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Molecular Orbital Theory of the Electronic Structure of Molecules. 33. The Effect of α-Electropositive Substituents on the Stabilities of Carbenium Ions

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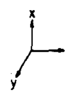
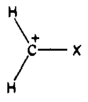
Abstract: The effect of substituents, X, on the stabilities of α-substituted methyl, ethyl, and vinyl cations is studied by standard ab initio procedures. X is varied systematically along the whole series of the first short period substituents, Li, BeH, BH_2, CH_3, NH_2, OH, and F. SiH_3 was included because of the availability of experimental evidence. It is found that electropositive substituents can be extremely effective in stabilizing carbenium ions. Lithium stabilizes the ethyl and vinyl cations even better than the best π donor, the amino group; BeH, BH_2, and SiH_3 are roughly as effective as CH_3. The methyl cation is the most sensitive to π donors, while the vinyl cation is the most sensitive to σ donors. Consequently, the α-lithiovinyl cation is more stable than the α-lithioethyl cation, and BeH is more effective than OH for the stabilization of the vinyl cation. The binding energies of the simple Lewis acids H^+, Li^+, BeH^+, BH_2^+, and CH_3^+ to the carbenes $:CH_2$, $:CHCH_3$, and $:C{=}CH_2$ follow the order: $H^+ > CH_3^+ > BH_2^+ > BeH^+ > Li^+$. The basicity sequence of the carbenes toward all these Lewis acids is $:CHCH_3 > :CH_2 > :C{=}CH_2$.

Although carbenium ions, α-substituted by metals or metalloid elements, have often been invoked in the literature,[2-4] a clear understanding of the effects of such electropositive substituents is lacking. Very little quantitative evidence exists except for silicon which is found to be deactivating relative to carbon.[5] α-Metallocarbenium ions involving Ag,[2] Rh,[3] Ru,[3] Pt,[4] and other transition metals[3] may be involved[2e] as intermediates in the catalyzed isomerization of strained hydrocarbons[2,3] and in solvolysis reactions.[4] The well known stable transition metal carbenes[6] may display "carbenium ion character" [6,7] but very few of the complexes bear a positive charge and can truly be described as α-metallocarbenium ions.[6,7] To our knowledge, our paper is the first to examine systematically (either qualitatively or quantitatively) the effect of different metals on the stabilities of simple carbenium ions in comparison with the more common nonmetallic substituents.

We use here standard ab initio procedures[8] to study the effect of substituents, X, on the stabilities of α-substituted methyl (**1**), ethyl (**2**), and vinyl (**3**) cations. X is varied along the whole series of first short period substituents, Li, BeH, BH_2, CH_3, NH_2, OH, and F. SiH_3 is also included because of the availability of experimental evidence.[5]





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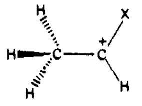

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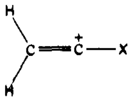

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Method

Calculations were carried out using the ab initio SCF-MO Gaussian 70 series of programs.[8] Each structure of **1** was fully optimized using the minimal RHF/STO-3G method,[9a] followed by a single calculation at the extended RHF/4-31G level.[9b,c] Standard geometries[10a,b] were assumed for **2** and **3**, but in **2** the optimized C^+-X bond length from the corresponding **1** was incorporated, and in **3** the C^+-X bond length was minimized (RHF/STO-3G). The carbenium center in **2** is taken to be trigonal with standard bond lengths based on the optimized geometry (RHF/STO-3G) of the ethyl cation ($C\text{-}C^+ = 1.49$, $C^+\text{-}H = 1.12$).[10c] In **3** the carbenium center is assumed to be linear with a $C{=}C^+$ bond length of 1.20 Å, taken from the optimized geometry (RHF/STO-3G) of the vinyl cation.[10d] Standard values[10a,b] were used for the $HC{=}C^+$ bond angle and the $H\text{-}C{=}$ bond lengths (120° and 1.08 Å, respectively). For the α-amino cations, planar arrangements around nitrogen with bond angles of 120° were used. Although this is probably not the preferred amino geometry for **1** and **2** with X = perpendicular NH_2 or for **3** with X = planar NH_2, this assumption simplifies calculation and interpretation.

Table I. Optimized Structures[a] (RHF/STO-3G) of α-Substituted Methyl Cations (**1**) and the Optimized C^+–X Bond Lengths in α-Substituted Vinyl Cations (**3**)

Substituent ($X = YH_n$)	α-Substituted methyl cations (**1**): Bond lengths, Å: C^+–Y	C^+–H	Y–H	Bond angles, deg: ∠HCY	∠CYH	∠HCYH dihedral	Optimized C–Y bond length (Å) in **3**
H	1.120[e]	1.120[e]					1.106[h]
Li	2.085	1.110		126.4			2.019
BeH	1.803	1.115	1.296	124.0	180.0		1.750
Planar BH_2[b]	1.692	1.116	1.163	122.8	115.9	180.0	1.527
Perpendicular BH_2[c]	1.562	1.115	1.170	122.6	116.9	90.0	1.647
CH_3	1.484[f]	1.115[f]	*f*	*f*	*f*	*f*	1.480[k]
Perpendicular NH_2[c]	1.392	1.127	1.024	122.0	119.7	90.0	1.283
Planar NH_2[b]	1.292	1.103	1.038	120.1	121.8	180.0	1.353
OH[d]	1.271[g]	1.114[g]	1.003[g]	*j*	114.7[g]	180.0[g]	1.270
F	1.265[h]	1.127[h]		122.7[h]			1.263
SiH_3	1.941[i]	1.113[i]	1.425[i]	123.9[i]	102.4[i]	90.0	

[a] Assuming C_{2v} symmetry for the YC^+H_2 groups in **1** and the YC^+–CH_2 group in **3**. [b] The YH_2 group and YC^+H atoms in **1** or the YC^+C atoms in **3** lie in the same plane. [c] The YH_2 group and the YC^+H or the $YC^+{=}CH_2$ atoms define two perpendicular planes. [d] In **1** the HOC^+H dihedral angle is 180°, in **3** the HOC^+ and the $={CH_2}$ atoms define two perpendicular planes. [e] D_{3h} symmetry. From ref 16c. [f] Structure with C_s symmetry. For more structural detail, see ref 16c. [g] From ref 16c. Structure with C_s symmetry. [h] From ref 16c. [i] Assuming local C_{3v} symmetry at silicon. [j] ∠COH = 114.7, ∠HCO = 123.0, with HCOH cis, ∠HCH = 12.6. [k] Fully optimized structure from ref 31.

Table II. Calculated Energies (RHF/STO-3G and RHF/4-31G) of α-Substituted Methyl (**1**), Ethyl (**2**), and Vinyl (**3**) Cations

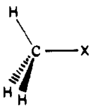
Substituent ($X = YH_n$)	Energy, hartrees: **1**[a] RHF/STO-3G	**1**[a] RHF/4-31G	**2**[b] RHF/STO-3G	**2**[b] RHF/4-31G	**3**[c] RHF/STO-3G	**3**[c] RHF/4-31G
H	−38.779 48[h]	−39.171 29[h]	−77.405 94	−78.192 57	−76.165 40[h]	−76.977 53[h]
Li	−45.619 72	−46.117 93	−84.221 05	−85.114 36	−83.029 72	− 83.950 58
BeH	−53.248 41	−53.796 94	−91.862 25	−92.806 47	−90.652 36	−91.624 68
Planar BH_2[d]	−63.739 48	−64.388 26	−102.357 20	−103.402 60	−101.164 95	−102.239 72
Perpendicular BH_2[e]	−63.769 31	−64.420 28	−102.383 58	−103.430 06	−101.133 79	−102.20631
CH_3	−77.408 06[h]	−78.194 96	−116.024 10[j]	−117.208 64[a,l]	−114.792 96[a,m]	−116.000 48[a,m]
Perpendicular NH_2[e,f]	−93.105 97	−94.129 93	−131.711 71	−133.143 42	−130.588 55	−132.025 19
Planar NH_2[d,f]	−93.234 85[h]	−94.245 19	−131.839 70	−133.246 17	−130.500 38	−131.946 07
OH[g]	−112.707 02[h]	−113.974 86[h]	−151.317 99	−152.983 35	−150.063 13	−151.752 61
F	−136.272 79[h]	−137.891 67[h]	−174.898 80[a,k]	−176.918 97[a,k]	−173.634 67	−175.669 91
SiH_3	−325.619 29[i]					

[a] Fully optimized structures (RHF/STO-3G). [b] Using standard geometries[10] incorporating the optimized C^+–X bond lengths from **1**. [c] Using standard geometries[10] and optimizing the $={C^+}$–X bond length. [d] The YH_2 group and the YC^+H atoms in **1** and **2** or the YC^+C atoms in **3** lie in the same plane. [e] The YH_2 group and the YC^+H or the $YC^+{=}C$ atoms define two perpendicular planes. [f] Using a planar arrangement around nitrogen. [g] In **1** and **2** the HOC^+H dihedral angle is 180°, in **3** the HOC^+ and the $={CH_2}$ atoms define two perpendicular planes. [h] From ref 16c. [i] Assuming C_{3v} symmetry at silicon. [j] From ref 10c. [k] From ref 16f. The calculated RHF/STO-3G energy for the standard geometry structure[10] is −174.896 28. [l] From ref 13d. [m] From ref 31.

Results and Discussion

The optimized geometries (RHF/STO-3G) of the α-substituted methyl cations (**1**) and the optimized C^+–X bond length in the vinyl cations (**3**) are given in Table I.

The total energies of **1**, **2**, and **3** using the STO-3G and the 4-31G basis sets are presented in Table II. The total energies of the corresponding neutral molecules, CH_3X (**4**), CH_3CH_2X (**5**), and $H_2C{=}CHX$ (**6**), in their most stable conformations



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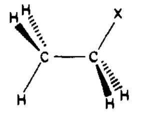

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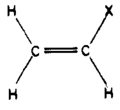

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are collected in Table III. The Mulliken[11] charge distribution (RHF/STO-3G) and the population of the formally empty $2p_\pi(C^+)$ orbital in **1** ($2p_y(C^+)$ using the axes indicated) are presented in Table IV. The net π transfer is equal to the population of the $2p_\pi(C^+)$ orbital. The σ charge transfer from X to the H_2C^+ group which is given in the last column of Table IV is calculated by subtracting the net π transfer to H_2C^+ from the total charge on X.

The stabilities of the α-substituted cations **1**, **2**, and **3** are compared with those of the parent methyl, ethyl, and vinyl cations, respectively, by means of the isodesmic reactions[12] 1, 2, and 3. The results are shown in Table V.

$$CH_2X^+ + CH_4 \rightarrow CH_3^+ + CH_3X \qquad (1)$$

$$H_3CC^+HX + CH_3CH_3 \rightarrow CH_3CH_2^+ + CH_3CH_2X \quad (2)$$

$$CH_2{=}C^+X + CH_2{=}CH_2 \rightarrow CH_2{=}C^+H + CH_2{=}CHX \qquad (3)$$

A positive energy in Table V indicates a greater stabilization in the cation than in the corresponding neutral molecule. Previous experience shows that the error in isodesmic reactions, especially with the 4-31G basis set, is generally of the order of 2-5 kcal/mol.[12,13] The agreement between the STO-3G and 4-31G results in Table V is fair except for X = Li, OH, and F where the RHF/STO-3G stabilization energies are substantially higher.[14] In the following discussion we will refer to the

Table III. Calculated Energies (RHF/STO-3G and RHF/4-31G) of Monosubstituted Methanes (**4**), Ethanes (**5**), and Ethylenes (**6**)[a]

	Energy, hartree					
	4[b]		**5**[c]		**6**[c]	
Substituent	RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G
H	−39.726 86[d]	−40.139 76[d]	−78.305 49[i]	−79.114 84[k]	−77.071 21[l]	−77.920 50[k]
Li	−46.421 59[e]	−46.959 57[h]	−84.992 73[j]	−85.926 01[h]	−83.784 03[j,m]	−84.747 03[j,m]
BeH	−54.153 21[e]	−54.732 90[h]	−92.725 23[j]	−93.701 52[h]	−91.508 03[j,n]	−92.517 16[j,n]
BH_2	−64.667 69[f]	−65.346 30[h]	−103.243 02[j]	−104.319 19[h]	−102.025 22[j,o]	−103.140 16[j,o]
CH_3	−78.306 18[d]	−79.115 82[d]	−116.885 12[j]	−118.092 11[k]	−115.656 68[l]	−116.902 03[k]
NH_2	−94.032 86[d]	−95.064 98[d]	−132.612 25[i]	−134.049 04[k]	−131.384 75[l]	−132.870 15[k]
OH	−113.549 19[d]	−114.867 16[d]	−152.129 49[i]	−153.854 11[k]	−150.908 80[l]	−152.664 22[k]
F	−137.169 06[d]	−138.856 86[d]	−175.752 12[i]	−177.841 54[k]	−174.529 41[l]	−176.646 01[k]
SiH_3	−326.511 06[g]					

[a] All molecules in their most stable conformations. [b] Fully optimized (RHF/STO-3G). [c] Standard geometries.[10] [d] From ref 16c. [e] From ref 21b. [f] From ref 21a. [g] From ref 27. [h] From ref 10b. [i] From ref 10c. [j] This study. [k] From ref 12. [l] From ref 13c. [m] The C–Li bond optimized (RHF/STO-3G) at 1.935 Å. [n] The C–Be bond was optimized (RHF/STO-3G) at 1.663 Å. [o] For the planar geometry (CCBH dihedral angle = 0°), the C–B bond was optimized (RHF/STO-3G) at 1.542 Å.

Table IV. Total Charges and Population[a] of Certain Orbitals in α-Substituted Methyl Cations (**1**)

Substituent[b] (X = YH_n)	Total Charges				Population of $2p(C^+)$	σ charge transfer to $^+CH_2$[e]
	C^+	H's on C^+	Y[c]	YH_n[d]		
H	0.225	0.516	0.258	0.258	0.0	0.258
Li	0.096	0.288	0.618	0.618	0.0	0.618
BeH	0.117	0.414	0.427	0.470	0.0	0.470
Planar BH_2	0.160	0.432	0.351	0.407	0.0	0.407
Perpendicular BH_2	0.121	0.454	0.301	0.423	0.089	0.334
CH_3	0.239	0.446	−0.206	0.316	0.314[f]	0.182
Perpendicular NH_2	0.386	0.438	−0.442	0.176	0.103	0.073
Planar NH_2	0.200	0.414	−0.282	0.386	0.576	−0.190
OH	0.284	0.450	−0.117	0.266	0.491	−0.225
F	0.390	0.512	0.098	0.098	0.348	−0.250
SiH_3	0.049	0.384	0.773	0.567	0.032	0.535

[a] Using the Mulliken population analysis.[11] [b] For geometry definitions see the corresponding footnotes in Table II. [c] The charge of the heavy atom of the substituent. [d] The total charge on the substituent (heavy atom and hydrogens bonded to it). [e] See text. [f] A population of 0.112 was reported for the standard geometry in ref 10c.

Table V. Calculated Stabilization Energies (RHF/STO-3G and RHF/4-31G) for α-Substituted Methyl, Ethyl, and Vinyl Cations[a]

	Stabilization energies, kcal/mol					
	Reaction 1		Reaction 2		Reaction 3	
Substituent	RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G
Li	91.3	79.6	80.2	69.4	95.1	91.9
BeH	26.7	20.4	22.9	17.1	31.5	31.7
Planar BH_2	12.0	6.5	8.6	3.6	28.6	26.7
Perpendicular BH_2	30.7	26.6	25.1	20.8	9.0	5.7
CH_3	30.9	29.9	24.1	22.5	25.9	25.2
Perpendicular NH_2	12.9	21.0	−0.6	10.4	68.8	61.5
Planar NH_2	93.8	93.3	79.7	74.7	13.5	11.8
OH	66.0	47.8	55.2	32.3	37.7	19.7
F	32.1	2.1	29.0	−0.2	6.9	−20.8
SiH_3	34.9					

[a] Using the energies in Tables II and III for the cations and the neutral molecules, respectively.

more reliable RHF/4-31G results except for X = SiH_3 where they are not available. The results for the three series of cations are qualitatively similar and our discussion concentrating on the substituted methyl cations (**1**) is equally applicable to **2** and **3**.

Three effects determine the ability of an α substituent to stabilize carbenium ions: σ inductive effects, lone pair π donation, and hyperconjugation. π donation has been believed to be the most effective[15,16] and is exemplified by the high barriers (e.g., 73.2 kcal/mol for rotation around the C–N bond in $C^+H_2NH_2$, Table II) and by the high Mulliken populations of the formally empty cationic 2p orbital[16d,e] (Table IV). The higher electronegativity of hydroxy and fluorine (resulting in a stronger σ withdrawal, Table IV) and their reduced π-donor abilities (see the $2p_\pi(C^+)$ population in Table IV) are responsible for their lower stabilization energies.[16b] The effect of π-donor substituents on the stability of methyl and ethyl has been analyzed extensively elsewhere[15,18] and will not be discussed further here.

Surprisingly, we find that the electropositive substituents, despite their lack of p or d electrons,[17] can be extremely effective in stabilizing carbenium ions. Lithium stabilizes the

Table VI. Calculated Dissociation Energies of the Cations **1**, **2**, and **3** to Lewis Acids X^+ and Methylene, Ethylidene, and Vinylidene, Respectively[a]

	Dissociation energies, kcal/mol					
	Reaction 5		Reaction 6		Reaction 7	
Lewis acid	RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G
H^+	255.5	227.1	273.6	244.7	236.4	204.6
Li^+	70.3	47.3	72.6	49.2	66.3	41.3
BeH^+	132.6	98.8	142.8	108.9	124.9	89.7
BH_2^{+}[b]	139.7	111.7	150.1	122.1	126.7	97.4
CH_3^+	160.8	134.5	172.4	147.3[b]	141.1	111.5

[a] The carbenes are taken as singlets; for energies see ref 16c. The energies of X^+ are from ref 33. [b] For the most stable conformation of the cation.

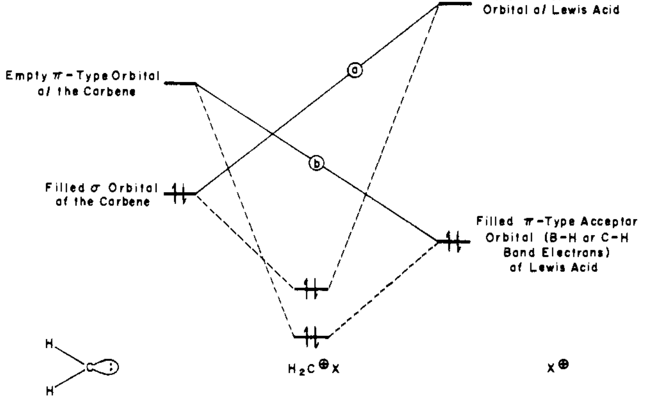

Figure 1. Schematic orbital interaction diagram between methylene and a Lewis acid X^+. The antibonding orbitals of H_2C^+X are omitted for clarity.

ethyl and vinyl cations even more than the best π donor, the amino group, and BeH is more effective than hydroxy for the vinyl cation. This large stabilization is due primarily to σ donation as indicated by the σ charge transfer of 0.618 and 0.470 electron from Li and BeH, respectively, to the CH_2 moiety; the $2p_y(C^+)$ orbital remains empty (Table IV). These cations can therefore be described as resonance hybrids, e.g., $H_2C^+\text{-}Li \leftrightarrow H_2C\text{:}\ Li^+$, where the contribution of the carbenic structure decreases with increasing electronegativity, Li > BeH > BH_2. Even with X = Li, considerable charge (+0.384) is still present on the CH_2 group showing a large contribution of the carbocationic resonance hybrid. All the cations are stable toward dissociation to X^+ and the corresponding singlet carbene. For X = Li and BeH the dissociation energies are 47.3 and 98.8 kcal/mol, respectively (see Table VI and discussion below). Based on these considerations we prefer to describe **1**, **2**, and **3** (X = Li, BeH) as carbenium ions rather than as weakly complexed metal carbenes.[18] Lithium and BeH substituents are not very practical,[20] but our results are illustrative and suggest that other electropositive groups may stabilize carbenium ions strongly.

It is interesting to note that the $Li\text{-}C^+$, $HBe\text{-}C^+$, and planar $H_2B\text{-}C^+$ bond lengths (2.085, 1.803, and 1.692 Å) are all longer than those in the corresponding neutral molecules (2.009, 1.691, and 1.570).[21a,b] This contrasts with the shortening found for X = CH_3, NH_2, OH, and F at the STO-3G level.

Hyperconjugation is chiefly responsible for stabilization provided by CH_3 and BH_2. This is shown most clearly by $C^+H_2\text{-}BH_2$ which in the perpendicular conformation allowing hyperconjugation is 20.1 kcal/mol more stable than the planar form.[21] The inductive effect in the latter leads to a stabilization of only 6.5 kcal/mol. Double hyperconjugation, i.e., between the π_{BH_2} and the $2p_y(C^+)$ orbitals and between the π_{CH_2} and the $2p_x(B)$ orbitals, results in a shortening (0.130 Å) of the C-B bond length in the perpendicular relative to the planar form.[21] For the substituted vinyl cation $CH_2{=}C^+\text{-}BH_2$, hyperconjugation between the π_{BH_2} and the $2p_x(C^+)$ orbitals and conjugation between the π_{CC} and the $2p_y(B)$ orbitals[22] operate in a similar manner to stabilize the planar form. It should be noted that α-BH_2 (in its best conformation) is only roughly comparable to α-CH_3 in its stabilizing ability, and α-BeH, which is superior to α-CH_3 in the vinyl cation, is actually inferior to α-CH_3 for the methyl and ethyl cations. A carbenium ion α substituted with a $B(OCH_3)_2$ group was recently postulated as a possible intermediate in the solvolysis[23a] and the thermal decomposition[23b] of tertiary α-chloroboronates.

Silicon is the metalloid element for which the most quantitative data on the effect of substitution on a carbocation center is available.[5] Solvolysis of $(CH_3)_3Si\text{-}C(CH_3)_2Br$ is 38 000 times slower than $(CH_3)_3C\text{-}C(CH_3)_2Br$.[5d] However, much smaller deactivating effects, relative to carbon, are found in other experiments. Thus, the Hammett-Brown σ^+ constant of p-$Si(CH_3)_3$, derived from solvolysis of p-$(CH_3)_3SiC_6H_4C(CH_3)_2Cl$, is +0.02 vs. −0.26 for p-$C(CH_3)_3$.[24] In detrimethylsilylation,[5c,25a] and in bromination-detrimethylsilylation,[25b] a p-$Si(CH_3)_3$ group is slightly activating, relative to H, but deactivating (by a factor of approximately 20-30) relative to a p-methyl substituent.

The comparison of the stabilizing effect of silyl and methyl substituents involves the energy of the isodesmic reaction 4.

$$H_3SiCH_2^+ + CH_3CH_3 \rightarrow CH_3CH_2^+ + CH_3SiH_3 \quad (4)$$

This has been studied previously by Eaborn, Feichtmayr, Horn, and Murrell.[26] Using a minimal Slater basis and assumed geometries, they obtained $\Delta E = -6.2$ kcal/mol indicating that silyl is *less* effective than methyl in stabilizing the carbenium center. This conclusion was reinforced[26] by the addition of d functions on silicon, which changed ΔE to −16.0 kcal/mol.

Our investigation goes somewhat further than that of Eaborn et al. in that we have carried a partial geometry optimization of $H_3SiCH_2^+$ at the RHF/STO-3G level (Table I). This led to a sharp increase in the $C^+\text{-}Si$ distance from 1.866 Å in methylsilane[27] to 1.941 Å in the ion. This parallels the long bonds to C^+ noted above for other electropositive groups. If optimized geometries are used for all species in (4), the RHF/STO-3G value for ΔE is +4.0 kcal/mol, indicating that silyl is *more* effective than methyl. If a single set of d functions is added to the silicon basis (STO-3G*),[27,28] this changes only slightly to $\Delta E = +2.2$ kcal/mol. Thus, it appears that silyl is somewhat more stabilizing than methyl if $C^+\text{-}X$ bond lengths are optimized. The slower solvolysis of $(CH_3)_3Si\text{-}C(CH_3)_2Br$ relative to $(CH_3)_3C\text{-}C(CH_3)_2Br$[5] may be due, at least in part, to solvation or ground state effects and not just to stability differences between α-silyl and α-alkyl carbenium ions.

The comparison of SiH_3 and CH_3 in the stabilization of a cationic center (RHFSTO-3G) indicates a stronger inductive but a weaker hyperconjugative effect. The population (Table IV) of the 2p(C^+) orbital in $H_3CCH_2^+$ (0.134 electron) is much higher than in $H_3SiCH_2^+$ (0.032 electron) indicating greater hyperconjugative electron donation from the CH_3 than the SiH_3 group.[29] The H_3Si-C^+ bond is 0.46 Å longer than the H_3C-C^+ bond, and this should affect the degree of orbital overlap. The inductive σ donation by the α-SiH_3 group is, however, much higher (0.535 vs. 0.182 for SiH_3 and CH_3, respectively, Table IV).

Comparing the three series of carbenium ions, **1-3**, we find that the methyl cation is the most sensitive to π donors, while the vinyl cation is the most sensitive to σ donors. Thus, fluorine has the strongest destabilizing effect and lithium exerts the strongest stabilizing effect in the vinylic series. This higher sensitivity to the inductive effect[30] results in the unexpected result that an α-hydroxy substituent is less effective than methyl in stabilizing the vinyl cation and fluorine is highly destabilizing even relative to hydrogen. The ethyl cation is 15 kcal/mol more stable than the vinyl cation[31] and the energy gap between the two series is even larger for the hydroxy and fluorine substituents. This gap is reduced by electropositive substituents; the α-lithiovinyl cation is more stable than the α-lithioethyl cation.

Interaction of Lewis Acids with Carbenes

In relation to recent ICR studies[32] and as part of a general study[21b,33] of the interaction of simple charged Lewis acids (e.g., H^+, Li^+, BeH^+, BH_2^+, and CH_3^+) with different bases we report here their interaction with several carbenes. The dissociation energies of H^+, Li^+, BeH^+, BH_2^+, and CH_3^+ to methylene, ethylidene, and vinylidene are given by reactions 5, 6, and 7, respectively, and the calculated values are presented in Table VI. The dissociation of the cations is assumed to proceed with spin conservation so that singlet carbenes are formed. This assumption has computational advantages as the problems associated with the comparison of molecules with different multiplicities are avoided.[34]

$$^{+}CH_2X \rightarrow H_2C{:} + X^+ \tag{5}$$

$$CH_3C^{+}HX \rightarrow H_3CCH{:} + X^+ \tag{6}$$

$$H_2C{=}C^{+}X \rightarrow H_2C{=}C{:} + X^+ \tag{7}$$

The acid-base interaction can be described as involving the empty orbital of X^+ and the lone pair electrons of the carbene (Figure 1, interaction a). With hydrogen[33] as the Lewis base the calculated acidity order is: $H^+ > CH_3^+ > BeH^+ > BH_2^+ > Li^+$. This order was rationalized in terms of the nature of the acid's vacant orbital and the electronegativity of the central atom.[33]

A different acidity order is found here (Table VI), $H^+ > CH_3^+ > BH_2^+ > BeH^+ > Li^+$. In particular, BH_2^+, which is a very weak acid toward H_2, is a rather strong acid toward carbenes. The different order exhibited here is due primarily to the presence of a low lying empty 2p orbital in the carbene base. This makes hyperconjugation possible if the Lewis acid has available filled π_{XH_2} orbitals such as those of BH or CH bonds (interaction b of Figure 1). Thus BH_2^+ becomes a stronger acid than BeH^+, since it can adopt a conformation in which hyperconjugation can occur.

It should be emphasized that the best calculations performed on these systems are only at the RHF/4-31G level. The earlier work[33] on H_2 as a base shows that absolute values of such binding energies are changed considerably if polarization functions and correlation corrections are added. However, the RHF/4-31G method did give the same acidity order as the most sophisticated level used.[33]

The basicities of the carbenes toward all the Lewis acids investigated here follows the order: $H_3CCH{:} > H_2C{:} > H_2C{=}C{:}$. The lower basicity of vinylidene relative to methylene may be due to the fact that the lone pair electrons in the former are in an sp orbital which is lower in energy than the sp^2 orbital in methylene. Thus, interaction a (Figure 1) is weaker in vinylidene. Inductive donation by the methyl and a better dispersal of the positive charge in the cation are features contributing to the higher basicity of ethylidene.

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Molecular Orbitals from Group Orbitals. 3. Quantitative Perturbational Molecular Orbital Analysis of ab Initio SCF–MO Wave Functions[1]

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Abstract: The use of qualitative perturbational molecular orbital (PMO) methods to interpret or predict the results of ab initio SCF–MO calculations has become common. However, because quantitative definitions of fragment orbitals and a rigorous PMO formalism within the framework of SCF–MO theory have not existed, it has not been possible to analyze quantitatively the results of SCF–MO computations in terms of interactions between molecular fragments. In the present work, both the PMO formalism and a quantitative definition of fragment orbitals have been developed within the framework of SCF–MO theory. These developments permit a quantitative PMO analysis to be performed which is as rigorous as the SCF–MO calculation itself. Alternative methods also exist for the description of the interactions between molecular fragments. One of these, discussed in the present work, involves an energy partitioning and population analysis in terms of fragment orbitals. To illustrate these various procedures, computations are reported on two problems of current interest, viz., rotation in ethane and in propylene.

The capabilities of theoretical organic chemistry have expanded greatly in recent years. Two developments, especially, are responsible. The first is the discovery of the Woodward–Hoffmann rules,[2] which has focused attention upon the frontier[3] and perturbational molecular orbital (PMO) methods[4] for the analysis of chemical reactions. The second is the increasing accessibility of well documented computer programs[5] and associated technology, which allow nonempirical SCF–MO computations to be performed on systems of reasonable size and chemical interest. It is now well established that ab initio calculations within the Hartree–Fock approximation reproduce faithfully the static and dynamic stereochemical properties of all classes of molecular systems.[6]

In its original formulation,[4] the PMO method was founded upon the hypothesis that the reaction of a system A with another system B to form a new system AB can be rationalized in terms of the mutual perturbations of the *molecular* orbitals of A and B. Subsequently,[1,7] the method was extended to the treatment of conformational problems, the assumption being made that the stable structure of a molecule can be regarded as the result of a chemical reaction (or orbital interaction) between the different functional groups into which the molecule can be dissected conceptually. The advantage of such an approach is that the description of the total electronic structure of a molecule is simplified considerably if the molecule can be treated as two or more assemblies of atoms, i.e., functional groups, rather than individual atoms.[8] The latter forms the basis of the LCAO–MO formalism. The approach has been justified by the observation that a molecular fragment is a near-transferable quantum mechanical entity.[7a,9]

Although the PMO formalism requires a definition of the orbitals of the interacting moieties regardless of the nature of the problem, there are some fundamental differences between the analysis of a chemical reaction and the analysis of a con-