484 J. Am. Chem. Soc. 1983, 105, 484-488

Lithium-Stabilized Methanonium Ions, $CLi_{5-n}H_n^+$. A Theoretical Study

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Received March 24, 1982

Abstract: With the exception of CH_4Li^+, all lithiated CH_5^+ cations are indicated by ab initio molecular orbital calculations to be highly stabilized species. In agreement with the mass spectroscopic observation of these ions, all possible dissociation modes are highly endothermic. At the 3-21G level of calculation, the proton affinities of the lithiated methanes are very large, ranging from 259 kcal/mol for CH_3Li to 318 kcal/mol for CLi_4. The Li^+ cation affinity of methane is low, 9 kcal/mol, but much larger values are found for CH_3Li (52), CH_2Li_2 (77), $CHLi_3$ (87), and CLi_4 (83). Calculation on some of these species using a larger basis set and including electron correlation suggests that these values may even be underestimated. The $CLi_{5-n}H_n^+$ species, examined with regard to a number of geometrical possibilities, are found to prefer the following structures: CH_4Li^+, Ia (C_{3v}); $CH_3Li_2^+$, IIa (D_{3h}); $CH_2Li_3^+$, IIIa (C_{2v}); $CHLi_4^+$, IVa (C_{3v}); and CLi_5^+, Va (D_{3h}). Prospects for the experimental observation of these ions in condensed media are discussed.

The methanonium ion, CH_5^+, is the pentacoordinate carbocation prototype.[2,3] Although it has not been observed directly in condensed media,[2] CH_5^+ is highly stable in the gas phase.[3] Dissociation into CH_3^+ and hydrogen is endothermic by 42 ± 2 kcal/mol. How can such pentacoordinate carbonium ions best be stabilized by simple substituents? If suitable groups can be found, it might be possible to observe such ions directly in solution under suitable conditions. In this paper, we show that replacement of two or more hydrogens in CH_5^+ by lithium leads to species indicated to be highly stable thermodynamically.

This work was suggested both by our earlier theoretical studies on lithiated carbocations[4,5] and by mass spectroscopic detection of all members of the set: CH_4Li^+ (I),[6] $CH_3Li_2^+$ (II),[6,7] $CH_2Li_3^+$ (III),[7] $CHLi_4^+$ (IV),[7] and CLi_5^+ (V).[5,7,8] Recent work by Lagow[5,7] and by Wu[8] has been particularly stimulating. Prior ab initio calculations indicated that CH_4Li^+ was not very stable toward dissociation[9] but that $CH_3Li_2^+$ would require nearly 50 kcal/mol for dissociation into methyllithium and the lithium cation.[4] It thus appeared likely that the higher lithiated carbonium ions would be highly stable as well. This prediction has been verified for CLi_5^+.[5] We now report a comprehensive examination of the structures and energies of all five of the lithiated carbonium ions, I–V. The results are compared with those for the lithiated carbenium ions, CH_2Li^+, $CHLi_2^+$, and CLi_3^+, which are also highly stabilized species.[4,10]

Table I. Absolute (au) and Relative (kcal/mol) Energies

species	HF/3-21G[a,b]	rel	HF/4-31G[c]	rel
CH_4Li^+ (Ia, C_{3v})	−47.17946 (0)	0.0	−47.38709	0.0
(Ib, C_{2v})	−47.17712 (1)	1.5	−47.38476	1.5
(Ic, C_{3v})	−47.17258 (2)	4.3	−47.38051	4.1
(Id, C_{4v})	−47.01780 (3)	101.5		
$CH_3Li_2^+$ (IIa, D_{3h})	−54.02484 (0)	0.0	−54.27598	0.0
(IIb, C_s)	−54.01690 (1)	5.0	−54.26791	5.1
$CH_2Li_3^+$ (IIIa, C_{2v})	−60.83847 (0)	0.0	−61.13195	0.0
(IIIb, D_{3h})	−60.78275 (2)	35.0		
$CHLi_4^+$ (IVa, C_{3v})	−67.64683 (0)	0.0	−67.98406	0.0
(IVb, C_{2v})	−67.64239 (1)	2.8	−67.97896	3.2
(IVc, C_{4v})	−67.63057 (1)	10.2	−67.96708	10.7
CLi_5^+ (Va, D_{3h})	−74.45440 (0)	0.0	−74.83337	0.0
(Vb, C_{4v})	−74.45313 (1)	0.8	−74.83147	1.2
H_2 ($D_{\infty h}$)	−1.12296		−1.12683	
HLi ($C_{\infty v}$)	−7.92984		−7.97735	
Li_2 ($D_{\infty h}$)	−14.76925		−14.86088	
CH_4 (T_d)	−39.97688		−40.13977	
CH_3Li (C_{3v})	−46.75248		−46.96000	
CH_2Li_2 (C_{2v})	−53.52480		−53.77541	
$CHLi_3$ (C_{3v})	−60.31791		−60.61063	
CLi_4 (T_d)	−67.13154		−67.46685	
Li^+ (K_h)	−7.18709		−7.23326	
CH_3^+ (D_{3h})	−39.00913		−39.17512	
CH_2Li^+ (C_{2v})	−45.91361		−46.11907	
$CHLi_2^+$ (C_{2v})	−52.76156		−53.00844	
CLi_3^+ (D_{3h})[d]	−59.58603		−59.87562	
CH_5^+ (C_s)	−40.16056		−40.32715	

[a] Integer in parentheses gives the number of negative eigenvalues in the force constant matrix. [b] See ref 5, 10, and 25. [c] See ref 4, 5, and 10. [d] Singlet; triplet estimated to be 6–7 kcal/mol lower in energy; see ref 10.

Computational Methods. The GAUSSIAN76[11] and GAUSSIAN80[12] series of programs and standard computational procedures were used. The standard 3-21G and 4-31G (5-21G for lithium is implied) basis sets were employed to calculate geometries. Various alternative structures for the ions were examined to ensure that

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[1] (a) Erlangen. (b) Hyderabad. (c) Pittsburgh.

[2] Olah, G. A.; Klopman, G. A.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 3261.

[3] Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6119 and references cited therein. Bohme, D. K.; Mackay, G. I.; Schiff, H. I. *J. Chem. Phys.* **1980**, *73*, 4978.

[4] Jemmis, E. D.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 527.

[5] Jemmis, E. D.; Chandrasekhar, J.; Würthwein, E.-U.; Schleyer, P. v. R.; Chinn, J. W.; Landro, F. J.; Lagow, R. J.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4275.

[6] Stucky, G., private communication. See ref 4, footnote 17. Also see: Eastes, W.; Ross, U.; Thoennies, J. P. *J. Chem. Phys.* **1979**, *70*, 1652; Ellenbroek, T.; Gierz, U.; Noll, M.; Thoennies, J. P. *Ibid.* **1982**, *86*, 1153; Brown, T. L. *Ann. N.Y. Acad. Sci.* **1966**, *136*, 95.

[7] Chinn, J. W.; Gurak, J.; Landro, F. J.; Lagow, R. J., unpublished observations, 1980. Gurak, J. A.; Chinn, J. W., Jr.; Lagow, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 2637.

[8] Wu, C. H., unpublished observations, 1981. See: Wu, C. H.; Ihle, H. R. *Chem. Phys. Lett.* **1979**, *61*, 54.

[9] (a) Jemmis, E. D., unpublished calculations, 1976. (b) Boldyrev, A. I.; Charkin, O. P. *Zhur. Strukt. Khim.* **1979**, *20*, 969; *J. Struct. Chem.* **1979**, *20*, 838.

[10] Chandrasekhar, J.; Pople, J. A.; Seeger, R.; Seeger, U.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 3651 and references cited therein.

[11] Binkley, J. S.; Whiteside, R. A.; Hariharan, P.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. *QCPE* **1979**, *11*, 368.

[12] Binkley, J. S.; Whiteside, R.; Krishnan, R.; Seeger, R.; Schlegel, H. B.; DeFrees, D. J.; Pople, J. A. *QCPE* **1981**, *13*, 406. For the 3-21G basis set, see: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

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Table II. Higher Order (6-31G*//HF/3-21G) Absolute Energies (au) of CH_4Li^+ and $CH_3Li_2^+$ [a]

species	HF/6-31G*	MP2	MP3	MP4DQ	MP4SDQ
CH_4Li^+ (Ia, C_{3v})	−47.44586 (0.0)	−47.58724 (0.0)	−47.60324 (0.0)	−47.60567 (0.0)	−47.60667 (0.0)
(Ib, C_{2v})	−47.44354 (1.5)	−47.58433 (1.8)	−47.60039 (1.8)	−47.60286 (1.8)	−47.60387 (1.8)
(Ic, C_{3v})	−47.43797 (5.0)	−47.57606 (7.0)	−47.59213 (7.0)	−47.59478 (6.8)	−47.59582 (6.8)
(Id, C_{4v})	−47.29511 (94.6)	−47.45073 (85.7)	−47.46655 (85.8)	−47.46831 (86.2)	−47.46913 (86.3)
$CH_3Li_2^+$ (IIa, D_{3h})	−54.33040 (0.0)	−54.48302 (0.0)	−54.49609 (0.0)	−54.49762 (0.0)	−54.49879 (0.0)
(IIb, C_s)	−54.32575 (2.9)	−54.47621 (4.3)	−54.49003 (3.8)	−54.49204 (3.5)	−54.49338 (3.4)

[a] Relative energies (kcal/mol) are in parentheses.

Table III. 3-21G Harmonic Frequencies (cm^{-1}) (Zero-Point Energies, kcal/mol)

CH_4Li^+	$CH_3Li_2^+$	$CH_2Li_3^+$	$CHLi_4^+$	CLi_5^+
256.9 (e)	145.2 (a_2'')	161.1 (b_1)	149.4 (e)	101.9 (e')
327.3 (a_1)	205.6 (e')	226.5 (a_1)	274.6 (a_1)	304.0 (e')
1425.1 (a_1)	460.6 (a_1')	297.7 (b_2)	303.0 (e)	326.4 (a_2'')
1537.7 (e)	643.8 (a_2'')	481.4 (b_1)	522.8 (a_1)	337.4 (e'')
1727.1 (e)	829.5 (e'')	498.8 (a_1)	595.7 (e)	495.6 (a_1')
3110.7 (a_1)	1495.3 (e')	634.8 (b_2)	726.5 (e)	535.6 (a_1')
3204.0 (e)	3159.2 (a_1')	684.7 (a_1)	768.1 (a_1)	664.4 (a_2'')
3287.3 (a_1)	3315.0 (e')	778.7 (b_2)	2710.2 (a_1)	675.4 (e')
		813.2 (a_2)		
		1481.2 (a_1)		
		2897.1 (a_1)		
		2933.4 (b_1)		
(30.9)	(23.0)	(17.0)	(11.2)	(6.9)

the global energy minimum was located. In this search, the MNDO program,[13] parameterized for lithium by Thiel and Clark,[14] was helpful in locating stationary points on the potential energy hypersurface. These were then subjected to geometry optimization at the HF/3-21G and HF/4-31G ab initio levels. The HF/3-21G stationary points were characterized by diagonalizing the force constant matrix and determining the number of negative eigenvalues. True minima have no such imaginary frequencies; chemical transition structures have one. The geometry of each of the stationary points calculated at the HF/3-21G level is given in Figure 1.

Table I summarizes the energies of the species studied along with the number of imaginary frequencies found. Included in this table are the energies of other reference molecules needed for the thermodynamic evaluations summarized in Tables IV and V. Higher level calculational results are given in Table II. The 3-21G harmonic frequencies for the global minima are listed in Table III. Comparison with experimental results for a wide variety of molecules has shown that these values are approximately 11–12% too large but can serve as a guide to the experimental evaluation of these particular molecules.[12] All heats of reaction given below have been corrected for zero-point vibrational energies by using these harmonic frequencies.

Results and Discussion

Geometries and Energies. CH_4Li^+. The lithium cation–methane complex has been studied earlier.[9] At all levels, the face lithiated C_{3v} form (Ia) is the most stable, although the energetic preference over the edge- (Ib, C_{2v}) and corner-lithiated (Ic, C_{3v}) form is not large. By imposition of C_{4v} symmetry, a pyramidal geometry (Id) was also investigated. It proved to be much higher in energy.

The only minimum is Ia; Ib is a transition structure for movement of lithium from one methane face to another, while Ic and Id are higher-order stationary points.

Table II gives the energy separation of these species using the more extensive 6-31G* basis set[15] and includes the effect of electron correlation through fourth-order Møller–Plesset perturbation theory with all single, double, and quadruple excitations (MP4SDQ).[16] The geometries used for these calculations were

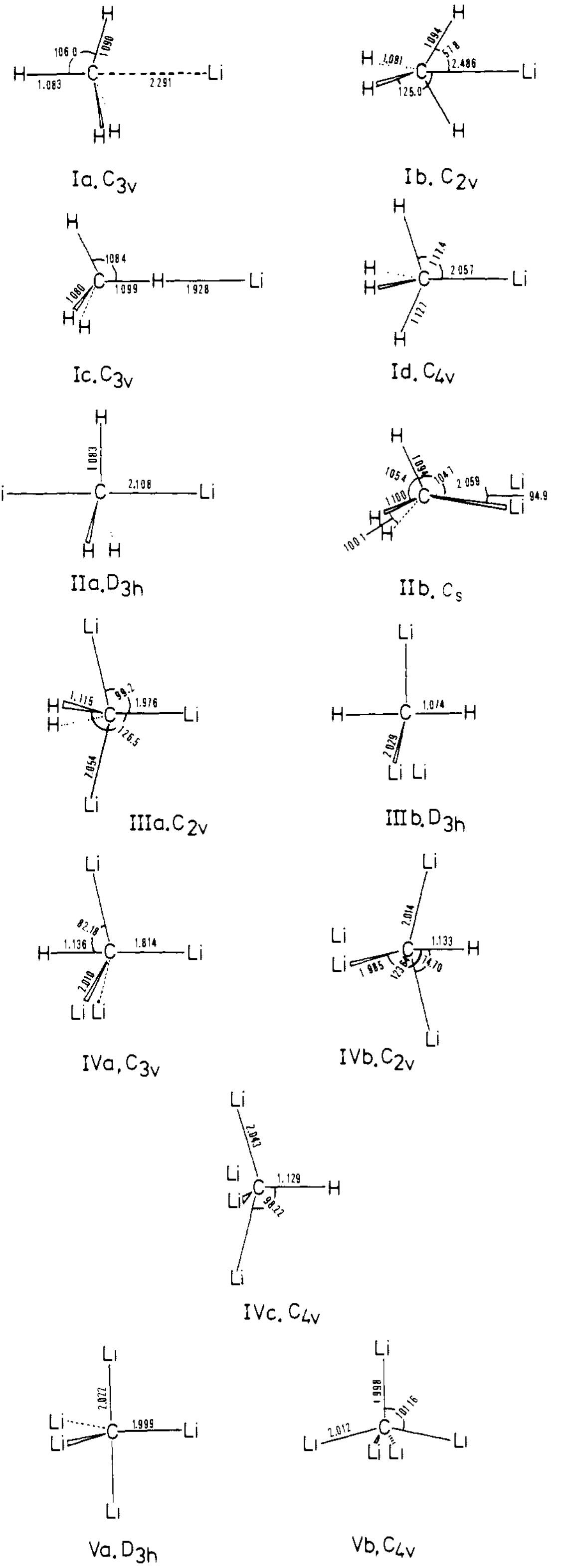

Figure 1. Geometries of the stationary points (3-21G//3-21G): bond lengths (Å), angles (deg).

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(13) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(14) Thiel, W.; Clark, T., to be published.

(15) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(16) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

Table IV. Dissociation Energies of Pentacoordinate $CLi_{5-n}H_n^+$ Ions[a] (kcal/mol)

	4-31G//4-31G (3-21G//3-21G) dissociation energies toward loss of				
ion	Li^+ (eq 1)	H^+ (eq 2)	H_2 (eq 3)	HLi (eq 4)	Li_2 (eq 5)
CH_5^+		113.3 (110.0)[b]	9.7 (13.8)[c]		
CH_4Li^+	8.0 (8.9)	259.5 (259.5)	76.7 (79.6)	141.2 (142.8)	
$CH_3Li_2^+$	51.3 (52.9)	306.0 (305.7)	80.1 (80.0)	107.8 (107.0)	148.9 (153.0)
$CH_2Li_3^+$	75.3 (77.3)	319.3 (318.9)	74.6 (74.7)	85.0 (85.3)	93.3 (95.4)
$CHLi_4^+$	86.0 (87.0)	318.7 (317.6)		76.8 (76.7)	69.6 (70.3)
CLi_5^+	82.0 (83.7)				58.1 (59.5)

[a] All values include the 3-21G zero-point correction. [b] Experimental value: 127 kcal/mol, ref 3. [c] Experimental value: 42 ± 2 kcal/mol, ref 3. For higher level theoretical results, see ref 21.

Table V. 4-31G//4-31G (3-21G//3-21G) Stabilization of Carbocations by Lithium Substitution[a] (kcal/mol)

carbenium ions	stabilization energy (eq 6)	carbonium ions	stabilization energy (eq 7)
CH_2Li^+	−76.5 (−79.6)	CH_4Li^+	−146.2 (−148.3)
$CHLi_2^+$	−118.1 (−123.0)	$CH_3Li_2^+$	−189.5 (−192.0)
CLi_3^+	−144.6 (−150.3)	$CH_2Li_3^+$	−210.2 (−214.0)
		$CHLi_4^+$	−228.3 (−232.4)
		CLi_5^+	−243.1 (−248.8)

[a] Values include the ZPE correction.

those found at the HF/3-21G level. There is good agreement in the small energy separation between the global minimum (Ia) and the C_{2v} (Ib) structures. The corner-lithiated (Ic, C_{3v}) form is found to be less stable when electron correlation is included, and the C_{4v} structure (Id) is found to be somewhat more stable than indicated by the 3-21G results, though still very high in energy (86 kcal/mol).

The various possible modes of dissociation of CH_5^+ and of the $CLi_{5-n}H_n^+$ ions are summarized by eq 1–5. The data, presented

$$CH_{5-n}Li_n^+ \rightarrow Li^+ + CH_{5-n}Li_{n-1} \quad (1)$$

$$CH_{5-n}Li_n^+ \rightarrow H^+ + CH_{4-n}Li_n \quad (2)$$

$$CH_{5-n}Li_n^+ \rightarrow H_2 + CH_{3-n}Li_n^+ \quad (3)$$

$$CH_{5-n}Li_n^+ \rightarrow HLi + CH_{4-n}Li_{n-1}^+ \quad (4)$$

$$CH_{5-n}Li_n^+ \rightarrow \rightarrow Li_2 + CH_{5-n}Li_{n-2}^+ \quad (5)$$

in Table IV, show that CH_4Li^+ (Ia) dissociates most easily into methane and the lithium cation (eq 1); this reaction, at 3-21G, is endothermic by only 8.9 kcal/mol (9.7 kcal/mol at HF/6-31G*). Including electron correlation (MP4SDQ/6-31G*) increases this value to 11.0 kcal/mol. This enthalpy loss would be compensated approximately by the entropy gained on dissociation at 20 °C. Hence, CH_4Li^+ should only be observed experimentally in the gas phase at lower temperatures.[6]

This low heat of dissociation is easily comprehended by examining the gross atomic charges obtained from a 3-21G Mulliken population analysis.[17] These atomic charges for all of the global $CLi_{5-n}H_n^+$ minima are shown in Figure 2; average atomic charges for these and other pertinent species are summarized in Table VI. The lithium atom maintains virtually a full positive charge (+0.890) in CH_4Li^+ and the C–Li bond is quite long (2.291 Å). This can be compared with a bond length of 2.003 Å in methyllithium where the lithium atom has a charge of only +0.480. For this reason, Li^+ and CH_4 are only relatively weakly associated. However, other lithium cation–saturated hydrocarbon complexes have been observed, e.g., with cyclohexane[18,19] and with isobutane.[19] The dissociation energies in these instances are considerably larger, 24 kcal/mol for the cyclohexane complex.

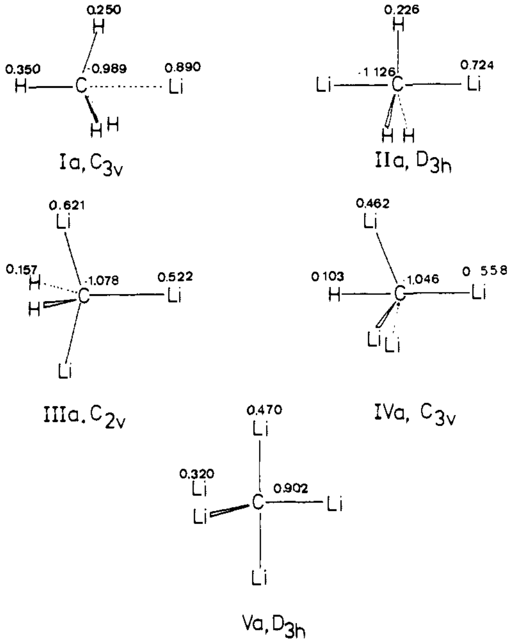

Figure 2. Atomic charges: obtained from 3-21G Mulliken population analyses.

Table VI. Atomic Charges Obtained from 3-21G//3-21G Mulliken Population Analysis

species[a]	charge (C)	charge (H)	charge (Li)
CH_5^+ (C_s)	−0.934	+0.387[b]	
CH_4Li^+ (C_{3v})	−0.989	+0.275[b]	+0.890
$CH_3Li_2^+$ (D_{3h})	−1.126	+0.226	+0.724
$CH_2Li_3^+$ (C_{2v})	−1.078	+0.157	+0.598
$CHLi_4^+$ (C_{3v})	−1.046	+0.103	+0.494
CLi_5^+ (D_{3h})	−0.902		+0.380
CH_4 (T_d)	−0.794	+0.192	
CH_3Li (C_{3v})	−0.905	+0.142	+0.480
CH_2Li_2 (C_{2v})	−0.923	+0.142	+0.320
$CHLi_3$ (C_{3v})	−0.873	+0.154	+0.239
CLi_4 (T_d)	−0.806		+0.202
CH_3^+ (D_{3h})	−0.181	+0.394	
CH_2Li^+ (C_{2v})	−0.384	+0.282	+0.820
$CHLi_2^+$ (C_{2v})[c]	−0.573	+0.197	+0.688
CLi_3^+ (D_{3h})[c]	−0.651		+0.550

[a] Lowest energy forms unless indicated. [b] Average values. [c] Singlet forms, see ref 10.

Additional energies summarized in Table IV indicate that other modes of dissociation are unfavorable. The reverse of eq 3 is the heat of hydrogenation. The value for CH_2Li^+ is 67 kcal/mol higher than that indicated for CH_3^+! Similarly, the proton affinity (eq 2) of methyllithium, 259 kcal/mol, is extremely large for a neutral molecule. The experimental proton affinity of methylamine, 214 kcal/mol, provides a comparison.[20] However, the proton affinity of the methyl anion is much larger, 416.6 kcal/mol.[20]

We have already seen that the calculated dissociation energy of CH_4Li^+ to give Li^+ and CH_4 (eq 1) increases somewhat at higher theoretical levels. Similarly, the values in Table IV for

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(17) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 1841, 2338, 2343.

(18) Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5920.

(19) Hodges, R. V.; Beauchamp, J. L. *Anal. Chem.* **1976**, *48*, 825.

(20) Bowers, M. T., Ed. *Gas Phase Ion Chem.* **1979**, *2*, 1, 87.

the endothermic dissociation of CH_5^+ are too low, by ca. 14 kcal/mol for loss of H^+ (eq 2) and by ca. 30 kcal/mol for loss of H_2 (eq 3), when compared with experiment[3] or with larger basis set calculations which include the effects of electron correlation.[21] To examine this further, we evaluated eq 2–4 for CH_4Li^+ at the MP4SDQ/6-31G** level which includes polarization functions on all atoms. The energies of eq 2–4, 271.3, 101.8, and 165.2 kcal/mol., respectively, were all higher than the Table IV values, by about 12, 24, and 23 kcal/mol. When reference data becomes available, eq 1–5 can also be evaluated with the higher level data for $CH_3Li_2^+$ in Table II.

From these results one can conclude that all of the numbers given in Table IV are probably too low.

$CH_3Li_2^+$. This ion has been considered in detail already.[4] At MP4SDQ/6-31G*//HF/3-21G, the D_{3h} geometry (IIa) is 3.4 kcal/mol more stable than the C_s alternative (IIb). In agreement with the mass spectroscopic observation of this ion, all possible dissociation modes (eq 1–5) are indicated to be very unfavorable: loss of Li^+ costs 52 and loss of H_2 80 kcal/mol. The proton affinity of CH_2Li_2, 306 kcal/mol, is even larger than that of methyllithium and approximates the value found experimentally for the iodide ion.[20] Carbonium ions with two or more lithium atoms are highly stable species thermodynamically.

$CH_2Li_3^+$. Geometry searches indicated the C_{2v} structure, IIIa, to be the most stable form of $CH_2Li_3^+$. The D_{3h} alternative, IIIb, with the two hydrogens apical and the three lithiums equatorial, was less stable by 35 kcal/mol and gave two negative eigenvalues on the force constant matrix. Other geometries based on C_s and C_{2v} symmetry converted to IIIa. The same was true of IIIb; thus, IIIa appears to be the only stable geometry on the $CH_2Li_3^+$ potential energy surface. Like IIa, IIIa has two apical lithiums in a roughly trigonal-bipyramidal structure. The third lithium occupies the equatorial position but some widening of the Li–C–Li angles results.

In general, the C–H bonds in this set of ions are strong and covalent, while the C–Li interactions have more ionic character. As a conceptual model, CH_2^{2-}, with nearly the same geometry as the CH_2 moiety in IIIa, would interact with three Li^+ cations without much structural perturbation. In a similar way, CH_3^-, which differs little in energy between D_{3h} and C_{3v} forms, would interact with two Li^+ cations. IIa is somewhat lower in energy than IIb.

$CHLi_4^+$. Three basic structures, IVa–c, for $CHLi_4^+$ were examined, but only one minimum (IVa) was found at 3-21G. Two structures were based on tetrahedral CLi_4: face protonated (C_{3v}, IVa), and edge protonated (C_{2v}, IVb). The third structure, IVc (C_{4v}), has the highest symmetry possible. The lowest energy structure at both 3-21G and 4-31G, IVa, also has roughly trigonal-bipyramidal geometry, but the single hydrogen is apical instead of equatorial. The Li–C–Li angles between equatorial and apical lithiums again are widened. The same is true in IVb, a trigonal-bipyramidal arrangement with hydrogen equatorial.

CLi_5^+. The fully lithiated methanonium ion, CLi_5^+, prefers D_{3h} symmetry (Va). This appears to be the only minimum on the potential energy surface. By imposition of C_{4v} symmetry, transition structure Vb can be calculated; it lies only 1 kcal/mol higher in energy than Va. Thus, the preferred structures of CLi_5^+, D_{3h}, and of CH_5^+, C_s, are basically different. In the latter, the preference of the three-center, two-electron CH_2 bond for a cyclic arrangement dominates. In CLi_5^+, the C-Li bonds have much more ionic character. Hence, the natural preference for AX_5 molecules to adopt D_{3h} symmetry is observed. In this pentacoordinate arrangement, the five substituent atoms are as equidistant as possible.

The trends in the dissociation energies of the lithiated methanonium ions summarized in Table IV can be easily discussed in terms of the atomic charges shown in Figure 2 and Table VI. As one proceeds along the series CH_4Li^+, $CH_3Li_2^+$, $CH_2Li_3^+$, $CHLi_4^+$, and CLi_5^+, there is a decrease in the positive charge on both the hydrogen and lithium atoms. This would require an increase in the energy necessary to remove a lithium cation or a proton. Since the charge on lithium is always greater than that on hydrogen, lithium cation loss is always easier. The energy required to dissociate into HLi or Li_2 (monomers) decreases along the same series. This reflects the relatively greater increase in stabilization of carbenium ions by additional lithium substitution. The loss of H_2, on the other hand, is nearly equally unfavorable for all three lithiated carbonium ions.

Stabilization Energies. Lithium substitution stabilizes both carbenium ions (tricoordinate) and carbonium ions (pentacoordinate) to remarkably large extents. Isodesmic reactions (eq 6 and 7) can be employed to put the comparison on a common basis.

$$CH_3^+ + nCH_3Li \rightarrow CH_{3-n}Li_n^+ + nCH_4 \qquad (6)$$

$$CH_5^+ + nCH_3Li \rightarrow CH_{5-n}Li_n^+ + nCH_4 \qquad (7)$$

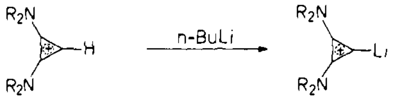
The stabilization energies, Table V, show carbonium ions to be even more favorably affected than carbenium ions; the *additional* stabilization for one, two, and three lithiums is 69.7, 71.4, and 65.6 kcal/mol, respectively. Although a leveling effect is noted, further lithiation enhances the stabilization of both types of carbocations; the magnitudes range from 41.6 kcal/mol in going from CH_2Li^+ to $CHLi_2^+$, to 14.8 kcal/mol ($CHLi_4^+$ vs. CLi_5^+). Electropositive substituents are very effective in delocalizing the positive charge by σ donation.

For calibration, the electron-deficient methyl cation is stabilized 40 kcal/mol by a methyl group and 78 kcal/mol by a NH_2 substituent.[22] These substituents are π donors. However, pentacoordinate carbonium ions have eight valence electrons and are not stabilized effectively in this manner. Thus, eq 8, evaluated

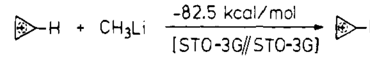
$$CH_5^+ + CH_3CH_3 \xrightarrow{-4\ \text{kcal/mol}} CH_3CH_4^+ + CH_4 \qquad (8)$$

with experimental data,[3] indicates the relatively modest stabilization afforded CH_5^+ by methyl substitution. (A second $C_2H_7^+$ isomer is 8 kcal/mol more stable, however).[3]

Prospects for Direct Observation in Condensed Phases. Since the indicated thermodynamic stabilities of IIa–Va are large, these ions might be observable in condensed phases, provided the right conditions can be found. Indeed, one lithiated carbocation has been prepared by direct hydrogen–lithium exchange in ether.[23] The stabilized cyclopropenium ion, VI, gives VII. Model calculations on the parent system (eq 9)[24] indicate that lithium stabilization of the cyclopropenium ion is almost as great as in the methyl cation (Table V). Strategies for the preparation of IIa–Va might involve either the protonation of polylithiated methane precursors or the interaction of various lithiated methanes with the lithium salts of bulky, nonnucleophilic and inert anions. Methyllithium and the higher lithiated methanes are highly associated, and the energy of protonation or lithiation must be sufficient to overcome the association energy. We have not yet



VI VII



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[21] Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A.; Radom, L. *J. Am. Chem. Soc.* **1976**, *98*, 3436. Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *Ibid.* **1981**, *103*, 5649.

[22] Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 1291. Clark, T.; Schleyer, P. v. R. *Tetrahedron Lett.* **1979**, 4641.

[23] Weiss, R.; Priesner, C.; Wolf, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 446.

[24] Clark, T., unpublished calculations. $C_3Li_3^+$ is particularly stable[9a] and will be reported subsequently.

[25] Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive", 2nd ed.; Carnegie-Mellon University Press: Pittsburgh, PA, July, 1981.

probed these energetic relationships calculationally. Nevertheless, experiments aimed at the preparation of IIa–Va in solution, in matrix isolation, or in the bulk solid phase would seem to hold considerable promise.

Acknowledgment. This work was facilitated by a NATO grant and a von Humboldt Award (to J.A.P.) and was supported at Erlangen by the Fonds der Chemischen Industrie and at Carnegie-Mellon by NSF Grant CHE-79-01061-01. We thank R. Lagow and C. H. Wu for information prior to publication and T. Clark for assistance.

Registry No. I, 73579-16-5; II, 69728-30-9; III, 83862-78-6; IV, 83862-79-7; V, 83862-80-0.

Reaction of Atomic Carbon with Ammonia. The Mechanism of Formation of Amino Acid Precursors†

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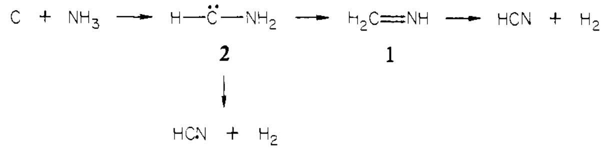
Abstract: The reactions of arc-generated carbon atoms with ammonia have been investigated. Primary reactions of C_1 are NH inserton and hydrogen abstraction. The NH insertion leads to methyleneamine (**1**) and HCN. The hydrogen abstraction proceeds in a stepwise manner to generate CH_2, which reacts with NH_3 to produce CH_3NH_2. Hydrolysis of the nonvolatile residue from this reaction produces the amino acids glycine, alanine, *N*-methylglycine, *β*-alanine, and aspartic acid. Serine is also formed when H_2O is included with the reactants. The mechanism of formation of the amino acid precursors is discussed. Labeling experiments (^2H and ^{13}C) rule out a hydrogen cyanide polymer as a major precursor to the amino acids.

In a recent preliminary communication,[1] we reported that amino acids were produced when arc-generated carbon vapor is cocondensed at −196 °C with aqueous ammonia or by the hydrolysis of the products of the reaction between carbon vapor and anhydrous ammonia.[2] In this paper, we shall discuss the primary products of the reaction of carbon with ammonia and present evidence concerning the mechanism of formation of amino acid precursors. Since carbon,[3,4] ammonia,[4] and water[5] have all been detected as extraterrestrial species, these studies may provide information concerning the mechanism of formation of extraterrestrial amino acids such as those which have been detected in meteorites[6] and lunar samples.[7]

Results and Discussion

Reactions are typically carried out by condensing gaseous reactants with carbon vapor on the walls of a reactor at −196 °C. At the conclusion of the reaction, volatile products are removed at room temperature and the residue is hydrolyzed with 6 N HCl. Treatment of the hydrolysate with acidic 1-butanol followed by trifluoroacetic anhydride forms the *N*-trifluoroacetyl *n*-butyl esters of the amino acids,[8] which are analyzed by gas chromatography–mass spectrometry (GC–MS).[9] Yields of volatile products are shown in Table I and those of the amino acids under various sets of reaction conditions are listed in table II. Total yields are on the order of 4.7% based on carbon vaporized. Amino acids that have been detected are glycine, alanine, *β*-alanine, *N*-methylglycine, and aspartic acid. When aqueous ammonia is used as a reactant, serine is also observed. While most of the products can be rationalized from the reaction of atomic carbon, acetylene has been shown to be a product of C_2 reactions.[10]

Mechanism of Formation of Glycine. Cacace and Wolf[11] have investigated the reaction of nucleogenic carbon atoms with NH_3 and have demonstrated that methyleneamine, **1**, is a primary product. The methyleneamine is undoubtedly formed by insertion of carbon into an NH bond of ammonia to generate aminomethylene, **2**, which rearranges to **1**. We find that a number of products observed in the present study may also be rationalized in terms of the intermediacy of **1**. Hydrogen cyanide, a major product, most probably arises via the decomposition of either energetic **1** or **2**. The reaction of $C(^1D)$ with NH_3 to form **1** is exothermic by 164 kcal/mol,[12] and this excess energy could be directed into the production of HCN.



$$C + NH_3 \longrightarrow \underset{\mathbf{2}}{H{-}\ddot{C}{-}NH_2} \longrightarrow \underset{\mathbf{1}}{H_2C{=}NH} \longrightarrow HCN + H_2$$

$$\mathbf{2} \longrightarrow HCN + H_2$$

Table I. Volatile Products and Their Yields in the Reaction of Carbon (88 mmol) with NH_3 (104 mmol)

product	yield, mmol
HCN	8.7×10^{-1}
C_2H_2	1.1×10^{-1}
CH_3NH_2	2.5
$CH_3C{\equiv}N$	4.6×10^{-1}

In the preliminary account of this work, we proposed that the precursor to glycine was aminoacetonitrile, **3**, which could be

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† Dedicated to Professor William von E. Doering on the occasion of his 65th birthday.

(1) Shevlin, P. B.; McPherson, D. W.; Melius, P. *J. Am. Chem. Soc.* **1981**, *103*, 7006–7007.

(2) For recent reviews of the chemistry of atomic carbon, see: (a) Skell, P. S.; Havel, J. J.; McGlinchey, M. J. *Acc. Chem. Res.* **1973**, *6*, 97–105. (b) MacKay, C. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. II, pp 1–42. (c) Shevlin, P. B. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. I, pp 1–36.

(3) Feldman, P. D.; Brune, W. H. *Astrophys. J.* **1976**, *209*, L45–L48.

(4) Keller, H. U. *Space Sci. Rev.* **1976**, *18*, 641–684.

(5) Zuckerman, B. *Nature (London)* **1977**, *268*, 491–495.

(6) Kvenvolden, K.; Lawless, J.; Pering, K.; Peterson, E.; Flores, J.; Ponnamperuma, C.; Kaplan, I. R.; Moore, C. *Nature (London)* **1970**, *228*, 923–926.

(7) (a) Fox, S. W.; Harada, K.; Hare, P. E. *Space Life Sci.* **1972**, *3*, 425–431. (b) Fox, S. W.; Harada, K.; Hare, P. E. *Geochim. Cosmochim. Acta, Suppl. 3* **1972**, *2*, 2109–2118. (c) Fox, S. W.; Hare, P. E.; Harada, K. *Subcell. Biochem.*, in press.

(8) Roach, D.; Gehrke, C. W. *J. Chromatogr.* **1969**, *44*, 268–278.

(9) Leimer, K. R.; Rice, R. H.; Gehrke, C. W. *J. Chromatogr.* **1977**, *141*, 121–144.

(10) Skell, P. S.; Harris, R. F. *J. Am. Chem. Soc.* **1966**, *88*, 5933–5934.

(11) Cacace, F.; Wolf, A. P. *J. Am. Chem. Soc.* **1965**, *87*, 5301–5308.

(12) DeFrees and Hehre (DeFrees, D. J.; Herhe, W. J. *J. Phys. Chem.* **1978**, *82*, 391–393) have determined the ΔH_f of **1** to be 26.4 ± 3.2 kcal/mol.

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