(CF_3)_2CH^- + (CH_3)_3COH$	9.6×10^{-12}	9.6×10^{-10}	373.3
$(CF_3)_2CD^- + (CH_3)_3COH$	1.8×10^{-11}		
$(CF_3)_2CH^- + CH_3OH$	$\approx 5 \times 10^{-13}$[d]		379.2
$(CF_3)_2CH^- + H_2O$	$\approx 2 \times 10^{-13}$[d]		390.8

[a] Averages of three kinetic runs at $P_{He} = 0.5$ Torr, $\bar{v} = 80$ m s^{-1}, and 298 K, given in cm^3 $molecule^{-1}$ s^{-1}. Although the reproducibility of the rate constants was ≤±8%, the possible systematic uncertainties in calibrations suggest that their accuracy is ±20%. [b] Given in cm^3 $molecule^{-1}$ s^{-1}. Reference 16. [c] Reference 4a. Given in kcal mol^{-1}, ±2 kcal mol^{-1}. [d] Rate constants were not determined with $(CF_3)_2CD^-$. [e] Reference 15.

In our kinetic studies of these ion–molecule reactions, we maintain the 65 cm reaction distance, which is directly related to reaction time in flow experiments, as a constant, but we vary the concentration of ROH added to the flow. At each new concentration of added ROH, we measure the signal intensity of $(CF_3)_2CH^-$ or $(CF_3)_2CD^-$. Under pseudo-first-order conditions with [ROH] in large excess compared to the ion concentration, the decay slope of the plot of log ion signal versus increasing [ROH] added was readily converted into the bimolecular rate constant by equations already given.[14b] In adduct-forming reactions, termolecular collisional stabilization of the adduct with the buffer gas to remove excess vibrational energy is assumed.

The alcohols, obtained from commercial sources, were dried and distilled just prior to use, and a constant-boiling center fraction was transferred to glass storage bulbs after three freeze-pump-thaw degassing cycles. The synthesis of $(CF_3)_2C{=}N_2$ was previously given.[1]

Results

Kinetics. The kinetic studies of the reactions of $(CF_3)_2CH^-$ and $(CF_3)_2CD^-$ with the ROH molecules exhibited excellent pseudo-first-order decays of the ion signals at *m/z* 151 and 152, respectively. The observed rate constants, k_{total}, and those calculated for the collision limit, k_{LAN}, are listed in Table I (see footnote *a* in Table I for additional information).

Reactions of $(CF_3)_2CH^-$ and $(CF_3)_2CD^-$ with $(CF_3)_2CHOH$. The fast reaction of $(CF_3)_2CH^-$ with $(CF_3)_2CHOH$ (ΔH°_{acid} = 348.4 ± 2 kcal mol^{-1})[15] proceeded by the two primary reaction channels shown in eq 1 with formation of the cluster ion $(F\text{-}H)^-OCH(CF_3)_2$ (*m/z* 187)[2] (eq 1a) and the product of H^+ transfer $CF_3CH_2O^-$ (*m/z* 167) (eq 1b) which is 15.6 ± 4 kcal mol^{-1} exothermic, along with the secondary reaction of clustering of $(CF_3)_2CHO^-$ with $(CF_3)_2CHOH$ (eq 3). As larger concentrations of $(CF_3)_2CHOH$ were added, it was also obvious that a secondary

$$\underset{m/z\ 167}{(CF_3)_2CHO^-} + HOCH(CF_3)_2 \xrightarrow{He} \underset{m/z\ 335}{(CF_3)_2CHO^-(HOCH(CF_3)_2)} \qquad (3)$$

cluster ion exchange (*m/z* 187 → *m/z* 335) was occurring (eq 4). Addition of a small concentration of $(CF_3)_2CHOH$ (~2 ×

$$\underset{m/z\ 187}{(FH)^-OCH(CF_3)_2} + HOCH(CF_3)_2 \rightarrow \underset{m/z\ 335}{(CF_3)_2CHO^-(HOCH(CF_3)_2)} + HF \qquad (4)$$

10^{11} molecules cm^{-3}) to the helium flow containing only $(CF_3)_2CH^-$

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[11] Schleyer, P. v. R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141–1150.

[12] Roy, M.; McMahon, T. B. *Can. J. Chem.* **1985**, *63*, 708–715.

[13] Bierbaum et al. (Bierbaum, V. M.; Filley, J.; DePuy, C. H. *J. Am. Chem. Soc.* **1985**, *197*, 2818–2820) describe the only reference of which we are aware suggesting a gas-phase E1cb elimination process. This suggestion was based on the large kinetic deuterium isotope effects for the reactions of H_2N^- and HO^- with Et_2O giving EtO^-.

[14] (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 2194–2203. (b) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *Ibid.* **1980**, *102*, 6491–6498.

[15] $\Delta H^{\circ}_{acid}((CF_3)_2CHOH)$ = 348.4 ± 2 kcal mol^{-1} from ΔG°_{acid}-$((CF_3)_2CHOH)$ = 340.8 ± 2 kcal mol^{-1} (private communication from Professor R. W. Taft) assuming ΔS°_{acid} = 25.5 cal mol^{-1} deg^{-1} at 298 K.

gave the ions at *m/z* 167 (39%), 187 (42%), and 335 (19%) at this early stage of reaction. The presence of the cluster exchange reaction in eq 4 requires that 42% is a minimum value for the extent of the elimination channel.

Reaction of $(CF_3)_2CD^-$ (*m/z* 152) with $(CF_3)_2CHOH$ proceeded with the same rate constant and produced the three product anions at *m/z* 167, 187, and 335 in the same ratio as was observed in the reaction with $(CF_3)_2CH^-$; no deuterium was incorporated in these negative ions. We also observed that the starting ion at *m/z* 152 did *not* undergo D/H exchange in its reaction with $(CF_3)_2CHOH$ through ~90% decay of its original ion signal intensity.

Reactions of $(CF_3)_2CH^-$ and $(CF_3)_2CD^-$ with CF_3CH_2OH. The PA's of $(CF_3)_2CH^-$ and $CF_3CH_2O^-$ (PA = 364.4 ± 2 kcal mol^{-1})[4a] are equal within experimental error. Thus, H^+ transfer between $(CF_3)_2CH^-$ and CF_3CH_2OH would be thermoneutral and is expected to be slow. It was, therefore, surprising to observe a rapid decay of the signal for the *m/z* 151 ion as small concentrations of CF_3CH_2OH were added to the flow containing $(CF_3)_2CH^-$. The rate constant for the decay of $(CF_3)_2CH^-$ (Table I) was 76% of the collision limit.[16] The primary products were the cluster ion $(FH)^-OCH_2CF_3$ (*m/z* 119)[2] and a small amount of HF_2^- (*m/z* 39). While HF_2^- slowly decayed probably by F^- transfer to CF_3CH_2OH, the ion at *m/z* 119 underwent secondary clustering with CF_3CH_2OH to yield the ions at *m/z* 219 and 319 (eq 5–8).

$$\underset{m/z\ 151}{(CF_3)_2CH^-} + HOCH_2CF_3 \xrightarrow{0.90} \underset{m/z\ 119}{(FH)^-OCH_2CF_3} + CF_3CH{=}CF_2 \quad (5a)$$

$$\xrightarrow{0.10} \underset{m/z\ 39}{FHF^-} + ? \quad (5b)$$

$$\underset{m/z\ 119}{(HF)^-OCH_2CF_3} + HOCH_2CF_3 \xrightarrow{He} \underset{m/z\ 219}{(HF)^-OCH_2CF_3(HOCH_2CF_3)} \quad (6)$$

$$\underset{m/z\ 219}{(FH)^-OCH_2CF_3(HOCH_2CF_3)} + HOCH_2CF_3 \xrightarrow{He} \underset{m/z\ 319}{(HF)^-OCH_2CF_3(HOCH_2CF_3)_2} \quad (7)$$

$$\underset{m/z\ 39}{FHF^-} + HOCH_2CF_3 \rightarrow \underset{m/z\ 119}{(FH)^-OCH_2CF_3} + HF \quad (8)$$

The reaction of $(CF_3)_2CD^-$ (*m/z* 152) with CF_3CH_2OH proceeded in a manner similar to that described above with no D/H exchange in $(CF_3)_2CD^-$ through 80% of its reaction and with the same collision limited rate constant as was measured with $(CF_3)_2CH^-$. In the early stages of the reaction (5 to 15% decay of $(CF_3)_2CD^-$), the major primary product cluster ion was now found to be composed of 70% $(FH)^-OCH_2CF_3$ (*m/z* 119)[2] and 30% $(FD)^-OCH_2CF_3$ (*m/z* 120)[2] following correction for the presence of 2% $(CF_3)_2CH^-$ in the starting ion and the (M + 1) isotope of the *m/z* 119 ion. A small amount of FHF^- was again observed, but FDF^- (*m/z* 40) was not present. No loss of deuterium was observed as the primary cluster ions *m/z* 119 and 120 underwent further clustering with CF_3CH_2OH to yield $(FH)^-OCH_2CF_3(HOCH_2CF_3)$ (*m/z* 219)[2] and $(FD)^-OCH_2CF_3(HOCH_2CF_3)$ (*m/z* 220),[2] respectively. These experiments were not followed far enough to determine if H/D exchange occurred in the formation of the cluster ions *m/z* 319 and 320.

Reactions of $(CF_3)_2CH^-$ and $(CF_3)_2CD^-$ with *tert*-Butyl Alcohol. Since $\Delta H°_{acid}((CH_3)_3COH)$ = 373.3 ± 2 kcal mol^{-1},[4a] H^+ transfer between $(CH_3)_3COH$ and $(CF_3)_2CH^-$ is endothermic by 9 kcal mol^{-1} and would not be observed. The reaction of $(CF_3)_2CH^-$ with $(CH_3)_3COH$ occurred with a much smaller rate constant (Table I) and gave only $F^-(HOC(CH_3)_3)_2$ (*m/z* 167)[2] as the apparent primary product. Slow secondary clustering of this product ion was observed, yielding a very small amount of $F^-(HOC(CH_3)_3)_3$ (*m/z* 241).[2] These reactions are shown in eq 9 and 10.

$$\underset{m/z\ 151}{(CF_3)_2CH^-} + 2HOC(CH_3)_3 \rightarrow \underset{m/z\ 167}{F^-(HOC(CH_3)_3)_2} + CF_2{=}CHCF_3 \quad (9)$$

$$\underset{m/z\ 167}{F^-(HOC(CH_3)_3)_2} + HOC(CH_3)_3 \xrightarrow{He} \underset{m/z\ 241}{F^-(HOC(CH_3)_3)_3} \quad (10)$$

Although we were not able to detect the monosolvate cluster ion $F^-(HOC(CH_3)_3)$ (*m/z* 93) in this reaction, it could be that the *m/z* 93 ion was converted to the disolvate *m/z* 167 ion due to the relatively large flows of $(CH_3)_3COH$ required to even partially decay $(CF_3)_2CH^-$ in this slow reaction. To determine if this was possible, we examined the cluster-forming reaction between F^- and $(CH_3)_3COH$. Fluoride ion was generated from NF_3 by dissociative electron attachment in the upstream end of the FA. Addition of $(CH_3)_3COH$ produced the monosolvate cluster ion at the collision limit[16] ($k_{total} = 1.1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}) following the decay of the F^- signal. Secondary formation of disolvate cluster ion was also rapid. To obtain the apparent bimolecular rate constant for the secondary clustering step (eq 11), the reaction data were computer modeled with use of a program of consecutive first-order reactions. The apparent bimolecular rate contant for the termolecular reaction 11 was found to be 6×10^{-10} cm^3 molecule^{-1} s^{-1}. Since this secondary cluster forming step is ~60 times greater than k_{total} for reaction 9 under these conditions, we could not have observed $F^-(HOC(CH_3)_3)$ (*m/z* 93) under these reaction conditions.

$$\underset{m/z\ 93}{F^-(HOC(CH_3)_3)} + (CH_3)_3COH \xrightarrow{He} \underset{m/z\ 167}{F^-(HOC(CH_3)_3)_2} \quad (11)$$

The reaction of $(CF_3)_2CD^-$ (*m/z* 152) with $(CH_3)_3COH$ occurred with a rate constant (Table I) almost twice that measured for reaction 9. This suggested that an additional channel was available to destroy $(CF_3)_2CD^-$ which was not observed with $(CF_3)_2CH^-$ and $(CH_3)_3COH$. The product ions through 75% decay of the *m/z* 152 ion were varying amounts of $(CF_3)_2CH^-$ (*m/z* 151), the product of D/H exchange, and the cluster ions $F^-(HOC(CH_3)_3)_2$ (*m/z* 167) and $F^-(HOC(CH_3)_3)_2(CD_3CN)$ (*m/z* 211) (eq 12 and 13). The cluster ion at *m/z* 211 appears to be formed by clustering of the *m/z* 167 ion with excess CD_3CN present in the flow used as the D atom source in preparing the starting *m/z* 152 ion. The branching fractions in eq 12 were obtained at an early stage in the decay of the *m/z* 152 ion and represent the "best" values for this slow reaction.

$$\underset{m/z\ 152}{(CF_3)_2CD^-} + HOC(CH_3)_3 \xrightarrow{0.54} \underset{m/z\ 151}{(CF_3)_2CH^-} + DOC(CH_3)_3 \quad (12a)$$

$$\xrightarrow[(CH_3)_3CHOH]{0.46} \underset{m/z\ 167}{F^-(HOC(CH_3)_3)_2} + CF_3CD{=}CF_2 \quad (12b)$$

$$\underset{m/z\ 167}{F^-(HOC(CH_3)_3)_2} + CD_3CN \xrightarrow{He} \underset{m/z\ 211}{F^-(HOC(CH_3)_3)_2(CD_3CN)} \quad (13)$$

The absence of deuterium in the cluster ion at *m/z* 167 from the reaction of $(CF_3)_2CD^-$ with $HOC(CH_3)_3$ was unexpected. To estimate the rate of D/H exchange in these cluster ions, mixtures

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(16) The collision limited rate constants for these reactions were calculated by Langevin ion-induced dipole theory since the gas-phase dipole moment for $(CF_3)_2CHOH$ is unknown. Therefore, the comparisons of k_{LAN} will be more meaningful for all of the ROH molecules. See the following (Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 1, Chapter 3) for a discussion of the methods for calculating these rate constants. Molecular polarizabilities were calculated by the method of Miller and Savchik (Miller, K. J.; Savchik, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7206). The k_{LAN} values for the reactions of $(CF_3)_2CH^-$ with $(CF_3)_2CHOH$, CF_3CH_2OH, and $(CH_3)_3COH$ were 7.0×10^{-10}, 6.8×10^{-10}, and 9.6×10^{-10} cm^3 molecule^{-1} s^{-1}, respectively.

of $F^-(DOC(CH_3)_3)$ and $F^-(DOC(CH_3)_3)_2$, and of $F^-(DOC(CH_3)_3)_2$ and some $F^-(DOC(CH_3)_3)_3$ were separately generated by adding different concentrations of $(CH_3)_3COD$ to a flow containing F^- ($NF_3 + e^- \rightarrow F^-$). As expected, the monosolvated cluster ion $F^-(DOC(CH_3)_3)$ signal decayed rapidly (see above) when $(CH_3)_3COH$ was added to the flow forming principally $F^-(DOC(CH_3)_3)(HOC(CH_3)_3)$ (m/z 168) along with a small amount (<2%) of $F^-(HOC(CH_3))_2$ (m/z 167). Addition of $(CH_3)_3COH$ to a flow containing mainly $F^-(DOC(CH_3)_3)_2$ (m/z 169) along with a minor amount of $F^-(DOC(CH_3)_3)_3$ (m/z 244) demonstrated that the major loss of the m/z 169 cluster ion was by a slow bimolecular alcohol molecule exchange ($k_{\mathrm{total}} = 7.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) shown in eq 14 with further clustering

$$\underset{m/z\ 169}{F^-(DOC(CH_3)_3)_2} + (CH_3)_3COH \rightarrow \underset{m/z\ 168}{F^-(DOC(CH_3)_3)(HOC(CH_3)_3)} + (CH_3)_3COD \tag{14}$$

of this m/z 168 ion to give the cluster $F^-(DOC(CH_3)_3)(HOC(CH_3)_3)_2$ at m/z 243 ion being even slower ($k_{\mathrm{app}} \approx 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}). Since the rate constant for the alcohol exchange (eq 14) is so small, the presence of $(CH_3)_3COD$ in this flow would have little effect on reversing the exchange observed of the ions m/z 168 → m/z 169. From the results of these experiments, we conclude that had deuterium been present in >10% in the original cluster product ion formed in the reaction of $(CF_3)_2CD^-$ with $(CH_3)_3COH$ it would have been observed. This was not the case.

Reactions of $(CF_3)_2CH^-$ and $(CF_3)_2CD^-$ with CH_3OH and H_2O. Very small rate constants were determined for the reactions of $(CF_3)_2CH^-$ with CH_3OH ($\Delta H^\circ_{\mathrm{acid}} = 379.2 \pm 2$ kcal mol^{-1})[4a] and with H_2O ($\Delta H^\circ_{\mathrm{acid}} = 390.8 \pm 2$ kcal mol^{-1})[4a] (Table I) which were close to our lower limit of measurement (10^{-13} cm^3 molecule^{-1} s^{-1}). The first product ion detected from the reaction of $(CF_3)_2CH^-$ with CH_3OH (eq 15) was $F^-(HOCH_3)_2$ (m/z 83) along with a trace of $F^-(HOCH_3)_3$ (m/z 115), the latter ion probably formed

$$\begin{array}{c} (CF_3)_2CH^- + 2CH_3OH \rightarrow \underset{m/z\ 83}{F^-(HOCH_3)_2} + CF_3CH{=}CF_2 \\ \mathrm{He}\downarrow CH_3OH \\ \underset{m/z\ 115}{F^-(HOCH_3)_2} \end{array} \tag{15}$$

by secondary clustering of the m/z 83 ion with CH_3OH. The initial product ion observed from the reaction with H_2O was $F^-(H_2O)_3$ (m/z 73) with further clustering yielding a trace of $F^-(H_2O)_4$ (m/z 91) (eq 16).

$$\begin{array}{c} (CF_3)_2CH^- + 3H_2O \rightarrow \underset{m/z\ 73}{F^-(H_2O)_3} + CF_3CH{=}CF_2 \\ \mathrm{He}\downarrow H_2O \\ \underset{m/z\ 91}{F^-(H_2O)_4} \end{array} \tag{16}$$

The reactions of $(CF_3)_2CD^-$ with CH_3OH and H_2O produced the same cluster ions as were observed with $(CF_3)_2CH^-$. However, since these product ion signals were very small, we can only place an upper limit for their deuterium content of ≤30%. Some D/H exchange in $(CF_3)_2CD^-$ (→ $(CF_3)_2CH^-$) was observed in both reactions, but precise values were impossible to determine from the small ion signals observed for the exchanged ion at m/z 151.

Discussion

Structures of the Negative Ions at m/z 151 and 152. We pointed out in the introduction that deprotonation of fluoroethane yielded the hydrogen-bonded structure $H_2C{=}CH{-}H{\cdot\cdot}F^-$ rather than the carbanion[10-12] while deprotonation of F_3CCH_3 produced the carbanion $F_3CCH_2^-$[11,13] stabilized by negative hyperconjugation based on ab initio calculations. Roy and McMahon[12] used experimental observations to assign structures to certain negative ions not calculated; "The anions derived from "deprotonation" of ethyl fluoride and other fluoroethanes are found *not* to readily abstract a proton from stronger gas phase acids as would be expected of a carbanion but rather readily transfer F^-, a result quite reasonable for a hydrogen-bonded F^- adduct." The results obtained with $C_2HF_4^-$ and $C_2F_5^-$ led them to suggest that $C_2HF_4^-$ was the hydrogen-bonded olefin··F^- adduct and $C_2F_5^-$ was the carbanion.

In the present study, one or both CF_3 groups can negatively hyperconjugate with the lone pair of electrons at C_2 of $(CF_3)_2CH^-$. This stabilization could account for the lower proton affinity of $(CF_3)_2CH^-$ (PA = 364 ± 2 kcal mol^{-1})[17] compared to that of $CF_3CH_2^-$ (PA = 375 ± 3 kcal mol^{-1}).[4a] We also observed fast H^+ transfer (eq 1b) competitive with F^- transfer (eq 1a) in the reaction of $(CF_3)_2CH^-$ with $(CF_3)_2CHOH$ contrary to the findings of Roy and McMahon given above. Formation of the two product ions $(CF_3)_2CHO^-$ and $(FH)^-OCH(CF_3)_2$[2] was shown *not* to arise from partial dissociation of an excited cluster ion $[(FH)^-OCH(CF_3)_2]^*$ (eq 17) since no P_{He} effect was observed on the eq 1a/eq 1b branching ratio at low concentrations of added alcohol as P_{He} was varied from 0.5 to 1.1 torr.

$$FH + (CF_3)_2CHO^- \nleftarrow [(FH)^-OCH(CF_3)_2]^* \xrightarrow{\mathrm{He}} (FH)^-OCH(CF_3)_2 \tag{17}$$

The above data rule out the hydrogen-bonded complex $F_2C{=}C(CF_3)H{\cdot\cdot}F^-$ as the exclusive structure for the ion at m/z 151. However, an equilibrating pair of anions $[F_2C{=}C(CF_3)H{\cdot\cdot}F^- \rightleftarrows (CF_3)_2CH^-]$ might accommodate the above data as well as the observations of (i) $(FD)^-OCH_2CF_3$ in the product ions from the reaction of $(CF_3)_2CD^-$ with CF_3CH_2OH and (ii) that D/H exchange was competitive with F^- transfer observed in the reactions of the deuteriated anion with $(CH_3)_3COH$, CH_3OH, and H_2O. If this suggestion of an equilibrating pair of anions is correct, both structures must have similar heats of formation. Since $\Delta H_f^\circ((CF_3)_2CH^-) = -330.1 \pm 2$ kcal mol^{-1},[1] we need only to reasonably estimate $\Delta H_f^\circ(F_2C{=}C(CF_3)H{\cdot\cdot}F^-)$ to test this suggestion.

This is done by using the equation $\Delta H_f^\circ(F_2C{=}C(CF_3)H{\cdot\cdot}F^-) = \Delta H_f^\circ(F_2C{=}C(CF_3)H) + \Delta H_f^\circ(F^-) - D^\circ(F_2C{=}C(CF_3)H{\cdot\cdot}F^-)$. The sum of the first two ΔH_f°s[4,18] is −290.4 kcal mol^{-1} (see next section). This requires that the binding energy in the hydrogen-bonded olefin··F^- complex is ≈40 kcal mol^{-1} to have $\Delta H_f^\circ((CF_3)_2CH^-) \approx \Delta H_f^\circ(F_2C{=}C(CF_3)H{\cdot\cdot}F^-)$. The binding energy of F^- to C_2H_4 in the hydrogen-bonded complex $H_2C{=}C{-}H{-}H{\cdot\cdot}F^-$ was calculated to be 9.1 kcal mol^{-1} with the 3-21+G basis set[11] and 2 kcal mol^{-1} with the 4-31+G basis set;[12] a value of 5 kcal mol^{-1} was estimated for this binding energy from experimental data.[12] The expected increase in the gas-phase acidity of the C–H bond in $F_2C{=}C(CF_3)H$ compared with that in C_2H_4 ($\Delta H^\circ_{\mathrm{acid}} = 406$ kcal mol^{-1})[19] should follow the reported correlation between gas-phase acidity and hydrogen bond energy to F^-.[3] However, the hydrogen bond energy in the acetylene··F^- complex ($\Delta H^\circ_{\mathrm{acid}}(C_2H_2) = 375.4$ kcal mol^{-1})[4a] calculated to be 20.1 kcal mol^{-1} at the 3-21+G level[11] and 12.8 at the 4-31+G level should reasonably serve as an upper limit for such unsaturated CH hydrogen bonds to F^-. Since this is far less than the required 40 kcal mol^{-1} established above, we conclude that the hydrogen-bonded structure $F_2C{=}C(CF_3)H{\cdot\cdot}F^-$ is significantly higher in energy than the carbanion $(CF_3)_2CH^-$ and that the latter is the only structure contributing to the negative ion at m/z 151.

Thermochemistry of the E1cb Elimination Steps. In order to achieve the elimination reactions observed in the Results section, the reactant $(CF_3)_2CH^-$ ion and alcohol must overcome the sizable F^- affinity of the olefin $CF_3CH{=}CF_2$ represented in eq 18; ΔH°(eq 18) = −39.7 kcal mol^{-1}. This is calculated by using heats

$$CF_3CH{=}CF_2 + F^- \rightarrow (CF_3)_2CH^- \tag{18}$$

of formation common to these elimination reactions, $\Delta H_f^\circ((CF_3)_2CH^-) = -330.1$ kcal mol^{-1},[1] $\Delta H_f^\circ(CF_3CH{=}CF_2)$ =

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[17] PA($(CF_3)_2CH^-$) = 364 ± 2 kcal mol^{-1} was determined experimentally by using the bracketing method.[1] Using the relationship $\Delta H_f^\circ((CF_3)_2CH^- = \Delta H_f^\circ((CF_3)_2CH_2) + \mathrm{PA}((CF_3)_2CH^-) - \Delta H_f^\circ(H^+)$, $\Delta H_f^\circ((CF_3)_2CH^-) = -330.1 \pm 2$ kcal mol^{-1} was calculated by using $\Delta H_f^\circ((CF_3)_2CH_2) = -326.9$ kcal mol^{-1} based on group additivities.[18]

[18] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

[19] DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051–4053.

−229.9 kcal mol^{-1},[18] and $\Delta H_f°(F^-) = -60.5$ kcal mol^{-1}.[4a]

The reaction of $(CF_3)_2CH^-$ with $(CF_3)_2CHOH$ (eq 1) involves the only alcohol investigated where H^+ transfer is exothermic, $\Delta H°$(eq 1b) = −15.6 ± 4 kcal mol^{-1}, and represents <39% of the product-forming channels. To calculate $\Delta H°$(eq 1a), we require $\Delta H_f°((FH)^-OCH(CF_3)_2)$ which we calculate to be −475.7 kcal mol^{-1} [20] using the relationship $\Delta H_f°((FH)^-OCH(CF_3)_2 = \Delta H_f°(HF) + \Delta H_f°((CF_3)_2CHO^-) - D°((FH)^- \text{–} OCH(CF_3)_2)$,[20] the latter being the binding enthalpy of the cluster ion.[3] We calculate $\Delta H°$(eq 1a) = −8.4 kcal mol^{-1}.

In the elimination channel 5a for the reaction of $(CF_3)_2CH^-$ with CF_3CH_2OH, $\Delta H_f°((FH)^-OCH_2CF_3) = -306.6$ kcal mol^{-1},[20,21] and we calculate $\Delta H°$(eq 5a) = +0.6 kcal mol^{-1}.[14,16] This small reaction endothermicity is not in agreement with the large rate constant for this elimination reaction. The fluoride ion binding energy to CF_3CH_2OH ($D°(F^- \text{–} HOCH_2CF_3) = -39.1$ kcal mol^{-1})[3] reported by Larson and McMahon is slightly less than the calculated fluoride ion affinity of $CF_3CH{=}CF_2$ (eq 18). Since the former binding energy was experimentally determined from equilibrium measurements while the latter F^- affinity depends on calculated $\Delta H_f°$ for $CF_3CH{=}CF_2$ and $(CF_3)_2CH_2$, we assume that the small cumulative errors are present in the latter calculated values and eq 5a is, in fact, modestly exothermic. Similar errors probably also apply to $\Delta H°$(1a), but their magnitude is unknown. However, such errors might explain the amounts of elimination versus H^+ transfer in reaction 1 with channels 1a and 1b actually having more similar reaction exothermicities.

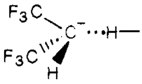
The negative ion elimination product from the reaction of $(CF_3)_2CH^-$ with *one* $(CH_3)_3COH$ molecule (reaction 9) would be the *tert*-butyl alcohol solvated fluoride ion, $F^-(HOC(CH_3)_3)$.[3] We calculate $\Delta H_f°(F^-(HOC(CH_3)_3) = -168.5$ kcal mol^{-1} [22] and $\Delta H° = +6.4$ kcal mol^{-1} for the formation of $F^-(HOC(CH_3)_3)$ as the negative ion product. In calculating this heat of reaction, only the $\Delta H_f°$'s of the starting ion $(CF_3)_2CH^-$ [17] and product olefin $CF_3CH{=}CF_2$ involve calculated values using group additivities; the remaining two values are experimentally determined. We believe that the errors in these calculations are <6 kcal mol^{-1}. On the basis of this consideration, the elimination reaction yielding the monosolvate $F^-(HOC(CH_3)_3)$ (m/z 93) is *endothermic* and the *m/z 93 cluster negative ion is not generated in this reaction.* The alternative explanation is to form $F^-(HOC(CH_3)_3)_2$ (m/z 167) directly as the product where the binding energy of the second *tert*-butyl alcohol molecule allows this channel to be exothermic, e.g., $D°((CH_3)_3CO^- \text{–} (HOC(CH_3)_3) = 20.4$ kcal mol^{-1}.[23]

For the very slow elimination reaction of $(CF_3)_2CH^-$ with CH_3OH assuming formation of the monosolvate negative ion $F^-(HOCH_3)$, we calculate $\Delta H_f°(F^- \text{–} (HOCH_3)) = -126.1$ kcal mol^{-1} [24] and $\Delta H° = +10.1$ kcal mol^{-1}.[24] Similarly, for the reaction of $(CF_3)_2CH^-$ with H_2O, we calculate $\Delta H_f°(F^-(H_2O)) = -141.6$ kcal mol^{-1} [25] and $\Delta H° = +16.4$ kcal mol^{-1} [25] for generation of the monohydrate ion $F^-(H_2O)$. The magnitudes of these reaction endothermicities require that multisolvated F^- ions are directly produced in both of these reactions which accounts for the smaller rate constants measured in these reactions.

Mechanism of the Elimination Reactions between $(CF_3)_2CH^-$ and ROH Molecules. We pointed out in the introduction that the reactions of anionic bases, B^-, with fluorinated alkanes forming fluoride cluster ions could involve an ROH assisted *syn*-E2 or *syn*-E1cb elimination via a transition state or an intermediate, respectively, with the conjugate acid of the base, BH, hydrogen bonding to carbon and to the fluorine of a C–F bond (eq 2). In the present experiments, BH = ROH and the hydroxyl proton would be coordinated to C_2 and the fluorine of a neighboring C–F bond in the carbanion $(CF_3)_2CH^-$ in this mechanism. However, we believe that the results from the reactions of $(CF_3)_2CH^-$ and $(CF_3)_2CD^-$ with $(CH_3)_3COH$ require an additional mechanism to be considered for fluoride cluster ion formation, that of coordination of the ROH molecule only to the fluorine in the carbanion setting up an ROH assisted *anti*-E1cb elimination mechanism.[26] This coordination of ROH would be expected to be most favorable with the negative hyperconjugating fluorine located anticoplanar to the C_2 electron pair.[12]

The reactions of $(CF_3)_2CH^-$ and $(CF_3)_2CD^-$ with $(CH_3)_3COH$ where H^+ transfer was endothermic by 9 kcal mol^{-1} occurred with rate constants that were about 50 times smaller than the rate constants for the reactions with $(CF_3)_2CHOH$ and CF_3CH_2OH. The reaction of $(CF_3)_2CH^-$ with $(CH_3)_3COH$ identified $F^-(HOC(CH_3)_3)_2$ (m/z 167) as the primary product ion of the alcohol assisted elimination reaction based on the thermochemical discussion given above. The results of the reaction between $(CF_3)_2CD^-$ and $(CH_3)_3COH$ showed D/H exchange in the carbanion but no observable (<0.5%) incorporation of deuterium into the elimination product ion $F^-(HOC(CH_3)_3)_2$ (eq 12) in spite of the fact that both of these product-forming channels had essentially the same rate constant. If the ROH assisted *syn*-E1cb elimination mechanism had been operating with formation of $F^-(DOC)(CH_3)_3)$ as the primary elimination product following D/H exchange at C_2 (54% observed), we would have expected to find considerable $F^-(DOC(CH_3)_3)(HOC(CH_3)_3)$ (m/z 168), formed by secondary clustering of $F^-(DOC(CH_3)_3)$ with $(CH_3)_3COH$, in the product ion signals. Although the m/z 168 cluster ion was not observed in the present experiment with $(CF_3)_2CD^-$, it was readily formed in the clustering reaction of $F^-(DOC(CH_3)_3)$ (generated separately) with $HOC(CH_3)_3$.

A feature of the above summary which we believe is important in describing the mechanism of the elimination product forming channel is that *two* $(CH_3)_3COH$ molecules are required to complex with $(CF_3)_2CH^-$ before $F^-(HOC(CH_3)_3)_2$ can separate. Let us assume that the first molecule of $(CH_3)_3COH$ coordinates to C_2 of the carbanion as in **1**. This will localize the negative charge primarily between C_2 of the carbanion and O of the coordinated alcohol. As the second $(CH_3)_3COH$ coordinates to **1**, these are the two sites available for hydrogen bonding. On the basis of this analysis, coordination of the second molecule of $(CH_3)_3COH$ would be expected to yield the products of overall H^+ transfer, $(CF_3)_2CH_2$ and $(CH_3)_3CO^-(HOC(CH_3)_3)$, at a rate at least competitive with that of elimination. The 20.4 kcal mol^{-1} binding energy of the homoconjugate cluster $((CH_3)_3CO^-(HOC(CH_3)_3)$[23] would overcome the 9 kcal mol^{-1} endothermicity of H^+ transfer between $(CF_3)_2CH^-$ and a *single* $(CH_3)_3COH$ molecule.[27] Since the $(CH_3)_3CO^-(HOC(CH_3)_3)$ cluster ion was not observed in these experiments, we do not believe that structure **1** is directly involved in the generation of the elimination product cluster ion $F^-(HOC(CH_3)_3)_2$.



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However, **1** is considered to be involved in the slow but significant amount of exchange in $(CF_3)_2CD^-$ in the reaction with

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(20) This is calculated by using $\Delta H_f°(HF) = -64.8$ kcal mol^{-1}.[4a] $\Delta H_f°((CF_3)_2CHO^-) = -385.9$ kcal mol^{-1} from $\Delta H_f°((CF_3)_2CHOH) = -367.1$ kcal mol^{-1} (calcd)[18] and $\Delta H°_{acid}((CF_3)_2CHOH) = 348.4$ kcal mol^{-1},[15] and the experimentally determined cluster binding enthalpy $D°((FH) \text{–} {}^-OCH(CF_3)_2) = 25$ kcal mol^{-1}.[3]

(21) $\Delta H_f°(CF_3CH_2OH) = -207.0$ kcal mol^{-1},[4a] $\Delta H_f°(CF_3CH_2O^-) = -209.8$ kcal mol^{-1},[4a] and $D°((FH) \text{–} {}^-OCH_2CF_3) = 32$ kcal mol^{-1}.[3]

(22) $\Delta H_f°((CH_3)_3COH) = -74.7$ kcal mol^{-1},[4a] and $D°(F^- \text{–} (HOC(CH_3)_3) = 33.3$ kcal mol^{-1}.[3]

(23) Caldwell, G.; Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 4660–4667.

(24) $\Delta H_f°(CH_3OH) = -36.0$ kcal mol^{-1},[4a] and $D°(F^- \text{–} (HOCH_3)) = 29.6$ kcal mol^{-1}.[3]

(25) $\Delta H_f°(H_2O) = -57.8$ kcal mol^{-1},[4a] and $D°(F^- \text{–} (H_2O)) = 23.3$ kcal mol^{-1}.[3]

(26) Our use of syn and anti to describe these ROH assisted E1cb elimination mechanisms is to specify the probable geometric relationship of the C–F bond to be broken relative to the orbital containing the "unshared" pair of electrons at C_2 of the carbanion.

(27) McDonald et al. (McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 7586) reported the "anion-switching" proton transfer in the reaction of $c\text{-}C_5H_5^-$ with $HOCH_2CF_3$. In this case, the intermediate hydrogen bonded complex $[c\text{-}C_5H_5^-(HOCH_2CF_3)]$ was observed to proceed to the products $c\text{-}C_5H_6$ and $CF_3CH_2O^-(HOCH_2CF_3)$ as a result of the secondary reaction of the intermediate complex with an additional CF_3CH_2OH molecule where $2k_1 = k_2$.

$(CH_3)_3COH$ which is illustrated in eq 19. Formation of complex

$$\begin{tikzcd}
(CF_3)_2CD^- + (CH_3)_3COH \arrow[r, shift left] & (CF_3)_2CD^-/HOC(CH_3)_3 \arrow[l, shift left] \arrow[d, shift right] \\
\underset{\mathbf{3}}{(CF_3)_2CH^-/DOC(CH_3)_2} \arrow[r, shift left] \arrow[d] & \underset{\mathbf{2}}{(CF_3)_2CDH/{}^-OC(CH_3)_3} \arrow[l, shift left] \arrow[u, shift right] \\
(CF_3)_2CH^- + DOC(CH_3)_3 & (19)
\end{tikzcd}$$

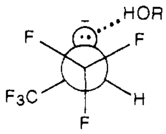
2 takes advantage of the 10–20 kcal mol^{-1} exothermic generation of the ion–molecule collision complexes due to ion–dipole and ion–induced dipole attractive forces. While **2** cannot separate because of the endothermicity of the H^+ transfer, **2** can transfer deuterium, yielding **3** which separates and completes the process of D/H exchange.[28] The essential doubling of the rate constant for the reaction of $(CF_3)_2CD^-$ with $(CH_3)_3COH$ (elimination and D/H exchange) compared to that for the reaction of $(CF_3)_2CH^-$ with $(CH_3)_3COH$ (elimination only) strongly suggests that *the two processes of elimination and D/H exchange are separate and occur with similar rate constants.*

The above discussion leads us to conclude that the product-forming channels in the reactions of $(CF_3)_2CH^-$ and $(CF_3)_2CD^-$ with $(CH_3)_3COH$ occur by coordination of the alcohol to *two different sites* of the carbanion, (i) at C_2 of the carbanion for D/H exchange and (ii) at fluorine of a CF_3 group for generation of the cluster ion $F^-(HOC(CH_3)_3)_2$. This conclusion of separate coordination sites by the alcohol molecules explains why (a) H^+ transfer did not occur at C_2 which would require two $(CH_3)_3COH$ molecules and (b) deuterium was not observed in the elimination product $F^-(HOC(CH_3)_3)_2$ with the $DOC(CH_3)_3$ formed by D/H exchange at the carbanion C_2 simply being lost to the flow components. It also explains why the D/H exchange in $(CF_3)_2CD^-$ was so slow *if* a major coordination site in the carbanion was at fluorine as well as at C_2. That the cluster ion $[(CF_3)_2CH^-(HOC(CH_3)_3)]$ was not observed requires that formation of this ion (k_1) with the alcohol coordinated to fluorine is slow and rate limiting while coordination of the second $(CH_3)_3COH$ molecule and elimination of $F^-(HOC(CH_3)_3)_2$ (k_2) is fast with $k_2 > 10k_1$ (eq 20).[27] The rather large concentrations of $(CH_3)_3COH$ present

$$(CF_3)_2CH^- + HOC(CH_3)_3 \xrightarrow{k_1} [F_3C{-}CH{-}CF_2{-}F^-{\cdot\cdot}HOC(CH_3)_3] \xrightarrow[HOC(CH_3)_3]{k_2} F^-(HOC(CH_3)_3)_2 + CF_3CH{=}CF_2 \quad (20)$$

in the flow for this slow reaction occurring in only one out of every 100 collisions eliminate the possibility of directly observing the carbanion–alcohol cluster ion with such kinetic constraints.[29]

We believe that these results are best interpreted in terms of the two structures **4** and **5** with R = $C(CH_3)_3$ where **4** yields the product ions of D/H exchange and the complex **5** forms the ion products of the ROH assisted *anti*-E1cb elimination.[26] ROH



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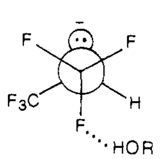

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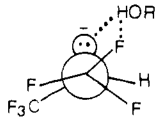

6

assisted *syn*-E1cb elimination[26] shown in eq 2 would proceed via intermediate **6**. In the present case where R = $C(CH_3)_3$, the intramolecular hydrogen bonding in **6** must overcome the severe eclipsing interactions, especially between F on C_1 and the CF_3 group at C_2, and potential steric problems between the bulky *tert*-butyl group and other atoms in the complex. We doubt that such a structure would be stable enough to survive long enough to collide with a second $(CH_3)_3COH$ molecule which is required to effect the elimination of $F^-(HOC(CH_3)_3)_2$.

In the fast reaction of $(CF_3)_2CH^-$ with $(CF_3)_2CHOH$ occurring at nearly the collision limit, both of the channels of elimination (eq 1b, $\Delta H° = -8.4$ kcal mol^{-1}) and of H^+ transfer (eq 1a, $\Delta H° = -15.6$ kcal mol^{-1}) are exothermic. The results from the reaction of the deuteriated carbanion $(CF_3)_2CD^-$ (*m/z* 152) with $(CF_3)_2CHOH$ demonstrated that the H^+ transfer step in this collision limited reaction was *not* reversible since (i) D/H exchange in *m/z* 152 (→ *m/z* 151) was not observed[27] and (ii) *no* deuterium was observed in the fluoride cluster ion elimination product. Removal of F^- from $(CF_3)_2CH^-$ by this alcohol molecule *must* occur with concomitant formation of the $(HF)^-OCH(CF_3)_2$ cluster ion because of the large F^- affinity of the olefin $CF_3CH{=}CF_2$. This is observed in the formation of the major product ion at *m/z* 187 in eq 1a which is due to the large binding energy of F^- to $HOCH(CF_3)_2$ ($D°(F^-{-}HOCH(CF_3)_2) = 48.1$ kcal mol^{-1}).[3] Since HF is a weaker gas-phase acid than $HOCH(CF_3)_2$, the structure of this cluster is considered to be that of H^+ transfer $(FH)^-OCH(CF_3)_2$,[2] with $D°((FH){-}^-OCH(CF_3)_2) = 25$ kcal mol^{-1}.[3] Although these results appear to be most consistent with the mechanism involving two separate sites in the carbanion for coordination of the alcohol molecule leading to reaction, we cannot rule out the possibility of the ROH assisted *syn*-E1cb mechanism in this reaction.

Proton transfer between $(CF_3)_2CH^-$ and CF_3CH_2OH was expected to be slow if it was thermally neutral or nonexistent if H^+ transfer was endothermic. The single primary product from this fast, collision-limited reaction was $(FH)^-OCH_2CF_3$ (*m/z* 119)[2] (eq 5a), the product of CF_3CH_2OH assisted elimination of F^- from $(CF_3)_2CH^-$. The corresponding cluster ion product from the reaction of $(CF_3)_2CD^-$ with CF_3CH_2OH was composed of 70% $(FH)^-OCH_2CF_3$ (*m/z* 119) and 30% $(FD)^-OCH_2CF_3$ (*m/z* 120).[2] This latter result showed that some H/D exchange had occurred in the collision of $(CF_3)_2CD^-$ with CF_3CH_2OH according to eq 21. However, D/H exchange in $(CF_3)_2CD^-$ was not observed

$$(CF_3)_2CD^- + HOCH_2CF_3 \rightarrow (CF_3)_2CD^-/HOCH_2CF_3 \rightleftarrows (CF_3)_2CHD/{}^-OCH_2CF_3 \rightleftarrows \underset{\mathbf{7}}{(CF_3)_2CH^-/DOCH_2CF_3} \quad (21)$$

during the reaction with CF_3CH_2OH requiring that cluster ion **7** does *not* separate to yield $(CF_3)_2CH^-$ (*m/z* 151). Elimination of F^- assisted by CF_3CH_2OD from **7** must then occur to produce the deuterium containing cluster ion at *m/z* 120.

That no D/H exchange was observed in the carbanion $(CF_3)_2CD^-$ through 80% of its decay while 30% of the elimination product anion was $(FD)^-OCH_2CF_3$ in the reaction of $(CF_3)_2CD^-$ with CF_3CH_2OH means that every collision proceeds to the elimination product anions in agreement with the kinetics of the reaction. However, these facts require that D/H exchange did occur at some point in the collision encounter between $(CF_3)_2CD^-$ and $HOCH_2CF_3$ in forming $(FD)^-OCH_2CF_3$. Generation of this product ion may be the result of the ROH assisted *syn*-E1cb elimination mechanism with the accompanying D/H exchange at C_2 which could be due to the larger acidity (greater binding energy to the carbanion) and smaller steric bulk of CF_3CH_2OH compared to $(CH_3)_3COH$. Alternatively, the $CF_3CH_2OH(D)$ molecules coordinated at C_2 may migrate to a fluorine within the collision complex and effect the *anti*-E1cb elimination process. Since $(FD)^-OCH_2CF_3$ makes up 30% of the elimination product ions, at least 60% of the CF_3CH_2OH molecules must first coordinate at C_2 of the carbanion; the exact percentage depends on the unknown magnitude of the isotope effect in the D/H exchange in eq 21. Any residual amount of the elimination product $(FH)^-OCH_2CF_3$ would then be assigned to direct coordination of CF_3CH_2OH to fluorine of a CF_3 group and loss of $(FH)^-OCH_2CF_3$. The increased acidity and expected larger binding energy of CF_3CH_2OH over that of $(CH_3)_3COH$ to the carbanion accounts for the larger amount of coordination at C_2 in this example.

We believe that the most probable reason why deuterium was not found in the elimination product anion from the reaction of $(CF_3)_2CD^-$ with $(CF_3)_2CHOH$ but was observed in the products

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from the reaction with CF_3CH_2OH is that H^+ transfer is exothermic by 15.6 kcal mol^{-1} in the former reaction. This excess energy is deposited in the vibrational manifolds of the components of the complex of H^+ transfer $[(CF_3)_2CDH/^-OCH(CF_3)_2]$ which reduces the lifetime of the complex and separation occurs. The increased steric bulk of $(CF_3)_2CHOH$ compared to CF_3CH_2OH may also contribute to the separation of this complex.

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Pressure Effects on the Intervalence Transfer Electronic Absorption Band of the Mixed-Valence Bis(fulvalene)diiron Monocation in Various Media[†]

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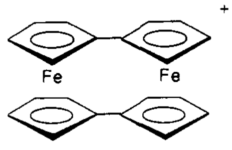
Abstract: The pressure dependence of the two intervalence transfer (IT) electronic absorption bands of the mixed-valence bis(fulvalene)diiron cation is examined in various media. In general, a blue shift with increasing pressure is seen for both IT bands in all media. The blue shifting is attributable to an intramolecular effect, where an increase in pressure leads to an increase in the energy separation between the bonding ground and antibonding excited states of the IT transition. At high pressures and to variable degrees in the different media (crystal lattice, PMMA polymer, intercalated into zeolite 13X) compression leads to intermolecular effects on the energy of the two IT bands. Data obtained for the zeolite-intercalated bis(fulvalene)diiron cation are analyzed in terms of the PKS vibronic model. Values for the electronic and vibronic coupling parameters are obtained from spectra measured in the range of 11–138 kbar. The value of the PKS electronic coupling factor ϵ was shown to increase by a factor of ~1.5 over this pressure range. The degree of valence localization in the bis(fulvalene)diiron cation can be changed appreciably with pressure. From $|\epsilon|$ and the PKS vibronic coupling factor λ evaluated for the low-energy IT band it was calculated that $|\epsilon|/\lambda^2$, a ratio that characterizes the valence localization, increases continuously from 0.59 at 11 kbar to 0.78 at 89 kbar.

Pressure tuning spectroscopy (PTS) has been shown to be effective in studying the energy perturbations on valence orbitals resulting from pressure-induced compression of condensed phases.[3] Compression of crystals consisting of molecular units or large molecular ions leads to a reduction in interatomic and intermolecular distances which increases the overlap of valence orbitals. An electronic absorption band for a molecular moiety will shift to either higher or lower energy dependent on the balance between intramolecular and intermolecular effects of compression. In the case of intramolecular effects, an excitation from a bonding to an antibonding orbital should increase in energy with an increase in pressure. On the other hand, as a result of attractive van der Waals intermolecular interactions, a bonding to antibonding excitation localized on one molecular unit will generally shift to lower energy upon an increase in the pressure. This shift to lower energy as a result of intermolecular effects reflects the greater polarizability of the excited-state molecule with an electron in the antibonding orbital compared to the ground-state molecule.

Very recently we reported[4] the effect of pressure-induced freezing on the energy of the intervalence transfer (IT) electronic absorption band of binuclear mixed-valence complexes in solution. The energy of the IT band was monitored as the pressure was increased until, at pressures less than 10 kbar, the solutions froze. Essentially no shifts of the IT bands were observed, which is in marked contrast to the prediction of the dielectric continuum model[5,6] for the solvent reorientation contribution to the energetics of the IT band.

In view of the interesting results obtained for the IT bands of mixed-valence complexes in solution, PTS was applied to the study of IT bands of mixed-valence complexes in the solid state. The hemihydroquinone picrate salt of bis(fulvalene)diiron monocation (I), compound **1**, was selected for this initial PTS study on solids with pressures up to 163 kbar.



I

Mixed-valence cation I has been the object of considerable investigation.[7–20] The two iron ions in various salts of cation I

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