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Ylide Dications: An Examination of First- and Second-Row Systems[1]

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Abstract: Ab initio molecular orbital calculations using split-valence plus polarization basis sets and incorporating electron correlation have been used to examine the ylide dications CH_2XH^{2+} and their conventional isomers CH_3X^{2+} (X = NH_2, OH, F, PH_2, SH, and Cl). Although highly exothermic fragmentation processes exist for the ylide dications, the barriers for such dissociations are calculated to be substantial. The ylide dications lie in relatively deep potential wells and are predicted to be observable species. In contrast, the more conventional CH_3X^{2+} dications are found to have little or no barrier to dissociation and/or rearrangement. Calculated ionization energies are compared with Q_{min} values recently reported from charge-stripping experiments.

It is well-known that simple ylides (CH_2XH) are not particularly stable species and generally lie considerably higher in energy than their conventional isomers (CH_3X).[3,4] In contrast, it has recently been found that *ylidions*[5] ($CH_2XH^{\bullet+}$), which represent examples of *distonic*[6] radical cations (species in which the charge and radical sites are formally separated), are generally quite stable and frequently lie lower in energy than their conventional isomers ($CH_3X^{\bullet+}$). For example, the methyleneoxonium radical cation ($CH_2OH_2^{\bullet+}$) is found[7a–c] to be substantially more stable than the methanol radical cation ($CH_3OH^{\bullet+}$) (by 45 (theory)[7a] or 29 (experimental)[7c] kJ mol^{-1}). We have found[8] that a continuation of this trend accompanies further ionization. Thus, whereas the methyleneoxonium dication ($CH_2OH_2^{2+}$) lies in a deep potential well, the methanol dication (CH_3OH^{2+}) is not a stable entity, consistent with experimental results.[9]

In this paper, we explore the generality of the above results through calculations on the *ylide dications* (CH_2XH^{2+}) and their conventional isomers (CH_3X^{2+}) for a variety of first- and second-row substituents (X = NH_2, OH, F, PH_2, SH, and Cl).[10]

Although gas-phase dications were originally regarded as a curiosity and only observed incidentally in the course of normal mass spectrometric and collisional-activation studies, there has been considerable recent interest in such species.[11,12] This has arisen to a large extent through advances in experimental techniques which are designed specifically for the study of dications and which utilize charge-stripping,[13] double-charge-transfer,[14] photon double ionization,[15] and Auger[16] processes.

Method and Results

Standard ab initio molecular orbital calculations were carried out using modified versions[17,18] of the Gaussian 80[19] and Gaussian

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(3) See, for example: (a) Mitchell, D. J.; Wolfe, S.; Schlegel, H. B. *Can. J. Chem.* **1981**, *59*, 3280. (b) Pople, J. A.; Raghavachari, K.; Frisch, M. J.; Binkley, J. S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 6389. (c) Dixon, D. A.; Dunning, T. H.; Eades, R. A.; Gassman, P. G. *J. Am. Chem. Soc.* **1983**, *105*, 7011.

(4) For an excellent review of ylide chemistry, see: Morris, D. G. *Surv. Prog. Chem.* **1983**, *10*, 189.

(5) For recent reviews dealing with ylidions, see: (a) Radom, L.; Bouma, W. J.; Nobes, R. H.; Yates, B. F. *Pure Appl. Chem.* **1984**, *56*, 1831. (b) Schwarz, H. *Shitsuryo Bunseki* **1984**, *32*, 3.

(6) Defined in: (a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805. For a comprehensive bibliography, see: (b) Yates, B. F.; Bouma, W. J.; Radom, L. *Tetrahedron*, in press. Recent references include: (c) Wesdemiotis, C.; Danis, P. O.; Feng, R.; Tso, J.; McLafferty, F. W. *J. Am. Chem. Soc.* **1985**, *107*, 8059. (d) Burgers, P. C.; Holmes, J. L.; Terlouw, J. K.; van Baar, B. *Org. Mass Spectrom.* **1985**, *20*, 202. (e) Hammerum, S.; Ingemann, S.; Nibbering, N. *Org. Mass Spectrom.* **1985**, *20*, 314. (f) Sack, T. M.; Cerny, R. L.; Gross, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 4562.

(7) (a) Bouma, W. J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2929. (b) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2930. (c) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *J. Am. Chem. Soc*, **1982**, *104*, 2931. (d) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.*, in press.

(8) Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 5484.

(9) (a) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 2931. (b) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *Can. J. Chem.* **1983**, *61*, 2305. (c) Maquin, F.; Stahl, D.; Sawaryn, A.; Schleyer, P. v. R.; Koch, W.; Frenking, G.; Schwarz, H. *J. Chem. Soc., Chem. Commun.* **1984**, 504.

(10) We note that an extension of the first-row substituents to include X = CH_3 would give rise to the $C_2H_6^{2+}$ species, for which it is well established that the global minumum corresponds to an ylide dication with a $CH_2CH_4^{2+}$ structure. See: (a) Schleyer, P. v. R.; Kos, A. J.; Pople, J. A.; Balaban, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 3771. (b) Lammertsma, K.; Olah, G. A.; Barzaghi, M.; Simonetta, M. *J. Am. Chem. Soc.* **1982**, *104*, 6851.

(11) For leading recent references to experimental studies, see: (a) Hanner, A. W.; Abbey, L. E.; Bostwick, D. E.; Burgess, E. M.; Moran, T. F. *Org. Mass Spectrom.* **1982**, *17*, 19. (b) Rabrenovic, M.; Proctor, C. J.; Ast, T.; Herbert, C. G.; Brenton, A. G.; Beynon, J. H. *J. Phys. Chem.* **1983**, *87*, 3305. (c) Rye, R. R.; Houston, J. E. *J. Chem. Phys.* **1983**, *78*, 4321. (d) Brehm, B.; Fröbe, U.; Neitzke, H.-P. *Int. J. Mass Spectrom. Ion Processes* **1984**, *57*, 91. (e) Kingston, R. G.; Guilhaus, M.; Brenton, A. G.; Beynon, J. H. *Org. Mass Spectrom.* **1985**, *20*, 406. (f) Fournier, P. G.; Fournier, J.; Salama, F.; Richardson, P. J.; Eland, J. H. D. *J. Chem. Phys.* **1985**, *83*, 241. (g) Koch, W.; Schwarz, H.; Maquin, F.; Stahl, D. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 305. (h) Koch, W.; Maquin, F.; Stahl, D.; Schwarz, H. *Chimia* **1985**, *39*, 376. (i) Lablanquie, P.; Nenner, I.; Millie, P.; Morin, P.; Eland, J. H. D.; Hubin-Franskin, M. J.; Delwiche, J. *J. Chem. Phys.* **1985**, *82*, 2951. (j) Samson, J. A. R.; Masuoka, T.; Pareek, P. N. *J. Chem. Phys.* **1985**, *83*, 5531. (k) Dujardin, G.; Winkoun, D. *J. Chem. Phys.* **1985**, *83*, 6222. (l) Mathur, D.; Badrinathan, C.; Rajgara, F. A.; Raheja, U. T. *Chem. Phys.* **1986**, *103*, 447. (m) Burdick, G. W.; Appling, J. R.; Moran, T. F. *J. Phys. B* **1986**, *19*, 629.

(12) For leading references to theoretical studies, see ref 8 and 11h and: (a) Lammertsma, K.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 7. (b) Koch, W.; Maquin, F.; Schwarz, H.; Stahl, D. *J. Am. Chem. Soc.* **1985**, *107*, 2256.

(13) (a) Higgins, W.; Jennings, K. R. *J. Chem. Soc., Chem. Commun.* **1965**, 99. (b) Beynon, J. H.; Fontaine, A. E. *Ibid* **1966**, 717. For leading recent references, see: (c) Ast, T. *Adv. Mass Spectrom.* **1980**, *8*, 555. (d) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77. (e) Kingston, E. E.; Brenton, A. G.; Beynon, J. H.; Flammang, R.; Maquestiau, A. *Int. J. Mass Spectrom. Ion Processes* **1984**, *62*, 317. (f) Guilhaus, M.; Boyd, R. K.; Brenton, A. G.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 209. (g) Kingston, E. E.; Beynon, J. H.; Ast, T.; Flammang, R.; Maquestiau, A. *Org. Mass Spectrom.* **1985**, *20*, 546.

(14) See ref 13d and: (a) Appell, J.; Durup, J.; Fehsenfeld, F. C.; Fournier, P. *J. Phys. B* **1973**, *6*, 197. (b) Cooks, R. G.; Ast, T.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *11*, 490.

(15) (a) Tsai, B. P.; Eland, J. H. D. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 143. (b) Cosby, P. C.; Moller, R.; Helm, H. *Phys. Rev. A* **1983**, *28*, 766. (c) Curtis, D. M.; Eland, J. H. D. *Int. J. Mass Spectrom. Ion Phys.* **1985**, *63*, 241. (d) Dujardin, G.; Winkoun, D.; Leach, S. *Phys. Rev. A* **1985**, *31*, 3027.

(16) (a) Stalherm, D.; Cliff, B.; Hillig, H.; Melhorn, W. *Z. Naturforsch., A: Astrophys. Phys. Chem.* **1969**, *24*, 1728. (b) Spohr, R.; Bergmark, T.; Magnusson, N.; Werme, L. O.; Nordling, C.; Siegbahn, K. *Phys. Scr.* **1970**, *2*, 31. (c) Moddeman, W. E.; Carlson, T. A.; Krause, O.; Pullen, B. P. *J. Chem. Phys.* **1971**, *55*, 2317. For leading references, see: (d) Netzer, F. P.; Mathew, J. A. D. *J. Electron Spectrosc. Relat. Phenom.* **1979**, *16*, 359. (e) Jennison, D. R. *Phys. Rev. A* **1981**, *23*, 1215. (f) Thomson, M.; Baker, M. D.; Christie, A.; Tyson, J. F. *Auger Electron Spectroscopy*; Wiley: New York, 1985.

(17) Farnell, L.; Nobes, R. H.; Poppinger, D.; Yates, B. F., unpublished results.

(18) Baker, J.; Nobes, R. H.; Poppinger, D., unpublished results.

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Table I. Calculated Total Energies[a] (Hartrees) and Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1}) for First-Row Systems

	HF/3-21G[b]	HF/6-31G*	HF/6-31G**	MP2/6-31G**	MP3/6-31G**	ZPVE[b]
$CH_2NH_3^{2+}$, **1a**	−93.841 67	−94.360 88	−94.376 50	−94.653 36	−94.678 17	172.7
TS(**1a** $\rightarrow CH_2^{\cdot+} + NH_3^{\cdot+}$), **4a**	−93.760 92	−94.271 89	−94.287 60	−94.527 08	−94.557 96	152.0
TS(**1a** $\rightarrow CH_2NH_2^+ + H^+$), **5a**	−93.718 13	−94.238 69	−94.250 09	−94.544 29	−94.562 39	154.3
NH_2^+ ($^1A_1$)	−54.822 90[c]	−55.127 29[c]	−55.135 07	−55.257 88	−55.277 55	48.3
NH_2^+ ($^3B_1$)	−54.915 51[c]	−55.208 52[c]	−55.217 03[c]	−55.319 84[c]	−55.335 45[c]	44.1
$NH_3^{\cdot+}$ ($^2A_2''$)	−55.576 26[c]	−55.873 24[c]	−55.884 89[c]	−56.028 63[c]	−56.045 17[c]	89.5
$CH_2NH_2^+$	−93.862 84[c]	−94.383 18[c]	−94.394 71[c]	−94.690 86[c]	−94.710 39[c]	152.7
$HCNH_2^{\cdot+}$	−93.208 62[c]	−93.725 39[c]	−93.735 62[c]	−93.996 61[c]	−94.014 86[c]	110.7
$CH_2NH^{\cdot+}$	−93.197 93[c]	−93.717 48[c]	−93.725 55[c]	−93.978 84[c]	−94.000 85[c]	101.9
$HCNH_2^{2+}$	−92.568 72	−93.084 46	−93.096 25	−93.358 08	−93.372 77	98.7
CH_2NH^{2+}	−92.481 39	−93.001 54	−93.011 08	−93.270 20	−93.286 75	83.0
$CH_2OH_2^{2+}$, **1b**	−113.511 22	−114.129 33	−114.147 53	−114.438 78	−114.454 62	138.9
TS(**1b** $\rightarrow CH_2^{\cdot+} + OH_2^{\cdot+}$), **4b**	−113.393 42	−114.010 47	−114.027 42	−114.276 54	−114.302 42	111.8
TS(**1b** $\rightarrow CH_2OH^+ + H^+$), **5b**	−113.393 59	−114.028 52	−114.039 20	−114.338 99	−114.350 68	115.6
OH^+ ($^1\Sigma^+$)	−74.434 29[c]	−74.830 25[c]	−74.836 91[c]	−74.954 53[c]	−74.972 90[c]	17.7
OH^+ ($^3\Sigma^-$)	−74.569 91[c]	−74.968 75[c]	−74.974 63[c]	−75.074 66[c]	−75.089 24[c]	17.4
$OH_2^{\cdot+}$ ($^2B_1$)	−75.207 89[c]	−75.615 31[c]	−75.628 20[c]	−75.773 97[c]	−75.787 28[c]	48.6
CH_2OH^+	−113.514 14[c]	−114.156 43[c]	−114.167 13[c]	−114.468 50[c]	−114.480 75[c]	100.6
$HCOH^{\cdot+}$	−112.864 89[c]	−113.503 67[c]	−113.513 03[c]	−113.785 48[c]	−113.794 40[c]	71.0
$HCOH^{2+}$	−112.234 09	−112.863 21	−112.872 51	−113.150 45	−113.152 07	67.1
CH_2FH^{2+}, **1c**	−137.242 47	−137.984 57	−137.996 44	−138.274 92	−138.285 60	91.5
TS(**1c** $\rightarrow CH_2^{\cdot+} + FH^{\cdot+}$), **4c**	−137.151 59	−137.887 90	−137.899 47	−138.133 33	−138.154 68	74.1
TS(**1c** $\rightarrow CH_2F^+ + H^+$), **5c**	−137.199 75	−137.948 08	−137.952 86	−138.232 09	−138.240 54	76.3
F^+ (^1D)	−98.123 67	−98.632 61	−98.632 61	−98.728 60	−98.744 29	0.0
F^+ (^3P)	−98.278 75[c]	−98.792 06[c]	−98.792 06[c]	−98.869 63[c]	−98.879 92[c]	0.0
$FH^{\cdot+}$ ($^2\Pi$)	−98.967 43[c]	−99.489 60[c]	−99.496 80	−99.626 13	−99.635 30	17.4
CH_2F^+	−137.328 02[c]	−138.093 79[c]	−138.097 79	−138.382 39	−138.389 56	75.3
$HCF^{\cdot+}$	−136.668 03[c]	−137.433 77[c]	−137.436 12[c]	−137.693 60[c]	−137.696 70[c]	35.8
HCF^{2+}	−135.861 39	−136.698 58	−136.701 86	−136.967 25	−136.962 50	35.9
CH_3^+	−39.009 13[c]	−39.230 64[c]	−39.236 29	−39.346 52	−39.364 49	87.0
$CH_2^{\cdot+}$ ($^2A_1$)	−38.347 47[c]	−38.566 19[c]	−38.570 60	−38.649 32	−38.664 44	45.0
H_2	−1.122 96[c]	−1.126 83	−1.131 33	−1.157 65	−1.163 14	27.9
$H_2^{\cdot+}$	−0.583 15[c]	−0.584 07[c]	−0.594 48[c]	−0.594 48[c]	−0.594 48[c]	12.4

[a] Based on 6-31G*-optimized geometries unless otherwise noted. [b] Based on 3-21G-optimized geometries. [c] From ref 38.

82[20] programs. Optimized structures were obtained with the 3-21G$^{(*)}$ and 6-31G* basis sets.[21,22] The spin-unrestricted Hartree–Fock (UHF) formalism was used for open-shell species and also for those transition structures connecting singlet molecules with their doublet fragments. Restricted Hartree–Fock (RHF) calculations were performed in remaining cases, unless otherwise noted. Improved relative energies were determined through single-point calculations with the 6-31G** basis set[22] and with valence-electron correlation incorporated by using Møller–Plesset perturbation theory terminated at second (MP2) and third (MP3) order.[23] Vibrational frequencies were calculated at the 3-21G$^{(*)}$//3-21G$^{(*)}$ level in order to characterize stationary points on the surface as minima (representing equilibrium structures) or saddle points (representing transition structures) and to allow zero-point vibrational contributions to relative energies to be evaluated. The latter were scaled by 0.9 to allow for the overestimation of vibrational frequencies at this level of theory. Our best relative energies correspond to MP3/6-31G**//6-31G* values with zero-point correction, calculated directly for first-row systems or estimated for second-row systems by using the additivity approximation[24]

$$\Delta E(\text{MP3/6-31G}^{**}) \approx \Delta E(\text{MP3/6-31G}^{*}) + \Delta E(\text{HF/6-31G}^{**}) - \Delta E(\text{HF/6-31G}^{*}) \quad (1)$$

Unless otherwise noted, these are the values given in the text.

Calculations are reported for the ylide dications (CH_2XH^{2+}), their conventional isomers (CH_3X^{2+}), five pairs of possible fragmentation products ($CH_2^{\cdot+} + XH^{\cdot+}$, $CH_3^+ + X^+$, $CH_2X^+ + H^+$, $CHX^{\cdot+} + H_2^{\cdot+}$, and $CHX^{2+} + H_2$), and the various transition structures for rearrangement and dissociation. The search for transition structures for C–X fragmentation in the CH_3X^{2+} dications (e.g., $CH_3PH_2^{2+} \rightarrow CH_3^+ + PH_2^+$) was restricted to the singlet surface. The optimized transition structures were found to be stable with respect to allowing spin contamination.

Ionization energies were calculated, for comparison with experimental charge-stripping data, both in a conventional manner, as a difference in energies of the doubly charged ions (from the present work) and the singly charged ions (from ref 7d), and by using an equations-of-motion approach.[25] The latter calculations were carried out at the partial third-order level[26] using the MOLECULE,[27] EPSCF,[28] and EOM[29] packages. The core orbitals and virtual orbitals lying above 2 hartrees in energy were neglected in the EOM calculations. Such an approach has been previously found to be successful in the calculation of ionization energies.[30]

Calculated total energies are presented in Tables I and II and relative energies in Tables III and IV. Optimized structures (6-31G* with 3-21G$^{(*)}$ values in parentheses) and schematic energy profiles are displayed as Figures 1–12 within the course of the discussion. The ylide dications and their conventional

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(19) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406.

(20) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A., Carnegie-Mellon University, Pittsburgh, PA 15213.

(21) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(22) (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797. (c) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(23) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

(24) (a) Nobes, R. H.; Bouma, W. J.; Radom, L. *Chem. Phys. Lett.* **1982**, *89*, 497. (b) McKee, M. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 4673.

(25) For leading references, see: Correia, N.; Baker, J. *J. Phys. Chem.* **1985**, *89*, 3861.

(26) Baker, J. *Chem. Phys.* **1983**, *79*, 117.

(27) Almlöf, J. Report 74-29, Institute of Physics, University of Stockholm, Sweden.

(28) Beebe, N. H.; Purvis, G. D.; Kurtz, H. A., Quantum Theory Project, University of Florida, Gainesville, FL 32611.

(29) Baker, J., EOM, Department of Quantum Chemistry, University of Uppsala, Sweden.

(30) See, for example: Baker, J.; Pickup, B. T. *Mol. Phys.* **1983**, *49*, 651.

Table II. Calculated Total Energies[a] (Hartrees) and Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1}) for Second-Row Systems

	HF/3-21G$^{(*)}$[b]	HF/6-31G*	HF/6-31G**	MP2/6-31G*	MP3/6-31G*	ZPVE[b]
$CH_2PH_3^{2+}$, **1d**	−378.775 51	−380.630 10	−380.641 60	−380.815 91	−380.847 27	142.1
$CH_3PH_2^{2+}$, **2d**	−378.752 20	−380.601 93	−380.613 71	−380.814 26	−380.840 27	143.7
TS(**2d** → **1d**), **3d**	−378.737 02	−380.592 97	−380.607 64	−380.806 62	−380.833 82	139.2
TS(**1d** → $CH_2^{\cdot+}$ + $PH_3^{\cdot+}$), **4d**	−378.704 97	−380.558 87	−380.570 73	−380.719 45	−380.751 92	124.4
TS(**1d** → $CH_2PH_2^+$ + H^+), **5d**	−378.625 78	−380.473 09	−380.481 95	−380.692 61	−380.715 09	120.4
TS(**2d** → CH_3^+ + PH_2^+), **6d**	−378.730 95	−380.586 60	−380.597 59	−380.777 24	−380.808 46	141.4
TS(**2d** → $CH_2PH_2^+$ + H^+), **7d**	−378.625 48	−380.471 18	−380.480 37	−380.702 54	−380.721 98	123.4
PH_2^+ ($^1A_1$)	−339.871 01	−341.506 55	−341.511 44	−341.586 22	−341.605 27	39.5
PH_2^+ ($^3B_1$)	−339.870 31	−341.506 42	−341.511 79	−341.571 46	−341.586 45	38.7
$PH_3^{\cdot+}$ ($^2A_1$)	−340.493 97	−342.131 56	−342.139 00	−342.213 46	−342.231 05	68.5
$CH_2PH_2^+$	−378.743 13	−380.587 99	−380.597 01	−380.814 43	−380.838 92	121.1
$HCPH_2^{\cdot+}$	−378.105 87	−379.947 91	−379.954 91	−380.117 53	−380.144 22	81.3
$CH_2PH^{\cdot+}$	−378.130 97	−379.975 04	−379.981 26	−380.162 77	−380.189 57	91.1
$HCPH_2^{2+}$	−377.480 44	−379.326 45	−379.334 59	−379.516 18	−379.543 92	79.5
CH_2PH^{2+}	−377.534 62	−379.383 35	−379.390 23	−379.558 57	−379.588 07	84.8
$CH_2SH_2^{2+}$, **1e**	−434.725 04	−436.796 19	−436.807 97	−437.012 75	−437.041 58	119.8
CH_3SH^{2+}, **2e**	−434.644 24	−436.709 18	−436.720 50	−436.958 76	−436.984 48	112.5
TS(**2e** → **1e**), **3e**	−434.642 51	−436.709 09	−436.720 36	−436.957 34	−436.983 26	110.3
TS(**1e** → $CH_2^{\bullet+}$ + $SH_2^{\bullet+}$), **4e**	−434.671 08	−436.737 33	−436.749 23	−436.919 24	−436.952 72	103.1
TS(**1e** → CH_2SH^+ + H^+), **5e**	−434.622 42	−436.686 27	−436.694 16	−436.922 79	−436.945 57	99.5
TS(**2e** → CH_3^+ + SH^+), **6e**	−434.622 96	−436.692 22	−436.702 38	−436.903 72	−436.936 41	115.2
SH^+ ($^1\Sigma^+$)	−395.787 87	−397.635 81	−397.640 26	−397.727 44	−397.747 36	16.9
SH^+ ($^3\Sigma^-$)	−395.878 66	−397.727 88	−397.731 88	−397.806 16	−397.822 99	16.9
$SH_2^{\cdot+}$ ($^2B_1$)	−396.476 39	−398.326 99	−398.334 66	−398.425 31	−398.444 16	42.1
CH_2SH^+	−434.743 74	−436.807 11	−436.814 65	−437.046 50	−437.069 91	99.8
$HCSH^{\cdot+}$ (cis)	−434.093 34	−436.153 69	−436.159 70	−436.356 18	−436.381 26	59.1
$HCSH^{2+}$	−433.450 79	−435.515 80	−435.523 01	−435.743 86	−435.762 99	54.9
CH_2ClH^{2+}, **1f**	−495.791 12	−498.100 11	−498.110 35	−498.333 24	−498.358 68	92.6
TS(**1f** → $CH_2^{\cdot+}$ + $ClH^{\bullet+}$), **4f**	−495.738 25	−498.035 02	−498.045 61	−498.229 53	−498.261 28	75.5
TS(**1f** → CH_2Cl^+ + H^+), **5f**	−495.716 17	−498.019 81	−498.023 93	−498.261 06	−498.281 49	72.4
Cl^+ (^1D)	−456.836 30	−458.914 15	−458.914 15	−459.013 43	−459.033 21	0.0
Cl^+ (^3P)	−456.935 94	−459.015 02	−459.015 02	−459.100 49	−459.116 27	0.0
$ClH^{\bullet+}$ ($^2\Pi$)	−457.553 04	−459.633 97	−459.640 28	−459.742 17	−459.759 35	17.2
CH_2Cl^+	−495.846 33	−498.149 92	−498.153 58	−498.393 73	−498.414 01	70.7
$HCCl^{\cdot+}$	−495.195 05	−497.496 95	−497.499 16	−497.719 16	−497.737 35	32.5
$HCCl^{2+}$	−494.541 82	−496.848 67	−496.851 26	−497.094 58	−497.103 91	36.9
CH_3^+	*c*	*c*	*c*	−39.325 14	−39.341 58	*c*
$CH_2^{\cdot+}$ ($^2A_1$)	*c*	*c*	*c*	−38.635 21	−38.649 41	*c*
H_2	*c*	*c*	*c*	−1.144 10	−1.149 24	*c*
$H_2^{\bullet+}$	*c*	*c*	*c*	−0.584 07	−0.584 07	*c*

[a] Based on 6-31G*-optimized geometries unless otherwise noted. [b] Based on 3-21G$^{(*)}$-optimized geometries. [c] See Table I.

Table III. Calculated Relative Energies[a] (kJ mol^{-1}) for First-Row Systems

	HF/3-21G	HF/6-31G*	HF/6-31G**	MP2/6-31G**	MP3/6-31G**	MP3/6-31G**[b]
$CH_2NH_3^{2+}$, **1a**	0	0	0	0	0	0
TS(**1a** → $CH_2^{\cdot+}$ + $NH_3^{\bullet+}$), **4a**	212	234	233	332	316	297
TS(**1a** → $CH_2NH_2^+$ + H^+), **5a**	324	321	332	286	304	287
$CH_2^{\cdot+}$ + $NH_3^{\bullet+}$	−215	−206	−207	−65	−83	−117
$CH_2NH_2^+$ + H^+	−56	−59	−48	−98	−85	−103
CH_3^+ + NH_2^+ ($^1A_1$)	25	8	13	129	95	61]
CH_3^+ + NH_2^+ ($^3B_1$)	−218	−206	−202	−34	−57	−95
$HCNH_2^{\cdot+}$ + $H_2^{\cdot+}$	131	135	122	164	181	136
$CH_2NH^{\cdot+}$ + $H_2^{\cdot+}$	159	156	148	210	218	165
$HCNH_2^{2+}$ + H_2	394	393	391	361	373	332
CH_2NH^{2+} + H_2	623	610	615	592	599	544
$CH_2OH_2^{2+}$, **1b**	0	0	0	0	0	0
TS(**1b** → $CH_2^{\bullet+}$ + $OH_2^{\cdot+}$), **4b**	309	312	315	426	400	375
TS(**1b** → CH_2OH^+ + H^+), **5b**	309	265	284	262	273	252
$CH_2^{\cdot+}$ + $OH_2^{\cdot+}$	−116	−137	−135	41	8	−33
CH_2OH^+ + H^+	−8	−71	−51	−78	−69	−103
CH_3^+ + OH^+ ($^1\Sigma^+$)	178	180	195	362	308	277
CH_3^+ + OH^+ ($^3\Sigma^-$)	−178	−184	−166	46	2	−29
$HCOH^{\cdot+}$ + $H_2^{\cdot+}$	166	109	105	155	173	123
$HCOH^{2+}$ + H_2	405	366	377	343	366	326
CH_2FH^{2+}, **1c**	0	0	0	0	0	0
TS(**1c** → $CH_2^{\bullet+}$ + $FH^{\bullet+}$), **4c**	239	254	255	372	344	328
TS(**1c** → CH_2F^+ + H^+), **5c**	112	96	114	112	118	105
$CH_2^{\cdot+}$ + $FH^{\cdot+}$	−190	−187	−186	−1	−37	−63
CH_2F^+ + H^+	−225	−287	−266	−282	−273	−288
CH_3^+ + F^+ (^1D)	288	319	335	525	464	460
CH_3^+ + F^+ (^3P)	−119	−100	−84	154	108	104
$HCF^{\cdot+}$ + $H_2^{\cdot+}$	−23	−87	−90	−35	−15	−54
HCF^{2+} + H_2	678	418	429	394	420	395

[a] Based on the total energies in Table I. [b] With zero-point correction (see text).

Table IV. Calculated Relative Energies[a] (kJ mol^{-1}) for Second-Row Systems

	HF/3-21G$^{(*)}$	HF/6-31G*	HF/6-31G**	MP2/6-31G*	MP3/6-31G*	MP3/6-31G**[b]	MP3/6-31G**[c]
$CH_2PH_3^{2+}$, **1d**	0	0	0	0	0	0	0
$CH_3PH_2^{2+}$, **2d**	61	74	73	4	18	18	19
TS(**2d** → **1d**), **3d**	101	97	89	24	35	27	24
TS(**1d** → $CH_2^{\cdot+}$ + $PH_3^{\cdot+}$), **4d**	185	187	187	253	250	249	233
TS(**1d** → $CH_2PH_2^+$ + H^+), **5d**	393	412	419	324	347	354	334
TS(**2d** → CH_3^+ + PH_2^+), **6d**	117	114	116	102	102	103	103
TS(**2d** → $CH_2PH_2^+$ + H^+), **7d**	394	417	423	298	329	335	318
$CH_2^{\cdot+}$ + $PH_3^{\cdot+}$	-173	-178	-179	-86	-87	-88	-114
$CH_2PH_2^+$ + H^+	85	111	117	4	22	28	10
CH_3^+ + PH_2^+ ($^1A_1$)	-275	-281	-279	-251	-261	-259	-273
CH_3^+ + PH_2^+ ($^3B_1$)	-273	-281	-280	-212	-212	-211	-226
$HCPH_2^{\cdot+}$ + $H_2^{\cdot+}$	227	258	242	300	312	297	242
$CH_2PH^{\cdot+}$ + $H_2^{\cdot+}$	161	186	173	181	193	180	134
$HCPH_2^{2+}$ + H_2	452	464	461	409	405	402	370
CH_2PH^{2+} + H_2	309	315	315	297	289	289	263
$CH_2SH_2^{2+}$, **1e**	0	0	0	0	0	0	0
CH_3SH^{2+}, **2e**	212	228	230	142	150	151	145
TS(**2e** → **1e**), **3e**	217	229	230	145	153	154	146
TS(**1e** → $CH_2^{\cdot+}$ + $SH_2^{\cdot+}$), **4e**	142	155	154	245	233	233	218
TS(**1e** → CH_2SH^+ + H^+), **5e**	269	289	299	236	252	262	244
TS(**2e** → CH_3^+ + SH^+), **6e**	268	273	277	286	276	280	276
$CH_2^{\cdot+}$ + $SH_2^{\cdot+}$	-259	-255	-255	-125	-137	-137	-167
CH_2SH^+ + H^+	-49	-29	-18	-89	-74	-63	-81
CH_3^+ + SH^+ ($^1\Sigma^+$)	-189	-184	-180	-105	-124	-120	-134
CH_3^+ + SH^+ ($^3\Sigma^-$)	-427	-426	-421	-311	-323	-317	-332
$HCSH^{\cdot+}$ + $H_2^{\cdot+}$	128	154	141	190	200	188	145
$HCSH^{2+}$ + H_2	397	403	403	328	340	340	307
CH_2ClH^{2+}, **1f**	0	0	0	0	0	0	0
TS(**1f** → $CH_2^{\cdot+}$ + $ClH^{\cdot+}$), **4f**	139	171	170	272	256	255	239
TS(**1f** → CH_2Cl^+ + H^+), **5f**	197	211	227	190	203	219	201
$CH_2^{\cdot+}$ + $ClH^{\cdot+}$	-287	-263	-264	-116	-131	-133	-160
CH_2Cl^+ + H^+	-145	-131	-114	-159	-145	-128	-148
CH_3^+ + Cl^+ (^1D)	-143	-117	-105	-14	-42	-30	-35
CH_3^+ + Cl^+ (^3P)	-404	-382	-370	-243	-260	-248	-253
$HCCl^{\cdot+}$ + $H_2^{\cdot+}$	34	50	44	79	98	92	49
$HCCl^{2+}$ + H_2	332	327	335	249	277	285	260

[a] Based on the total energies in Table II. [b] Estimated by using the additivity approximation of eq 1. [c] MP3/6-31G** value with zero-point correction (see text).

Table V. Calculated Central Bond Lengths (Å) for MP2/6-31G*-Optimized Structures

species	neutral	monocation	dication[a]
CH_3NH_2	1.465[b]	1.431[c]	
CH_2NH_3	1.559[d]	1.470[c]	1.420
CH_3OH	1.424[b]	1.405[d]	
CH_2OH_2	1.805[e]	1.468[d]	1.314
CH_3F	1.392[d]	1.310[f]	
CH_2FH	g	1.557[f]	1.366
CH_3PH_2	1.857[d]	1.798[d]	1.712
CH_2PH_3	1.674[d]	1.765[d]	1.865
CH_3SH	1.814[d]	1.786[d]	1.649
CH_2SH_2	1.635[d]	1.759[d]	1.674
CH_3Cl	1.778[d]	1.765[d]	
CH_2ClH	1.691[d]	1.770[d]	1.656

[a] MP2(full)/6-31G* total energies for $CH_2NH_3^{2+}$, $CH_2OH_2^{2+}$, CH_2FH^{2+}, $CH_3PH_2^{2+}$, $CH_2PH_3^{2+}$, CH_3SH^{2+}, $CH_2SH_2^{2+}$, and CH_2ClH^{2+} are −94.624 40, −114.413 69, −138.260 12, −380.831 67, −381.831 59, −436.983 59, −437.030 08, and −498.348 32 hartrees, respectively. [b] From ref 38. [c] From: Yates, B. F.; Nobes, R. H.; Radom, L. *Chem. Phys. Lett.* **1985**, *116*, 474. [d] From ref 7d. [e] From: Harding, L. B.; Schlegel, H. B.; Krishnan, R.; Pople, J. A. *J. Phys. Chem.* **1980**, *84*, 3394. [f] From ref 40. [g] No ylide-like minimum found.

isomers where appropriate were reoptimized at MP2/6-31G* to allow comparisons at this level of theory with recent results for the corresponding neutral and monocationic species.[7d] Optimized bond lengths (MP2/6-31G*) for the central C–X bond in CH_3X^{n+} and CH_2XH^{n+} (n = 0, 1, and 2) are presented in Table V. Unless otherwise stated, geometric comparisons in the text refer to the MP2/6-31G* values.

Discussion

Methyleneammonium ($CH_2NH_3^{2+}$) and Methylamine ($CH_3NH_2^{2+}$) Dications. Optimized structures for the methyleneammonium dication (**1a**) and related species are presented in Figure 1. **1a** has been studied previously by ab initio techniques in an investigation[31] of π-electron donation by the NH_3^+ group in substituted cations and in a study[32] of CH_4X^{2+} dications. Our higher level calculations confirm the previously reported[31] structure for $CH_2NH_3^{2+}$ and, in addition, show that the eclipsed and staggered conformations are almost equivalent energetically. From Table V, it can be seen that the C–N bond length of 1.420 Å in

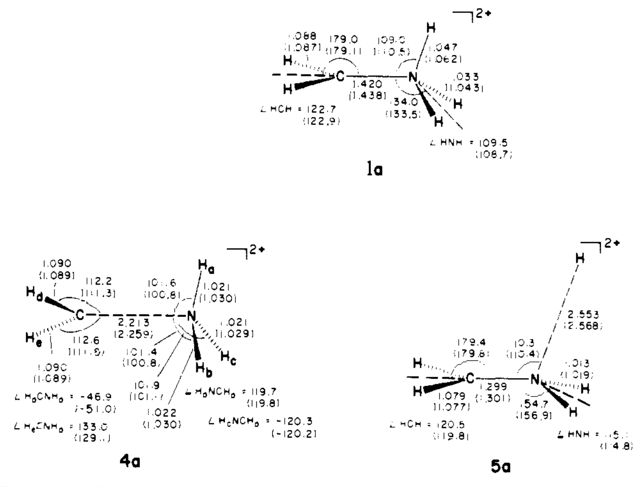

Figure 1. Optimized structures for the methyleneammonium dication ($CH_2NH_3^{2+}$, **1a**) and related systems.

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[31] Paddon-Row, M. N.; Santiago, C.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6561.

[32] Lammertsma, K. *J. Am. Chem. Soc.* **1984**, *106*, 4619.

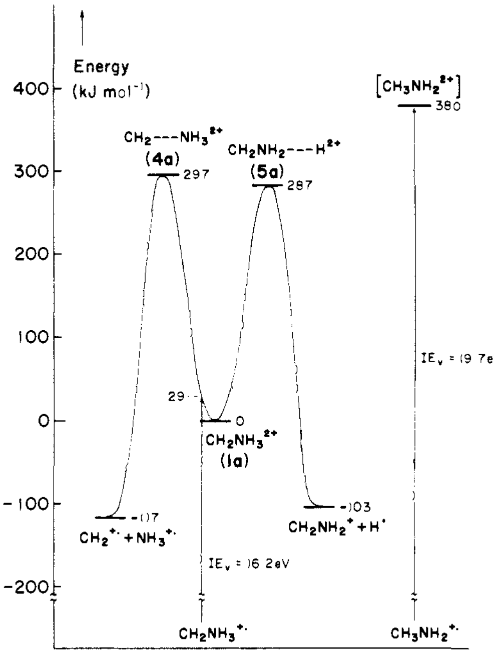

Figure 2. Schematic energy profile for dissociative processes in the methyleneammonium dication (**1a**).

$CH_2NH_3^{2+}$ is shorter than the 1.470 Å calculated for the radical cation $CH_2NH_3^{\bullet+}$ and the 1.559 Å calculated at the same level for the neutral CH_2NH_3. It is even shorter than the C–N bond length of 1.465 Å in neutral CH_3NH_2. The shortening may be attributed to hyperconjugative electron donation from the NH_3^+ group into the formally vacant p orbital at carbon. As might have been anticipated, for **1a** there is considerable flattening of the bonds at the carbon atom which is now formally a carbenium center.

The methylamine dication ($CH_3NH_2^{2+}$) is found to be unstable with respect to the 1,2-hydrogen shift that yields **1a**. This contrasts with the potential surface for the corresponding radical cations which showed[33,34] a barrier of 168 kJ mol^{-1} separating $CH_3NH_2^{\bullet+}$ from $CH_2NH_3^{\bullet+}$.

The schematic potential energy profile of Figure 2 shows that $CH_2NH_3^{2+}$ is thermodynamically unstable with respect to fragmentation products $CH_2^{\bullet+} + NH_3^{\bullet+}$ (by 117 kJ mol^{-1}) and $CH_2NH_2^+ + H^+$ (by 103 kJ mol^{-1}). However, the barriers to such dissociations are substantial (297 and 287 kJ mol^{-1}, respectively). Thus $CH_2NH_3^{2+}$ lies in a deep potential well, consistent with its experimental observation in charge-stripping mass spectrometry experiments;[9] these are discussed in more detail below.

We should point out that homolytic bond fission of the type $CH_2NH_3^{2+} \rightarrow CH_2^{\bullet+} + NH_3^{\bullet+}$ is not expected to be particularly well described by a single-configuration treatment. Indeed, for related dicationic fragmentations we have been able recently to demonstrate[35] that there is only slow convergence of the Møller–Plesset perturbation expansion of the energy of the transition structure, leading to a substantial overestimation of the barrier to fragmentation. The slow convergence appears to be associated with spin contamination in the UHF wave function.[35,36] The principal consequence in the present series of molecules is that the barriers for homolytic fragmentation, $CH_2XH^{2+} \rightarrow CH_2^{\bullet+} + XH^{\bullet+}$, as calculated at our highest theoretical level, are likely to be too high by as much as 100 kJ mol^{-1}. However, the qualitative conclusions are not affected by this correction in that there remain substantial residual barriers to homolytic fragmentation.

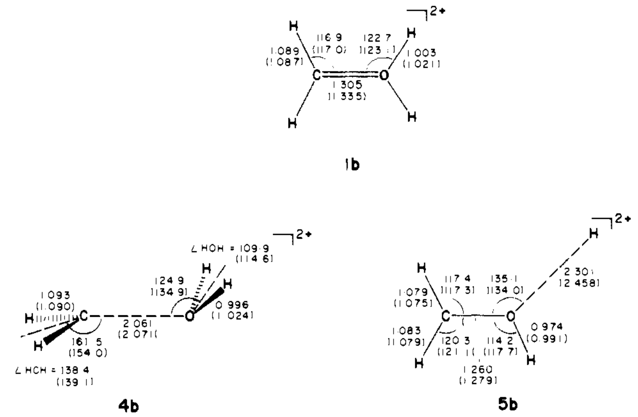

Figure 3. Optimized structures for the methyleneoxonium dication ($CH_2OH_2^{2+}$, **1b**) and related systems.

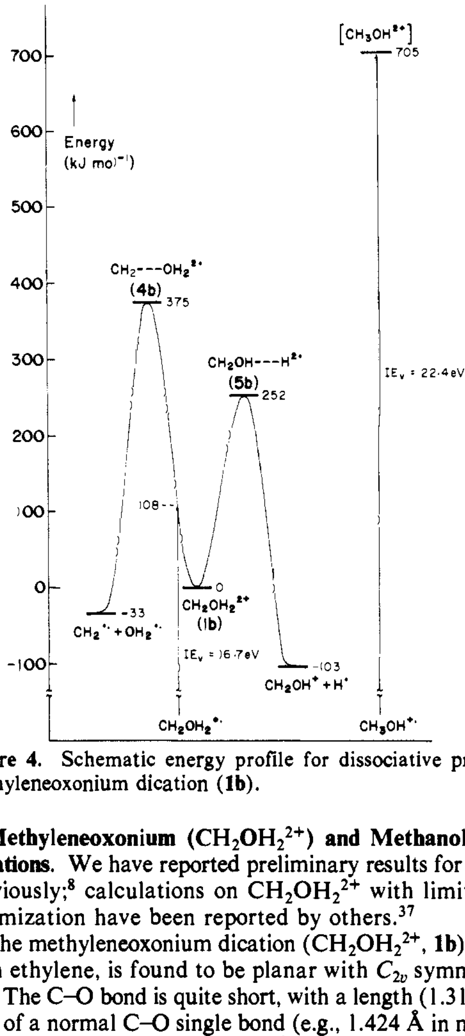

Figure 4. Schematic energy profile for dissociative processes in the methyleneoxonium dication (**1b**).

Methyleneoxonium ($CH_2OH_2^{2+}$) and Methanol (CH_3OH^{2+}) Dications. We have reported preliminary results for these systems previously;[8] calculations on $CH_2OH_2^{2+}$ with limited geometry optimization have been reported by others.[37]

The methyleneoxonium dication ($CH_2OH_2^{2+}$, **1b**), isoelectronic with ethylene, is found to be planar with C_{2v} symmetry (Figure 3). The C–O bond is quite short, with a length (1.314 Å) between that of a normal C–O single bond (e.g., 1.424 Å in methanol) and a C–O double bond (e.g., 1.221 Å in formaldehyde).[38] The C–O length is similar to that of the ethylenic C=C double bond (1.336 Å).[38] The shortness of the C–O bond may be attributed to strong delocalization from the lone pair on oxygen into the formally vacant p orbital at carbon.

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[33] Bouma, W. J.; Dawes, J. M.; Radom, L. *Org. Mass Spectrom.* **1983**, *18*, 12.

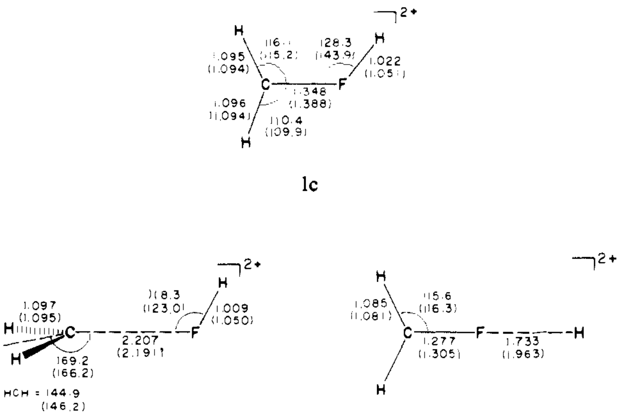
[34] Frisch, M. J.; Raghavachari, K.; Pople, J. A.; Bouma, W. J.; Radom, L. *Chem. Phys.* **1983**, *75*, 323.

[35] Gill, P. M. W.; Radom, L., submitted for publication.

[36] Handy, N. C.; Knowles, P. J.; Somasundram, K. *Theor. Chim. Acta* **1985**, *68*, 87.

[37] (a) Strausz, O. P.; Kozmutza, C.; Kapuy, E.; Robb, M. A.; Theodorakopoulos, G.; Csizmadia, I. G. *Theor. Chim. Acta* **1978**, *48*, 215. (b) Strausz, O. P.; Kapuy, E.; Kozmutza, C.; Robb, M. A.; Csizmadia, I. G. *J. Mol. Struct.* **1982**, *89*, 235. (c) Novoa, J. J. *J. Mol. Struct., Theochem* **1985**, *121*, 29.

[38] Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; Krishnan, R.; DeFrees, D. J.; Schlegel, H. B.; Pople, J. A. *Carnegie-Mellon Quantum Chemistry Archive*; Department of Chemistry, Carnegie-Mellon University: Pittsburgh, PA, 1983.



1c

4c **5c**

Figure 5. Optimized structures for the methylenefluoronium dication (CH_2FH^{2+}, **1c**) and related systems.

As with $CH_2NH_3^{2+}$, $CH_2OH_2^{2+}$ is thermodynamically unstable with respect to fragmentation products (Figure 4), lying 33 kJ mol^{-1} above $CH_2^{\bullet+}$ + $OH_2^{\bullet+}$ and 103 kJ mol^{-1} above CH_2OH^+ + H^+. However, the barriers to such dissociation processes are large, the lower energy decomposition pathway, i.e., via **5b** to give CH_2OH^+ + H^+, requiring 252 kJ mol^{-1}.[39]

The methanol dication (CH_3OH^{2+}) is found to fall apart on both the 3-21G and 6-31G* surfaces. Geometry optimization, starting with the $CH_3OH^{\bullet+}$ structure, leads under an RHF constraint to a weak complex (**8b**) of $HCOH^{2+}$ and H_2, but this no longer bears any resemblance to methanol. The complex **8b** lies substantially higher in energy (by 312 kJ mol^{-1}) than **1b**. With UHF calculations, such an optimization results in the highly exothermic production of $HCOH^{\bullet+}$ + $H_2^{\bullet+}$ (lying 170 kJ mol^{-1} below **8b**).

Methylenefluoronium (CH_2FH^{2+}) and Fluoromethane (CH_3F^{2+}) Dications. The methylenefluoronium dication (**1c**) is isoelectronic with formaldimine ($CH_2{=}NH$). Its preferred structure (Figure 5) is planar, in contrast to the orthogonal C_s structure of the radical cation ($CH_2FH^{\bullet+}$);[40] the C–F bond (1.366 Å) is slightly shorter than normal C–F single bonds (e.g., 1.392 Å in CH_3F), but the degree of shortening is markedly less than in the $CH_2OH_2^{2+}$ case. Thus, although the planar structure of CH_2FH^+ suggests that one of the lone pairs on fluorine is involved in π-bonding to carbon,[41] Coulombic repulsion appears to play a larger role here than in the oxygen case.

The methylenefluoronium dication (**1c**) lies in a somewhat shallower well than does $CH_2NH_3^{2+}$ and $CH_2OH_2^{2+}$. The barrier to the highly exothermic (by 288 kJ mol^{-1}) fragmentation to CH_2F^+ + H^+ is reduced to 105 kJ mol^{-1}.

The fluoromethane dication is found to be unstable. With RHF calculations, dissociation to give H^+ + CH_2F^+ can take place without a barrier.

Methylenephosphonium ($CH_2PH_3^{2+}$) and Methylphosphine ($CH_3PH_2^{2+}$) Dications. The methylenephosphonium dication has a preferred staggered conformation (**1d**, Figure 7) with a near-planar carbenium center. The alternative eclipsed conformation (**1d**^{e}) lies higher in energy by just 0.2 kJ mol^{-1} and is confirmed by frequency calculations to be located at a saddle point on the surface; i.e., it represents the transition structure for internal rotation. The C–P bond length in $CH_2PH_3^{2+}$ is 1.865 Å, which is longer than the C–P bond in the ylidion (1.765 Å) and longer than a normal C–P single bond (e.g., 1.857 Å in CH_3PH_2). Hyperconjugative interactions in $CH_2PH_3^{2+}$ appear to be less important than in $CH_2NH_3^{2+}$, as might have been anticipated.

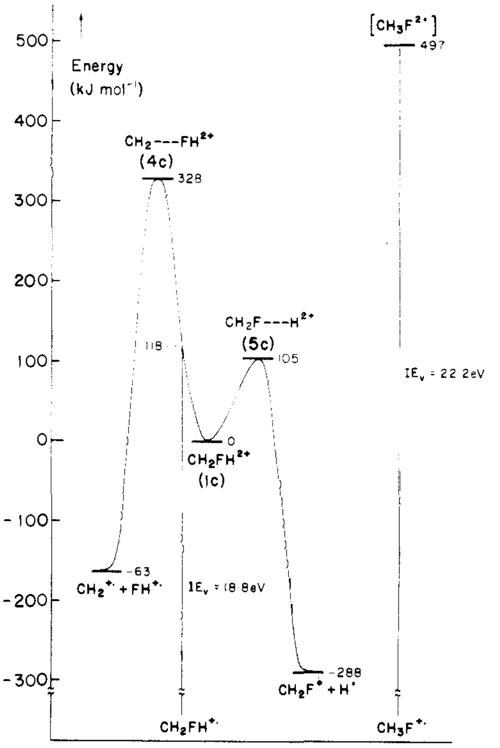


Figure 6. Schematic energy profile for dissociative processes in the methylenefluoronium dication (**1c**).

For the methylphosphine dication, the eclipsed conformation (**2d**^{e}) is marginally favored at the 3-21G$^{(*)}$ level of theory. However, we find that at our highest level the preferred conformation is staggered (**2d**), with the barrier to rotation via the eclipsed form being again just 0.2 kJ mol^{-1}. The C–P bond length of 1.712 Å in $CH_3PH_2^{2+}$ is shorter than both the 1.798 Å in singly charged $CH_3PH_2^{\bullet+}$ and the 1.857 Å in neutral CH_3PH_2. Frequency calculations show that $CH_3PH_2^{2+}$ (**2d**) is a true minimum on the 6-31G* potential surface. However, the barrier to rearrangement via transition structure **3d** (Figure 8) is very small, and the barrier may disappear entirely at higher levels of theory.

The lowest energy decomposition pathway for $CH_2PH_3^{2+}$ (**1d**) involves hydrogen migration (via **3d**) followed by C–P bond rupture (via **6d**) to give CH_3^+ + PH_2^+. This process has a barrier of 103 kJ mol^{-1} and an exothermicity of 273 kJ mol^{-1}. Higher energy processes include direct breakage of the C–P bond in **1d** to give $CH_2^{\bullet+}$ + $PH_3^{\bullet+}$ and fragmentation to give $CH_2PH_2^+$ + H^+, the latter being slightly endothermic.

Methylenesulfonium ($CH_2SH_2^{2+}$) and Methanethiol (CH_3SH^{2+}) Dications. In contrast to the methyleneoxonium dication (isoelectronic with ethylene) which has a planar structure (**1b**), the methylenesulfonium dication (isoelectronic with silaethylene) has an anti (C_s) structure, strongly bent at sulfur (**1e**, Figure 9). Although this result might appear surprising at first glance, it is consistent with the greater pyramidality of H_3S^+ compared with H_3O^+ (bond angles of 96.9° and 113.1°, respectively, at HF/6-31G*) and also reflects a reduced tendency for delocalization of the lone pair on sulfur into the formally vacant p orbital on the adjacent carbon. Nevertheless, the C–S bond in $CH_2SH_2^{2+}$ is quite short, with a length (1.674 Å) which is considerably less than that of the C–S bond in neutral methanethiol (1.814 Å).

The preferred conformation of the methanethiol dication is eclipsed (**2e**), the barrier to internal rotation via the staggered structure (**2e**^{s}) being 11 kJ mol^{-1}. The calculated structure (**2e**) resembles a complex of $HCSH^{2+}$ + H_2 (or of $HCSH^{\bullet+}$ + $H_2^{\bullet+}$) in that the C–S bond is short (1.649 Å) and the symmetry-equivalent C–H bonds are unusually long (1.217 Å).

Although CH_3SH^{2+} (**2e**) is found to be a minimum in this study, its rearrangement to $CH_2SH_2^{2+}$ (**1e**) via a 1,2-hydrogen shift requires only 1 kJ mol^{-1}, and it is quite probable that at higher levels of theory this barrier for rearrangement would disappear

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[39] Similar results were obtained recently[37c] but at a less precise level of theory.

[40] Bouma, W. J.; Yates, B. F.; Radom, L. *Chem. Phys. Lett.* **1982**, *92*, 620.

[41] Strong π-donation from fluorine has recently been invoked to explain the calculated shortening of C–F lengths in the series CF_2, $CF_2^{\bullet+}$, and CF_2^{2+}: Koch, W.; Frenking, G. *Chem. Phys. Lett.* **1985**, *114*, 178.

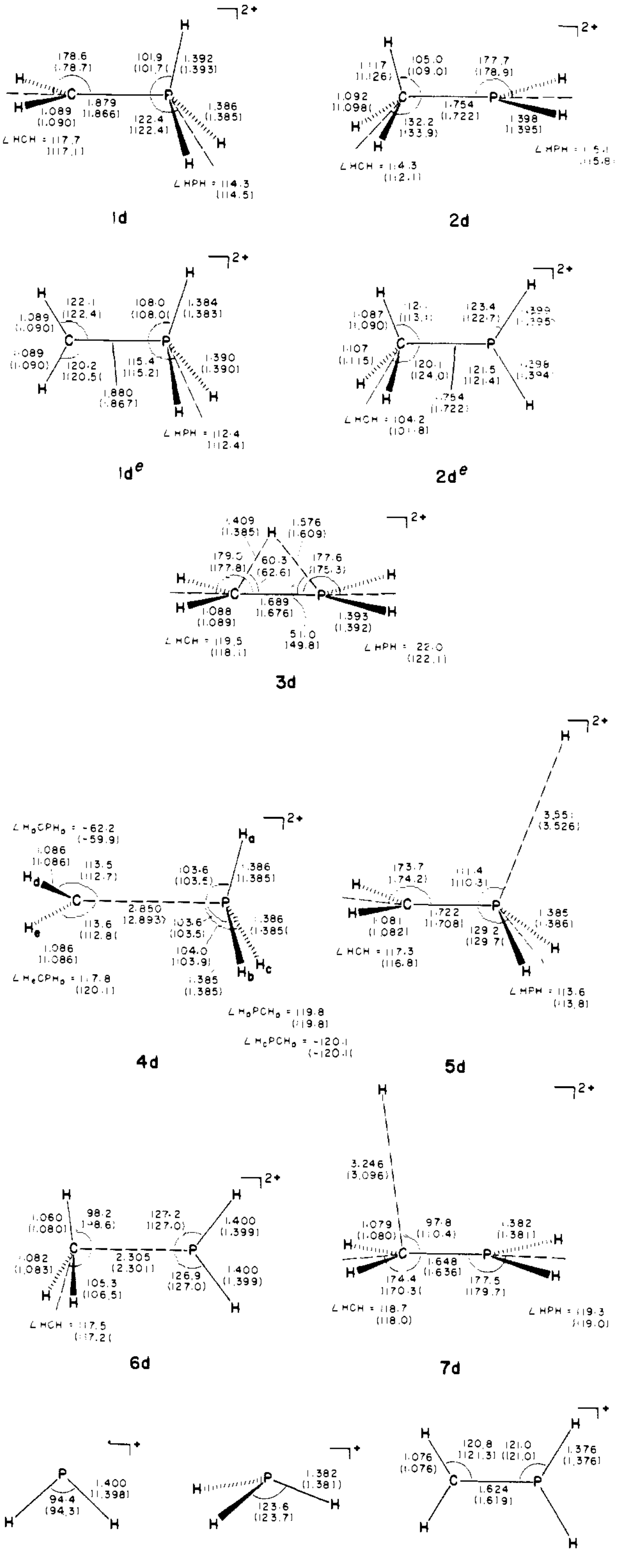

Figure 7. Optimized structures for the methylenephosphonium dication ($CH_2PH_3^{2+}$, **1d**) and related systems.

altogether. For its part, $CH_2SH_2^{2+}$ lies in a moderately deep well, with barriers of 218 and 244 kJ mol^{-1} to fragmentation to $CH_2^{\bullet+}$ + $SH_2^{\bullet+}$ and CH_2SH^+ + H^+, respectively.

In contrast to the situation for $CH_2PH_3^{2+}$, hydrogen migration in $CH_2SH_2^{2+}$ followed by C–S bond rupture to give CH_3^+ + SH^+ is not expected to be a competitive process for decomposition of $CH_2SH_2^{2+}$ since this would require 58 kJ mol^{-1} more energy than direct rupture of the C–S bond.

The search for a transition structure for formation of CH_2SH^+ + H^+ from CH_3SH^{2+} was unsuccessful. Test calculations suggest that there is a very large barrier to proton loss from the carbon of CH_3SH^{2+}. Indeed, the lower energy pathway probably involves a 1,2-hydrogen shift (via **3e**), followed by proton loss from the sulfur.

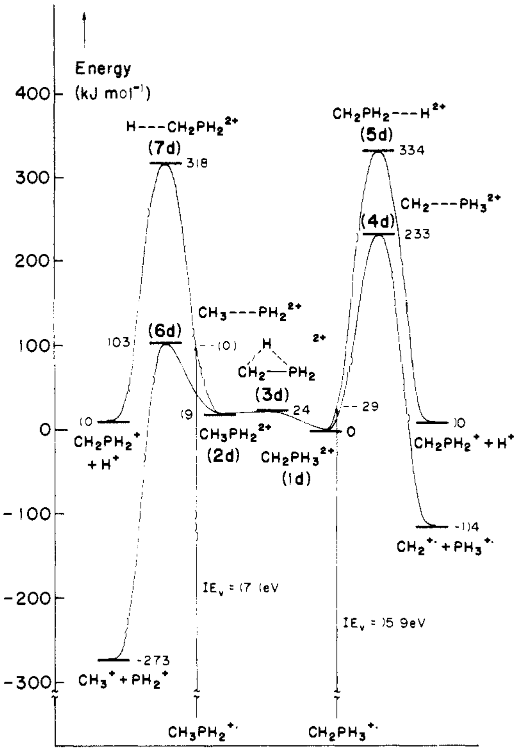

Figure 8. Schematic energy profile for dissociative processes in the methylenephosphonium dication (**1d**).

Methylenechloronium (CH_2ClH^{2+}) and Chloromethane (CH_3Cl^{2+}) Dications. The methylenechloronium dication (**1f**, Figure 11) is planar, with a C–Cl length (1.656 Å) considerably shorter than that of normal C–Cl bonds (e.g., 1.778 Å in chloromethane). Although the C–Cl bond in **1f** is still longer than that in CH_2Cl^+ (1.588 Å), the degree of shortening relative to neutral CH_3Cl is much greater than that calculated for CH_2FH^{2+}. This is somewhat surprising since it is usually held that second-row atoms have a smaller tendency to participate in π-bonding than do first-row atoms[42] and suggests the reduced importance of coulombic repulsion in the second-row system. As with CH_2FH^{2+}, the planar geometry of CH_2ClH^{2+} contrasts markedly with the twisted C_1 structure predicted[7d] for the ylidion, $CH_2ClH^{\bullet+}$.

The methylenechloronium dication (**1f**) lies in a much deeper potential well than CH_2FH^{2+}, with barriers to decomposition to CH_2Cl^+ + H^+ and $CH_2^{\bullet+}$ + $ClH^{\bullet+}$ of 201 and 239 kJ mol^{-1}, respectively.

The chloromethane dication is not stable, and any structure bearing some resemblance to neutral chloromethane lies very high in energy on the potential surface at both 3-21G$^{(*)}$ and 6-31G*. Optimizations at these levels show that CH_3Cl^{2+} dissociates without a barrier to CH_3^+ + Cl^+.

CH_3X^{2+} Dications. In our search for possible CH_3X^{2+} structures, we explored two further avenues. First, we looked for low-lying triplet structures of CH_3X^{2+}, having found that for several of the X^+ cations (X = NH_2, OH, F, SH, and Cl) the triplet lies much lower in energy than the singlet.[43] In each case, however, the triplet CH_3X^{2+} dications were found to dissociate spontaneously (either to CH_3^+ + X^+ or to CH_2X^+ + H^+).

The second avenue of exploration was concerned with determining whether any planar CH_3X^{2+} dications might be stable structures. It is well established that the parent methane dication, CH_4^{2+}, prefers a square-planar (D_{4h}) structure.[44] We searched

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[42] For an illuminating discussion, see: Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

[43] For example, the calculated energy difference between F^+ (^1D) and F^+ (^3P) is 356 kJ mol^{-1} at MP3/6-31G** in favor of the triplet.

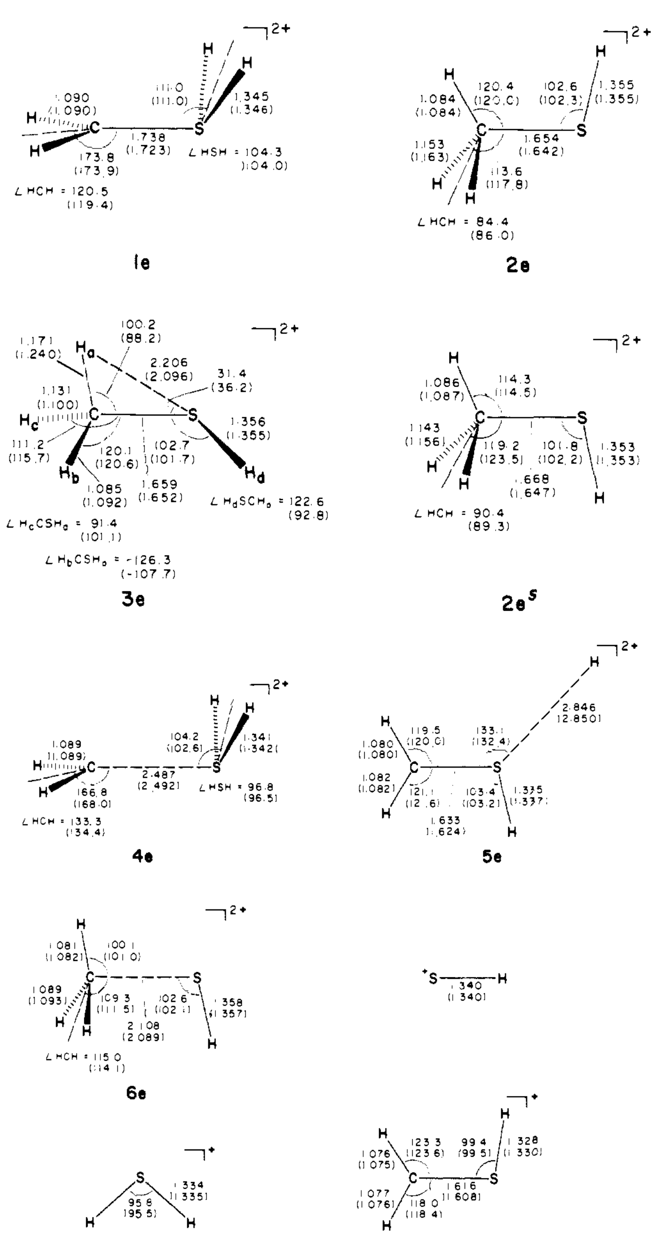

Figure 9. Optimized structures for the methylenesulfonium dication ($CH_2SH_2^{2+}$, **1e**) and related systems.

the individual CH_3X^{2+} surfaces at various levels of theory (including optimizations at the MP2/6-31G* level) but were unable to find any planar structures which are located at minima on these surfaces.

It would appear that the CH_3X^{2+} dications are not particularly stable species. For those systems that do reside at a local minimum on the potential surface (X = PH_2, SH), the positive charge is concentrated on X (e.g., for $CH_3PH_2^{2+}$ the Mulliken charges are distributed +1.64 (PH_2) and +0.36 (CH_3)). For more electronegative X (X = NH_2, OH, F, Cl), double ionization becomes more difficult and the CH_3X^{2+} dications become unstable with respect to dissociation.

Comparative Data for Possible Fragmentation Products of Ylide Dications. It is of interest to compare theoretical and experimental relative energies for the possible fragmentation products of the ylide dications, as shown in Table VI. For the first-row substituents (X) the thermodynamically preferred fragmentation products correspond to CH_2X^+ + H^+, whereas for the second-row substituents the CH_3^+ + X^+ pair is preferred. It should be noted with respect to the latter situation that, except for PH_2^+, the ground state for all the X^+ cations is a triplet.

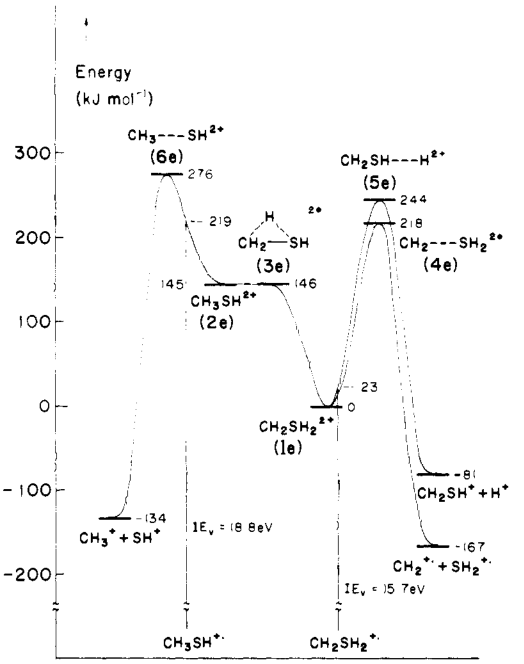

Figure 10. Schematic energy profile for dissociative processes in the methylenesulfonium dication (**1e**).

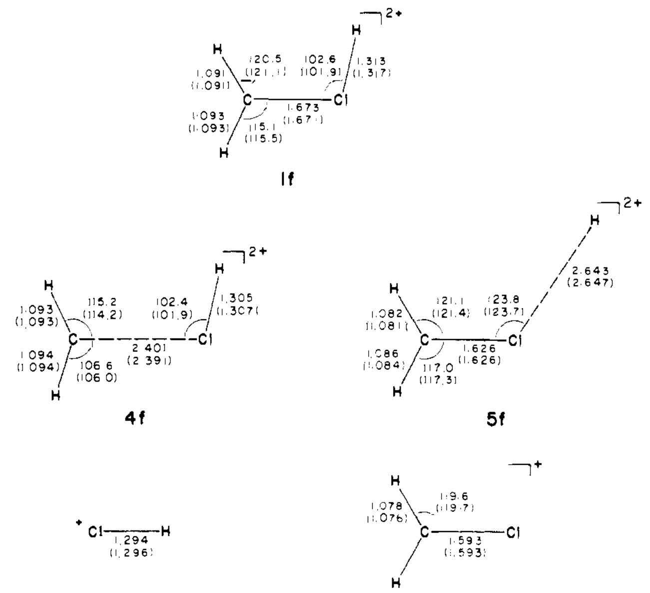

Figure 11. Optimized structures for the methylenechloronium dication (CH_2ClH^{2+}, **1f**) and related systems.

Table VI. Theoretical[a] and Experimental[b] Relative Energies (kJ mol^{-1}) for Possible Fragmentation Products of Ylide Dications

	$CH_2^{\cdot+}$ + $XH^{\cdot+}$		CH_2X^+ + H^+		CH_3^+ + X^+	
X	theor	exptl	theor	exptl	theor	exptl
NH_2	0	0	14	-54[c]	22	19
OH	0	0	-70	-128	4	6
F	0	0	-225	-301[c]	167	182
PH_2	0	0	124		-159	-182
SH	0	0	86	7[d]	-165	-151
Cl	0	0	12	-41[c,e]	-93	-69

[a] MP3/6-31G** values with zero-point vibrational contribution (from Tables III and IV). [b] From $\Delta H_f°_0$ data in ref 45a, unless otherwise noted. [c] $\Delta H_f°_{298}$ value for CH_2X^+ corrected to 0 K with the aid of calculated vibrational frequencies. [d] $\Delta H_f°_0$ for CH_2SH^+ from ref 45b. [e] $\Delta H_f°_{298}$ for CH_2Cl^+ from ref 45c.

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(44) (a) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 3436. (b) Pople, J. A.; Tidor, B.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1982**, *88*, 533. (c) Siegbahn, P. E. M. *Chem. Phys.* **1982**, *66*, 443.

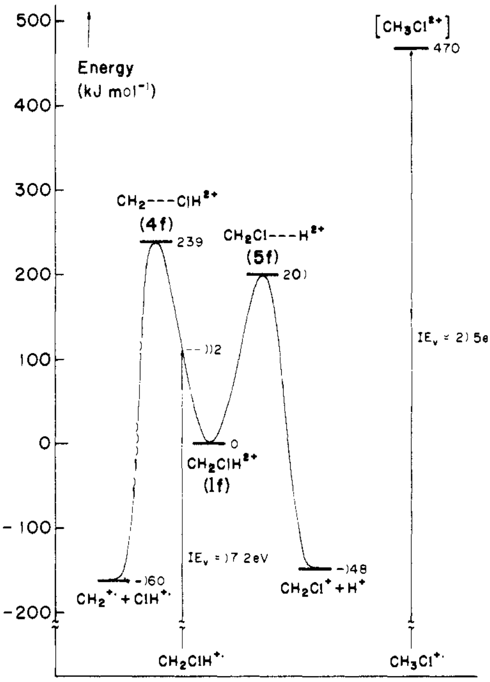

Figure 12. Schematic energy profile for dissociative processes in the methylenechloronium dication (**1f**).

There is good agreement between the calculated relative energies of the $CH_2^{\bullet+}$ + $XH^{\bullet+}$ and CH_3^+ + X^+ pairs and experimental values.[45] These comparisons (with the exception of X = PH_2 for which PH_2^+ is a ground-state singlet) are all isogyric,[46] i.e., the number of electron pairs is conserved, and are well-handled at the MP3/6-31G** level of theory.

The comparisons of $CH_2^{\bullet+}$ + $XH^{\bullet+}$ with CH_2X^+ + H^+, on the other hand, are nonisogyric *for all X*. There is consequently a large correlation contribution to the relative energies, which results in the $CH_2^{\bullet+}$ + $XH^{\bullet+}$ pair being artificially favored when the incorporation of electron correlation is incomplete. The magnitude of the error at the MP3/6-31G** level lies in the quite narrow range 65 ± 15 kJ mol⁻¹. In a similar manner, there is an error of 23 kJ mol⁻¹ in the (nonisogyric) comparison of $CH_2^{\bullet+}$ + $PH_3^{\bullet+}$ and CH_3^+ + PH_2^+, referred to above.

Support for these arguments comes from relative energies calculated at the MP4/6-31G** level[47] which lead to somewhat reduced errors for the nonisogyric comparisons. For example, the energy of $CH_2NH_2^+$ + H^+ relative to $CH_2^{\bullet+}$ + $NH_3^{\bullet+}$ is 1 kJ mol⁻¹ (MP4/6-31G**) compared with 14 (MP3/6-31G**) and −54 (experimental) kJ mol⁻¹. Again, for CH_3^+ + PH_2^+ relative to $CH_2^{\bullet+}$ + $PH_3^{\bullet+}$, the MP4/6-31G** energy is −163 kJ mol⁻¹ compared with −159 (MP3/6-31G**) and −182 (experimental) kJ mol⁻¹. There is a smaller difference, as might have been expected, between MP4 and MP3 results for the isogyric comparisons. For example, for CH_3^+ + NH_2^+ relative to $CH_2^{\bullet+}$ + $NH_3^{\bullet+}$ the values are 22 (MP3/6-31G**), 22 (MP4/6-31G**), and 19 (experimental) kJ mol⁻¹.

Calculated Ionization Energies and Relationship with Charge-Stripping Mass Spectrometry Experiments. Charge-stripping mass spectrometry experiments have been carried out[9] for most of the systems examined in the present study. In general, intense peaks corresponding to [CH_3X^{2+}] were found[9a,b] in the spectra of $CH_2XH^{\bullet+}$ but not in the spectra of $CH_3X^{\bullet+}$.[48] Experimental Q_{min} values have been reported[9c] for X = NH_2, OH, F, SH, and Cl and vertical ionization energies calculated[9c] for the fluorine and oxygen systems. It is of interest to make comparisons with the present theoretical predictions. Vertical and adiabatic ionization energies and calculated excess energies (ΔE = $IE_v - IE_a$) obtained in the present study are presented in Table VII, together with the available experimental Q_{min} values.

Table VII. Calculated[a] Vertical (IE_v, eV) and Adiabatic (IE_a, eV) Ionization Energies, Calculated[a] Excess Energies (ΔE, kJ mol⁻¹), and Experimental[b] Q_{min} Values (eV)

process	IE_v	EOM[c]	IE_a	ΔE	Q_{min}
$CH_2NH_3^{\bullet+} \rightarrow CH_2NH_3^{2+}$	16.2	15.8	15.9	29	18.9
$CH_3NH_2^{\bullet+} \rightarrow CH_3NH_2^{2+}$	19.7				17.7
$CH_2OH_2^{\bullet+} \rightarrow CH_2OH_2^{2+}$	16.7		15.6	108	16.5
$CH_3OH^{\bullet+} \rightarrow CH_3OH^{2+}$	22.4	21.6			16.3
$CH_2FH^{\bullet+} \rightarrow CH_2FH^{2+}$	18.8		17.6	118	17.9
$CH_3F^{\bullet+} \rightarrow CH_3F^{2+}$	22.2	21.9			17.2
$CH_2PH_3^{\bullet+} \rightarrow CH_2PH_3^{2+}$	15.9		15.6	29	
$CH_3PH_2^{\bullet+} \rightarrow CH_3PH_2^{2+}$	17.1		16.2	81	
$CH_2SH_2^{\bullet+} \rightarrow CH_2SH_2^{2+}$	15.7	15.4	15.5	23	19.8
$CH_3SH^{\bullet+} \rightarrow CH_3SH^{2+}$	18.8		18.1	75	20.2
$CH_2ClH^{\bullet+} \rightarrow CH_2ClH^{2+}$	17.2		16.1	112	17.5
$CH_3Cl^{\bullet+} \rightarrow CH_3Cl^{2+}$	21.5				18.2

[a] MP3/6-31G** values, with zero-point vibrational contribution where appropriate. [b] From ref 9b. [c] Vertical ionization energies (eV), as calculated with the EOM approach (see text) and the 6-31G** basis set.

We can see immediately from Table VII that whereas the experimental Q_{min} values are generally quite similar for $CH_2XH^{\bullet+}$ and $CH_3X^{\bullet+}$ isomers (with $Q_{min}(CH_2XH^{\bullet+}) > Q_{min}(CH_3X^{\bullet+})$ for first-row systems), the theoretical ionization energies for the two isomers are significantly different (with $IE(CH_2XH^{\bullet+}) < IE(CH_3X^{\bullet+})$). Our results support the suggestion[9c] that CH_2XH^{2+} ions are formed from both $CH_2XH^{\bullet+}$ and $CH_3X^{\bullet+}$ in the charge-stripping experiments. A possible rationalization is that formation of CH_2XH^{2+} dications from $CH_3X^{\bullet+}$ arises through prior rearrangement of $CH_3X^{\bullet+}$ to give vibrationally excited $CH_2XH^{\bullet+}$ radical cations. This would be consistent with the generally smaller values of Q_{min} observed for $CH_3X^{\bullet+}$ compared with $CH_2XH^{\bullet+}$.

Additional evidence that the Q_{min} values obtained through charge-stripping of $CH_3X^{\bullet+}$ ions do not correspond to formation of CH_3X^{2+} dications comes from alternative procedures for calculating the energy for the vertical ionization process $CH_3X^{\bullet+} \rightarrow CH_3X^{2+}$. In the first place, provided that the geometries of CH_3X and $CH_3X^{\bullet+}$ are similar, then the various single and double ionization energies are related by

$$IE_v(CH_3X^{\bullet+} \rightarrow CH_3X^{2+}) \approx IE_v(CH_3X \rightarrow CH_3X^{2+}) - IE_v(CH_3X \rightarrow CH_3X^{\bullet+}) \quad (2)$$

This allows values for the ionization process $CH_3X^{\bullet+} \rightarrow CH_3X^{2+}$ to be obtained from an independent set of experimental data. For example, the lowest double ionization energy of CH_3OH ($IE_v(CH_3OH \rightarrow CH_3OH^{2+})$) has been measured[49] in a double-charge-transfer experiment as 33.2 ± 0.5 eV. Combining this with the literature[50] value for IE_v ($CH_3OH \rightarrow CH_3OH^{\bullet+}$) of 10.90 eV leads to a vertical ionization energy for the process $CH_3OH^{\bullet+} \rightarrow CH_3OH^{2+}$ of 22.3 eV. This is close to the theoretically calculated value of 22.4 eV (Table VII) but differs significantly from the Q_{min} value reported in the charge-stripping experiment.

In addition, the vertical ionization energies calculated by using the alternative equations-of-motion approach are quite close to those from the conventional calculations. For example, the EOM procedure leads to $IE_v(CH_3OH^{\bullet+} \rightarrow CH_3OH^{2+})$ = 21.6 eV and $IE_v(CH_3F^{\bullet+} \rightarrow CH_3F^{2+})$ = 21.9 eV, results which are close to our directly calculated values of 22.4 and 22.2 eV, respectively (Table VII). Thus, both theory and experiment indicate that the

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(45) (a) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *6*. (b) Butler, J. J.; Baer, T.; Evans, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 3451. (c) Martin, R. H.; Lampe, F. W.; Taft, R. W. *J. Am. Chem. Soc.* **1966**, *88*, 1353.

(46) Pople, J. A.; Frisch, M. J.; Luke, B. T.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1983**, *17*, 307.

(47) (a) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91. (b) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(48) An intense charge-stripping peak was observed,[9b] however, in the spectrum of $CH_3SH^{\bullet+}$.

(49) Appell, J.; Durup, J.; Fehsenfeld, F. C.; Fournier, P. *J. Phys. B* **1974**, *7*, 406.

(50) Levin, R. D.; Lias, S. G. *Ionization Potential and Appearance Potential Measurements 1971–1981*; U.S. Government Printing Office: Washington, DC, 1982.

energies for the process $CH_3X^{\bullet+} \rightarrow CH_3X^{2+}$ are considerably higher than the Q_{min} values obtained through charge stripping of $CH_3X^{\bullet+}$ cations.[51]

Comparison of the experimental Q_{min} values with the calculated ionization energies shows moderate (though by no means perfect) agreement for the ylide dications CH_2XH^{2+} when X = OH (Q_{min} = 16.5 eV, IE_v = 16.7 eV, IE_a = 15.6 eV), X = F (Q_{min} = 17.9 eV, IE_v = 18.8 eV, IE_a = 17.6 eV), and X = Cl (Q_{min} = 17.5 eV, IE_v = 17.2 eV, IE_a = 16.1 eV). However, there are major discrepancies for X = NH_2(Q_{min} = 18.9 eV, IE_v = 16.2 eV, IE_a = 15.9 eV) and X = SH (Q_{min} = 19.8 eV, IE_v = 15.7 eV, IE_a = 15.5 eV). The theoretical values in these two instances are supported by EOM calculations and by higher level conventional calculations. Thus, for X = NH_2 the calculated IE_v values are 16.2 (MP3/6-31G**), 16.2 (MP4/6-31G**), 15.8 (EOM/6-31G**), and 16.3 eV (MP3/6-311G**)[52] compared with the experimental Q_{min} of 18.9 eV, while for X = SH the calculated IE_v values are 15.7 (MP3/6-31G**) and 15.4 eV (EOM/6-31G**) compared with the experimental Q_{min} value of 19.8 eV. The disagreement between theory and experiment is sufficiently large that reinterpretation of the experimental data could be in order.

Finally, we note that the significant differences between IE_v and IE_a values for a number of systems (X = OH, F, PH_2, and Cl) reflect a marked difference between the geometry of the ylidion ($\dot{C}H_2XH^+$) and the ylide dication (CH_2XH^{2+}) in these cases. This effect would not, however, account for the discrepancy noted above between the theoretical and experimental ionization energies.

Concluding Remarks

Ylide dications (CH_2XH^{2+}), although thermodynamically unstable with respect to fragmentation products, are found to lie in moderately deep potential wells and should be observable species. In contrast, their conventional isomers (CH_3X^{2+}) can rearrange or fragment with little or no barrier. The calculated ionization energies corresponding to production of ylide dications from ylidions are generally in moderate agreement with experimental Q_{min} values. However, there are a number of discrepancies, and a reexamination of the experimental data is suggested in these cases. The calculations indicate that production of CH_3X^{2+} dications from $CH_3X^{\bullet+}$ is a high-energy process, and the experimental Q_{min} values for such systems are likely to correspond to production of the isomeric CH_2XH^{2+} dications.

Registry No. $CH_2NH_3^{2+}$, 103884-69-1; $CH_3NH_2^{2+}$, 103958-76-5; $CH_2OH_2^{2+}$, 83584-97-8; CH_3OH^{2+}, 99674-12-1; CH_2FH^{2+}, 103751-46-8; CH_2F^{2+}, 103958-74-3; $CH_2PH_3^{2+}$, 103884-70-4; $CH_3PH_2^{2+}$, 103958-77-6; $CH_2SH_2^{2+}$, 103884-71-5; CH_3SH^{2+}, 103958-75-4; CH_2ClH^{2+}, 103884-72-6; CH_3Cl^{2+}, 103958-73-2; Ph_2^+, 12339-26-3; $Ph_3^{\cdot+}$, 29724-05-8; $CH_2PH_2^+$, 59025-96-6; $HCPH_2^{\cdot+}$, 98077-14-6; $CH_2PH^{\cdot+}$, 89387-22-4; SH^+, 12273-42-6; $SH_2^{\cdot+}$, 77544-69-5; CH_2SH^+, 54043-03-7; $HCSH^{\cdot+}$, 61356-81-8; Cl^+, 24203-47-2; $ClH^{\bullet+}$, 12258-94-5; CH_2Cl^+, 59000-00-9; $HCCl^+$, 89877-51-0; $HCCl_2^+$, 103904-09-2; $CH_2^{\bullet+}$, 15091-72-2; H_2, 1333-74-0; $H_2^{\bullet+}$, 12184-90-6; CH_3^+, 14531-53-4.

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[51] Further information on the stabilities and lifetimes of the CH_3X^{2+} species might be obtained from state of the art photoionization or Auger spectroscopy experiments.

[52] The 6-311G** basis set is described in: Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

A MCSCF Study of Homoaromaticity and the Role of Ion Pairing in the Stabilization of Carbanions

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Abstract: The bicyclo[3.2.1]octa-3,6-dien-2-yl anion (I), the anion I lithium cation complex, the allyl anion (X), the allyl radical, the allyl anion lithium cation complex, the ethene molecule, and the ethene lithium cation complex have been studied by means of multiconfigurational SCF (MCSCF) and analytical gradients. The calculations have been confined to minimal and split-valence basis sets. The large distance between the C_2 olefinic bridge and the C_3 carbanionic bridge of anion I and the short C_6–C_7 bond distance imply bishomoaromaticity to be negligible. According to these results, homoaromaticity is not responsible for the observed stability in many potentially homoaromatic carbanions. The stability of anion I in the gas phase is instead explained in terms of a simple electrostatic model, where the quadrupole moment in the C_2 olefinic bridge stabilizes the charge in the C_3 carbanionic bridge. This model agrees quantitatively with experiment. Calculations on the anion I lithium cation complex showed that in solution an additional attractive interaction between the C_2 olefinic bridge and the lithium cation can contribute. This additional interaction is estimated to stabilize the carbanion–lithium ion pair in the gas phase by about 16 kcal/mol. However, the stabilizing interactions of anion I in solution (quadrupole–charge and counterion–anion interactions) will be reduced by solvent shielding. The relative ratios of the different stabilizing interactions are therefore difficult to estimate. The geometrical findings of this paper have been verified by a recent X-ray experiment.

The concept of homoaromaticity has been controversial since it was introduced by Winstein almost 30 years ago.[1] Although homoaromatic stabilization of carbocations is well established,[2] more recent work concludes that homoaromaticity is not expected to be of importance in carbanions and neutral compounds, including radicals.[3] This conclusion about carbanions is based upon theoretical studies of the prototype of bishomoaromatic anions, i.e., the bicyclo[3.2.1]octa-3,6-dien-2-yl anion (I),[4] and other

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[†] University of Lund.

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[1] (a) Applequist, D. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 4012. (b) Winstein, S. *J. Am. Chem. Soc.* **1959**, *81*, 6524. For reviews, see: (c) Winstein, S. *Q. Rev., Chem. Soc.* **1969**, *23*, 141. Winstein, S. *Spec. Publ.—Chem. Soc.* **1967**, *21*, 5. (d) Winstein, S. *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. 3, Chapter 22, p 965. (e) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106. (f) Warner, P. M. *Top. Nonbenzenoid Aromat. Chem.* **1976**, 2.

0002-7863/86/1508-6554$01.50/0