entage. We observe significant mixing of the four highest occupied MOs with those lying lower in energy. At this intermolecular separation it is apparent that a simple extension of the monomeric four-orbital model to the dimer is not justified. The strong overlaps of the monomer wave functions at this distance constitute a large perturbation that is inconsistent with a simple coupled chromophore model.

In Figure 3 we present the INDO calculated UV–vis spectra of the BChlb dimer. What is most striking is the appearance of a strong absorption at 9339 cm^{-1} with an oscillator strength of 0.939. This represents a 3590-cm^{-1} red shift relative to the average of the BChlb monomers. This absorption is composed of 90% dimer HOMO → LUMO (MOs 188 → 189) and has a strong y polarization. Note in Figure 1 that the y axis runs from N3 to N1 of BChlb-L. The Qy transition for BChlb monomers exhibit a major shift of charge density from the ring III side to the ring I side of the macrocycle.[13] In the dimer this shift in electron density is also observed, and, as the monomer y axes are roughly antiparallel, there is a net electron density shift toward the center of the dimer structure in the HOMO–LUMO transition. The configurations 186 → 189 and 187 → 189 mix in the configuration interaction (CI) to give a pair of transitions that bracket the 9339-cm^{-1} transition at 6880 cm^{-1} (0.032) and 11 616 cm^{-1} (0.147), respectively. It is interesting to speculate on the possible role that the calculated transition at 6880 cm^{-1} may play in electron transfer. Although there were no unacceptable steric hinderances in the crystal structure, slight geometric relaxation of some elements of the dimer may affect the MO splitting and hence this absorption. As well, the degree of the red shift is sensitive to the interplanar distance with the monomer spectrum being regenerated at large enough separation.[16] An analysis of these effects in addition to the charge-transfer characteristics of the remaining low-energy transitions and their modulation by electric fields is under investigation.

Although other mechanisms may be contributory and important, we have demonstrated that dimer formation within van der Waals radii for BChlb results, by itself, in a significant red shift with roughly a doubling in the oscillator strength of the long wavelength transition relative to the respective monomers. That a large red shift appears to be a consequence of this particular dimer formation should not be surprising. Large red shifts of the long wavelength transition in crystals of methylbacteriopheophorbide-*a* have been observed experimentally and attributed to π–π interactions between the staggered macrocycle rings.[5] The BChlb macrocycles in the X-ray structure are quite close and appear to behave as a true supermolecule rather than two interacting monomers. Petke and Maggiora showed in theoretical calculations that Mg porphyrin–porphyrin dimers which were within van der Waals distances behaved as a true dimer.[14,15] Also our initial results appear to suggest some charge-transfer characteristics may be inherent in the dimer itself and be quite low lying.[16] It should be noted that the calculated effects of charges upon the UV–vis spectrum of chlorophylls and bacteriochlorophylls are known to be significant.[6,13] Thus the possibility exists that the presence of the proper electric field created by nearby polar substituents or secondary protein structures (α-helices) could have a strong effect on the charge-transfer characteristics of the BChlb dimer in vivo. Furthermore, the Qy transition dipole moments for the isolated BChlb monomers are roughly antiparallel and displaced with an overlapping of ring I for both monomers. Although unable to account for the proper magnitude in the red shift, classical exciton theory shows that this relative configuration will result in a larger red shift than were the transition dipoles at right angles or were the macrocycles fully overlapping.[17,18]

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On the Existence of Alkyl Carbanions in the Gas Phase

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Recently, we introduced a new method for the regiospecific generation of gas-phase carbanions by means of collision-induced decarboxylation of organic carboxylate anions in an FT-ICR (eq 1).[1] We have now adapted this method for use in our flowing

$$RCO_2^- \rightarrow R^- + CO_2 \tag{1}$$

afterglow–triple quadrupole instrument[2] and have explored the scope of the method with respect to the kinds of carbanions that can be produced. We describe here an experimental evaluation of the absolute stabilities of alkyl carbanions, as well as the observation of several new species synthesized by reaction 1.

The procedure involves generation of the carboxylate anion in the flow tube by means of fluorodesilylation of the appropriate trimethylsilyl ester.[3] The carboxylate ion is extracted from the flow tube and mass-selected with the first quadrupole. Decarboxylation is effected by means of collision-induced dissociation (CID) in the second quadrupole and the resulting fragment ions are mass-analyzed with the third quadrupole. By monitoring the intensity of R^- as a function of the carboxylate ion axial kinetic energy, we can also obtain an experimental threshold energy for reaction 1.[4]

We have conducted a general survey of the low-energy CID of carboxylate anions and conclude that decarboxylation is a universal fragmentation pathway for such ions.[5] A key observation is that the acetate anion can be decarboxylated to produce a low yield of the methyl anion (eq 2).[6] The fact that we can observe such a "fragile", weakly bound species as CH_3^- with our

$$CH_3CO_2^- \xrightarrow{CID} CH_3^- + CO_2 \tag{2}$$

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Table I. Upper Bounds for Gas-Phase Acidities Derived from Experimental Decarboxylation Thresholds

			ΔH_{acid} (RH), kcal/mol	
carboxylate	E_T, eV[a]	R^-	this work[b]	lit[c]
$CF_3CO_2^-$	1.70	CF_3^-	377	377.0
$CH_3CO_2^-$	2.74	CH_3^-	420	416.6
$NCCH_2CO_2^-$	1.44	$NCCH_2^-$	368	372.9
$H_2C{=}CHCO_2^-$	2.41	$H_2C{=}CH^-$	401	406[d]
$CH_3C(O)CO_2^-$	2.10	CH_3CO^-	382	390[e]
$CH_3OC(O)CO_2^-$	1.60	CH_3OCO^-	384	<390[f]
$CF_3CH_2CH_2CO_2^-$	2.65	$CF_3CH_2CH_2^-$	403	
$CH_2{=}CHCH_2CO_2^-$	1.74	$CH_2{=}CHCH_2^-$	392	391.9
$(CH_2)_2CHCO_2^-$	2.75	$(CH_2)_2CH^-$	413	412[d]
$CH_3C(O)CH_2CH_2CO_2^-$	2.41	$CH_3C(O)CH_2CH_2^-$	409	
$C_6H_5CO_2^-$	2.74	$C_6H_5^-$	406	400.7[g]
$C_6H_5CH_2CO_2^-$	1.29	$C_6H_5CH_2^-$	382	380.8

[a] Threshold center-of-mass translational energy for reaction 1. Estimated uncertainty ±0.15 eV. [b] Calculated ΔH_{acid} from eq 4. Estimated uncertainty ±3.5 kcal/mol. [c] Gas-phase acidities taken from ref 14 unless otherwise noted. [d] Reference 10. [e] Reference 3b. [f] Reference 12. [g] Reference 16.

technique ($EA(CH_3) = 1.8$ kcal/mol)[7] suggests that *virtually any carbanion with a positive electron binding energy greater than 1–2 kcal/mol should also appear from CID of the corresponding carboxylate.*

In our CID survey, several alkylcarboxylate anions were exceptional in that CID produced *no* detectable carbanions (indeed, no fragment ions at all). For example, CID of propionate, 2-methylpropionate, 3-methylbutyrate, and 2,2-dimethylpropionate anions (the putative ethyl, *sec*-propyl, isobutyl, and *tert*-butyl anion precursors) results in no detectable fragment ions under a variety of conditions of collision energy and target-gas pressure. Similarly, although both cyclopropyl[1] and 1-methylcyclopropyl anions can be generated by collision-induced decarboxylation, no fragment ions are observed from CID of cyclopentyl- or cyclohexylcarboxylate anions. At high collision energies (> 10 eV, lab), cyclobutylcarboxylate anion undergoes an inefficient fragmentation to form an ion of *m/z* 71 (presumably the acrylate anion), but no cyclobutyl anion can be detected.

The absence of any detectable fragment ions resulting from CID of the various saturated cyclic and acyclic carboxylate anions noted above leads us to believe that although these anions also undergo collision-induced decarboxylation, the "carbanion" so produced is unstable and immediately ejects an electron. Alternative fragmentation routes such as dehydration or dehydrogenation that would result in stable anions are not observed,[5b] and electron detachment from the parent carboxylate should not be kinetically nor energetically competitive.[8] Moreover, this scenario is consistent with the predicted instability of alkyl anions larger than CH_3^- based on both theory[9] and experiment.[10] On the basis of calculated flight times for an ion through the third quadrupole to the ion multiplier, we can estimate an upper limit of about 25 μs for the lifetime of the ethyl, *sec*-propyl, isobutyl, *tert*-butyl, cyclobutyl, cyclopentyl, and cyclohexyl "anions".

In spite of the instability of the C_2–C_4 alkyl carbanions, it appears possible that certain of the larger alkyl carbanions can be stable. In such species, alkyl group polarizability may counterbalance destabilizing inductive effects.[11] For example, although isobutyl anion cannot be observed, substitution of a methyl group for the β-hydrogen results in a (weakly) bound neopentyl anion. This remarkable anion is produced in low but measureable yield from CID of 3,3-dimethylbutyrate anion (eq 3).

$$(CH_3)_3CCH_2CO_2^- \xrightarrow{\text{CID}} (CH_3)_3CCH_2^- + CO_2 \qquad (3)$$

Collision-induced decarboxylation provides a route to the regiospecific formation of many substituted and/or unsaturated carbanions that would be difficult or impossible to generate by conventional chemical ionization methods. We have used the method to generate a variety of novel anions, including acetyl[3b] (I), methoxycarbonyl[12] (II), α-chloroethyl (III), 3,3,3-trifluoropropyl (IV), β-acetylethyl (V), and β-(trimethylsilyl)ethyl (VI).

CH_3CO^- I $\quad$ CH_3OCO^- II $\quad$ CH_3CHCl^- III $\quad$ $CF_3CH_2CH_2^-$ IV

$CH_3C(O)CH_2CH_2^-$ V $\quad$ $(CH_3)_3SiCH_2CH_2^-$ VI

The threshold energy (E_T) for reaction 1 provides an upper limit for the energy required for heterolytic cleavage of the R^-–CO_2 bond[13] and can be related to the gas-phase acidity for the conjugate acid of the carbanion RH (eq 4). In most cases the limiting values

$$\Delta H_{\text{acid}}(\text{RH}) = E_T + \Delta H_f(\text{RCO}_2\text{H}) + \Delta H_{\text{acid}}(\text{RCO}_2\text{H}) - \Delta H_f(\text{CO}_2) - \Delta H_f(\text{RH}) \qquad (4)$$

for the gas-phase acidity of RH derived from the measured threshold energy for decarboxylation show good agreement with the literature values[14] (Table I). This, combined with the fragmentation pattern of the parent carboxylate, allows verification of the identity of the carbanion. It also provides a means to estimate gas-phase proton affinities for novel anions such as the β-acetylethyl anion V, a positional isomer of the more stable butanone enolates ($\Delta H_{\text{acid}}(CH_3COCH_2CH_3) = 368$ kcal/mol).[14]

Through the use of potentially reactive collision gases at pressures enabling multiple collisions of both parent and fragment ions, we are also able to examine the ion–molecule reactions of the carbanions produced by decarboxylation. For example, CID of 3-butenoate anion with O_2 target gas results in formation of the allyl anion, and under multiple-collision conditions, O_2^- is also formed (eq 5).[15] In contrast, O_2–CID of propionate anion does *not* produce O_2^- under similar conditions of pressure and collision energy. This indicates that O_2^- is a genuine reaction product from a bimolecular electron transfer reaction of allyl anion with O_2, rather than from free electron scavenging or from an electron transfer reaction of the kinetically excited carboxylate ion.

$$CH_2{=}CHCH_2CO_2^- \xrightarrow[-CO_2]{\text{CID}} CH_2{=}CHCH_2^- \xrightarrow{O_2} O_2^- \qquad (5)$$

Further investigations of the scope of this decarboxylation technique and the properties of regiospecifically generated carbanions are in progress.

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