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STABILIZATION OF METHYL CATIONS BY SECOND ROW SUBSTITUENTS

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Abstract. With the exception of PH_2 (*vs*. NH_2) all second row substituents, Na, MgH, AlH_2, SiH_3, SH and Cl, stabilize methyl cations more effectively than their first row counterparts.

The effect of PH_2, SH, and Cl substituents on the stability of methyl cations have been compared with NH_2, OH, and F.[1-3] The same is true of SiH_3 *vs*. CH_3.[4] The effects of the more electropositive elements of the second row have not yet been considered. We have therefore carried out an *ab initio* study of the CH_2X^+ cations, where X = Na, MgH and AlH_2. In order to obtain a complete picture at a uniform level of theory and to estimate stabilization energies not considered earlier,[1-3] we have included all second row substituents. This complements a similar study involving first row groups.[4] Calculations were performed using the Gaussian 70[5] and Gaussian 76[6] series of programs with full geometry optimization[7] at both the minimal STO-3G[8] and STO-3G*[9] basis set levels. The latter includes a set of d-orbitals on the second row atoms. These calculations are designated STO-3G//STO-3G and STO-3G*//STO-3G*, respectively. The results are presented in the Table.

The three effects contributing to the stabilization energies (defined in the Table, footnote a), σ-donation, π-donation, and hyperconjugation, have been discussed for substituents of the first period[4] so that we can now compare first and second row substituent effects directly within this interprative framework.

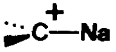
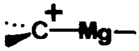
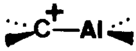
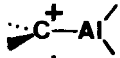
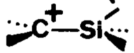
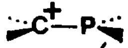
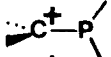
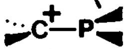
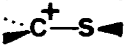
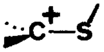
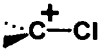
σ-Donation: All elements of the second period of eight, except chlorine, are more electropositive than carbon.[10] The sigma stabilizing effect[4] is therefore superimposed on the other stabilizing factors for most of the second row substituents. Surprisingly, the sigma stabilization in CH_2Na^+ (130 to 140 kcal mol^{-1}) is larger than that in CH_2Li^+ (91.3 kcal mol^{-1} at STO-3G),[4] despite the similar electronegativities of these metals.[10] MgH and AlH_2 (STO-3G stabilization energies 75 and 56 kcal mol^{-1}, respectively) are better able to stabilize the cationic center than are BeH and BH_2 (26.7 and 30.7 kcal mol^{-1}, respectively)[4]; the second row elements are more electropositive. SiH_3 similarly is 4 kcal mol^{1} more effective than CH_3 (STO-3G).[4] The large stabilization energies found for CH_2Na^+ and CH_2MgH^+ have important consequences. We have recently proposed that lithiomethyl cation, CH_2Li^+, and its derivatives may be intermediates in the reaction of lithium carbenoids.[11] The high thermodynamic stability of the sodium and magnesium metallo-carbenium ions suggests that carbenoids involving these metals may react similarly.

Hyperconjugation: The rotation barrier in $CH_2AlH_2^+$ is calculated to be 5.4 kcal mol^{-1} at STO-3G and 4.8 kcal mol^{-1} at STO-3G*. The STO-3G barrier for $CH_2BH_2^+$ is 18.7 kcal mol^{-1}.[4] Hyperconjugative electron donation, which only takes place in the perpendicular form, is therefore a great deal weaker for AlH bonds than for BH. The greater length of the CAl bond and the polarization of the AlH bonds towards H serve to weaken the hyperconjugative effect. Similarly, CH_3 hyperconjugates better than SiH_3.[4] In general, second row substituents should not hyperconjugate as well as their first row analogs.

π-Donation: Bernardi *et al.*[2] have observed the order of π-donation to CH_2^+ center to be $P > S \geqslant N > O > Cl > F$. Our calculations agree, but also point out other factors which affect the overall stabilization of CH_2X^+ ions. PH_2 is clearly a very strong π-donor; the rotation barrier from the all-planar $CH_2PH_2^+$ to the C_{2v} perpendicular form, with the C-PH_2 moiety held planar, is 97.6 kcal mol^{-1} at STO-3G, and 115.9 kcal mol^{-1} at STO-3G*. This corresponds closely to the π-stabilization energy. The energy difference between the perpendicular C_{2v} species and the C_s form, in which the PH_2 group is allowed to pyramidalize, is, however, 71.2 kcal mol^{-1} (STO-3G; 90.1 kcal mol^{-1} at STO-3G*).[12] The energy required to make the C-PH_2 moiety planar reduces the effective π-stabilization. PH_2 is therefore actually a weaker stabilizing group than NH_2 (stabilization energies 93.4[4] (STO-3G) and 55-62 kcal mol^{-1} for $CH_2NH_2^+$ and $CH_2PH_2^+$ respectively) despite its inherently superior π-donating ability. Experimentally, stabilization by a $N(CH_3)_2$ group is 27 kcal mol^{-1} better than by $P(CH_3)_2$.[13] The rotation barrier in CH_2SH^+ is calculated to be 44.8 (STO-3G), 53.8 (STO-3G* and 36.5[1] (4-31G) kcal mol^{-1}, the stabilization energy for the planar form (67.6 (STO-3G) or 84.4 (STO-3G*) kcal mol^{-1}) is somewhat larger than that (66.0 kcal mol^{-1}(STO-3G))[4] obtained for CH_2OH^+. This confirms SH to be a better π-donor than OH to CH_2^+.[1-3] The experimental stabilization energies are OH = 60 kcal mol^{-1} and SH = 64 kcal mol^{-1}.[13] As with CH_2F^+,[9] the results for CH_2Cl^+ are likely to be unreliable using minimal basis sets, so that conclusions as to the relative π-donor strengths of the two halogens are uncertain at the theoretical levels employed here. The experimental values are 26 kcal mol^{-1} and 32 kcal mol^{-1} for F and Cl, respectively.[13]

Binding Energies: As for the first row groups,[4] the binding energies (see Table, footnote b) of electropositive substituents are high, so that $NaCH_2^+$, $HMgCH_2^+$, $H_2AlCH_2^+$ are better regarded as metallocarbenium ions, rather than carbene complexes ($CH_2\colon \rightarrow M^+$). The C-Si bond in $H_3SiCH_2^+$ is indicated to be very strong. This ion and its much more stable isomer, $CH_3SiH_2^+$, have been discussed previously.[4,14]

Table: TOTAL ENERGIES (a.u.), STABILIZATION ENERGIES (ΔH_{stab}), AND BINDING ENERGIES FOR CH_2X^+ CATIONS.

	STO-3G//STO-3G			STO-3G*//STO-3G*		
Ion and Geometry	Total Energy	ΔH_{stab}[a,c]	Binding Energy[b]	Total Energy	ΔH_{stab}[a,c]	Binding Energy[b,d]
	-198.21635	-140.0	-37.3	-198.21925	-133.9	-39.1
	-236.00020	-75.0	-71.6	-236.00452	-64.3	-72.8
	-278.46359	-50.2	-71.0	-278.49399	-48.1	-81.3
	-278.47215	-55.5	-76.4	-278.50158	-52.9	-86.0
	-325.61965	-34.7	-100.6	-325.67700	-33.2	-109.4
	-376.36560	-55.9	-	-376.42573	-61.2	-
	-376.21010	+41.7	-	-376.24106	+54.7	-
	-376.32361	-29.6	-	-376.38459	-35.4	-
	-432.0639	-67.6	-	-432.11621	-84.4	-
	-431.98497	-22.8	-	-432.03042	-30.6	-
	-492.78345	-4.8	-	-492.82584	-20.1	-

[a] The energy (kcal mol^{-1}) for the reaction $CH_3^+ + CH_3X \rightarrow XCH_2^+ + CH_4$.

[b] The energy (kcal mol^{-1}) for the reaction CH_2 (singlet) + $X^+ \rightarrow XCH_2^+$.

[c] STO-3G//STO-3G and STO-3G*//STO-3G* energies for CH_3X are taken from ref. 9 and from T.W. Bentley, J. Chandrasekhar and P. v. R. Schleyer, unpublished.

[d] STO-3G//STO-3G and STO-3G*//STO-3G* energies for X^+ are: Na^+ -159.78462 and -159.78462, MgH^+ -197.51377 and -197.51626, AlH_2^+ -239.08706 and -239.99215 SiH_3^+ -287.08706[14] and -287.13043.

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References

1. F. Bernardi, I. G. Csizmadia, H. B. Schlegel, and S. Wolfe, Can. J. Chem., 53, 1144 (1975).
2. F. Bernardi, I. G. Csizmadia, and N. D. Epiotis, Tetrahedron, 31, 3085 (1975).
3. F. Bernardi, A. Mangini, N. D. Epiotis, J. R. Larson, and S. Shaik, J. Am. Chem. Soc., 99, 7465 (1977).
4. Y. Apeloig, P. v. R. Schleyer, and J. A. Pople, J. Am. Chem. Soc., 99, 1291 (1977).
5. W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, QCPE Program No. 236 Indiana University, Bloomington, Indiana (1973).
6. J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, QCPE Program No. 368, Indiana University, Bloomington, Indiana (1979).
7. The STO-3G and STO-3G* optimum geometries for the CH_2X^+ ions are available from the authors, and will be published subsequently.
8. W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys., 51, 2769 (1970).
9. J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, J. Chem. Phys., 64, 5142 (1976).
10. See F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", third edition, Wiley-Interscience, New York, 1972, p. 115.
11. T. Clark and P. v. R. Schleyer, J. C. S. Chem. Comm., in press.
12. For a discussion of inversion barriers in AH_3 molecules see W. Cherry and N. D. Epiotis, J. Am. Chem. Soc., 98, 1135 (1976).
13. R. W. Taft, R. H. Martin and F. W. Lampe, J. Am. Chem. Soc., 87 2490 (1965)
14. Y. Apeloig and P. v. R. Schleyer, Tetrahedron Lett., 4647 (1977).

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