

Gas-Phase Reactions of the Methyl Anion

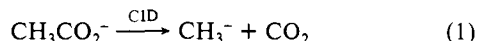
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Abstract: We report the first direct observations of ion/molecule reactions of the methyl anion CH_3^- in the gas phase. Methyl anions are generated by means of collision-induced dissociation (CID) of CH_3CO_2^- or $\text{CH}_3\text{CH}_2\text{O}^-$ in a flowing afterglow-triple quadrupole instrument. Ion/molecule reactions of CH_3^- can be observed when CID is effected in the presence of reactive gases under appropriate conditions of collision energy and reactant gas pressure. Following fragmentation of the precursor ion, methyl anion reactions take place within the collision cell under nonthermal conditions. For a given neutral reactant, only those product ions that are unique to CH_3^- are reported. Reflecting its strongly basic character [$\Delta H^\circ_{\text{acid}}(\text{CH}_4) = 416.6$ kcal/mol] and its low electron-binding energy [$\text{EA}(\text{CH}_3) = 1.8$ kcal/mol], CH_3^- abstracts a proton from $\text{CH}_2=\text{CH}_2$ and NH_3 and transfers an electron to O_2 , OCS , CS_2 , and C_6F_6 . Nucleophilic addition/elimination reactions are observed both with aprotic reagents such as N_2O and with protic substrates such as propionaldehyde. Results of reactions with a variety of other substrates are also presented.

The methyl anion CH_3^- arguably can be considered the archetype of organic anions, but virtually nothing is known of its gas-phase chemistry. The major obstacle encountered in attempts to study the chemistry of CH_3^- is the difficulty of generating this ion under conditions appropriate for the observation of ion/molecule reactions. Although CH_3^- can be observed in the low-pressure negative-ion mass spectra of several organic species,¹⁻⁴ numerous other reactive anions are also formed and CH_3^- is but a minor constituent of the resulting complex mixtures. Chemical ionization methods such as proton abstraction, fluorodesilylation, and other methods developed to generate carbanions⁵⁻¹² fail utterly to produce CH_3^- . Even the amide ion NH_2^- , the most basic reagent ion readily available [$\Delta H^\circ_{\text{acid}}(\text{NH}_3) = 403.6$ kcal/mol],⁵ is far too weak to deprotonate CH_4 [$\Delta H^\circ_{\text{acid}}(\text{CH}_4) = 416.6$ kcal/mol].¹¹⁻¹³ Moreover, it is likely that collisional detachment of the weakly bound electron of CH_3^- [$\text{EA}(\text{CH}_3) = 1.8$ kcal/mol]¹³ would occur under the high-pressure conditions or at the long interaction times that are usually required for the study of ion/molecule reactions and thereby preclude the observation of CH_3^- .¹⁴

Recently, we described how CH_3^- can be produced by collision-induced decarboxylation of CH_3CO_2^- in a flowing afterglow-triple quadrupole instrument (eq 1).¹⁵ Herein we report



that ion/molecule reactions of CH_3^- can be observed when de-

carboxylation is effected in the presence of reactive gases at appropriate pressures. We describe an experimental protocol for identifying CH_3^- reactions and present results from the first systematic experimental investigation of the gas-phase chemistry of CH_3^- .

Experimental Section

The experiments described in this paper were carried out in a flowing afterglow-triple quadrupole instrument (Figure 1).^{16,17} Briefly, the instrument consists of a 1-m-long, 7-cm-diameter stainless steel flow tube, through which a constant flow of helium buffer gas is maintained by a Roots blower. For these experiments, the buffer gas pressure was 0.30 Torr and the buffer flow rate was 130 (STP) cm^3/s . Primary ions generated in the upstream ion source (electron ionization, EI, at 70 eV and emission current of 0.40-0.50 mA) are carried downstream by the helium buffer, where they can react with neutral reagents added through fixed or movable inlets. The resulting ions are sampled through a 1-mm-diameter orifice in the nose cone partition separating the flow tube from the differentially pumped detection chamber, which is maintained at less than 5×10^{-5} Torr. A low, attractive potential (0.1-1.5 V) is applied to the molybdenum disk that contains the sampling orifice in order to optimize collection of the negative ions.

The sampled ions are focused into the triple quadrupole analyzer and examined by standard quadrupole mass analysis or by tandem mass spectrometry.¹⁸ The ions are detected at the exit of the third quadrupole (Q3) by a conversion dynode and Channeltron particle multiplier. Pressures in the collision chamber (Q2) were measured with an MKS Baratron capacitance manometer. Collision energies (laboratory frame) are given by the Q2-rod offset voltage, and the energy axis origin is located by retarding potential analysis.

Because of the complex trajectories described by ions in the quadrupole collision cell and the fact that collision cross sections for the ion/molecule pairs considered here are unknown, we are unable to define rigorously the upper bound of pressure for single-collision conditions. However, we have developed a number of empirical tests that signal the onset of effects due to multiple collisions.¹⁶ The tests involve monitoring the appearance of secondary ion/molecule reaction products when a reactive gas is present in Q2 or, alternatively, the onset of nonlinearity in the pressure dependence of sequential dissociation reactions. For parent ion axial kinetic energy in excess of ~ 1 eV (lab), the various diagnostic tests indicate that effects of multiple collisions become manifest at collision gas pressures greater than $(5-10) \times 10^{-5}$ Torr, depending upon the collision gas used and the collision energy.

Quantitative measurements of threshold energies for CID in the second quadrupole region are carried out at collision gas pressures corresponding to single-collision conditions ($P_{\text{Q2}} < 5 \times 10^{-5}$ Torr). Ion/molecule reactions of the methyl anions produced by CID can be ob-

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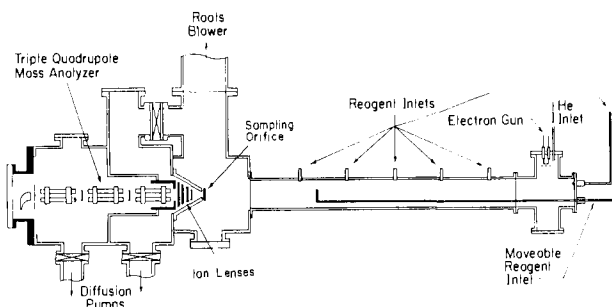
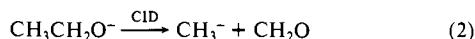


Figure 1. The flowing afterglow-triple quadrupole instrument.

served only in multiple-collision conditions, and most were studied at reactant gas pressures of $(3\text{--}5) \times 10^{-4}$ Torr. It should be noted that reaction conditions within Q2 are nonthermal and not well-characterized. Particularly under multiple-collision conditions, the distribution of collision energies is broad and indeterminate, and the actual number of collisions suffered by ions will also be described by an unknown distribution function.

Methyl anions were generated in the central quadrupole by CID of either CH_3CO_2^- , m/z 59 (eq 1) or $\text{CH}_3\text{CH}_2\text{O}^-$, m/z 45 (eq 2), depending



upon which region of the mass spectrum was being examined for CH_3^- reaction products.¹⁹ The availability of alternative sources for CH_3^- is desirable because the intense and collision-broadened signal of the precursor ion can obscure detection of a product ion with a similar mass (± 2 amu). Acetate ions were produced in the flow tube by three different methods. The reaction of NH_2^- (from dissociative electron capture by NH_3) with acetic anhydride $[(\text{CH}_3\text{CO})_2\text{O}]$ produces a high yield of CH_3CO_2^- (and presumably the neutral products $\text{NH}_3 + \text{CH}_2=\text{C}=\text{O}$).²³ This reaction avoids rapid formation of the unwanted cluster ions $(\text{CH}_3\text{CO}_2\text{H})_n\text{CH}_3\text{CO}_2^-$ that are the major products of deprotonation of acetic acid under flowing afterglow conditions. Direct electron ionization of acetic anhydride also produces acetate ions, albeit in relatively low yield. Fluorodesilylation⁶⁻⁸ of trimethylsilyl acetate, which was prepared *ex situ* by mixing acetic anhydride with excess bis(trimethylsilyl)acetamide, produces an intermediate yield of acetate. For the fluorodesilylation method, the vial containing the crude mixture was connected directly to the flow tube inlet, and the head vapors were allowed to react with fluoride ion, which was generated by dissociative capture of energetic electrons by CF_4 or SF_6 . In the experiments involving $\text{CH}_3\text{CH}_2\text{O}^-$ as the CH_3^- precursor, $\text{CH}_3\text{CH}_2\text{O}^-$ was generated by base-induced elimination of ethylene from diethyl ether²⁴ or by deprotonation of ethanol.

Collisional activation with argon target gas of CH_3CO_2^- produced by dissociative electron capture by acetic anhydride results only in CH_3^- fragment ions (Figure 2a). However, low-level impurity ions could be detected in the CID spectrum of CH_3CO_2^- produced by the reaction of NH_2^- with acetic anhydride. These impurity ions appeared at m/z 17 and 41 and were assigned to OH^- and HC_2O^- , respectively. These ions

(19) Our observation of CH_3^- resulting from CID of CH_3CO_2^- and $\text{CH}_3\text{CH}_2\text{O}^-$ can be contrasted with previous studies of the high-energy CID reactions of $\text{CH}_3\text{CH}_2\text{O}^-$, CH_3CO_2^- , and the related ion CH_3COS^- by Bowie and co-workers, in which CH_3^- was not detected.^{20,21} Only H_2 loss from $\text{CH}_3\text{CH}_2\text{O}^-$ was observed,²⁰ and on the basis of nonappearance of fragment ions from CH_3CO_2^- and CH_3COS^- , it was concluded that both species are "stable" with respect to fragmentation.²¹ However, in a recent reinvestigation of CH_3CO_2^- by this same group,²² CH_3^- is reported as a minor fragment ion among several others, including CH_2CO_2^- , CHCO_2^- , CO_2^- , and HC_2O^- .

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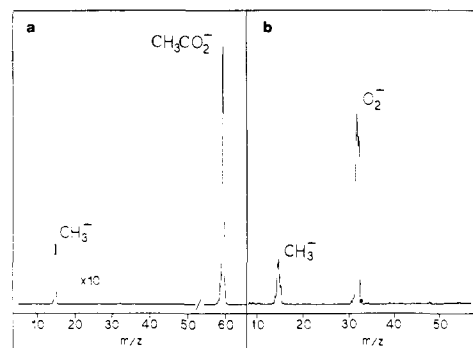
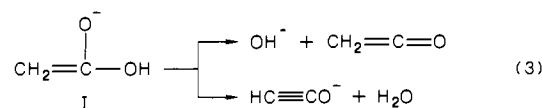


Figure 2. Collision-induced dissociation spectra of CH_3CO_2^- illustrating the formation of CH_3^- and its subsequent reaction with O_2 : (a) argon target gas at a pressure of 3×10^{-5} Torr and a CH_3CO_2^- ion axial kinetic energy of 15 eV; (b) oxygen target gas at a pressure of 4×10^{-4} Torr and a CH_3CO_2^- ion axial kinetic energy of 13 eV. The CH_3CO_2^- ion signal (not shown) is approximately 50 times more intense than the O_2^- product ion signal under these conditions.

may result from CID of traces of the enolate tautomer (I) of the acetate anion (eq 3), which may be formed by nonspecific deprotonation by the



strongly basic NH_2^- ion of acetic acid contaminant in the acetic anhydride.²²

Low-level impurity ions were also detected in the CID spectrum of CH_3CO_2^- produced by fluorodesilylation of trimethylsilyl acetate. These ions appeared at m/z 19 and 39 and were assigned to F^- and $\text{F}^-(\text{HF})$, arising from dissociation of $\text{F}^-(\text{HF})_2$ (m/z 59). Clusters of HF with CH_3CO_2^- could also be detected in the flow tube and appeared to be enhanced by incomplete derivatization of the acid. Apparently, HF is produced when fluorodesilylation is attempted in the presence of free acetic acid, although the mechanism that leads to HF production is not clear. When these low-level impurities interfered with the identification of CH_3^- reaction products, the experiments were repeated with an alternative CH_3CO_2^- production method.

Materials. All reagent gases were obtained from commercial suppliers and were of the following purities: He (99.995%), Ar (99.995%), CH_3Cl (99.5%), CH_4 (99.0%), CO_2 (99.5%), OCS (97.5%), CF_4 (99.9%), $\text{CH}_2=\text{CH}_2$ (99.5%), $\text{CF}_3\text{CF}=\text{CF}_2$ (99.5%), 1,3-butadiene (99.0%), NH_3 (99.99%), N_2O (99.0%), O_2 (99.5%), SF_6 (99.8%), SO_2 (99.98%). Deuterium-labeled compounds were obtained from Aldrich Chemical Co. with the following isotopic purities: D_2O (99.8% d), acetic anhydride- d_6 (99+% d), acetic acid- d_4 (99.5% d). Liquid reagents were also obtained commercially. Benzene was stored over molecular sieves to ensure dryness; all liquid samples were subjected to several freeze-pump-thaw cycles prior to use to remove dissolved gases.

Results and Discussion

Reactions of CH_3^- can be observed when collision-induced decarboxylation of CH_3CO_2^- (or CID of $\text{CH}_3\text{CH}_2\text{O}^-$) is effected by reactive gases at pressures that permit multiple ion/molecule collisions within Q2. Acetate anions are generated in the flow tube and mass-selected at the first quadrupole (Q1), such that only ions of m/z 59 enter Q2. The reactive gas is admitted to Q2, which is enclosed in shrouding to permit the attainment of moderate pressures (up to 10^{-3} Torr). The acetate ions selected at Q1 undergo collisions in Q2 and are decarboxylated to yield CH_3^- (Figure 2a).¹⁹ In subsequent collisions, CH_3^- can react with the collision gas. The fragment ions produced by CID, the product ions resulting from ion/molecule reactions, and the remaining parent acetate ions are then mass-analyzed at Q3 (Figure 2b).

Although the initial CH_3CO_2^- collision in Q2 will be relatively energetic, e.g., 5 eV c.m. (center of mass), subsequent collisions may be less energetic due to momentum transfer. The lower energy collisions can lead to ion/molecule reactions involving both the CH_3^- fragment ions and the CH_3CO_2^- parent ion. Moreover, collisional detachment of the weakly bound electron of CH_3^- may lead to a source of free electrons, and potentially to electron capture by the collision gas. Thus, it is important to recognize

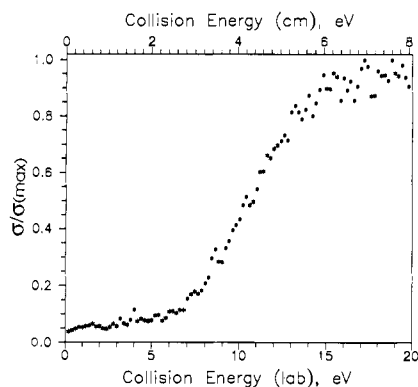


Figure 3. Plot of normalized CH_3^- ion intensity as a function of CH_3CO_2^- ion kinetic energy in the center-of-mass frame (upper scale) and the laboratory frame (lower scale). Argon target gas at a pressure of 5×10^{-5} Torr (single-collection conditions). The solid line represents a linear fit of the steeply rising portion of the appearance curve. The Doppler-corrected threshold energy from this experiment is 2.70 eV.

that ions appearing from reactive-gas CID of CH_3CO_2^- are not necessarily products from ion/molecule reactions of CH_3^- . The possible competing processes (endothermic and exothermic reactions of the parent carboxylate ion, capture of detached electrons, and unimolecular decomposition of primary reaction products) can lead to ambiguities if the resulting ions coincide in mass with predicted CH_3^- reaction products. Because of this potential interference, we established several strict criteria that must be fulfilled by an ion in order to identify it as a bona fide CH_3^- reaction product. The requirements and the rationale behind them are as follows:

1. The initial collision of CH_3CO_2^- in Q2 may result in decarboxylation, reaction of CH_3CO_2^- with the target gas, or scattering. It is only *after* collision-induced decarboxylation that CH_3^- is actually present and able to undergo reactive collisions with the target gas. Therefore, ions that can be observed in single-collision conditions ($P_{\text{Q2}} < 5 \times 10^{-5}$ Torr) are immediately ruled out as CH_3^- reaction products. Note that this requirement may preclude identification of a legitimate CH_3^- product that has the same mass as a CH_3CO_2^- product. In certain favorable reactions (specifically, electron transfers), product ions could be detected at pressures as low as 8×10^{-5} Torr, which therefore marks the onset of multiple collisions for these reactions. All CH_3^- reactions identified herein were observed only at or above 8×10^{-5} Torr.

2. Below the effective appearance potential for CH_3^- , any ions that are formed in Q2 necessarily arise from reactions of the *parent* ion (CH_3CO_2^- or $\text{CH}_3\text{CH}_2\text{O}^-$). Therefore, our second requirement is that the appearance potential for a CH_3^- reaction product be equal to or greater than the appearance potential for CH_3^- .

3. For each of the experiments described, the reaction conditions were duplicated with CD_3CO_2^- as a precursor for deuterium-labeled methyl anion. We imposed the requirement that all ions to be identified as CH_3^- reaction products must be observed in the CD_3^- experiment as well. Product ions that result from addition or condensation reactions should show an appropriate isotope shift in the CD_3^- product ion mass spectrum according to the number of deuteriums incorporated.

4. We reported previously¹⁵ that collision-induced decarboxylation of $\text{CH}_3\text{CH}_2\text{CO}_2^-$ does not produced measurable signals of CH_3CH_2^- and attributed this observation to rapid electron detachment from the incipient carbanion.⁸ Thus, carrying out reactive-gas collisional activation of $\text{CH}_3\text{CH}_2\text{CO}_2^-$ provides a means to verify *in the absence of reactive carbanions* whether a product ion can arise from reactions of a kinetically excited carboxylate ion or by capture of detached electrons. Each experiment was therefore repeated with $\text{CH}_3\text{CH}_2\text{CO}_2^-$ as the parent ion.

Energetics. The appearance potential of CH_3^- from CID of CH_3CO_2^- was obtained by monitoring the CH_3^- signal intensity as a function of collision energy (Figure 3) and was corrected for

Table I. Gas-Phase Acidity of Methane Derived from CH_3^- Appearance Energies for CID of Various Precursor Ions

precursor ion	neutral fragment ^a	E_T , eV ^b	$\Delta H_{\text{acid}}(\text{CH}_4)$, ^c kcal/mol
CH_3CO_2^-	CO_2	2.74	420
$\text{CH}_3\text{CH}_2\text{O}^-$	CH_2O	2.27	416
$(\text{CH}_3)_2\text{CHO}^-$	CH_3CHO	2.10	416
$(\text{CH}_3)_3\text{CO}^-$	$(\text{CH}_3)_2\text{CO}$	1.93	414
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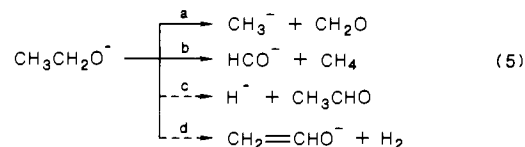
^a Identity inferred. ^b Threshold center-of-mass translational energy for appearance of CH_3^- from CID of the precursor ion. Estimated uncertainty is ± 0.15 eV. ^c Upper bound for CH_4 acidity calculated with use of eq 4, eq 6, or the analogous equation for the appropriate thermochemical cycle. Thermochemical data for the ions and neutral compounds taken from ref 5 and 28.

thermal motion of the target gas.^{25,26} The threshold decarboxylation energy so obtained is reproduced within experimental error for CID of CH_3CO_2^- produced by each of the three methods described in the Experimental Section. As we demonstrated previously,¹⁵ the threshold decarboxylation energy E_T (eq 1) provides a measure of the energy of heterolytic bond cleavage and can be related to the gas-phase acidity of CH_4 by a simple thermochemical cycle (eq 4). Using our measured value for E_T (1)

$$\Delta H_{\text{acid}}^{\circ}(\text{CH}_4) = E_T(1) + \Delta H_{\text{f}}^{\circ}(\text{CH}_3\text{CO}_2\text{H}) + \Delta H_{\text{acid}}^{\circ}(\text{CH}_3\text{CO}_2\text{H}) - \Delta H_{\text{f}}^{\circ}(\text{CO}_2) - \Delta H_{\text{f}}^{\circ}(\text{CH}_4) \quad (4)$$

of 2.74 ± 0.15 eV and appropriate thermochemical data from the literature,²⁷ we obtain a value of 420 ± 5 kcal/mol for $\Delta H_{\text{acid}}^{\circ}(\text{CH}_4)$.

Argon-CID of $\text{CH}_3\text{CH}_2\text{O}^-$ results in the production of CH_3^- (eq 5a) and HCO^- (eq 5b) by loss of formaldehyde and methane,



respectively. The channels shown in eq 5c and eq 5d have been observed previously from high-energy (keV) CID of ethoxide ion²⁰ and in the negative-ion mass spectrum of ethanol.¹ However, the relatively low parent ion resolution and low-mass detection cutoff (3 amu) of the triple quadrupole analyzer prevents the observation of these product ions with our instrument.

The corrected appearance potential for CH_3^- from CID of ethoxide is 2.27 ± 0.15 eV. This appearance potential, or CID threshold energy E_T (5a), can again be related to a heat of formation for CH_3^- and hence to the gas-phase acidity of CH_4 (eq 6).²⁹ Our experimental threshold energy yields a value of 418 ± 4 kcal/mol for $\Delta H_{\text{acid}}^{\circ}(\text{CH}_4)$.

$$\Delta H_{\text{acid}}^{\circ}(\text{CH}_4) = E_T(5a) + \Delta H_{\text{f}}^{\circ}(\text{CH}_3\text{CH}_2\text{OH}) + \Delta H_{\text{acid}}^{\circ}(\text{CH}_3\text{CH}_2\text{OH}) - \Delta H_{\text{f}}^{\circ}(\text{CH}_2\text{O}) - \Delta H_{\text{f}}^{\circ}(\text{CH}_4) \quad (6)$$

Methyl anion is also produced as a CID fragment from various other alkoxide anions, including $(\text{CH}_3)_2\text{CHO}^-$ and $(\text{CH}_3)_3\text{CO}^-$. We have measured CH_3^- appearance energies with these precursor ions and have evaluated $\Delta H_{\text{acid}}^{\circ}(\text{CH}_4)$ from appropriate thermochemical cycles. Table I summarizes the results for all of the

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(27) $\Delta H_{\text{f}}^{\circ}(\text{CH}_3\text{CO}_2\text{H}) = -103.3$ kcal/mol;²⁸ $\Delta H_{\text{acid}}^{\circ}(\text{CH}_3\text{CO}_2\text{H}) = 348.5$ kcal/mol;⁵ $\Delta H_{\text{f}}^{\circ}(\text{CO}_2) = -94.0$ kcal/mol;²⁸ $\Delta H_{\text{f}}^{\circ}(\text{CH}_4) = -17.8$ kcal/mol.²⁸

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(29) $\Delta H_{\text{acid}}^{\circ}(\text{CH}_3\text{CH}_2\text{OH}) = 378.0$ kcal/mol;^{5,30} $\Delta H_{\text{f}}^{\circ}(\text{CH}_3\text{CH}_2\text{OH}) = -56.1$ kcal/mol;²⁸ $\Delta H_{\text{f}}^{\circ}(\text{CH}_2\text{O}) = -26.0$ kcal/mol.²⁸

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Table II. Products from Ion/Molecule Reactions of CH_3^-

entry	reactant gas	products ^{a,b}	reaction ^c
1	O_2	$\text{CH}_3 + \text{O}_2^-$ (m/z 32)	ET
2	OCS	$\text{CH}_3 + \text{OCS}^-$ (m/z 60) $\text{CO} + \text{CH}_3\text{S}^-$ (m/z 47) $\text{CH}_2=\text{C}=\text{O} + \text{HS}^-$ (m/z 33)	ET AT(S) AE($\text{CH}_2=\text{C}=\text{O}$)
3	CS_2	$\text{CH}_3 + \text{CS}_2^-$ (m/z 76) $\text{CS} + \text{CH}_3\text{S}^-$ (m/z 47) $\text{CH}_2=\text{C}=\text{S} + \text{HS}^-$ (m/z 33)	ET AT(S) AE($\text{CH}_2=\text{C}=\text{S}$)
4	C_6F_6	$\text{CH}_3 + \text{C}_6\text{F}_6^-$ (m/z 186) $2\text{HF} + \text{C}_7\text{HF}_4^-$ (m/z 161) $3\text{HF} + \text{C}_7\text{F}_3^-$ (m/z 141)	ET AE(2HF) AE(3HF)
5	$\text{CF}_3\text{CF}=\text{CF}_2$	$2\text{HF} + \text{C}_4\text{HF}_4^-$ (m/z 125) $3\text{HF} + \text{C}_4\text{F}_3^-$ (m/z 105)	AE(2HF) AE(3HF)
6	N_2O	$\text{H}_2\text{O} + \text{HCN}_2^-$ (m/z 41) $\text{CH}_2\text{N}_2 + \text{OH}^-$ (m/z 17) CH_3SO_2^- (m/z 79)	AE(H_2O) AE(CH_2N_2) A
7	SO_2		A
8	CH_4^d		NR
9	$\text{CH}_2=\text{CH}_2$	$\text{CH}_4 + \text{C}_2\text{H}_3^-$ (m/z 27)	PT
10	C_4H_6 (1,3-butadiene)	$\text{CH}_4 + \text{C}_4\text{H}_5^-$ (m/z 53)	PT
11	C_6H_6 (benzene)	$\text{CH}_4 + \text{C}_6\text{H}_5^-$ (m/z 77)	PT
12	NH_3	$\text{CH}_4 + \text{H}_2\text{N}^-$ (m/z 16)	PT
13	CH_3Cl	$\text{CH}_4 + ^-\text{CH}_2\text{Cl}$ (m/z 49, 51)	PT
14	$\text{CH}_3\text{CH}_2\text{CHO}$	$\text{H}_2 + \text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2^-$ (m/z 71) or $\text{CH}_3\text{CHC}(\text{CH}_3)\text{O}^-$	AE(H_2)
15	$\text{CH}_2=\text{CHCHO}$	$\text{H}_2 + \text{CH}_2=\text{CHC}(\text{O})\text{CH}_2^-$ (m/z 69) or $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CO}^-$	AE(H_2)

^a Neutral product inferred. ^b CH_3^- produced in situ by CID of CH_3CO_2^- or $\text{CH}_3\text{CH}_2\text{O}^-$; reactant gas pressure, $3\text{--}5 \times 10^{-4}$ Torr; collision energy, 5–8 eV c.m. ^c ET, electron transfer; AT(X), X-atom transfer; AE(Y), addition of CH_3^- with elimination of Y; A, addition; NR, no reaction; PT, proton transfer. ^d Reaction of CD_3^- with CH_4 .

precursor ions examined. The final average value for $\Delta H_{\text{acid}}(\text{CH}_4)$ of 417 ± 4 kcal/mol is essentially identical with the accepted literature value of 416.6 ± 0.8 kcal/mol¹³ as well as with the value of 418.5 kcal/mol obtained from recent high-level calculations of gas-phase acidities.³¹

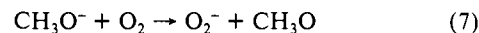
CH_3^- Reactions. The ion/molecule reactions of CH_3^- were examined with a variety of neutral reagents. In certain cases, ions that were predicted as products from CH_3^- reactions were also observed to result from reactive-gas collisional activation of $\text{CH}_3\text{CH}_2\text{CO}_2^-$. Such an observation is indicative of reactions of the parent carboxylate anion, and the contributions to the ion signal from authentic CH_3^- reaction products cannot be identified unambiguously. These reactions do not fulfill the criteria outlined above and, therefore, are omitted from the discussion save for certain pertinent details. The CH_3^- reactions that could be identified positively are summarized in Table II. The reactions observed include electron transfer, proton abstractions, and nucleophilic addition/elimination reactions. We consider it probable that collision-induced electron detachment from CH_3^- is also occurring, but do not have the means to detect this reaction.

The CH_3^- reactions were observed at low conversion, such that the product ion signal rarely exceeded 50% of the remaining CH_3^- signal. Under these conditions, secondary reactions of the initial CH_3^- -derived products are unlikely to be detected due to the relatively short ion residence times in Q2 (≤ 100 μs). The intensity of a CH_3^- reaction product typically attained a maximum value at collision energies of 5–8 eV c.m., above which the product ion intensity would usually decay. This behavior is appropriate for bimolecular ion/molecule reactions that proceed through a capture collision mechanism. At higher reactant ion kinetic energies, the lifetime of the collision complex decreases, and consequently, the probability of reaction decreases.

The efficiency of a given CH_3^- reaction can be estimated from the relative intensities of the product ion and CH_3^- in comparison with the ratio observed for the other reactions in Table II. Of all the CH_3^- reactions observed, electron transfer appears to be the most efficient in terms of both the yield of product ions and the pressure in Q2 at which the product ions could be detected. The proton-transfer reactions that can be ascribed unambiguously to CH_3^- are somewhat less efficient, with lower yields of product ions and higher collision gas pressures required to observe them. This apparent inefficiency results in part from the restrictions

imposed for identifying CH_3^- reaction products; the more acidic substrates that might be expected to react rapidly with CH_3^- are also deprotonated by carboxylate ions at high collision energy. For example, even a relatively weak acid such as D_2O [$\Delta H_{\text{acid}}(\text{D}_2\text{O}) = 392.8$ kcal/mol]³² is deprotonated by $\text{CH}_3\text{CH}_2\text{CO}_2^-$ at elevated energy. Because such a result violates the fourth requirement listed above, only deprotonations involving the weakest acids (e.g., ethylene and methyl chloride) are assigned to CH_3^- .

Oxygen. The O_2 collisional activation [(O_2)-CID] of CH_3CO_2^- is worth discussing in some detail, as it nicely illustrates the experimental method. The acetate anions are generated in the flow tube and mass-selected at Q1. As O_2 is added to the collision chamber and an attractive potential applied, ion/target collisions induce decarboxylation of CH_3CO_2^- , leading to production of CH_3^- . Below O_2 pressures of $\sim 5 \times 10^{-5}$ Torr, only CH_3^- and CH_3CO_2^- can be detailed (neglecting known impurity ions). When the O_2 pressure is increased, O_2^- can also be detected (Figure 2b). The appearance potential of O_2^- at $P_{\text{Q2}}(\text{O}_2) = 1.2 \times 10^{-4}$ Torr is ~ 4.0 eV, which is somewhat higher than the appearance potential of CH_3^- (ca. 2.5 eV at the same pressure) and corresponds to an energy regime in which CH_3^- is relatively abundant. The (O_2)-CID of CD_3CO_2^- results in formation of CD_3^- and, in multiple-collision conditions, O_2^- . In contrast, CID of $\text{CH}_3\text{OCO}_2^-$ (formed by direct addition of CH_3O^- to CO_2 in the flow tube) produces only CH_3O^- at O_2 pressures up to 5×10^{-4} Torr; no O_2^- can be detected. In this case electron transfer (eq 7) is more than



1 eV endothermic [$\text{EA}(\text{O}_2) = 0.440$ eV,³³ $\text{EA}(\text{CH}_3\text{O}) = 1.570$ eV³⁴]. The analogous experiment with $\text{CH}_3\text{CH}_2\text{CO}_2^-$ as the parent ion also does *not* produce measurable signals of fragment ions or of O_2^- . The electron transfer to O_2 from the parent carboxylate ions in all cases is more than 2.5 eV endothermic,³⁵ and the fact that O_2^- is not observed in (O_2)-CID of $\text{CH}_3\text{OCO}_2^-$ or of $\text{CH}_3\text{CH}_2\text{CO}_2^-$ indicates that electron transfer from the carboxylate ion is not an important source of O_2^- .

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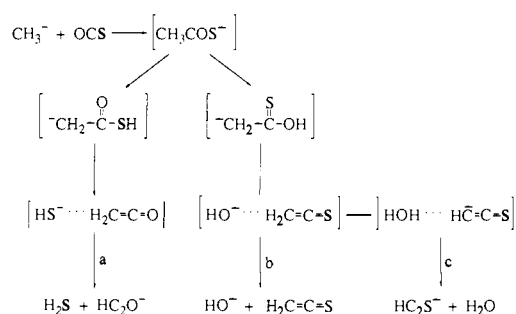
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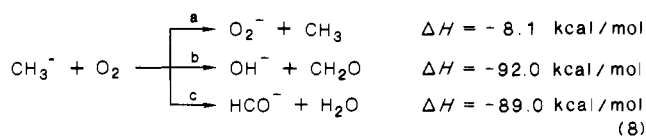
(35) Electron affinities of aliphatic carboxylates are typically greater than 3 eV: Cumming, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1.

(31) Siggel, M. R. F.; Thomas, T. D.; Saethre, L. J. *J. Am. Chem. Soc.* **1988**, *110*, 91.

Scheme I

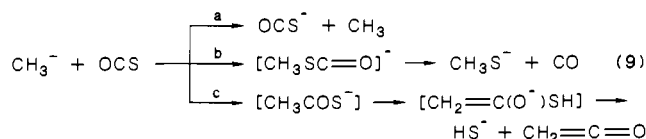


Electron transfer to O_2 occurs for several allylic anions,^{36,37} but competes with oxidative bond insertions and hydride transfers. Benzylic anions react with O_2 by oxidative insertion reactions but not electron transfer.³⁷ Although no free O_2^- is formed in the latter reaction, endothermic electron transfer has been proposed as a preliminary step with the oxidative insertion occurring within the collision complex prior to separation. The oxidation of CH_3^- by O_2 (eq 8b,c) is significantly more exothermic than the simple



electron transfer (eq 8a) that we observe to the exclusion of all other channels. However, the oxidation reactions require extensive rearrangement and could be disfavored due to shorter ion/molecule complex lifetimes under the nonthermal conditions in Q2.

Carbonyl Sulfide. (OCS)-CID of CH_3CO_2^- results in the formation of ions of m/z 15 (CH_3^-), 32, 33, 47, and 64. The signals at m/z 15, 33, and 47 are shifted to m/z 18 (CD_3^-), 34, and 50 in the (OCS)-CID spectrum of CD_3CO_2^- , and the m/z 64 signal cannot be resolved from the intense CD_3CO_2^- parent ion at m/z 62. Generating CH_3^- by (OCS)-CID of $\text{CH}_3\text{CH}_2\text{O}^-$ makes it possible to observe the mass region from m/z 57 to 62; ions are detected with m/z 60, 61, and 64. In contrast, (OCS)-CID of $\text{CH}_3\text{CH}_2\text{CO}_2^-$ does not produce any observable ions between m/z 10 and 70. The ions can be assigned as follows: m/z 32, O_2^- and/or S^- ; m/z 33, HS^- ; m/z 47, CH_3S^- ; m/z 60, OCS^- ; m/z 61 HCOS^- ; m/z 64, S_2^- . Of these ions, OCS^- , CH_3S^- , and HS^- can be identified as products of electron transfer (eq 9a), sulfur-atom transfer (eq 9b),^{7,38-41} and condensation³⁸⁻⁴¹ (eq 9c) reactions of CH_3^- with OCS.



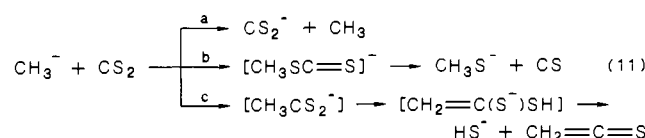
Although DS^- overlaps in mass with CD_3O^- , the latter ion (and consequently, attack at the oxygen terminus of OCS) nevertheless can be ruled out as a reaction product because CH_3O^- (m/z 31) is not observed in the reaction of CH_3^- with OCS. A condensation reaction proceeding via nucleophilic attack at the central carbon of OCS is implicated for the formation of HS^- (eq 9c). Inspection of the condensation reaction intermediates suggests several other potential reaction products (Scheme I), but only HS^- can be observed. This selectivity has been observed previously in reactions

of other anions with OCS ³⁸⁻⁴⁰ and probably arises from a preference for the cleavage that forms the weaker base HS^- [$\Delta H^\circ_{\text{acid}}(\text{H}_2\text{S}) = 352 \text{ kcal/mol}$]⁴² and the unfavorable energetics of proton transfer from $\text{CH}_2=\text{C}=\text{O}$ to HS^- [$\Delta H^\circ_{\text{acid}}(\text{CH}_2=\text{C}=\text{O}) = 365 \text{ kcal/mol}$].⁴³

In these experiments the signal at m/z 32 cannot be assigned with certainty, as it may arise from electron transfer to an O_2 impurity or from dissociation of OCS^- to CO and S^- . The HCOS^- (m/z 61) signal observed in (OCS)-CID of ethoxide maximizes at low collision energies, which is indicative of an exothermic or weakly endothermic reaction. Thus, HCOS^- probably arises from a hydride transfer (eq 10).⁴⁴ The S_2^- ion probably arises from a secondary reaction of S^- with OCS .



Carbon Disulfide. The reaction of CH_3^- with CS_2 produces three ions: one at m/z 76 that constitutes about 95% of the total product ion intensity, and two others at m/z 33 and 47 that together make up the remaining 5% of the product ions. The latter two ions shift to m/z 34 and 50 in the reaction of CD_3^- with CS_2 , reflecting the incorporation into the product ions of one and three deuterium atoms, respectively. The most intense product ion signal corresponds to CS_2^- produced by a bimolecular electron-transfer reaction of CS_2 with CH_3^- (eq 11a). The less intense signals at



m/z 33 and 47 are probably HS^- and CH_3S^- , which are formed by condensation (eq 11c) and sulfur atom transfer (eq 11b). These reactions appear to be significantly slower than electron transfer, on the basis of their lower yields.

These reactions are analogous to those observed for several other simple carbanions^{38,45} and other gas-phase anions such as H_2N^- , HO^- , CH_3O^- , $(\text{CH}_3)_2\text{N}^-$,³⁹ H_2P^- ,⁴⁰ and CH_2^- .⁴⁶ The electron-transfer channel (eq 11a) that is dominant in the methyl anion reaction with CS_2 has been reported only for the reaction of CH_2^- with CS_2 ,⁴⁶ but may also be important for other carbanions such as cyclopropyl anion.⁴⁵ Sulfur atom transfer (eq 11b), a minor channel for the methyl anion, can occur by direct carbanion attack at the sulfur atom and has been reported for the highly basic vinyl,^{38,45} cyclopropyl,⁴⁵ aryl,³⁸ and acetyl anions,⁷ and recently for CH_2^- .⁴⁶ Condensation with CS_2 (eq 11c) occurs for several other anions as well.^{38-40,45} When the neutral product of reactions like 11c contains acidic protons, the condensation reaction can be accompanied by proton transfer to form H_2S ;^{39,40,45} this would result in formation of HC_2S^- in the methyl anion reaction. This product is not observed under our experimental conditions. As in the (OCS)-CID spectrum, both S^- (or O_2^-) and S_2^- can be observed in (CS_2)-CID of CH_3CO_2^- (but not of $\text{CH}_3\text{CH}_2\text{CO}_2^-$).

Hexafluorobenzene. (C_6F_6)-CID of CH_3CO_2^- produces a relatively complex mixture of ions, many of which are attributable to reactions of CH_3CO_2^- with C_6F_6 . Some of the carboxylate reaction product ions can be identified as such on the basis of their pressure and collision energy dependence or by the incorporation of oxygen, but the definitive test was to carry out C_6F_6 collisional activation of $\text{CH}_3\text{CH}_2\text{CO}_2^-$. At low collision energies, the adduct of $\text{CH}_3\text{CH}_2\text{CO}_2^-$ with C_6F_6 is visible at m/z 259, along with the addition/elimination product $\text{C}_6\text{F}_5\text{O}^-$ at m/z 183.⁴⁷ At higher

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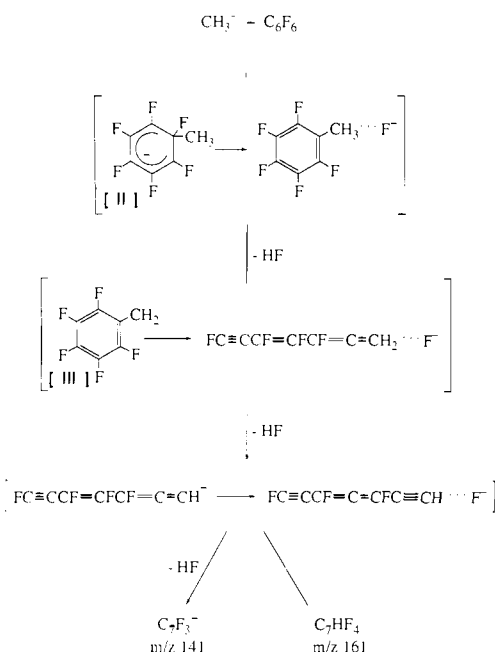
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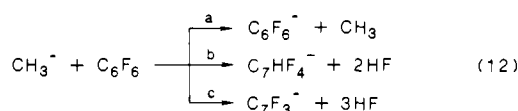
(41) DePuy, C. H.; Bierbaum, V. M. *Tetrahedron Lett.* **1981**, *22*, 5129.

Scheme II



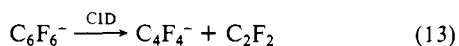
collision energies, additional signals appear at m/z 167 (C_6F_5^-), m/z 155 (C_5F_5^-), and m/z 117 (C_5F_3^-), which may result from fragmentation of the products (adduct and $\text{C}_6\text{F}_5\text{O}^-$) or from endothermic reactions. The fluoride ion F^- is also produced. Each of these ions is also observed in (C_6F_6)-CID of CH_3CO_2^- (adduct at m/z 245) and of CD_3CO_2^- (adduct at m/z 248). Accordingly, these product ions are assigned to carboxylate reactions. However, additional signals can be observed at m/z 186, 161, and 141 in (C_6F_6)-CID of CH_3CO_2^- . The signal at m/z 186 corresponds to C_6F_6^- formed by bimolecular electron transfer from CH_3^- and, like the CS_2 reaction, represents the dominant product ion. The substantially weaker signal at m/z 141 is unshifted in the (C_6F_6)-CID spectrum of CD_3CO_2^- , whereas the (still weaker) m/z 161 signal shifts to m/z 162. These two signals can be assigned to C_7F_3^- and C_7HF_4^- , respectively, arising from addition with elimination of two or three HF molecules.

That electron transfer is observed as the major channel for the reaction of CH_3^- with hexafluorobenzene (eq 12) is consistent with



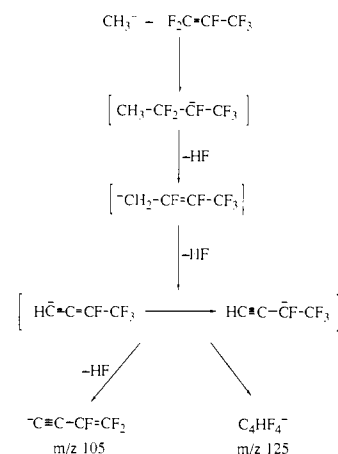
the expected exothermicity of the reaction [$\text{EA}(\text{C}_6\text{F}_6) = 0.52$ eV].⁴⁸ A mechanism for the addition/elimination reaction is proposed in Scheme II. It is probable that HF elimination is accompanied by ring opening in structure III because the alternative unsaturated cyclic structures would be highly strained. The intermediate species II and III are not observed; apparently, the addition reaction is sufficiently energetic that multiple HF loss is rapid.

An ion can also be detected at m/z 124 in (C_6F_6)-CID of both CH_3CO_2^- and CD_3CO_2^- (but not $\text{CH}_3\text{CH}_2\text{CO}_2^-$); this signal is assigned to C_4F_4^- , which probably arises from CID of the primary reaction product C_6F_6^- (eq 13).

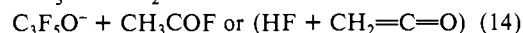


Hexafluoropropylene. ($\text{CF}_3\text{CF}=\text{CF}_2$)-CID of CH_3CO_2^- also results in the production of ions arising from reactions of both CH_3CO_2^- and CH_3^- . The dominant reaction product of the

Scheme III



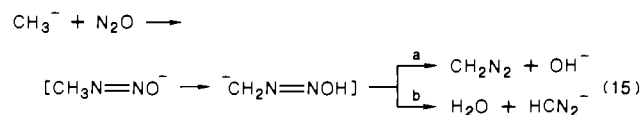
carboxylate ion with C_3F_6 appears at m/z 147 and corresponds to addition with elimination of acetyl fluoride (CH_3COF) or HF and CH_2CO (eq 14).⁴⁹ Fluoride ion, F^- , which is produced in $\text{CH}_3\text{CO}_2^- + \text{CF}_3\text{CF}=\text{CF}_2 \rightarrow$



low yield, can also arise from RCO_2^- . Other carboxylate product ion signals appear at m/z 97 ($\text{C}_2\text{F}_3\text{O}^-$), m/z 81 (C_2F_3^-), and m/z 69 (CF_3^-), but these are far weaker than the $\text{C}_3\text{F}_5\text{O}^-$ signal and probably result from CID of the carboxylate/ C_3F_6 adduct. Additional ion signals appear only in the (C_3F_6)-CID spectrum of CH_3CO_2^- (and of CD_3CO_2^-): one at m/z 105 and a weaker one at m/z 125 (m/z 105 and 126 for CD_3CO_2^-). These ions correspond to C_4F_3^- and C_4HF_4^- , arising from addition with elimination of two or three HF molecules.

Simple electron transfer to form C_3F_6^- is not observed. It is possible that electron transfer nevertheless occurs but that the product C_3F_6^- is not stable⁵⁰ and decomposes to F^- and C_3F_5 . Methyl addition to C_3F_6 is accompanied by HF elimination (Scheme III), and in analogy with the C_6F_6 reaction, the product resulting from loss of three HF molecules is more abundant than that for loss of two HF.

Nitrous Oxide. A number of studies have shown N_2O to be a versatile reagent for probing structures of carbanions.^{45,51-54} The CH_3^- reaction with N_2O proceeds via the characteristic pathway for primary carbanions:⁵⁴ addition with elimination of diazomethane (eq 15a) or water (eq 15b). Addition probably occurs



at the terminal nitrogen,^{55,56} and subsequent intramolecular proton transfer and fragmentation produces diazomethane and hydroxide ion. A second proton transfer can occur within the collision complex to yield HCN_2^- and water. This reactivity is directly analogous to that of other strong bases such as H_2N^- ,³⁹ H^{18}O^- ,⁵⁵ and allyl anion.⁵¹

Sulfur Dioxide. The reaction of CH_3^- with SO_2 produces an addition product CH_3SO_2^- (eq 16), observed at m/z 79 (m/z 82

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(50) We do not observe a stabilized C_3F_6^- radical anion in the flow tube where thermal electron capture and thermal bimolecular electron-transfer reactions are observed with species such as C_6F_6 .

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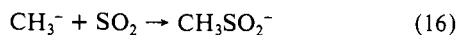
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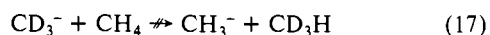
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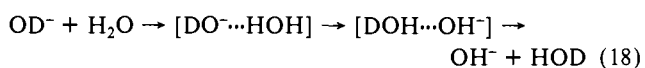


in the CD_3^- reaction). Because the reaction is carried out in a pressure regime in which termolecular stabilization of ion/molecule adducts is relatively inefficient, the lifetime of the unstabilized collision complex must be greater than $\sim 25 \mu\text{s}$. The addition reaction is the only channel that can be assigned to CH_3^- without ambiguity. Although electron transfer from CH_3^- to SO_2 is exothermic and probably occurs [$E_A(\text{SO}_2) = 1.097 \text{ eV}$],^{57,58} SO_2^- is also observed in (SO_2) -CID of $\text{CH}_3\text{CH}_2\text{CO}_2^-$, which indicates that electron transfer can occur from the parent carboxylate ion at high collision energies. The only other ion observed is SO_3^- , which may arise either from a reaction of the carboxylate ion or from secondary reactions of SO_2^- .

Methane. The reactions of CH_3^- with a series of weak acids are shown in entries 9–13 of Table II. The reaction with methane (8) was actually carried out with CD_3^- and CH_4 to enable detection of the potential CH_3^- product ion. However, no CH_3^- could be detected, indicating that the pseudosymmetrical proton transfer (eq 17) does not occur within the time scale of our experiment.

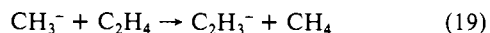


This negative result can be contrasted with the facile proton transfer observed for the $\text{OD}^-/\text{H}_2\text{O}$ system (eq 18), in which the

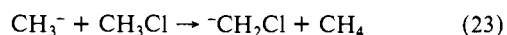
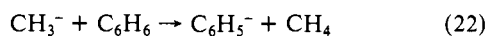
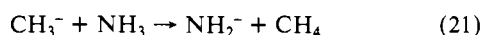


measured reaction rate constant reflects a proton transfer occurring on approximately three out of four ion/molecule encounters.⁵⁹ The origin of the difference in kinetics for the near-thermoneutral proton-transfer reactions between the hydroxide/water and methide/methane systems probably lies in the relative strengths of the intermolecular hydrogen bond formed in the intermediate collision complex.⁶⁰ Because carbon is much less electronegative than oxygen, the methide/methane interaction is much weaker than is the hydroxide/water interaction.⁶¹ As a result, the equilibrium carbon-carbon separation is relatively large in the association complex $[\text{H}_3\text{CH} \cdots \text{CH}_3^-]$, the proton has a large distance to traverse, and it encounters a substantial barrier. A recent calculation⁶² of the proton-transfer rate within the methide/methane complex yielded a value of $k_H(300) = 700 \text{ s}^{-1}$. A unimolecular reaction rate within the collision complex of this magnitude would render the overall bimolecular exchange reaction unobservable in our instrument.⁶³

Ethylene, Butadiene, Ammonia, Benzene, and Methyl Chloride. Proton transfer from ethylene [$\Delta H_{\text{acid}}(\text{C}_2\text{H}_4) = 406 \text{ kcal/mol}$]⁸ to CH_3^- does occur, albeit very slowly, to produce C_2H_3^- (eq 19).



Methyl anion also deprotonates 1,3-butadiene (eq 20), ammonia



(eq 21), benzene [eq 22; $\Delta H_{\text{acid}}(\text{C}_6\text{H}_6) = 400.7 \text{ kcal/mol}$],⁶⁴ and

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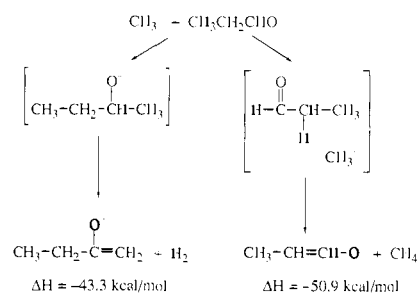
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(63) Assuming a lifetime for the $[\text{CH}_3^- \cdots \text{CH}_4]$ collision complex of less than 10^{-9} s , a barrier-crossing frequency of 700 s^{-1} at 300 K ⁶² corresponds to an effective bimolecular reaction rate coefficient of only $10^{-15} \text{ cm}^3/\text{molecule-s}$ at thermal energies. Although the barrier-crossing frequency increases slowly with energy,⁶² the frequency for back-dissociation to reactants also increases and apparently remains dominant under our experimental conditions.

Scheme IV

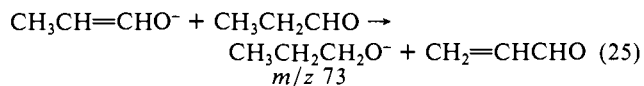
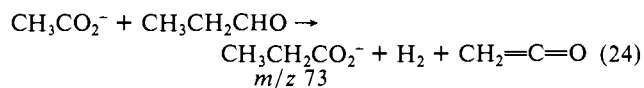


methyl chloride (eq 23; $\Delta H_{\text{acid}}(\text{CH}_3\text{Cl}) = 396 \text{ kcal/mol}$).⁶⁵ In (CH_3Cl) -CID of CH_3CO_2^- , Cl^- is also observed. However, because Cl^- appears in (CH_3Cl) -CID of $\text{CH}_3\text{CH}_2\text{CO}_2^-$ as well, it is not identified as a unique CH_3^- reaction product.

The methyl anion reactions with ammonia and water were carried out with deuterium-labeled reactants to probe for isotope exchange. Although deprotonation of the target gas occurs in both cases, the potential isotope-exchange products NHD^- (from $\text{CD}_3^- + \text{NH}_3$), OH^- (from $\text{CH}_3^- + \text{D}_2\text{O}$), or partially labeled methyl anions cannot be detected. In these systems, several factors can combine to disfavor isotope exchange. Not only would shorter lifetimes be expected for the energy-rich collision complexes that form in Q2, but the exothermicity of the initial proton transfer from ammonia or water to CH_3^- can further shorten the lifetime by releasing still more energy. Moreover, the binding energy in the resulting complexes, $[\text{NH}_2^- \cdots \text{CHD}_3]$ or $[\text{OD}^- \cdots \text{CH}_3\text{D}]$, will be quite weak, resulting only from ion-induced dipole forces. Finally, it is possible that rapid secondary self-exchange reactions may wash out any NHD^- or OH^- that is formed. Because D_2O is deprotonated by $\text{CH}_3\text{CH}_2\text{CO}_2^-$ at high collision energies to produce OD^- , the methyl anion reaction with D_2O is not included in Table II.

Propionaldehyde and Acrolein. The final two entries in Table II describe nucleophilic addition/elimination reactions of the methyl anion to substrates with acidic hydrogens [$\Delta H_{\text{acid}}^\circ(\text{CH}_3\text{CH}_2\text{CHO}) = 365.3 \text{ kcal/mol}$;⁶⁶ $\Delta H_{\text{acid}}^\circ(\text{CH}_2=\text{CHCHO}) \approx 365 \text{ kcal/mol}$ (estimated)].

Collisional activation of CH_3CO_2^- with propionaldehyde ($\text{CH}_3\text{CH}_2\text{CHO}$) results in the formation of several low-abundance ions, including the carboxylate adduct ion CH_3CO_2^- ($\text{CH}_3\text{CH}_2\text{CHO}$) (m/z 117), an aldehyde dimer ion $\text{CH}_3\text{CH}=\text{CHO}^-$ ($\text{CH}_3\text{CH}_2\text{CHO}$) (m/z 115), and its dehydration product at m/z 97. A signal observed at m/z 71 in the CID spectrum of CH_3CO_2^- shifts to m/z 74 (and possibly 73) in the CID spectrum of CD_3CO_2^- . This signal is assigned to the butanone enolate anion, which can arise from a CH_3^- -addition/ H_2 -elimination reaction (Scheme IV). A weak signal appears at m/z 73 for both CH_3CO_2^- and CD_3CO_2^- . With CD_3CO_2^- , a strong signal is also observed at m/z 57, which is obscured in CID of CH_3CO_2^- by the intense parent ion signal at m/z 59. The m/z 57 signal arises from the propionaldehyde enolate anion $\text{CH}_3\text{CH}=\text{CHO}^-$ and appears also for CID of $\text{CH}_3\text{CH}_2\text{CO}_2^-$, which indicates deprotonation by the carboxylate ion. Two processes may lead to formation of the m/z 73 ion in the CH_3CO_2^- CID spectrum: an inefficient addition/elimination reaction involving the parent ion (eq 24) or a secondary reaction, namely, hydride transfer, of the

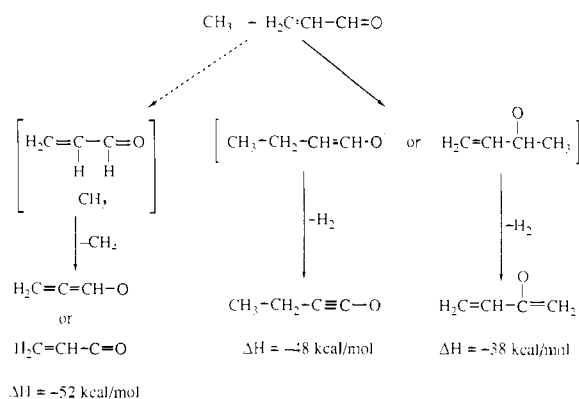


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Scheme V



propionaldehyde enolate anion (eq 25). Although the methyl anion undoubtedly participates in a proton-transfer reaction with propionaldehyde, only the butanone enolate anion is identified as a CH_3^- reaction product because the carboxylate ion also deprotonates propionaldehyde.

Acrolein, $\text{CH}_2=\text{CHCHO}$, reacts with CH_3^- and CH_3CO_2^- in a similar manner as does $\text{CH}_3\text{CH}_2\text{CHO}$. The carboxylate adduct $\text{CH}_3\text{CO}_2^- (\text{CH}_2=\text{CHCHO})$ and acrolein dimer $\text{CH}_2=\text{C}=\text{CHO}^- (\text{CH}_2=\text{CHCHO})$ are observed at m/z 115 and 111. Both dehydration and loss of ethylene (or CO) from the acrolein dimer ion are observed, producing weak signals at m/z 93 and 83. A product ion appearing at m/z 69 (m/z 71 for CD_3CO_2^-) is assigned to the addition/elimination reaction shown in Scheme V. A weak signal is detected at m/z 55 corresponding to deprotonated acrolein. In contrast to the case of $(\text{CH}_3\text{CH}_2\text{CHO})\text{-CID}$, low-mass fragments can be observed at m/z 27 (C_2H_3^-) and 43 ($\text{CH}_2=\text{CHO}^-$), which also appear in the CID spectrum of $\text{CH}_3\text{CH}_2\text{CO}_2^-$ and thus can be identified as reaction products of the carboxylate ion. Only the addition/elimination product observed at m/z 69 can be assigned unambiguously to a product of a CH_3^- reaction, although deprotonation is also a viable channel.⁶⁷

The observation of the addition/elimination channel is especially interesting. Kinetic studies of displacement reactions at carbonyl centers⁶⁸ suggest a double minimum potential energy profile, with the conventional tetrahedral adduct at the saddle point (or a local

(67) The aldehydic protons are also acidic enough to be abstracted by CH_3^- ; see ref 7.

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shallow minimum⁶⁹) and the minimum energy structures corresponding to hydrogen-bonded ion/molecule complexes. Thermal energy reactions that take place on such surfaces typically proceed with low efficiencies⁷⁰ (i.e., with rate constants significantly lower than the collision rate). In contrast, exothermic proton-transfer reactions are often quite rapid, with rate constants equal to or near the collision-limited values.⁷¹⁻⁷⁵ Nevertheless, our results demonstrate that nucleophilic addition of CH_3^- to both acrolein and propionaldehyde competes effectively with proton abstraction.

Conclusions

This study introduces a useful method for investigating the chemistry of anions that are otherwise difficult to prepare under conditions amenable to studies of ion/molecule reactions. The methyl anion can be generated by CID of CH_3CO_2^- , $\text{CH}_3\text{CH}_2\text{O}^-$, and other precursor ions, and when reactive neutral reagents are present in the collision chamber, ion/molecule reactions of CH_3^- can be observed. We have described an experimental protocol for identifying the gas-phase reactions of CH_3^- and distinguishing them from reactions of the kinetically excited precursor ions. The observed reactions of CH_3^- with various substrates are found to be consistent with its high basicity and nucleophilicity and its low electron-binding energy.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE-8502515). R.R.S. thanks the Alfred P. Sloan Foundation for a fellowship and S.T.G. is grateful to Rohm and Haas for a graduate fellowship administered by the Organic Division of the American Chemical Society.

Registry No. CH_3^- , 15194-58-8; CH_3CO_2^- , 71-50-1; $\text{CH}_3\text{CH}_2\text{O}^-$, 16331-64-9; $(\text{CH}_3)_2\text{CHO}^-$, 15520-32-8; $(\text{CH}_3)_3\text{CO}^-$, 16331-65-0; O_2 , 7782-44-7; OCS , 463-58-1; CS_2 , 75-15-0; C_6F_6 , 392-56-3; $\text{CF}_3\text{CF}=\text{CF}_2$, 116-15-4; N_2O , 10024-97-2; SO_2 , 7446-09-5; CH_4 , 74-82-8; $\text{CH}_2=\text{CH}_2$, 74-85-1; C_4H_6 (1,3-butadiene), 106-99-0; C_6H_6 , 71-43-2; NH_3 , 7664-41-7; CH_3Cl , 74-87-3; $\text{CH}_3\text{CH}_2\text{CHO}$, 123-38-6; $\text{CH}_2=\text{CH}-\text{CHO}$, 107-02-8.

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