On the Stability of Alkyl Anions.
A Molecular Orbital Theoretical Study

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Abstract: The proton affinities of the methyl anion and of other saturated alkyl anions have been calculated on the SCF level and also with the inclusion of electron correlation within the coupled electron pair approximation (CEPA) scheme. The results have given evidence that alkyl anions do not exist as stable compounds, i.e., that alkyl radicals have at most very small electron affinities.

I. Introduction

The electron affinities of alkyl radicals and thus the stability of alkyl anions are still not known experimentally. Even the existence of alkyl anions in the gas phase has not been proven so far. MO theoretical studies have mainly dealt with the methyl anion,[1-6] but SCF calculations on the ethyl anion have also been published.[6] On the methyl anion very good SCF calculations[1-3] and also calculations which include electron correlation[2-5] have been reported. The energies of the methyl anion and of the methyl radical were compared in some of the papers.[2,4,5] Driessler et al.[2] found within SCF the methyl radical to be 1.38 eV more stable than the methyl anion. Their computation of the electron correlation using the IEPA method[7] indicated that correlation might reverse the order of stability. They calculated the IEPA correlation energy of the anion to be 1.49 eV larger than that of the radical. Thus, a value of 0.11 eV was obtained for the (adiabatic) electron affinity of the methyl radical. Within the same basis set but with a Green's function method Cederbaum and Niessen,[4] on the other hand, obtained a negative value of −0.24 eV for the (vertical) electron affinity of the (planar) methyl radical. Those results cannot be regarded as final because of the following reasons.

(1) The basis set used was large but, of course, not complete. Since the number of electrons in the two systems compared (CH_3^- and CH_3) is different the contribution of electron correlation to the energy difference is large and one would have to extrapolate the correlation energy for a complete basis. Driessler et al. estimated that such an extrapolation might favor the anion over the radical by another 0.2 eV.

(2) Within IEPA the electron correlation energies are overestimated since the pair correlation energies are assumed to be additive. In order to avoid such addition errors the CEPA scheme[8] was developed. CEPA calculations on the methyl anion[3] show indeed an relatively large IEPA error for that molecule. Thus, the IEPA calculations of Driessler et al.[2] might have overestimated the stability of the anion relative to the radical.

Very recently Surrat and Goddard[5] reported on their calculations on the CH_3 cation, radical, and anion. They obtained a negative value for the adiabatic electron affinity of the CH_3 radical of −0.49 eV. They used a rather poor basis set but included a part of the relevant correlation effects. They concluded that the CH_3 anion is not stable vs. the decay into a CH_3 radical and an electron.

In order to avoid the comparison of the energies of two systems with a different number of electrons (here CH_3 and CH_3^-) we used a different approach for the theoretical determination of the electron affinity of the methyl anion. We calculated the protonation energy ΔH_{prot} of the methyl anion

$$CH_3^- + H^+ \rightarrow CH_4 \qquad (1)$$
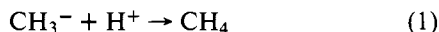
and used the experimental values for the dissociation energy D_0^0 of the CH bond in methane

$$CH_4 \rightarrow CH_3 + H$$
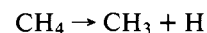
and of the ionization potential E_H of the hydrogen atom

$$H \rightarrow H^+ + e^-$$
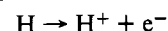
for the calculation of the electron affinity E_A of the methyl radical which is then obtained from the following relationship (cf. ref 6):

$$E_A = -\Delta H_{prot} + D_0^0 + E_H = -\Delta H_{prot} + 0.6784 \text{ au} \quad (2)$$

For D_0^0 a value of 112 kcal/mol was used (104 kcal/mol for the dissociation energy of the CH bond in CH_4 plus 8 kcal/mol as the correction for the zero point vibration).[10] The contribution of correlation energy to the protonation energy is expected to be small since the number and the type of electron pairs do not change during the protonation (eq 1). Hence, calculations which include electron correlation should yield the proton affinity with only a small absolute error.

II. The Proton Affinity of the Methyl Anion

The proton affinity of the methyl anion is obtained as the difference between the total energies of methane and of the methyl anion. We calculated these energies within SCF and with inclusion of the valence electron correlation using the CEPA scheme. Different basis sets of increasing sophistication were applied in order to study the sensitivity of the calculated proton affinity with respect to an improvement of the basis set. This point is of importance since the larger alkyl anions can be calculated with moderate basis sets only.

The results are listed in Table I. Starting from a 7.3/3 Huzinaga basis,[11] coupled to double ζ (DZ), flat functions[9] were successively added as indicated in the table (basis sets 1-5). Then, the same was done for a basis set which was augmented by polarization functions (basis sets 6-9): a set of d functions at the carbon atom (DZ + D) with an exponent of 1.0 and in addition a set of p functions at the hydrogens (DZ + D, P) with an exponent of 0.65. Finally, an extended basis set (EB) was applied which was based on a Huzinaga 9.5/5 basis augmented by two sets of d functions and one set of f functions at the carbon atom and two sets of p functions at the hydrogen atoms. The exponents of these polarization functions (as well as the quoted energies of methane) were taken from ref 3. In addition, several flat functions as listed in Table I (column 10) were included in the extended basis. In order to save computer time, the methyl anion was assumed to be planar in these calculations. The justification is the smallness of the inversion barrier of the pyramidal anion. According to CEPA calculations this barrier is smaller than 1 kcal/mol[3] (see section III). A CH bond length of 1.10 Å was assumed for methane as well as for the methyl anion. Only the values listed for the extended basis (column 10) refer to optimized CH bond

Table I. SCF and CEPA Energies for Planar CH_3^- and CH_4 (R_{CH} = 1.10 Å) Obtained with Various Basis Sets (Values in au)

Basis no.:		1	2	3	4	5	6	7	8	9	10
Type:		DZ	DZ	DZ	DZ	DZ	DZ + D	DZ + D,P	DZ + D,P	DZ + D,P	EB
+ flat functions at the C atom											
p (0.04)		−	+	+	+	+	+	+	+	+	+
p_z (0.01)		−	−	+	+	−	−	−	−	+	+
p_z (0.003)		−	−	−	+	−	−	−	−	−	+
s (0.04)		−	−	−	−	+	−	−	+	+	+
CH_4	$-E_{SCF}$	40.1395	40.1404	40.1404	40.1404	40.1406	40.1499	40.1655	40.1656	40.1656	40.2115
	$-E_{CEPA}$	40.2560	40.2579	40.2579	40.2579	40.2583	40.3006	40.3497	40.3501	40.3501	40.4221
CH_3^-	$-E_{SCF}$	39.3913	39.4539	39.4551	39.4552	39.4544	39.4605	39.4746	39.4748	39.4759	39.5186
SCF	ϵ	+0.0604	−0.0019	−0.0079	−0.0085	−0.0027	−0.0007	−0.0020	−0.0025	−0.0080	−0.0093
	ΔH_{prot}	0.7482	0.6865	0.6853	0.6852	0.6862	0.6893	0.6908	0.6908	0.6897	0.6929
CH_3^-	$-E_{CEPA}$	39.4979	39.5775	39.5803	39.5803	39.5793	39.6166	39.6583	39.6601	39.6623	39.7369
CEPA	ΔE_{corr}	0.1066	0.1237	0.1252	0.1251	0.1249	0.1561	0.1836	0.1853	0.1864	0.2183
	ΔH_{prot}	0.7581	0.6804	0.6776	0.6776	0.6790	0.6840	0.6914	0.6900	0.6878	0.6852

Table II. The Electron Affinity of the Methyl Radical Calculated (a) from the Proton Affinity and (b) from the Double Ionization of the Methyl Anion[a]

		Basis no.: 2	6	9	10
		Type: DZ	DZ + D	DZ + D,P	EB
CH_4	$-E_{SCF}$	40.1404	40.1499	40.1657	40.2115[b]
	ΔE_{IEPA}	0.1388	0.1752	0.2118	0.2401[b]
	ΔE_{CEPA}	0.1175	0.1507	0.1843	0.2106[b]
CH_3^-	$-E_{SCF}$	39.4539	39.4605	39.4759	39.5184
	ΔE_{IEPA}	0.1602	0.1942	0.2286	0.2644
	ΔE_{CEPA}	0.1237	0.1561	0.1864	0.2185
CH_3^+	$-E_{SCF}$	39.1786	39.1884	39.2045	39.2457
	ΔE_{IEPA}	0.0964	0.1253	0.1447	0.1636
	ΔE_{CEPA}	0.0848	0.1111	0.1295	0.1472
$E_A(CH_3\cdot)$ from $\Delta E(CH_3^-/CH_4)$					
	SCF	−5.1	−6.9	−7.1	−9.2
	IEPA	+8.3	+5.1	+3.4	+6.0
	CEPA	−1.3	−3.5	−5.8	−4.3
$E_A(CH_3\cdot)$ from $\Delta E(CH_3^-/CH_3^+)$					
	SCF	−54.2	−56.2	−56.6	−55.8
	IEPA	−14.2	−12.9	−3.9	+7.5
	CEPA	−29.8	−27.9	−20.9	−11.0

[a] The energy values are given in au; the values for the electron affinities E_A are given in kcal/mol. [b] Values taken from ref 3.

lengths for the anion (1.075 Å for SCF and 1.083 Å for CEPA) and 1.086 Å for methane.[3] From the results of Table I the following can be said about the effects of basis variation and of correlation.

1. Flat Functions. For a SCF calculation of a carbanion a basis set must contain at least one flat p function. Omission of flat functions (column 1) leads not only to positive values for the orbital energy ϵ of the lone pair but also to a considerably too large value for the protonation energy. (cf. ref 6). After one flat p function is included in the basis (columns 2 and 7), the addition of further flat functions (columns 3–5 and 7–9, respectively) seems to be of little relevance for the total energy and for the protonation energy of the anion while still having considerable influence on the orbital energy ϵ.

2. Polarization Functions. For the calculation of protonation energies the inclusion of polarization functions in the basis seems to be of minor importance. Within SCF polarization functions contribute only 2–3 kcal/mol to the CH bonding energy.

3. Correlation. The contribution of electron correlation to the calculated protonation energies is fairly small (~5 kcal/mol). The influence of the basis set on this contribution is fairly complicated. Basis 1 without any flat function is inadequate also for the description of electron correlation in the anion.

Thus, inclusion of correlation even increases the too large value of the protonation energy. In most basis sets (2–6 and 10) correlation favors the anion and thus decreases the protonation energy by 3–5 kcal/mol. The correlation effect is minimal, however, in the basis sets which include one set of d functions at the carbon atom and one set of p functions at the hydrogens. It seems that the basis sets in these cases are somewhat unbalanced.

4. Extended Basis. The extended basis yields for CH_3^- a SCF energy of 39.5186 au. Duke[1] reported a slightly lower value of 39.5195 au for the planar methyl anion. The basis he used was derived from a 10.6/6 Huzinaga basis which gives a 0.0022 au lower energy for the separate atoms 11 than the 9.5/5 basis. The better description of bonding with the extended basis leads within SCF to a slightly larger value for the protonation energy as compared with the smaller basis sets.

We conclude that protonation energies of carbanions can be satisfactorily obtained with moderate basis sets. For the methyl anion the protonation energy calculated within SCF with a DZ basis including one flat function (column 2) differs less than 1 kcal/mol from the protonation energy obtained from the correlation calculation with the extended basis (column 10) (The computation time ratio of the two calculations is ~1:1000.)

Table III. IEPA and NO Calculations for the Lone Pair of CH_3^- [a]

	Structure :	Planar			Pyramidal
	Basis type :	DZ + D	DZ + D,P	DZ + D,P	DZ + D,P
	No. :	6	9A	9B	9B
$CH_3^- -E_{SCF}$		39.4605	39.4768	39.4770	39.4813
$-E_{IEPA}$		39.4837	39.5032	39.5063	39.5089
$-E_{NO}$		39.4845	39.5096	39.5163	39.5111
ΔE_{IEPA}		0.0231	0.0263	0.0293	0.0276
ΔE_{NO}		0.0240	0.0327	0.0393	0.0298
$\Delta\Delta E_{NO/IEPA}$		0.0009	0.0064	0.0100	0.0022
NO-coeff c_1		0.979	0.937	0.838	0.974
c_2		−0.199	−0.344	−0.544	−0.212
$CH_3 -E_0$		39.5072	39.5216	39.5221	39.5066
$-E_{SCF}$		39.5157	39.5285	39.5290	39.5206
$E_{NO}(CH_3^-) - E_0(CH_3)$		0.0212	0.0120	0.0058	−0.0045

[a] Basis 9A is basis 9 + p_z at hydrogen with an exponent $\eta = 0.15$; basis 9B is basis 9A + p_z at carbon ($\eta = 0.003$) and d at carbon ($\eta = 0.20$).

III. The Electron Affinity of the Methyl Radical

From our CEPA calculations with the extended basis set we obtained a value for the proton affinity of the planar methyl anion of 430 kcal/mol. Insertion of this value in eq 2 leads to a negative value for the electron affinity of the methyl radical of −4 kcal/mol. Since the pyramidal form of the methyl anion lies energetically almost 1 kcal/mol below the planar structure[3] we obtain from our calculations an estimate for the adiabatic electron affinity of the methyl radical of −3 kcal/mol.

Before we discuss this value we would like to consider an alternate procedure for the determination of the electron affinity of the methyl radical which is based on the same calculation of the methyl anion and on a closed shell CEPA calculation of the methyl cation within the same basis. The electron affinity of the radical is then easily obtained from the energy difference of the anion and the cation and the accurately known ionization potential of the methyl radical of 9.84 eV.[12] With the extended basis (optimum bond lengths of CH_3^+: 1.080 Å for SCF and 1.089 Å for CEPA) this procedure yields a negative value for the electron affinity of the methyl radical of as much as −11 kcal/mol. However, in this case we compared two systems with a different number of electrons and the correlation effect is therefore large. With SCF the calculated electron affinity would be −56 kcal/mol.

In Table II the calculated electron affinities of the methyl radical as obtained by the two procedures are compared for different basis sets. While the SCF and the CEPA values extracted from the proton affinity of the anion are fairly stable, the absolute value of electron affinity computed from difference of the total CEPA energies of the anion and the cation decreases rapidly with increasing basis size. The values clearly show how unreliable it can be to compare energies which include correlation for systems with a different number of electrons (as long as one does not use extremely large basis sets).[13] The IEPA values are an illustration of the fact that the IEPA error in the anion is considerably larger than it is in the cation and in methane (cf. section IV).

A negative value for an electron affinity cannot be of any physical relevance and must be an artifact of the method used. If an electron cannot be bound by a radical than one should get zero for the electron affinity and the wave function of the anion should represent the wave function of the radical plus a free electron (in the form of a plane wave). Our closed-shell CEPA method, however, is not able to describe such a situation properly since (a) the basis is still not extensive enough to describe a free electron in space properly; (b) single excitations are not included in our CEPA scheme.

The two factors are not important as long as the electron in the anion is bound and represented by a closed-shell state. This

was proven by us by separate calculations which included single excitations from the lone pair.

Starting from a SCF calculation of the anion we performed for the lone pair not only a IEPA calculation but also an NO calculation according to Ahlrichs and Driessler.[14] This method gives the exact solution of a two-electron problem within a given basis. The difference between the IEPA energy (E_{IEPA} in Table III) and the NO energy (E_{NO}) represents mainly the contribution of single excitations to the energy. Table III lists the results for three different basis sets. As long as the basis is small (basis 6, column 1) the contribution of single excitations is small ($\sim 10^{-3}$ au) and the CI coefficient c_1 in the NO expansion is close to one, i.e., the basis does not provide the electron with the space needed for leaving the molecule. The total energy E_{NO} is considerably above the energy of the radical E_0 which is obtained with the core orbitals of the anion.

When the basis size is increased by the inclusion of more flat functions not only the contributions of the single excitations increase but also the CI coefficient c_2 increases, i.e., the wave function no longer represents a closed-shell state but rather a radical plus an extra electron. Thus, the energy difference between E_{NO} and E_0 of the CH_3 radical decreases and should vanish for an infinite basis.

When the same calculation is performed for the pyramidal structure we find the single excitation to be of minor importance even for the large basis. The CI coefficients show that the extra electron does not want to leave the molecule. The pyramidal methyl anion seems to have a vertical ionization potential larger than zero. However, its NO energy is higher than that of the planar CH_3^-. Thus, the planar CH_3 radical could be the minimum of the hypersurface and any value for the inversion barrier of the methyl anion might therefore be an artifact of the basis used: the smaller the basis the larger the inversion barrier will be.

We conclude in agreement with some previous calculations[4,5] that the methyl anion is in fact not stable vs. the loss of an electron, i.e., the methyl radical has no or at least an extremely small electron affinity. This result is surprising for two reasons: (a) In the methyl radical a low-lying singly occupied orbital is available for acception of an additional electron. (b) The SCF orbital energy of the highest occupied orbital in the methyl anion is negative (in planar CH_3^-, −0.25 eV, in the pyramidal form, −0.64 eV). Thus, the electron is in a bound state within SCF, even though SCF overestimates electron repulsion.

Obviously, the electron repulsion overcompensates the one-particle energy of about 10 eV (i.e., the MO energy of the singly occupied MO in the CH_3 radical) which is gained if a second electron is placed into the singly occupied MO. This phenomenon can be studied in a simpler example.

Table IV. IEPA Pair Energies of the Methyl Anion (au)[g]

Type of pairs	No. of Pairs	CH$_4$[e]	CH$_3^-$[f]	CH$_3^+$
CH$_3$ unit[a]	9	0.1533	0.1406	0.1634
Intra-CH; 1p, resp[b]	1	0.0330	0.0294	
Inter-CH$_3$/CH; 1p[c]	6	0.0543	0.0943	
IEPA (total)	16	0.2401	0.2644	0.1634
CEPA (total)	16	0.2106	0.2186	0.2470
CEPA/IEPA	16	0.877	0.827	0.900
1s correlation[d]	9	0.0437	0.0437	0.0436

[a] All pairs of a CH$_3$ subunit (three intraorbital and six interorbital pairs). [b] CH intraorbital pair for CH$_4$ and the lone pair intraorbital pair for CH$_3^-$, respectively. [c] All the interorbital pairs between the CH$_3$ subunit and a CH bond or the lone pair, respectively. [d] CEPA values for the 1s1s intraorbital pair plus all interorbital pairs between 1s and the valence orbitals. The inner-shell correlation was obtained with a modified basis consisting essentially of a fully uncontracted 9.5/5 Huzinaga basis augmented with flat functions. [e] Values taken from ref 3. [f] Planar. [g] Extended basis; of column 10 of Table I.

In the case of the H atom the orbital energy is −13.6 eV. When a second electron comes in and H$^-$ is formed the net energy gain is only 0.74 eV.[15] The orbital energy in H$^-$ is −1.25 eV. When the nuclear charge of the H atom is reduced the binding energy of the second electron falls off rapidly. At $z \approx 0.91$ the second electron is no longer bound, though the SCF orbital energy is still negative (−0.50 eV)[16] and though the orbital energy in the atom is still large (−11.3 eV).

Our results are at variance with a very recent estimate of Lowe[17] for the electron affinity of the methyl radical. He concluded from the fact that the extra electron in the methyl anion is in a bound MO that the electron affinity of the methyl radical should be at least as large as the electron affinity of the carbon atom, which is 1.27 eV. However, in the carbon atom anion we have only singly occupied p orbitals with parallel spins of the three unpaired electrons. That is completely different from the situation in the methyl anion where the extra electron is in a doubly occupied p (or hybrid) MO and will therefore experience much more electron repulsion then the extra electron in C$^-$. Much better founded seems to be the purely empirical relationship between bond strengths and electron affinities of radicals proposed be Streitwieser,[6] though the value of 4 kcal/mol he estimated for the electron affinity seems still to be too high. Our results can certainly not be reconciled with older experimental values for the electron affinity of the methyl radical which were obtained by magnetron techniques.[18]

IV. Analysis of the Correlation Energy Calculations

Table IV gives an analysis of the IEPA orbital pair energy contributions of the methyl anion in comparison with methane and the methyl cation. As the table shows, the intraorbital correlation of the lone pair in the anion is smaller than the electron correlation in a normal CH bond as in methane. The interorbital contributions between the lone pair and the CH$_3$ subunit, on the other hand, are considerably larger than the corresponding contributions between CH and the CH$_3$ subunit in methane. This is a consequence of the considerable penetration of the CH bonds by the diffuse lone pair. The interorbital pairs have usually (i.e., in the basis of well-localized MOs) the largest off-diagonal elements in the full CI treatment. Hence, the IEPA error (as compared with CEPA or a total CI treatment) tends to increase with an increase of the relative contribution of interorbital pairs to the total IEPA energy. Thus, the IEPA error in CH$_3^-$ is considerably larger than in methane or in CH$_3^+$.

In our CEPA calculations all valence electrons have been included. The inner shell correlation was supposed to be constant for the different systems (CH$_3^-$, CH$_3^+$, CH$_4$). In order to check this assumption we performed a calculation of the 1s correlation energy within an appropriate basis derived from the extended basis. The results, which have also been included in Table IV, show that the 1s correlation energy is a constant within 0.1 kcal/mol for the three systems considered.

V. Higher Alkyl Anions

After we have found that the methyl anion is not a stable compound we would like to discuss the stability of higher alkyl anions. For that purpose we calculated the proton affinities of the ethyl, *n*-propyl, and isopropyl anions. The results are listed in Table V. As starting points for the structures of the anions we used the structures of the corresponding hydrocarbons with one hydrogen atom removed. Then the carbon skeleton (CC bond lengths and CCC valence angles) was optimized within SCF with the basis set no. 6 (which includes a set of d functions and a set of flat p functions at each carbon atom). The following results were obtained for the alkyl anions.

1. For the ethyl anion the optimized CC bond length of 1.544 Å is very close to the corresponding value in ethane (1.530 Å within the same basis). Most favorable is the staggered conformation. The rotational barrier is calculated (with fixed geometry) to be only 2.2 kcal/mol as compared to 3 kcal/mol in ethane. The barrier toward inversion of the C-CH$_2^-$ group is computed to be 4 kcal/mol, which is slightly more than the corresponding value of the methyl anion (3 kcal/mol within

Table V. Proton Affinities of Alkyl Anions (au)

Type of calculation:	SCF	SCF	SCF	CEPA
Type :	DZ	DZ + D	DZ + D	DZ + D
Basis no. :	2	6	6A[a]	6A[a]
CH$_4$ total energy	−40.1404	−40.1499	−40.1500	−40.3010
CH$_3^-$ [b] total energy	−39.4549	−39.4647	−39.4656	−39.6199
ϵ	−0.0193	−0.0202	−0.0210	
ΔH prot	0.6855	0.6852	0.6844	0.6811
C$_2$H$_6$ total energy	−79.1205	−79.1468	−79.1474	−79.4320
C$_2$H$_5^-$ total energy	−78.4245	−78.4517	−78.4542	−78.7430
ϵ	−0.0064	−0.0078	−0.0100	
ΔH prot	0.6960	0.6951	0.6932	0.6890
C$_3$H$_8$ total energy	−118.1023	−118.1460	−118.2472	
n-C$_3$H$_7^-$ total energy	−117.4138	−117.4574	117.4589	
ϵ	−0.0177	−0.0192	−0.0205	
ΔH prot	0.6885	0.6886	0.6883	
i-C$_3$H$_7$ total energy	−117.4053	−117.4496	−117.4541	
ϵ	−0.0071	−0.0089	−0.0128	
ΔH prot	0.6970	0.6964	0.6931	

[a] Basis 6 plus one flat s function (exponent 0.04) at each carbon atom. [b] Pyramidal.

Table VI. Heats of Fragmentation of Alkyl Anions[a]

Reaction	Method	ΔH, kcal/mol
$C_2H_5^- \rightarrow C_2H_4 + H^-$	CEPA	3.3
	SCF	3.3
$i\text{-}C_3H_7^- \rightarrow C_3H_6 + H^-$	SCF	1.6
$n\text{-}C_3H_7^- \rightarrow C_2H_4 + CH_3^-$	SCF	18.1

[a] Basis 6A of Table V was used. H^- was calculated with the same basis, except that one flat s function ($\eta = 0.04$) was included (SCF energy -0.4845; IEPA energy -0.5057).

SCF and the same basis). The proton affinity of the ethyl anion comes out to be even larger than that of the methyl anion. Thus, methyl substitution tends even to destabilize a carbanion. Hyperconjugation between the lone pair and the vicinal CH bonds seems to be of minor importance. Considering the fact that the dissociation energy of a CH bond in ethane is smaller than in methane we predict that the ethyl radical is also not capable of accepting a further electron. The calculation which includes correlation shows also for the ethyl anion that correlation has little influence on the protonation energy.

2. In the *n*-propyl anion the two CC bonds are not equivalent. According to our calculations, the α CC bond length is 1.528 Å while the β CC bond is stretched to 1.551 Å, owing to the hyperconjugation with the lone pair. The CCC angle is enlarged to 117° as compared with 112° for propane. The proton affinity, which is about 3–4 kcal/mol lower than that of the ethyl anion, is an indication that the hyperconjugation of the lone pair with a CC bond is more effective than with a CH bond. Furthermore, the orbital energy ϵ of the lone pair is lower than in the case of the ethyl (and isopropyl) anion. Preferred is the conformation with the lone pair trans to the CC bond (the cis conformation is 3 kcal/mol and the gauche conformation with the lone pair perpendicular to the CCC plane is 4 kcal/mol higher in energy). The inversion barrier of the $C\text{-}CH_2^-$ group is calculated to be 3.8 kcal/mol, which is about the same as in the ethyl anion.

3. The optimum CC bond length in the isopropyl anion is 1.527 Å. The optimum CCC angle is 108°, somewhat smaller than in propane (112°). Remarkable is the large inversion barrier of the carbanionic center of 7 kcal/mol. The proton affinity is about the same as that of the ethyl anion. Thus, the second methyl substituent at the carbanionic center had no influence on the stability of the carbanion. The isopropyl anion, however, is less stable than the *n*-propyl anion.

We conclude that methyl substitution does not stabilize the negative charge in carbanions. Hence, alkyl anions are not stable vs. the loss of an electron. The heats of fragmentation of alkyl anions are very low (Table VI). That is another consequence of the low stability of alkyl anions and is quite different from the thermal properties of the corresponding cations. While the protonation of ethylene is very exothermic ($\sim$160

kcal/mol[19]) the addition of H^- to ethylene is exothermic by only about 3 kcal/mol.

References and Notes

(1) A. J. Duke, *Chem. Phys. Lett.*, **21**, 275 (1973).
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