

Films). These substrates were thoroughly cleaned by soxhlet extraction with *n*-hexane for several hours, followed by argon plasma cleaning for 15 min (Harrick PDC-3XG Plasma Cleaner). Optical parameters of the bare substrate were measured within 15 min after cleaning. IR spectrum of the bare substrate was used as reference and was measured within 1 h after cleaning.

**Pressure-area isotherms and deposition experiments** were performed on a computer-controlled Lauda film balance, placed in a laminar flow hood, and thermostated to 20 °C. Dipping and withdrawal rate of substrates was 1 cm/min, with a drying time of 5 min after each cycle. Samples of 0.1–0.7 mL of  $10^{-4}$ – $10^{-3}$  M solutions of the amphiphiles in chloroform/trifluoroacetic acid (95/5) or in chloroform/methanol (85/15) were used as spreading solutions. Double-distilled water (Corning Mega-Pure System MP-6A) was used as subphase for all experiments. Compressed monolayer films were stabilized for 1/2 h at constant pressure of 20 mN/m before depositions were initiated.

**Contact Angles** were measured by the sessile drop method, with a Rame-Hart contact angle goniometer. Contact angles were measured 1/2 h after film deposition and were remeasured after 24 h. Static advancing contact angles were measured by applying a drop on the surface with a micrometer syringe, and receding contact angles were measured by reducing the volume of the drop until the periphery of the drop retreated. Readings were taken approximately 30 s after the drop was applied at three different positions along the substrate, and the precision is  $\pm 2^\circ$ .

**Second-harmonic generation (SHG)** tests were performed by a weakly focused Q-switched Nd:YAG laser with the following characteristics: wavelength ( $\lambda = 2\pi c/\omega$ ) 1.06  $\mu\text{m}$ , pulse width  $\approx 8$  ns, pulse energy  $< 40$  mJ, beam size at the sample  $\approx 2.4$  mm (diameter). The second-harmonic radiation at 532 nm was detected in the 45° transmission geometry

through a high-f-number, spectrally filtered, high-efficiency collection system. This system provides substantial discrimination against incoherent emission and scattered radiation. Polarization control devices are located in the laser and detection branches. The samples are mounted on rotation/translation stages, which allow us to test the anisotropy of the samples' SHG properties. SHG intensities are measured relative to the SHG of quartz.

**IR-RA** measurements were taken with a FT-IR Nicolet-MX-1 spectrophotometer with a Harrick ATR attachment set at 75° incidence and Harrick Brewster angle Ge polarizer. Details of the optical set up used are described in ref 21b.

**Ellipsometric measurements** were performed on a Rudolph Research AutoEL-IV ellipsometer. The Auto-EL-IV is a microcomputer-controlled automatic-nulling ellipsometer. From the measured azimuths of polarizer and analyzer, the instrument computes two intermediate parameters,  $\Delta$  and  $\psi$ , which are then used to calculate the optical constants of bare surfaces and the thickness of transparent films on these surfaces. Measurements were performed at 633 nm with a tungsten-halogen lamp; the angle of incidence was 70°, and the refractive index used for the calculations was 1.45. The average value of at least three measurements, taken at different points along the substrate, was used for the calculations.

**Low-angle X-ray diffraction** was performed on a Rigaku powder diffractometer with a thin film attachment, with Cu K $\alpha$  radiation ( $\lambda = 1.54$  Å).

**Acknowledgment.** We thank Dr. J. van Mil for performing the X-ray measurements, Drs. E. Landau and G. Berkovic for discussions, and Yeda preindustrial funds for financial support. K.H. thanks the Max-Planck-Gesellschaft for a Minerva fellowship.

## Generation of Alkyl Carbanions in the Gas Phase

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**Abstract:** The scope and limitations of collision-induced decarboxylation of carboxylate negative ions as a method for generating gas-phase carbanions are described. Simple alkyl carbanions can be observed as fragments from a variety of aliphatic carboxylates, provided only that the carbanion has a lifetime toward electron detachment greater than  $\sim 25$   $\mu\text{s}$ . Several heretofore unknown alkyl carbanions have been observed, including the neopentyl anion, the 2- and 3-methylbutyl anions, cyclopropylmethyl anion, and cyclohexylmethyl anion, as well as cyclic and polycyclic carbanions such as the 1- and 2-methylcyclopropyl anions and the 1-bicyclopentyl anion. An empirical correlation between the electron affinities of primary alkyl radicals (RCH<sub>2</sub>) and the analogous alkoxy radicals (RO) is described that correctly predicts the stability and detectability of the corresponding primary carbanion fragments (RCH<sub>2</sub><sup>-</sup>) from collision-induced decarboxylation. A number of  $\alpha$ -substituted methyl anions and  $\beta$ -substituted ethyl anions have been formed by this method; both familiar and novel examples of these types of carbanions are described. The competing higher energy fragmentations and low-energy reactions of collisionally activated carboxylate ions are also discussed, including  $\beta$ -radical cleavages, remote-site fragmentations, and intramolecular isomerizations that occur prior to dissociation.

Carbanions play a central role in organic and organometallic chemistry because of their widespread synthetic utility in carbon-carbon and carbon-metal bond formation reactions.<sup>1-5</sup> For synthetic chemists, the isolated carbanion serves as a convenient "synthon", or idealized fragment, that assists in the design of synthetic procedures and permits description of reaction mechanisms in straightforward terms.<sup>6,7</sup> However, it is widely recognized that in solution the actual reactive anionic species are not free carbanions, but are closely associated with and stabilized by counterions and solvent molecules, and further may exist as aggregates.<sup>1-6,8,9</sup> Accordingly, a detailed understanding of the intrinsic properties and reactivities of isolated carbanions, along with the changes that accompany ion pairing, solvation, and aggregation, is an important goal of carbanion research.

Studies of the chemistry and properties of carbanions in the gas phase provide the means to probe the intrinsic reactivity of

these species and reveal the often dominating influence of the reaction medium on carbanion chemistry in solution. Although a great deal of information has been amassed from experimental studies for a wide variety of organic ions in the gas phase, as yet

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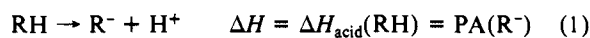
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very little is known about simple alkyl and cycloalkyl anions (i.e., conjugate bases of alkanes and cycloalkanes). Investigations of alkyl anions are impeded by the difficulties encountered in generating them in quantities sufficient to probe their reactivity (or even to detect). The standard methods that have been developed for the generation of gas-phase carbanions include dissociative electron attachment and chemical ionization approaches involving ion-molecule reactions such as deprotonation, substitution, and elimination.<sup>10,11</sup> Although the methyl anion can be observed as a minor constituent of the mixture of fragment ions formed by dissociative electron attachment to certain organic compounds,<sup>12</sup> neither this approach nor chemical ionization appears to be useful for the practical generation of larger alkyl anions. Alkanes are among the weakest organic acids known<sup>13</sup> and, with one recently reported exception,<sup>14</sup> none of the alkanes or cycloalkanes react with the usual deprotonating reagents (e.g.,  $\text{NH}_2^-$  and  $\text{OH}^-$ ) to produce alkyl anions by thermal energy proton transfers in the gas phase.<sup>15</sup>

In spite of the lack of experimental data on alkyl anions, theoretical investigations have allowed predictions to be made regarding their properties, structures, and stabilities.<sup>16-23</sup> A property often calculated because of its fundamental importance in carbanion chemistry is the proton affinity of the anion  $\text{PA}(\text{R}^-)$ , or, equivalently, the gas-phase acidity of the conjugate acid,  $\Delta H_{\text{acid}}(\text{RH})$  (eq 1). From the acidity  $\Delta H_{\text{acid}}(\text{RH})$ , the bond



dissociation energy  $D[\text{R}-\text{H}]$ , and the ionization potential of the hydrogen atom  $\text{IP}(\text{H})$ , the electron affinity (EA) of the radical R can be derived (eq 2). For the question of thermodynamic

$$\Delta H_{\text{acid}}(\text{RH}) = D[\text{R}-\text{H}] - \text{EA}(\text{R}) + \text{IP}(\text{H}) \quad (2)$$

stability of alkyl anions, the electron affinity of the corresponding radical is a critical parameter. When the electron affinity is negative, the anion is unstable with respect to the radical and a free electron and, in the absence of a kinetic barrier to electron detachment, would not be expected to exist as a long-lived isolated species. Bond dissociation energies are known for many alkanes; therefore, by calculating the acidity of an alkane, it is possible to predict whether the anion will be bound [i.e., whether  $\text{EA}(\text{R}) > 0$ ].

However, ab initio structure and energy calculations for anions do present some practical problems. The use of diffuse functions and an extended basis set with treatments for electron correlation becomes essential to describe adequately the binding of the extra electron.<sup>16</sup> When diffuse functions are omitted, even calculations using large basis sets can yield acidities that are as much as 40 kcal/mol higher than experimental values.<sup>16,17</sup> With the inclusion of diffuse functions, calculations using a large basis set with electron correlation can yield gas-phase acidities that are in close

agreement with experimental values.<sup>17-23</sup> For weakly bound anions, uncertainties and systematic errors associated with experimental or theoretical values of  $\Delta H_{\text{acid}}(\text{RH})$  and  $D[\text{R}-\text{H}]$  may well exceed the absolute value of  $\text{EA}(\text{R})$ , thus leaving open the question of whether  $\text{R}^-$  is bound. For example, if the values of  $\Delta H_{\text{acid}}(\text{CH}_4)$  derived from calculations at various high levels of theory are substituted into eq 2 with the known  $D[\text{CH}_3-\text{H}]$  of 104.8 kcal/mol,<sup>24</sup> negative values for  $\text{EA}(\text{CH}_3)$  result.<sup>18,19,21,23</sup> Only certain combinations of large basis sets and electron correlation treatments manage to achieve (perhaps fortuitously) a positive value for  $\text{EA}(\text{CH}_3)$ .<sup>20,25</sup> The methyl anion is known to exist as a stable anion bound by 1.8 kcal/mol,<sup>26</sup> but electron affinities for larger alkyl radicals have not been measured.

In spite of the difficulty of calculating accurate absolute values of acidity, calculated acidities at intermediate levels of theory show a good linear relationship with experimental values, even though the slope of the line typically exceeds unity.<sup>23</sup> Thus, it is feasible to predict relative acidities for alkanes and, hence, to estimate electron affinities for alkyl radicals. It is noteworthy that most ab initio calculations predict that in the gas phase ethane is a weaker acid than methane by 5-10 kcal/mol.<sup>18,22,23</sup> Results of calculations further suggest that ethyl, isopropyl, and *n*-propyl anions are unbound with respect to electron detachment.<sup>18,23,27</sup> Indeed, Schleyer and co-workers examined computationally a number of larger alkyl anion species and concluded that simple alkyl anions other than methyl and cyclopropyl anions are unbound and therefore should not be observable as long-lived species in the gas phase.<sup>28</sup>

In a recent report, DePuy and co-workers described a new experimental technique that yields estimates of gas-phase acidities for alkanes.<sup>29</sup> Their experimental results suggest that ethane and the secondary hydrogens in propane are less acidic than methane, whereas the tertiary hydrogen of isobutane is slightly more acidic than methane. From comparison of the predicted acidities with known bond dissociation energies, the resultant anions (ethyl, isopropyl, and *tert*-butyl) are predicted to be unbound, in accord with theoretical predictions of Schleyer et al.<sup>28</sup>

We have chosen to approach the question of stability of alkyl anions from a somewhat different experimental vantage point, wherefrom we systematically attempt to produce and detect directly isolated alkyl anions formed in the gas phase by means of activated unimolecular decomposition of appropriate precursors. Our method is conceptually akin to well-established techniques for production of reactive organic species by photolysis or pyrolysis.<sup>30-32</sup> These methods utilize a relatively stable precursor molecule that incorporates the desired reactive species masked by a functionality that is liberated as a stable molecule upon activation. Similar methods have been utilized in gas-phase ion experiments: for example, for the production of vinyl anions by base-induced elimination of  $\text{N}_2$  from substituted diazirines,<sup>33</sup> for the generation of silylenes and silaethylenes,<sup>34</sup> the keto tautomers of phenol,<sup>35</sup> nitrene and carbene radical ions,<sup>36</sup> and distonic ions.<sup>37,38</sup>

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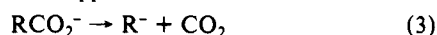
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To produce alkyl anions for the present study, we employ the technique of collision-induced decarboxylation of alkanolate ions  $\text{RCO}_2^-$  (eq 3).<sup>39,40</sup> This approach was used in an earlier ion

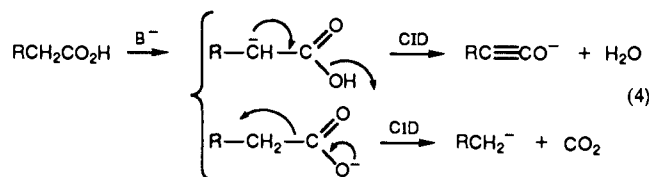


cyclotron resonance (ICR) study of  $\text{C}_3\text{H}_5^-$  ions.<sup>39</sup> These experiments demonstrated that decarboxylation produces isomeric  $\text{C}_3\text{H}_5^-$  ions from isomeric carboxylate precursors in a regioselective manner. We have now applied the decarboxylation method in a flowing afterglow-triple quadrupole instrument and have examined the dissociation products from more than 50 variously substituted carboxylate ions, including many alkyl and cycloalkyl carboxylates. A preliminary report of our investigations has appeared,<sup>40</sup> and herein we report in detail the results of a wider survey of the decarboxylation technique as applied to probing the stability of alkyl anions.

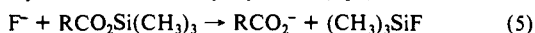
### Experimental Section

The decarboxylation experiments were carried out in a flowing afterglow instrument equipped with a triple quadrupole mass analyzer.<sup>41</sup> The apparatus consists of a 1-m-long, 7-cm-diameter stainless steel flow reactor, in which negative ions are generated by dissociative electron attachment and ion-molecule reactions. The ions are entrained in a constant flow of helium buffer gas (0.30–0.40 Torr, 130–190 STP  $\text{cm}^3/\text{s}$ ), which serves to transport them from the upstream source region to the 1-mm-diameter orifice leading to the analyzer chamber. As the ions are borne down the flow tube, they achieve thermal equilibrium through many thousands of nonreactive collisions with the buffer and reagent gases. The negative ions sampled from the plasma are focused into the triple quadrupole analyzer with electrostatic lenses located behind the sampling orifice. The first (Q1) and third (Q3) quadrupoles are ion mass filter elements, which are typically tuned to provide base-line resolution of adjacent ( $\pm 1$  amu) ion signals, and the second quadrupole (Q2) is a gas-tight "rf-only" unit that serves as a focusing collision cell for collision-induced dissociation (CID) experiments. The collision gas pressure in Q2 may be varied from  $\sim 2 \times 10^{-6}$  Torr, which represents the background pressure in the analyzer chamber, to  $\sim 5 \times 10^{-4}$  Torr and is measured with an MKS Baratron capacitance manometer. The axial kinetic energy of ions entering Q2 is defined in the laboratory frame of reference by the quadrupole rod offset voltage and may be varied over a range of  $\sim 0.3$ –200 V.

The method used for production of the carbanions ( $\text{R}^-$ ) of interest for the present study was decarboxylation by collisional activation of the conjugate base  $\text{RCO}_2^-$  of the appropriate carboxylic acid  $\text{RCO}_2\text{H}$  (eq 3). Several methods can be used to produce  $\text{RCO}_2^-$  ions in the flow tube. For example, dissociative electron attachment to the acid or its anhydride can be used to produce  $\text{RCO}_2^-$ . However, most of the carboxylic acids used for this study are not volatile enough for this approach to be useful under flowing afterglow conditions. Deprotonation of the free acids by  $\text{NH}_2^-$  or  $\text{OH}^-$  was avoided, in part because of their limited volatility, but also because we<sup>42</sup> and others<sup>43,44</sup> have observed that this can cause deprotonation at the carbon  $\alpha$  to the carboxyl group, leading to formation of the enolate tautomer, which can yield different fragments upon CID (eq 4).<sup>42</sup> The method used to prepare most of the carboxylates for this study

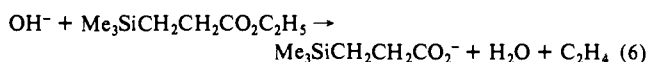


was fluorodesilylation of the trimethylsilyl esters (eq 5). The esters were



produced by mixing the free acids with a silylating agent [bis(trimethylsilyl)acetamide], and without further purification, the mixture was

admitted to the flow tube. The fluoride ion was generated by dissociative electron attachment to  $\text{SF}_6$  or  $\text{CF}_4$ . The method used for the preparation of  $\beta$ -(trimethylsilyl)propionate ion was base-induced elimination of ethylene from the ethyl ester (eq 6).



The  $\text{RCO}_2^-$  ions were mass-selected and activated by collisions with argon. For survey work, CID spectra were collected at collision energies varying from 0 to 70 eV in the laboratory frame of reference. To search for the carbanion produced by decarboxylation, the triple quadrupole was operated in single-ion detection mode and the activation conditions (collision energy and gas pressure) were varied to optimize the carbanion yield. To compensate for the low yields of some of the CID products, signal averaging of the mass spectra was employed.

**Materials.** Helium and argon gas were obtained from Air Reduction Co. at 99.995% purity, and  $\text{N}_2\text{O}$  was purchased from Matheson at 99.0% purity. Other reagents were obtained from commercial suppliers and used without further purification. All liquids were subjected to freeze-pump-thaw cycles when connected to the flow tube in order to remove dissolved gases.

The 3,3-dimethyl-4-pentenoic acid was synthesized by the Claisen rearrangement method of Dauben and Dietsche,<sup>45</sup> with 3-methyl-2-buten-1-ol and triethyl orthoacetate as the starting materials.

### Results and Discussion

Carboxylate ions  $\text{RCO}_2^-$  from more than 50 organic acids have been prepared in the flow tube by fluorodesilylation of the trimethylsilyl esters  $\text{RCO}_2\text{Si}(\text{CH}_3)_3$  and other methods. Each ion has been subjected to collisional activation in the triple quadrupole analyzer under a range of conditions of target gas pressure and collision energy. In Table I, we provide a summary listing of the carboxylate ions examined for the present study, along with a presentation of the CID results in terms of the observation or nonobservation of the corresponding carbanion fragments. Of the carboxylate ions examined, in all cases where decarboxylation of  $\text{RCO}_2^-$  would produce a carbanion fragment that has been generated previously by other means or is expected to be stable based on reliable theoretical studies, we have successfully produced  $\text{R}^-$  by CID. In most cases, decarboxylation appears to be the lowest energy fragmentation and is the major or exclusive process observed at collision energies up to  $\sim 5$  eV in the center of mass frame of reference. On the basis of the survey results, we expect that decarboxylation should be a universal fragmentation pathway for all carboxylate ions activated by low-energy collisions.

Several of the  $\text{RCO}_2^-$  species shown in Table I do not yield detectable quantities of carbanions arising from loss of  $\text{CO}_2$ . These species moreover do not yield significant quantities of ionic products from competing fragmentation processes. The most probable explanation for the absence of decarboxylation product ions is electron detachment from the incipient, unbound carbanion—perhaps even before it is completely free of the dissociating ionic complex. Whether decarboxylation and electron detachment occur simultaneously or in a stepwise fashion depends of unknown features of the relevant potential energy surfaces. However, it can be argued that electron detachment will most likely occur from the dissociating species when it begins to resemble structurally the R and  $\text{CO}_2$  products, both of which have negative electron affinities. At this point the system can cross to the repulsive (electron + R +  $\text{CO}_2$ ) surface. It is unlikely that electron detachment from the carboxylate ion is responsible for the absence of  $\text{R}^-$  for the following reasons. Electron affinities of  $\text{RCO}_2^-$ , where R is a simple alkyl group, are greater than 3 eV.<sup>46</sup> In contrast, for R =  $\text{C}_2\text{H}_5$  for example, the predicted enthalpy for dissociation of  $\text{RCO}_2^-$  to  $\text{R}^-$  and  $\text{CO}_2$  is  $\sim 2.9$  eV and for dissociation to R,  $\text{CO}_2$ , and an electron is only 2.6 eV. Moreover, there is some evidence that vibration-induced electron detachment from anions bound by 1 eV or more is relatively slow even in comparison to fragmentation processes of higher activation energies.<sup>47</sup> Thus,

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











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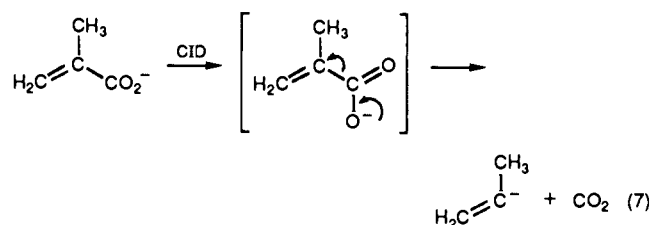
Table I. Selected Results of the Decarboxylation Survey<sup>a</sup>

		Alkanecarboxylates			
1	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	+	9	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+
2	CD <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	+	10	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+
3	CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	-	11	(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+
4	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	-	12	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	-
5	(CH <sub>3</sub> ) <sub>2</sub> CHCO <sub>2</sub> <sup>-</sup>	-	13	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	-
6	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	-	14	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>2</sub> CH <sub>3</sub> )CO <sub>2</sub> <sup>-</sup>	-
7	(CH <sub>3</sub> ) <sub>3</sub> CCO <sub>2</sub> <sup>-</sup>	-	15	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CO <sub>2</sub> <sup>-</sup>	-
8	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CO <sub>2</sub> <sup>-</sup>	-			
		Cycloalkanecarboxylates			
16		+	22		-
17		+	23		-
18		+	24		+
19		-	25		+
20		+	26		-
21		+			
		Unsaturated Carboxylates			
27	C <sub>2</sub> H <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	+	31	CH <sub>3</sub> CH <sub>2</sub> CH=CHCO <sub>2</sub> <sup>-</sup>	+
28	CH <sub>2</sub> =CHCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+	32	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+
29	CH <sub>3</sub> CH=CHCO <sub>2</sub> <sup>-</sup>	+	33	(CH <sub>3</sub> ) <sub>2</sub> C=CHCO <sub>2</sub> <sup>-</sup>	+
30	CH <sub>2</sub> =C(CH <sub>3</sub> )CO <sub>2</sub> <sup>-</sup>	+	34		+
		Substituted Propionates			
35	CH <sub>3</sub> CHClCO <sub>2</sub> <sup>-</sup>	+	40	CF <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CO <sub>2</sub> <sup>-</sup>	+
36	CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+	41	CF <sub>3</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+
37	HC≡CCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+	42	(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	- <sup>b</sup>
38	CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+	43	CH <sub>2</sub> =CHC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+
39	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+	44	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+
		Substituted Acetates			
45	BrCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+	49	NCCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+
46	ClCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+	50	CH <sub>3</sub> OCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	-
47	FCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+	51	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+
48	ICH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	+			

<sup>a</sup> + indicates that a product ion is observed from decarboxylation; - means that no decarboxylation product is observed. <sup>b</sup> A product ion is observed corresponding to loss of 44 amu, but is probably vinyl dimethyl siloxide from loss of CH<sub>4</sub> and CO; see text.

we expect that species such as C<sub>2</sub>H<sub>3</sub>CO<sub>2</sub><sup>-</sup> (3) that do not yield carbanions from loss of CO<sub>2</sub> nevertheless undergo decarboxylation, accompanied by rapid electron detachment.

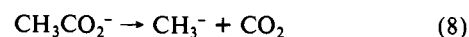
Identification of the product ions from decarboxylation requires that the mass to charge ratio (*m/z*) of the CID product ions reflects the loss of 44 amu. Preliminary structural assignment is based on the assumption that the fragmentation corresponds to a simple heterolytic bond cleavage, which produces CO<sub>2</sub> plus a carbanion that has the skeletal structure of the precursor carboxylate side chain and its anionic center at the carbon that originally had been bound to CO<sub>2</sub> (e.g., eq 7). The validity of



the structural assignment can be tested by examining the CID spectrum for evidence of alternative pathways also corresponding

to loss of 44 amu (e.g., loss of CH<sub>4</sub> and CO, of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>, of C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub>O, etc.), by examining the reactivity of the product carbanions with neutral reagents such as N<sub>2</sub>O,<sup>39,42</sup> and/or by measuring the appearance energy of the carbanion product.<sup>48</sup> The latter two probe methods require that the CID product be formed in high enough abundance that the signal-to-noise ratio is 100 or greater, but this was not the case for many of the alkyl carbanions discussed herein. Even so, rough estimates ( $\pm 1$  eV center of mass) of the appearance energies can be made and the collision energy dependence of the carbanion product yields examined.

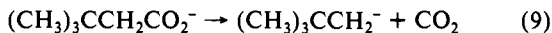
**Decarboxylation of Alkyl and Cycloalkyl Carboxylates: Primary Carbanions.** We have carried out decarboxylation studies for a number of acyclic and cyclic alkyl carboxylate ions (Table I). A significant finding for the present study is that decarboxylation of acetate ion yields the methyl anion CH<sub>3</sub><sup>-</sup> (eq 8).<sup>40,42</sup> The



formation of this weakly bound anion [EA(CH<sub>3</sub>) = 1.8  $\pm$  0.7 kcal/mol]<sup>26</sup> suggests that the decarboxylation method can be used

(48) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.*, following article in this issue.

to produce virtually any carbanion, provided that its electron binding energy exceeds  $\sim 2$  kcal/mol. The observation of a carbanion produced by CID in the triple quadrupole permits us to assign a lower limit of 25  $\mu$ s to the lifetime  $\tau$  of the anion, based on the estimated minimum flight time to the detector of a fragment ion produced in Q2. In our preliminary survey of the CID products of aliphatic carboxylate ions, we discovered that neopentyl anion could be detected as a product of the decarboxylation of 3,3-dimethylbutyrate ion (eq 9).<sup>40</sup> In view of the numerous predictions



of instability for gas-phase alkyl anions,<sup>18,27,28,49</sup> this observation is significant and convinced us that a systematic search might turn up other examples of stable alkyl anions.

The survey began with CID of propionate ion  $\text{CH}_3\text{CH}_2\text{CO}_2^-$ , the putative ethyl anion precursor. Decarboxylation of propionate does not produce a detectable signal of ethyl anion ( $m/z$  29) at any collision energy up to 50 eV in the laboratory frame.<sup>40,50</sup> For propionate-argon collisions, the laboratory energy range of 0–50 eV corresponds to 0–18 eV in the center of mass frame of reference (c.m.). For precursor carboxylates where decarboxylation yields stable anions, the threshold energy is typically near the reaction enthalpy for formation of the anion and  $\text{CO}_2$ ;<sup>48</sup> this energy falls in the range of 1.5–3 eV c.m., depending on the system. Clearly the collision energy range examined for propionate anion is adequate to effect decarboxylation, but the ethyl anion is not observed. If decarboxylation produces a transient ethyl anion, then it must decompose before reaching the detector; i.e.,  $\tau(\text{C}_2\text{H}_5^-) < 25 \mu\text{s}$ . Two possible decomposition pathways for the ethyl anion are hydride ejection (accompanied by formation of ethylene) and electron detachment. In neither case would the charged product be detectable in our instrument ( $\text{H}^-$  falls below the 3 amu low-mass cutoff of the triple quadrupole). From the estimated acidity of ethane,<sup>29</sup> we can compute that  $\text{H}^-$  loss is endothermic by 13 kcal/mol. If decomposition of the ethyl anion results solely from hydride loss, then there should be at least a 13 kcal/mol (0.6 eV) window of opportunity between the decarboxylation threshold energy (ca. 2–3 eV c.m.) and the hydride loss energy where the ethyl anion could be detected, but this is not the case. The more probable scenario is rapid electron detachment from the inchoate ethyl anion. This process would be expected because of the predicted thermodynamic instability of the ethyl anion.<sup>18,22,23,28,29</sup> Attempts to trap a transient ethyl anion by using reactive gases for collisional activation of propionate at pressures up to  $5 \times 10^{-4}$  Torr fail to yield reaction products attributable to  $\text{C}_2\text{H}_5^-$  or  $\text{H}^-$ .<sup>40</sup> Neither has it been possible as yet to trap any detached electrons with reagents such as  $\text{C}_6\text{F}_6$  or  $\text{CS}_2$ .<sup>40</sup> Collisional activation of propionate with  $\text{SO}_2$  yields  $\text{SO}_2^-$ , but it is likely that this ion arises by electron transfer from the parent carboxylate rather than from the ethyl anion.

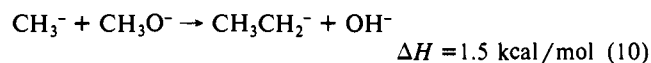
The fact that ethyl anion is unbound with respect to electron detachment whereas the methyl anion is bound indicates that the methyl substituent in  $\text{CH}_3\text{CH}_2^-$  destabilizes the anion relative to the radical. The methyl substituent effect on acidity is reversed for methane/ethane compared to water/methanol, methanol being a stronger gas-phase acid than water [ $\Delta H_{\text{acid}}(\text{CH}_3\text{OH}) = 380.5$  kcal/mol;  $\Delta H_{\text{acid}}(\text{H}_2\text{O}) = 390.8$  kcal/mol].<sup>46</sup> The acidity enhancement caused by methyl substitution in the water/methanol system has been ascribed to a two-electron hyperconjugative  $2p(\text{O}^-) - \pi^*(\text{CH}_3)$  interaction that acts to stabilize the methoxide anion relative to hydroxide.<sup>10,51,52</sup> There are some obvious

**Table II.** Electron Affinities for the R'X Species with X = O, NH,  $\text{CH}_2$

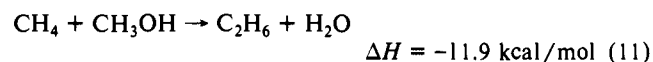
R'XH	EA(R'X), eV
OH	1.828 <sup>a</sup>
$\text{CH}_3\text{O}$	$1.570 \pm 0.022^b$
$\text{CH}_3\text{CH}_2\text{O}$	$1.726 \pm 0.033^c$
$(\text{CH}_3)_2\text{CHO}$	$1.839 \pm 0.029^c$
$(\text{CH}_3)_3\text{CO}$	$1.912 \pm 0.054^c$
$\text{NH}_2$	$0.75 \pm 0.06^d$
$\text{CH}_3\text{NH}$	$0.45 \pm 0.16^d$
$\text{CH}_3\text{CH}_2\text{NH}$	$0.66 \pm 0.20^d$
$(\text{CH}_3)_2\text{CHNH}$	$0.8 \pm 0.3^e$
$(\text{CH}_3)_3\text{CNH}$	0.85 <sup>f</sup>
$\text{CH}_3$	$0.078 \pm 0.030^g$
$\text{CH}_3\text{CH}_2$	$-0.28^h$
$\text{CH}_3\text{CH}_2\text{CH}_2$	$-0.08^h$
$(\text{CH}_3)_2\text{CHCH}_2$	$0.03^h$
$(\text{CH}_3)_3\text{CCH}_2$	$0.21^h$

<sup>a</sup> Reference 53. <sup>b</sup> Reference 54. <sup>c</sup> Reference 55. <sup>d</sup> Reference 56. <sup>e</sup> Reference 57. <sup>f</sup> Estimated for  $\Delta H_{\text{acid}}(\text{Me}_3\text{CNH}_2) \sim 396$  kcal/mol; see ref 58. <sup>g</sup> Reference 26. <sup>h</sup> Reference 29.

problems with this explanation; the  $2p(\text{O}^-)$  orbital is closer in energy to the occupied  $\pi(\text{CH}_3)$  than to the unoccupied  $\pi^*(\text{CH}_3)$ , so one would expect the four-electron destabilizing  $2p(\text{O}^-) - \pi(\text{CH}_3)$  interaction to be dominant. Moreover, because of the lower electronegativity of carbon, a carbon-based lone pair should be higher lying than an oxygen-based lone pair and thus *more* able to benefit from a stabilizing  $2p - \pi^*(\text{CH}_3)$  interaction. Finally, consider the hypothetical hydrogen–methyl exchange reaction in eq 10. Using literature values<sup>46</sup> for the relevant heats of formation



of  $\text{CH}_3^-$  (33.2 kcal/mol),  $\text{CH}_3\text{O}^-$  (–33.2 kcal/mol),  $\text{OH}^-$  (–32.7 kcal/mol), and  $\text{C}_2\text{H}_5^-$  [34.2 kcal/mol, assuming  $\Delta H_{\text{acid}}(\text{C}_2\text{H}_6) = 420$  kcal/mol]<sup>29</sup> yields an overall enthalpy for the hydrogen–methyl exchange of 1.5 kcal/mol. Thus, the stabilization afforded an oxyanion by a methyl substituent is only 1.5 kcal/mol greater than the stabilization afforded a carbanion, indicating that substituent effects in the anions alone cannot account for the reversal in the substituent effects on gas-phase acidity. For the analogous hypothetical hydrogen–methyl exchange in the conjugate acids (eq 11), we obtain  $\Delta H = -11.9$  kcal/mol [ $\Delta H_f(\text{CH}_4) = -17.8$



kcal/mol;  $\Delta H_f(\text{CH}_3\text{OH}) = -48.2$  kcal/mol;  $\Delta H_f(\text{C}_2\text{H}_6) = -20.1$  kcal/mol;  $\Delta H_f(\text{H}_2\text{O}) = -57.8$  kcal/mol].<sup>46</sup> Thus, in the neutral acids, methyl substitution at oxygen is *destabilizing* when com-

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(58) The electron affinity of  $\text{Me}_3\text{CNH}$  is not known, but can be derived from an estimated  $\Delta H_{\text{acid}}(\text{Me}_3\text{CNH}_2)$ . Comparison of the incremental effects on  $\Delta H_{\text{acid}}$  for the R'XH species for X = O and X = NH shows that substituting ethyl for methyl results in an increase of acidity of 3.1 kcal/mol for X = O and 3.8 kcal/mol for X = NH. Substitution of isopropyl for ethyl results in an increase of 1.9 kcal/mol for X = O and 2.1 kcal/mol for X = NH. Finally, substitution of *tert*-butyl for isopropyl with X = O results in an increase of 1 kcal/mol in acidity. If we assume an increase of  $\sim 1$  kcal/mol for X = NH as well, we can estimate  $\Delta H_{\text{acid}}(\text{Me}_3\text{CNH}_2)$  as 396 kcal/mol. This results in  $\text{EA}(\text{Me}_3\text{CNH}) = 0.85$  eV, assuming the N–H bond dissociation energy  $D[\text{Me}_3\text{CNH-H}] = 102$  kcal/mol.<sup>59</sup>

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(50) Although we have observed water loss when the parent anion is formed by proton abstraction from the free acid, we believe that water loss arises not from the aliphatic carboxylate ion, but from an enolate tautomer formed by  $\alpha$ -proton abstraction.<sup>42–44</sup>

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Table III. Alkoxy Anion-Alkyl Anion Electron Affinity Correlation

R'O <sup>-</sup>	EA(R'O)		R'CH <sub>2</sub> <sup>-</sup>	obsd? <sup>a</sup>
CH <sub>3</sub> O <sup>-</sup>	1.570 ± 0.022 <sup>b</sup>	52	C <sub>2</sub> H <sub>5</sub> <sup>-</sup>	-
CH <sub>3</sub> CH <sub>2</sub> O <sup>-</sup>	1.726 ± 0.033 <sup>c</sup>	53	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> <sup>-</sup>	-
(CH <sub>3</sub> ) <sub>2</sub> CHO <sup>-</sup>	1.839 ± 0.029 <sup>c</sup>	54	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> <sup>-</sup>	-
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O <sup>-</sup>	1.78 ± 0.15 <sup>d</sup>	55	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> <sup>-</sup>	-
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> O <sup>-</sup>	1.87 ± 0.16 <sup>d</sup>	56	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> <sup>-</sup>	+
CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )O <sup>-</sup>	1.95 ± 0.14 <sup>e</sup>	57	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> <sup>-</sup>	+
(CH <sub>3</sub> ) <sub>3</sub> CO <sup>-</sup>	1.912 ± 0.054 <sup>e</sup>	58	(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> <sup>-</sup>	+
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> O <sup>-</sup>	1.9 ± 0.2 <sup>f</sup>	59	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> <sup>-</sup>	-
CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> O <sup>-</sup>	1.9 ± 0.2 <sup>f</sup>	60	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> <sup>-</sup>	-
c-C <sub>5</sub> H <sub>9</sub> O <sup>-</sup>		61	c-C <sub>5</sub> H <sub>9</sub> CH <sub>2</sub> <sup>-</sup>	+
c-C <sub>6</sub> H <sub>11</sub> O <sup>-</sup>		62	c-C <sub>6</sub> H <sub>11</sub> CH <sub>2</sub> <sup>-</sup>	+
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> O <sup>-</sup>	2.0 ± 0.2 <sup>f</sup>	63	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>2</sub> <sup>-</sup>	-

<sup>a</sup> For the reaction R'CH<sub>2</sub>CO<sub>2</sub><sup>-</sup> → R'CH<sub>2</sub><sup>-</sup> + CO<sub>2</sub>. <sup>b</sup> Reference 54. <sup>c</sup> Reference 55. <sup>d</sup> Reference 60. <sup>e</sup> Reference 46. <sup>f</sup> Reference 61.

pared to methyl substitution at carbon, which is consistent with the expected destabilizing effect of a four-electron 2p-π(CH<sub>3</sub>) interaction in methanol. These interactions in the neutral acids dominate the methyl substituent effect on the gas-phase acidity of RXH (R = H, CH<sub>3</sub>; X = O, CH<sub>2</sub>).

The trends observed in the hydrocarbon acidities estimated by DePuy and co-workers<sup>29</sup> suggests that the acid-weakening effect of an α-methyl group is reversed for the second and third α substitutions; the secondary hydrogens in propane and the tertiary hydrogen in isobutane are more acidic than methane. However, because of the greater decrease in the C-H homolytic bond strengths along this series, the electron affinities for *sec*-propyl and *tert*-butyl radicals are negative. In spite of the predicted instability of the acyclic C<sub>2</sub>-C<sub>4</sub> alkyl anions, our observation of the neopentyl anion suggests that larger alkyl anions may exist as metastable or long-lived species in the gas phase. We have examined CID of the carboxylate precursors for the series of β-methyl-substituted anions: ethyl (CH<sub>3</sub>CH<sub>2</sub><sup>-</sup>), *n*-propyl (MeCH<sub>2</sub>CH<sub>2</sub><sup>-</sup>), isobutyl (Me<sub>2</sub>CHCH<sub>2</sub><sup>-</sup>), and neopentyl (Me<sub>3</sub>CCH<sub>2</sub><sup>-</sup>). Of these, only neopentyl was observed as a long-lived anion (τ > 25 μs). The other carboxylate ions (propionate, butyrate, and 3-methylbutyrate) yield no observable alkyl carbanions from decarboxylation at collision energies up to 50 eV lab. Observation of the neopentyl anion suggests that β-methyl substitution counteracts the destabilizing inductive effect of the α-alkyl substituent.

For the present investigation, we are concerned primarily with the electron binding energy of the alkyl anions, because this quantity will determine whether we can observe the anions from collision-induced decarboxylation. In Table II are listed electron affinities for the R'X radicals [EA(R'X); X = O, NH, CH<sub>2</sub>]. By considering the series of primary alkyl anions as substituted methyl anions R'CH<sub>2</sub><sup>-</sup>, we can compare the effects of the substituent R' for the analogous R'NH<sup>-</sup> and R'O<sup>-</sup> series. Inspection of Table II reveals a consistent trend in substituent effects on the relative stability of primary anions and the corresponding radicals as measured by the relevant electron affinities. Substitution of a methyl for a hydrogen directly at X (α substitution) results in destabilization of the anion relative to the radical; in all three systems (X = O, NH, CH<sub>2</sub>), the electron affinity of CH<sub>3</sub>X is decreased relative to HX. In contrast, β-methyl substitution in CH<sub>3</sub>X results in stabilization of the anion relative to the radical at each stage of substitution.

The significance of the observed trends in EA(R'X) becomes more obvious when the data of Table II are displayed as in Figure 1. The three curves show very similar shapes, which suggests that the R' substituent effects on EA in each series are similar. This qualitative correlation of substituent effects provides a predictive capability whereby we can identify potential candidates for stable R'CH<sub>2</sub><sup>-</sup> anions based on the EA of the analogous R'NH or R'O radicals. Indeed, from the fact that EA(Me<sub>3</sub>CNH) > EA(HO) and EA(Me<sub>3</sub>CNH) > EA(H<sub>2</sub>N), we might have predicted a priori that EA(Me<sub>3</sub>CCH<sub>2</sub>) > EA(CH<sub>3</sub>), i.e., that neopentyl anion is a stable species and therefore should be observable. Because more data are available for R'OH compounds than for R'NH<sub>2</sub>, we confine our attention to the former class of compounds

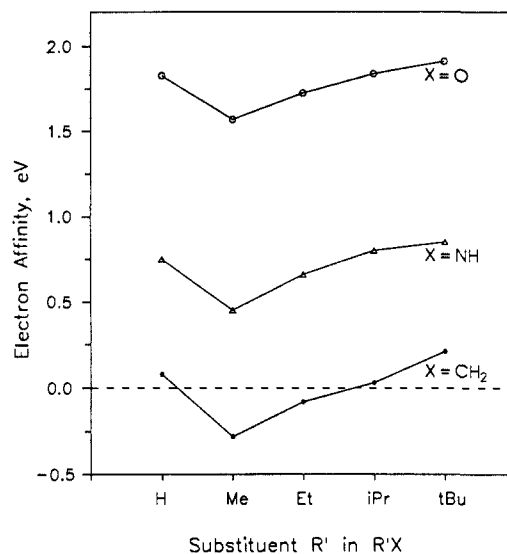


Figure 1. Electron affinity correlation for the R'X species.

in developing this correlation further. In Figure 1, the transition to stability with respect to electron detachment occurs for the carbanion series near R' = Me<sub>2</sub>CH, and the R'CH<sub>2</sub><sup>-</sup> carbanion with R' = Me<sub>3</sub>C is the first in the series that we can detect. The corresponding alkoxy species have EAs of 1.84 (Me<sub>2</sub>CHO) and 1.91 eV (Me<sub>3</sub>CO). On the basis of this qualitative correlation, we suggest that for any alkoxy R'O<sup>-</sup> with an electron binding energy in excess of ~1.9 eV, the analogous primary carbanion R'CH<sub>2</sub><sup>-</sup> should be bound with respect to electron detachment and, therefore, should be observable as a fragment from the CID of the corresponding carboxylate.

In Table III is listed a selection of alkoxides with electron binding energies both above and below 1.9 eV, along with the corresponding carbanions. The last column indicates whether or not the anion was detected in the CID spectrum of the parent carboxylate R'CH<sub>2</sub>CO<sub>2</sub><sup>-</sup>. Electron binding energies for cyclopentyl alkoxide and cyclohexyl alkoxide are not known, but can be estimated by comparison with secondary acyclic C<sub>5</sub> and C<sub>6</sub> alkoxides, e.g., 3-pentoxide and 2-methyl-3-pentoxide. The electron binding energies for these two ions are both 2.0 ± 0.2 eV,<sup>46</sup> and therefore, the analogous carbanions are expected to be bound with respect to electron detachment.

Note that whereas observation of the carbanion indicates that its lifetime with respect to electron detachment is greater than 25 μs, failure to observe the carbanion does not necessarily mean that it is unbound. The following qualitative comparison of the product ion yields for some of the carbanions R<sup>-</sup> listed in Table III reveals that electron binding energy, EA(R), is not the only factor that controls whether we can detect the carbanion in a CID spectrum. The yields of the alkyl anions observed can be extremely low. For example, the maximum yield of the methyl anion I<sup>-</sup>(CH<sub>3</sub><sup>-</sup>)/I(CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>) from decarboxylation of CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> at a pressure of 1 × 10<sup>-4</sup> Torr is ~0.002, corresponding to an apparent

decarboxylation cross section of approximately  $0.25 \text{ \AA}^2$ . The approximate maximum cross section observed for production of the neopentyl anion **58** is only  $\sim 0.02 \text{ \AA}^2$ , in spite of the higher electron binding energy predicted for the anion (4.8 kcal/mol)<sup>29</sup> compared to the methyl anion (1.8 kcal/mol).<sup>26</sup> The apparent cross section for production of 2-methylbutyl anion **57** is lower still, at  $0.005 \text{ \AA}^2$  or less. From the EA correlation in Table III, we would have predicted the electron binding energy of **57** to be greater than **58**, but the observed yield is lower. The signal intensities observed for such low yields are near the noise level in our instrument.

The failure to observe a carbanion from decarboxylation can be a result of several factors, which include insufficient parent ion abundance and autodetachment of electrons from a weakly bound carbanion, or the intrinsic instability of an unbound carbanion. Similarly, the low yield of some of the decarboxylation products that are observed may be a result of autodetachment of electrons from the carbanions, which are probably created with some vibrational excitation. The degree of vibrational excitation in the CID products undoubtedly increases as the number of atoms increases. Thus, although we would have predicted from the EA correlation that **59** and **60** are bound carbanions, we are unable to detect them on the time scale of these experiments. Similarly, although **63** would be predicted to be a bound carbanion from the correlation with the electron affinity of  $n\text{-C}_7\text{H}_{15}\text{O}^-$ , we cannot detect this carbanion from decarboxylation of **15**. In this particular case, the failure to observe the carbanion is probably in part a result of the relatively low volatility of the trimethylsilyl ester of octanoic acid, which limits the abundance of the precursor ion. Our technique is limited by the volatility of the neutral reagents to relatively small ( $< \text{C}_{10}$ ) carboxylate precursors.

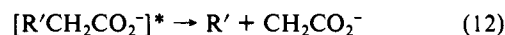
At this point, it is also important to consider the validity of identifying a particular ion signal as the carbanion arising from decarboxylation as opposed to a product of another CID process in which a loss of 44 amu occurs. We have observed in our survey work and from quantitative measurements of decarboxylation thresholds<sup>40,48</sup> that decarboxylation occurs near the thermodynamic limit, i.e., the onset for loss of  $\text{CO}_2$  occurs at collision energies that reflect the enthalpy for production of  $\text{CO}_2$  and a free anion from dissociation of  $\text{RCO}_2^-$ . The  $[\text{R}-\text{CO}_2]$  heterolytic bond energy for strongly basic anions (such as vinyl and methyl) is typically 2.5–3.0 eV. Our observed decarboxylation thresholds are consistent with the heterolytic bond energies; e.g., 2.67 eV is obtained for  $\text{CH}_3\text{CO}_2^-$ .<sup>42,48</sup> A carbanion produced by decarboxylation first appears at collision energies near 2.5 eV c.m. ( $\sim 5\text{--}15 \text{ eV lab}$ ). For most of the carboxylate ions studied, CID at energies up to 5 eV c.m. produces only the decarboxylation product in detectable yield. At higher collision energies (5–20 eV c.m.), products from other bond cleavage reactions begin to appear. Ion signals corresponding to losses of alkyl radicals from the side chain can be detected, sometimes accompanied by loss of the corresponding alkane (or alkene +  $\text{H}_2$ ).<sup>62–66</sup> At these higher collision energies, however, the ion signal of the alkyl anion from loss of  $\text{CO}_2$  often decreases in relative abundance, possibly as a result of vibration-induced electron detachment or a change in

the decarboxylation cross section.<sup>48</sup> In contrast, the radical cleavage processes become more prominent.

In order to determine the origin of a CID product it is essential to examine the collision energy dependence of the yield—particularly when the side chain in the carboxylate ion incorporates a propyl moiety that might be lost as propane, which has the same nominal mass as  $\text{CO}_2$  (44 amu). By observing the evolution of the CID spectrum for a particular carboxylate ion as the collision energy increases, it is possible to identify with some confidence products arising from decarboxylation versus homolytic bond cleavage, even when accurate appearance energies cannot be determined. Although it is impractical to make quantitative measurements of the decarboxylation threshold for product ions formed in very low yield, qualitative observations of the appearance energy ( $\pm 1 \text{ eV}$ ) can still be made and examined for consistency with the thermochemistry for heterolytic bond cleavage, as discussed above.

The observation of the primary carbanions ( $\text{R}'\text{CH}_2^-$ ) identified in Table III allows us to impose an upper limit on the gas-phase acidity of the corresponding alkanes  $\text{R}'\text{CH}_3$ . Accurate primary C–H bond dissociation energies are not known for larger alkanes, but can be estimated as  $98 \pm 2 \text{ kcal/mol}$ .<sup>59</sup> This value, combined with the knowledge that observation of  $\text{R}'\text{CH}_2^-$  indicates that  $\text{EA}(\text{R}'\text{CH}_2^-) > 0 \text{ eV}$ , results in  $\Delta H_{\text{acid}}(\text{R}'\text{CH}_3) < 412 \text{ kcal/mol}$  (eq 1) for  $\text{R}' = \text{isobutyl, sec-butyl, tert-butyl, cyclopentyl, and cyclohexyl}$ .

**Other Fragmentation Reactions.** In our preliminary report of the decarboxylation method, we reported that CID of several alkyl carboxylate ions results in no detectable fragment ions.<sup>40</sup> In these early studies, efforts were made to optimize conditions for decarboxylation, which generally proceeds most efficiently at collision energies below 30 eV lab (or  $\sim 5 \text{ eV c.m.}$ ).<sup>40,48</sup> Since that report, improvements in sensitivity and the use of an extended laboratory collision energy range of up to 75 eV have permitted the detection of products of the higher energy homolytic fragmentation processes alluded to in the previous section. In general, the fragments arising from these processes are not observed or are of extremely low intensity at collision energies below  $\sim 5 \text{ eV c.m.}$  The appearance energies of these fragment ions are in the range of 5–8 eV c.m., which almost certainly reflects a kinetic shift rather than a true thermochemical dissociation energy. A fragmentation process common to almost all of the alkanecarboxylates discussed thus far is homolytic cleavage of the carbon–carbon bond  $\beta$  to the carboxyl moiety, producing an alkyl radical (or fragments thereof) and the acetoxy radical anion (eq 12). In the series of carboxylate



ions  $\text{CH}_3\text{CH}_2\text{CO}_2^-$  (**3**),  $\text{MeCH}_2\text{CH}_2\text{CO}_2^-$  (**4**),  $\text{Me}_2\text{CHCH}_2\text{CO}_2^-$  (**6**), and  $\text{Me}_3\text{CCH}_2\text{CO}_2^-$  (**11**), the radical fragment lost in reaction 12 would be methyl, ethyl, isopropyl, and *tert*-butyl, respectively. It is of interest to note that the relative efficiency of formation of  $\text{CH}_2\text{CO}_2^-$  appears to track the stabilities of the accompanying radical fragments, i.e., the yield of acetoxy radical anion is least for CID of **3** and greatest for **11**.

Also observed for the carboxylates studied is the loss of alkyl radicals by homolytic cleavage at other sites along the side chain.<sup>62–66</sup> The products corresponding to bond cleavage at branch points are typically the most prominent of these. Thus for CID ( $> 5 \text{ eV c.m.}$ ) of 3-methylpentanoate (**9**), product ions are observed at  $m/z$  85 and 86, corresponding to loss of ethane and ethyl radical, respectively, and at  $m/z$  99 and 100, corresponding to loss of methane and methyl radical. At low collision energies ( $< 5 \text{ eV c.m.}$ ), only the 2-methylbutyl carbanion,  $m/z$  71, was detected. The acetoxy radical is the most prominent fragment from this carboxylate at high energies, and  $\text{CO}_2^-$  can be detected at somewhat lower abundance. Although linear  $\text{CO}_2$  has a negative electron affinity, bent  $\text{CO}_2^-$  can survive as a metastable ion with a lifetime of  $\sim 60 \mu\text{s}$ <sup>67,68</sup> and has been observed as a product of

(62) It has been suggested by Bowie and co-workers in their studies of alkanate CID<sup>63</sup> that the product ion arising by loss of 29 amu from 2-ethylbutyrate is produced by sequential loss of H and  $\text{C}_2\text{H}_4$  rather than loss of an ethyl radical. Similar mechanisms may hold for the homolytic fragmentations observed in the present study; we identify the neutral fragments as alkyl radicals and alkanes only for the sake of simplicity. Note also that what appears to be alkane loss may actually be  $[\text{alkene} + \text{H}_2]$  loss.<sup>64</sup>

(63) Stringer, M. B.; Bowie, J. H.; Eichinger, P. C. H.; Currie, G. J. *J. Chem. Soc., Perkin Trans. 2* **1987**, 385.

(64) (a) Tomer, K. B.; Crow, F. W.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 5487. (b) Jensen, N. J.; Tomer, K. B.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 2018. (c) Jensen, N. J.; Tomer, K. B.; Gross, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1863. (d) Adams, J.; Deterding, L. J.; Gross, M. L. *Spectrosc. Int. J.* **1987**, *5*, 199. (e) Adams, J.; Gross, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 4315.

(65) Wysocki, V. H.; Bier, M. E.; Cooks, R. G. *Org. Mass Spectrom.* **1988**, *23*, 627.

(66) Aurelle, H.; Treilhou, M.; Porme, D.; Savagnac, A.; Prome, J. C. *Rapid Commun. Mass Spectrom.* **1987**, *1*, 65.

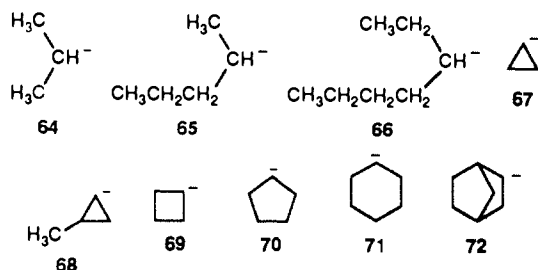
(67) Cooper, C. D.; Compton, R. N. *Chem. Phys. Lett.* **1972**, *14*, 29.

(68) Claydon, C. R.; Segal, G. A.; Taylor, G. A. *J. Chem. Phys.* **1970**, *52*, 3387.

endothermic electron transfer<sup>67,69</sup> and from high-energy (keV) CID of alkanoate ions.<sup>63</sup>

The fragment ions arising from alkane loss constitute a potential mass overlap with decarboxylation products if the alkane lost is propane. For example, because of the presence of an isopropyl group in 4-methylpentanoate (**10**), CID might be expected to result in loss of propane and production of an ion at  $m/z$  71, which is also the nominal mass of the decarboxylation product 3-methylbutyl anion (**56**). However, it is possible to identify the  $m/z$  71 ion observed as **56** on the basis of the observed energy dependence of the yield. Of the ions produced by radical cleavages, acetoxy radical anion is generally observed at the lowest collision energy. However, the  $m/z$  71 ion produced by CID of 4-methylpentanoate appears at collision energies below those at which the acetoxy radical anion can be observed and begins to decay as the collision energy is increased until the acetoxy anion and other radical cleavages are observed. Thus, we identify this  $m/z$  71 signal as **56**.

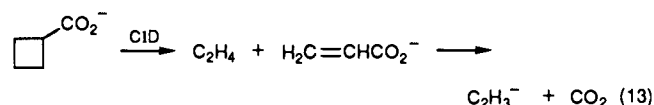
**Secondary Carbanions.** The electron affinity correlation of alkyl with alkoxy species discussed above and depicted in Figure 1 obviously cannot be used for secondary carbanions. The available data for secondary amide ions indicate that  $\alpha$ -methyl substitution destabilizes the anion relative to the radical for both the first and the second substituent: i.e.,  $EA(\text{Me}_2\text{N}) < EA(\text{MeNH}) < EA(\text{NH}_2)$ .<sup>46</sup> The alkyl radical electron affinities estimated by DePuy and co-workers suggest that the same trend holds for  $\alpha$ -methyl substitution at methyl for the first and second steps, but reverses for the third, i.e.,  $EA(\text{Me}_2\text{CH}) < EA(\text{Me}_3\text{C}) < EA(\text{MeCH}_2) < EA(\text{CH}_3)$ .<sup>29</sup> We have examined the CID spectra of a number of carboxylate precursors for acyclic secondary anions **64–66** and cyclic anions **67–72** and find that only the cyclopropyl anions **67** and **68** can be observed.



The cyclopropyl anion (**67**) might be likened to a severely distorted isopropyl anion (**64**), wherein the two methyl groups are bent back from the equilibrium geometry and linked together. This C–C–C bond angle distortion results in enhanced s-character in the C–H bonds of cyclopropane, an effect that has been linked to enhanced acidity.<sup>70</sup> From theoretical calculations and correlations of <sup>13</sup>C–<sup>1</sup>H coupling constants with percent s-character in the C–H bond, it might be expected that C–H bonds in cyclobutane would have enhanced s-character also, and thus that the acidity of cyclobutane would be enhanced relative to the secondary hydrogens of butane.<sup>71–73</sup> Interestingly, DePuy et al.<sup>29</sup> found that the hydrogens of cyclobutane are slightly less acidic than the secondary hydrogens in butane and that, in comparison with *sec*-butyl, the cyclobutyl anion is somewhat destabilized relative to the radical, unlike the cyclopropyl system. Thus, it appears that stabilizing or destabilizing effects other than rehybridization at the carbanion center are in operation in either or both the cyclopropyl and cyclobutyl species. We do not detect cyclobutyl anion in the CID spectrum of cyclobutanecarboxylate ion, and the anions of the larger ring systems (cyclopentane,

cyclohexane, and norbornane) are also not produced by CID.

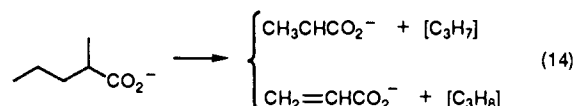
Although the cyclobutyl anion is not detected in the CID spectrum of cyclobutanecarboxylate, an ion signal of another fragmentation product is observed at relatively low energies (<7 eV c.m.) at  $m/z$  71, corresponding to loss of 28 amu. The yield of this ion increases with collision energy, and at higher energies, the vinyl anion ( $m/z$  27) can be observed. The fragment at  $m/z$  71 is probably the acrylate ion  $\text{CH}_2=\text{CHCO}_2^-$  resulting from loss of  $\text{C}_2\text{H}_4$  (eq 13). This elimination reaction is analogous to the



homolytic cleavages observed at high energies for the acyclic carboxylates and is probably facilitated by the release of ring strain in cyclobutanecarboxylate. The vinyl anion observed at higher collision energies can arise from further decomposition of the acrylate ion.

The carboxylate ions that were investigated by CID for production of acyclic secondary anions were 2-methylpropionate, 2-methylpentanoate, and 2-ethylhexanoate, the precursors for isopropyl (**64**), 2-pentyl (**65**), and 3-heptyl (**66**) anions, respectively. Activation of  $(\text{CH}_3)_2\text{CHCO}_2^-$  (**5**), the potential isopropyl anion precursor, does not yield a stable carbanion from decarboxylation. Based on the heat of formation for the anion calculated from the predicted acidity,<sup>29</sup> hydride loss is endothermic by more than 10 kcal/mol. Molecular hydrogen loss is endothermic by only a few kilocalories per mole, but no  $m/z$  41 ion resulting from  $\text{H}_2$  loss from isopropyl anion is detected. Thus, it appears that this anion experiences electron loss within less than 25  $\mu\text{s}$  of the decarboxylation event. The only fragmentation products observed from CID of **5** were  $\text{CO}_2^-$  and ions corresponding to loss of  $\text{CH}_3$  and  $\text{CH}_4$  ( $m/z$  72 and 71).

For CID of **8**, the situation is more complicated. The carboxylate ion incorporates a propyl moiety at a branch point, and cleavage of the carbon–carbon bond between the propyl group and the  $\alpha$ -carbon produces a resonance-stabilized methylacetoxy radical anion (eq 14) or the acrylate ion if the fragmentation is accompanied by hydrogen transfer or hydrogen atom loss. Thus,



both propyl radical and propane loss from the carboxylate might be expected to occur, and the fragment from propane loss coincides in nominal mass with the potential decarboxylation product  $m/z$  71. At collision energies of  $\sim 20$  eV, broad and very weak signals can be detected at about  $m/z$  41–45 and 71–72. The signals are enhanced at higher collision energies (7–15 eV c.m.) and can be resolved into discrete signals at  $m/z$  44, 45, 71, and 72. The energy dependence of the  $m/z$  71 ion signal intensity is more consistent with the usual behavior of a homolytic cleavage product than that of a decarboxylation product; i.e., the ion is observed only at collision energies greater than  $\sim 5$  eV c.m. and steadily increases in intensity with energy. Based on the accompanying propyl loss ( $m/z$  72) and the energy dependence of the  $m/z$  71 ion yield, we identify these ions as the methylacetoxy radical anion  $\text{CH}_3\text{CHCO}_2^-$  and the acrylate ion  $\text{CH}_2=\text{CHCO}_2^-$ , respectively.

No ion is observed to arise from loss of 44 amu from CID of 2-ethylhexanoate (**14**) (the potential precursor for **66**) at any collision energy. Fragment ions are observed that correspond to loss of ethyl radical and ethane ( $m/z$  113, 114), and loss of butyl radical and butane ( $m/z$  85, 86). Also observed is an ion signal at  $m/z$  71, which may arise by loss of methyl radical from the  $m/z$  86 ion or of propyl radical from the  $m/z$  114 ion. The acetoxy radical anion  $\text{CH}_2\text{CO}_2^-$ , so often observed from CID of  $\text{RCH}_2\text{CO}_2^-$ , is no longer detected in the CID spectra of the carboxylate precursors for secondary anions.

Signals are detected at  $m/z$  44 and 45 in the CID spectra of **8** and **14**, corresponding to  $\text{CO}_2^-$  and  $[\text{CHO}_2]^-$ , respectively. The

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(70) (a) Streitwieser, A., Jr.; Caldwell, R. A.; Young, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 529. (b) Streitwieser, A., Jr.; Owens, P. H.; Wolf, R. A.; Williams, J. E., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 5448.

(71) Foote, C. S. *Tetrahedron Lett.* **1963**, 579.

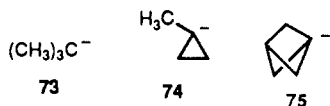
(72) Wiberg, K. B. *Tetrahedron Lett.* **1968**, *24*, 1083.

(73) Wiberg, K. B. In *Advances in Alicyclic Chemistry*; Hart, H., Karabatsos, G., Eds.; Academic Press: New York, 1968; Vol. 2.



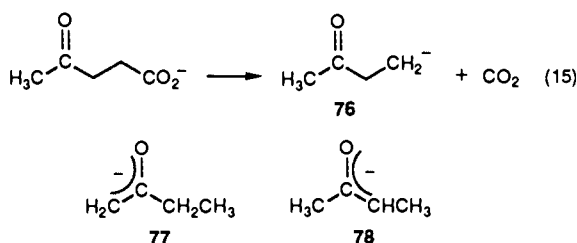
appearance of  $[\text{CHO}_2^-]$  is intriguing; this product is also observed in the CID spectrum of other carboxylate ions with  $\alpha$ -alkyl substituents: for example, **7**, **26**, and **34**. Its production appears to be enhanced by the presence of alkyl substituents at the  $\alpha$ -carbon and may involve hydride transfer from a nascent carbanion to  $\text{CO}_2$  or, alternatively, hydrogen atom transfer from an alkyl radical to a nascent  $\text{CO}_2^-$  ion. Because the  $m/z$  45 ion is observed only at the higher collision energies that also permit detection of  $\text{CO}_2^-$ , it seems probable that the mechanism for formation involves homolytic cleavage accompanied by hydrogen atom transfer within the activated complex; the product ion may be formate ion  $\text{HCO}_2^-$  or hydroxycarbonyl anion  $\text{HOC(O)}^-$ .

**Tertiary Carbanions.** We have examined the CID spectra of the carboxylate ion precursors of tertiary carbanions **73–75**. The

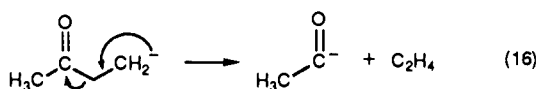


1-methylcyclopropyl anion (**74**) and the bridgehead [1.1.1]bicyclopentyl anion (**75**) are both observed as decarboxylation products of the appropriate precursor, whereas **73** cannot be detected in the CID spectra of 2,2-dimethylpropionate (**7**).<sup>40</sup> Results of computational studies and the experiments of DePuy and co-workers predict **73** to be unbound.<sup>28,29</sup> The bicyclopentyl anion **75** is of particular interest because it is, in essence, a distorted tertiary cyclobutyl anion. The bridging methylenes of **75** constrain the geometry of the bridgehead anion to be strongly pyramidal, which can stabilize the carbanion lone pair.<sup>73</sup> Kass and Chuo found that, in contrast to cyclobutane, bicyclobutane can be deprotonated by  $\text{NH}_2^-$  in a thermal reaction,<sup>14</sup> which reflects the enhanced acidity of bridgehead C–H bonds in highly strained rings.

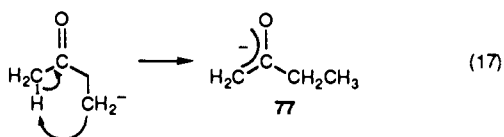
**$\beta$ -Substituted Ethyl Anions.** Although the ethyl anion itself is unbound, certain  $\beta$ -substituents X are capable of stabilizing the anion ( $\text{XCH}_2\text{CH}_2^-$ ) with respect to the radical. For example, decarboxylation of levulinate ion yields  $\beta$ -acetyethyl anion (**76**) (eq 15), an isomer of the lower energy primary and secondary



enolates of 2-butanone **77** and **78**. At collision energies below 5 eV c.m., the  $\beta$ -acetyethyl anion is the major CID product; a much smaller signal at  $m/z$  97 corresponding to loss of 18 amu ( $\text{H}_2\text{O}$  or  $\text{CH}_4 + \text{H}_2$ ) from the levulinate ion is also observed. At higher collision energy, additional CID products are observed at  $m/z$  43, which is probably the acetyl anion formed by loss of ethylene from the  $\beta$ -acetyethyl anion (eq 16), and at  $m/z$  55, which may be formed by methane loss from **76** or by decomposition of the  $m/z$  97 ion.



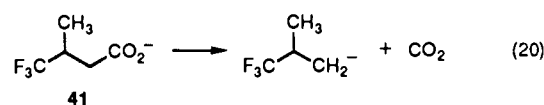
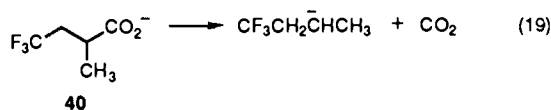
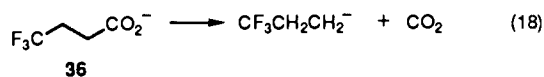
There exists a fairly obvious route for isomerization of a  $\beta$ -acetyethyl anion by an intramolecular proton-transfer reaction to form the primary butanone enolate (eq 17). To determine



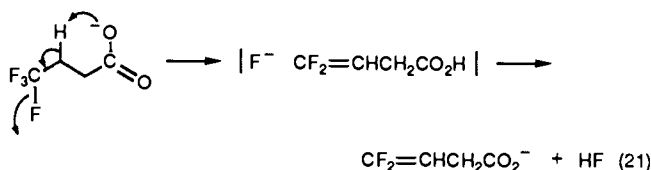
whether this reaction occurs, we consider the products that would

arise from further decomposition of the enolate ion at high collision energies and examine the higher energy ( $>8$  eV c.m.) CID spectrum of levulinate for the presence of these ions. The major CID products observed from an authentic primary butanone enolate **77** are the ketylenyl anion  $\text{HC}_2\text{O}^-$  ( $m/z$  41) and the acetyonyl radical anion  $\text{CH}_2\text{COCH}_2^-$  ( $m/z$  56); for an authentic secondary enolate **78**, the methyl anion ( $m/z$  15) and methylketylenyl anion ( $m/z$  55) are observed.<sup>74</sup> The observation of the acetyl anion and the absence of most of the decomposition products of the enolates in the CID spectrum of levulinate suggests that the extent of isomerization of the  $\beta$ -acetyethyl anion to the enolate structures is minimal.

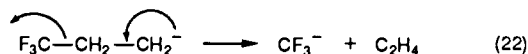
A  $\beta$ -trifluoromethyl substituent stabilizes not only the ethyl anion, but also the propyl and isopropyl anions. Unlike most of



the carboxylate ions examined here, the fluorinated carboxylates undergo numerous low-energy fragmentations besides  $\text{CO}_2$  loss. The lowest energy fragmentation product observed corresponds to HF loss. A possible mechanism for this decomposition is an intramolecular proton transfer accompanied by loss of  $\text{F}^-$ , which then abstracts a proton (eq 21). The product of HF loss can



undergo a second HF loss or  $\text{CO}_2$  loss; both products are detected for **36**, **40**, and **41**. Decarboxylation of **40** gave significantly less of the carbanion product than was observed for decarboxylation of **36** or **41**. The same pattern was observed for production of  $\text{CF}_3^-$  by CID of each of these carboxylates;  $\text{CF}_3^-$  was only a minor CID product of **40** but was a prominent product for **36** and **41**. This suggests that  $\text{CF}_3^-$  results from decomposition of the carbanions (e.g., eq 22).



Activation of 3-phenylpropionate ion (**44**) results in loss of 44 amu and formation of an ion of mass 105 as the sole ionic product at collision energies below  $\sim 20$  eV lab. At higher collision energies, signals are also observed at  $m/z$  77, corresponding to the phenyl anion, and at  $m/z$  58, corresponding to the acetoxy radical anion. By analogy with the decarboxylation results discussed thus far, we would identify the  $m/z$  105 ion as the  $\beta$ -phenylethyl anion  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2^-$ . However, recent studies by Nibbering and co-workers cast doubt on the viability of a  $\beta$ -phenylethyl anion as a long-lived species in the gas phase.<sup>75</sup> They concluded on the basis of isotope labeling experiments and reactivity studies that the long-lived  $\text{C}_8\text{H}_9^-$  ion formed by decarboxylation of  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CO}_2^-$  has the spiro[2.5]octadienyl structure **79**, which is a lower energy isomer of the  $\beta$ -phenylethyl anion. Although several other isomeric forms of the  $\text{C}_8\text{H}_9^-$  ion were identified as product ions formed by, for example, fluoro-desilylation of  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$  and deprotonation of

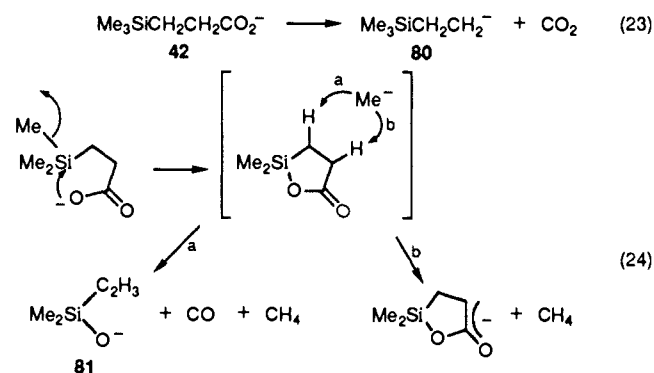
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(75) Maas, W. P. M.; van Keelen, P. A.; Nibbering, N. M. M. *Org. Mass Spectrom.*, in press.



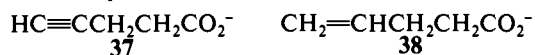
spiro[2.5]octadiene, no evidence was obtained for a persistent  $\beta$ -phenylethyl anion. Moreover, from an estimate of the acidity of the  $\beta$ -hydrogens in ethylbenzene and the C-H bond energy, Nibbering and co-workers derived an electron binding energy for the  $C_6H_5CH_2CH_2^-$  ion of  $0 \pm 3$  kcal/mol and concluded that a  $\beta$ -phenylethyl anion should be unbound with respect to electron detachment. However, we believe for the following reasons that the *nascent*  $C_8H_9^-$  ion formed by decarboxylation is indeed the  $\beta$ -phenylethyl isomer. The low yield of the  $m/z$  105 ion observed in the present decarboxylation study is a common feature of CID of carboxylate ions that yield weakly bound carbanions and is consistent with a low electron binding energy for the  $\beta$ -phenylethyl anion. We have found that CID of  $C_6H_5CH_2CH_2CH_2CO_2^-$  also produces  $C_8H_9^-$  (by loss of  $CH_2O$ ),<sup>76</sup> and from the threshold energy, we estimate  $\Delta H_{acid}(C_8H_{10}) = 406 \pm 5$  kcal/mol,<sup>48</sup> in good agreement with the value given by Nibbering et al. for the  $\beta$ -hydrogens of ethylbenzene:  $\Delta H_{acid} = 406 \pm 3$  kcal/mol.<sup>75</sup> These results are consistent with the formation of  $\beta$ -phenylethyl anion by decarboxylation of  $C_6H_5CH_2CH_2CO_2^-$  and CID of  $C_6H_5C-H_2CH_2CH_2O^-$ , although the ion may collapse eventually to the spiro[2.5]octadienyl structure (79). The phenide ion ( $m/z$  77) observed at higher collision energies can arise by ethylene loss from the  $\beta$ -phenylethyl anion, but is also reported to be a fragment from decomposition of 79.

In our preliminary communication of the present study,<sup>40</sup> we reported the production of  $\beta$ -trimethylsilylethyl anion (80) from CID of 42 (eq 23). Further examination of the CID spectrum



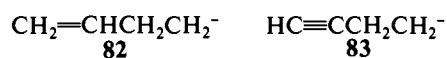
revealed an alternative pathway for loss of 44 amu by sequential loss of  $CH_4$  and  $CO$  (eq 24); an intermediate product from loss of  $CH_4$  could be detected. Measurement of the appearance energy for the  $m/z$  101 ion (from loss of 44 amu) yielded a value of 4.0 eV, which is well in excess of the estimated enthalpy for decarboxylation of ca. 2.5 eV. We have observed that appearance energies for decarboxylation products usually correlate well with the enthalpy change for decarboxylation<sup>48</sup> and, therefore, conclude that the  $m/z$  101 ion observed is probably 81. If an authentic  $\beta$ -trimethylsilylethyl anion is produced by decarboxylation, it is formed in much lower abundance than 81 and cannot be distinguished from it. Thus, determination by the present CID method of whether a  $\beta$ -trimethylsilyl substituent can in fact stabilize the ethyl anion must await labeling studies.

We have examined the CID spectra of two other potential precursors for  $\beta$ -substituted ethyl anions: the 4-pentynoate ion (37) and the 4-pentenoate ion (38). In both cases, anions can

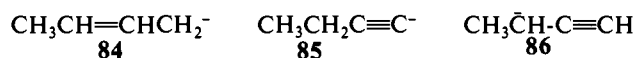


be observed at  $<5$  eV c.m. collision energy that correspond to loss of 44 amu. At higher collision energies, CID of 38 yields a small

amount of the vinyl anion and 37 yields the acetylide anion. These fragments may be produced by ethylene loss from the  $\beta$ -vinylethyl anion (homoallyl 82) and the  $\beta$ -acetylenylethyl anion (homo-

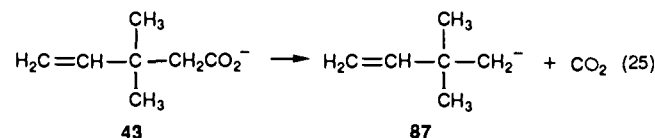


propargyl 83), respectively. The only other fragment ion observed is the acetoxy radical anion. Observation of the vinyl and acetylide anions is consistent with the apparently general process of ethylene loss from  $\beta$ -substituted ethyl anions. However, the appearance energies for the anions produced by loss of 44 amu are not consistent with the predicted thermochemistry for production of  $CO_2$  and 82 or 83.<sup>48</sup> Instead, the threshold energy for  $CO_2$  loss from 38 seems to reflect isomerization of the carbanion product to the allylic isomer 84, while the threshold energy for  $CO_2$  loss from



37 is more consistent with production of 85 or 86 than 83. If isomerization in fact occurs, the mechanism may involve intramolecular proton transfers in the carboxylate ion, either in the flow tube or upon collisional activation. If so, the production of vinyl and acetylide ions at high collision energies suggests that the isomerization is not complete, and that some fraction of the  $m/z$  55 or 53 ions formed by decarboxylation of 38 and 37 are intact  $XCH_2CH_2^-$  species, because vinyl and acetylide anions are not detected in the CID spectra of 84 or 86. However, the nature of appearance energy measurements is such that when an ion can be formed by two processes of similar energies, the measurement reflects the lower energy process (or perhaps some admixture of each if the lower energy process does not compete effectively).

In order to test the hypothesis of intramolecular rearrangement during CID of 38 and 37, the CID spectrum of 43 was examined.



In this ion, rearrangement to an allylic species is blocked by the methyl groups. Decarboxylation of 43 occurs with a threshold energy of  $2.55 \pm 0.1$  eV, which gives an upper limit to the acidity of the methyl hydrogens in 3,3-dimethylbutene (the conjugate acid of 87) of 409 kcal/mol,<sup>48</sup> about the same as that predicted for neopentane of 408.9 kcal/mol.<sup>29</sup> We expect that the acidity of the methyl hydrogens in 1-butene should also be of this magnitude ( $\sim 410$  kcal/mol),<sup>29</sup> whereas the appearance potential for  $C_4H_7^-$  ( $m/z$  55) from 38 suggests an acidity of the conjugate acid (butene) closer to 390 kcal/mol.<sup>48</sup> Thus, we conclude that some fraction of the 4-pentenoate ion population isomerizes such that allylic ions are produced along with the homoallyl anion.

**Substituted Methyl Anions.** In addition to the well-known benzyl ("phenylmethyl") and cyanomethyl anions,<sup>46</sup> each of the monohalogenated methyl anions  $FCH_2^-$ ,  $ClCH_2^-$ ,  $BrCH_2^-$ , and  $ICH_2^-$  has been produced by the decarboxylation method. To our knowledge, the fluoromethyl anion  $FCH_2^-$  has not been previously observed.<sup>77</sup> Halogen substituents are expected to stabilize the methyl anion, such that  $\Delta H_{acid}(CH_3X)$  is lower than  $\Delta H_{acid}(CH_4)$ .<sup>77,78</sup> Because the C-H bond dissociation energies in halomethanes are lowered only slightly in comparison with  $CH_4$  (e.g.  $D[ClCH_2-H]$ <sup>59</sup> = 101 kcal/mol versus  $D[CH_3-H]$ <sup>24</sup> = 104.8 kcal/mol), the overall effect of the halogen substituent is to stabilize the anion relative to the radical, conferring a greater electron affinity to  $CH_2X$  than  $CH_3$ .

Collisional activation of the  $XCH_2CO_2^-$  ions with  $X = Cl, Br,$  and  $I$  yields  $X^-$  as the major CID product, formed in what can be formulated as an intramolecular nucleophilic substitution re-

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action that also produces acetolactone as the neutral product.<sup>79</sup> These and some related cyclization processes of collisionally activated  $\beta$ -substituted alkoxides are the subject of a separate paper.<sup>80</sup> A related species that is of interest is the  $\alpha$ -chloropropionate ion (35), which yields both  $\text{Cl}^-$  and  $\text{CH}_3\text{CHCl}^-$  upon dissociation. The major decomposition product is  $\text{Cl}^-$ , probably formed by an activated intramolecular displacement analogous to that observed for the  $\text{XCH}_2\text{CO}_2^-$  species.<sup>80</sup> Decarboxylation yields the  $\alpha$ -chloroethyl anion, which, to our knowledge, has not previously been detected.<sup>81</sup> By analogy with fluorethane,<sup>81-83</sup> the  $\beta$ -hydrogens of chloroethane are likely to be (kinetically) much more acidic due to the exothermicity of decomposition to  $\text{Cl}^-$  and  $\text{C}_2\text{H}_4$  and the favorable kinetics of such elimination reactions.<sup>83,84</sup> In contrast, the acidity of the  $\alpha$ -hydrogen in chloroethane should be comparable to the acidity of  $\text{CH}_3\text{Cl}$  ( $\Delta H_{\text{acid}} = 396 \pm 3$  kcal/mol).<sup>77</sup> If  $\Delta H_{\text{acid}}(\text{CH}_3\text{CH}_2\text{Cl})$  is taken as  $\sim 395$  kcal/mol, the overall enthalpy of decomposition of the product ion  $\text{C}_2\text{H}_4\text{Cl}^-$  ion to  $\text{Cl}^-$  and  $\text{C}_2\text{H}_4$  is  $-44$  kcal/mol. The fact that  $\text{CH}_3\text{CHCl}^-$  can be detected indicates that there is a barrier to the 1,2 proton shift that would convert  $\text{CH}_3\text{CHCl}^-$  to  $^-\text{CH}_2\text{CH}_2\text{Cl}$  and, moreover, suggests that  $\alpha$  elimination to form  $\text{Cl}^-$  and ethylidene is also highly disfavored.<sup>85,86</sup>

In contrast to the anion-stabilizing effect of an  $\alpha$ -halogen substituent, replacement of hydrogen by methoxy in methane stabilizes the radical more than the anion, with the result that although  $\Delta H_{\text{acid}}(\text{CH}_3\text{OCH}_3) < \Delta H_{\text{acid}}(\text{CH}_4)$ ,  $\text{EA}(\text{CH}_3\text{OCH}_2) < 0$ .<sup>87</sup> We are unable to detect  $\text{CH}_3\text{OCH}_2^-$  formed by decarboxylation of methoxyacetate ion  $\text{CH}_3\text{OCH}_2\text{CO}_2^-$ . Also not observed is the methyl anion, a potential decomposition product of a short-lived  $\text{CH}_3\text{OCH}_2^-$  ion. Methoxide ion ( $\text{CH}_3\text{O}^-$ ) is formed at high collision energies,<sup>80</sup> along with the homolytic cleavage

products  $\text{OCH}_2\text{CO}_2^-$  ( $m/z$  74),  $\text{CH}_2\text{CO}_2^-$  ( $m/z$  58), and  $\text{CO}_2^-$  ( $m/z$  44).

### Conclusions

We have found that collision-induced decarboxylation is a useful method for production of highly reactive and weakly bound carbanions. We have used this method in a survey of CID of numerous alkanecarboxylate and cycloalkanecarboxylate ions and find evidence that several alkyl and cycloalkyl anions exist for more than 25  $\mu\text{s}$  in the gas phase. Among these are examples of primary carbanions, including the neopentyl anion, the 2- and 3-methylbutyl anions, cyclopentylmethyl anion, and cyclohexylmethyl anion, and secondary and tertiary carbanions such as 1- and 2-methylcyclopropyl anions and 1-bicyclopentyl anion. The decarboxylation method has been used to produce a variety of  $\alpha$ -substituted methyl anions,  $\beta$ -substituted ethyl anions, and vinylic carbanions. A simple correlation between electron affinities for primary alkyl radicals ( $\text{RCH}_2$ ) and the analogous alkoxy radicals ( $\text{RO}$ ) is described from which verifiable predictions can be made concerning the absolute stability and detectability of primary alkyl carbanions. In the following paper, we present results from quantitative analyses of the threshold energies for decarboxylation and describe a correlation of the measured threshold energies with the gas-phase acidities of the conjugate acids of the product carbanions.

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**Registry No.** 1, 71-50-1; 2, 21845-14-7; 3, 72-03-7; 4, 461-55-2; 5, 511-69-3; 6, 5711-68-2; 7, 29650-96-2; 8, 91150-70-8; 9, 91150-72-0; 10, 6699-33-8; 11, 22402-43-3; 12, 124891-60-7; 13, 124891-61-8; 14, 18035-91-1; 15, 74-81-7; 16, 18917-09-4; 17, 124891-62-9; 18, 124891-63-0; 19, 64274-59-5; 20, 64274-58-4; 21, 124891-64-1; 22, 45520-91-0; 23, 3198-23-0; 24, 70554-35-7; 25, 70554-37-9; 26, 124891-65-2; 27, 10344-93-1; 28, 54467-93-5; 29, 41824-21-9; 30, 124891-66-3; 31, 98571-46-1; 32, 124891-67-4; 33, 18358-40-2; 34, 73759-63-4; 35, 16336-84-8; 36, 112219-62-2; 37, 101917-31-1; 38, 20224-66-2; 39, 10402-70-7; 40, 124891-68-5; 41, 124891-69-6; 42, 59906-90-0; 43, 124891-70-9; 44, 826-17-5; 45, 68-10-0; 46, 14526-03-5; 47, 513-62-2; 48, 152-34-1; 49, 23297-32-7; 50, 20758-58-1; 51, 7631-42-7.

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