J. Am. Chem. Soc. **1988**, *110*, 1672-1678

Odd-Electron σ Bonds

Timothy Clark

Contribution from the Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, D-8520 Erlangen, Federal Republic of Germany. *Received March 5, 1987*

Abstract: The one- and three-electron bonded radical cation complexes obtained by combinations of the neutral hydrides of the elements Li–Ar with the corresponding radical cations have been investigated with MP2/6-31G* ab initio molecular orbital theory. The bond energies for the odd-electron σ bonds are found to range up to 55 kcal mol^{-1} and to depend exponentially on the energy, Δ_{IP}, required to transfer an electron from one partner in the complex to the other. A general equation is proposed to predict the dissociation energies of both one- and three-electron bonds in terms of Δ_{IP}, the bond energy of the symmetrical complexes, and a pre-exponential factor that is characteristic of the elements involved.

One- or three-electron bonds play an important role in radical chemistry and in many gas-phase processes involving radical ions. Despite this, relatively little is known about these odd-electron σ bonds, especially in comparison to the wealth of data available for conventional two-electron bonds. Baird[1] has treated three-electron bonds on the basis of simple molecular orbital theory and comes to the conclusion that the maximum strength of a three-electron bond is half that of the corresponding two-electron bond, but that the strength of the bond should fall off with increasing overlap integral. Baird has also pointed out that, whereas $He_2^{\bullet+}$ has a bond energy of 57 kcal mol^{-1},[2] the isoelectronic HeH$^\bullet$ radical is unbound.[3] Meot-Ner et al.[4] have treated what are essentially odd-electron bond energies in complexes between arenes and their radical cations using valence bond theory. They have pointed out that the bond strength depends strongly on the difference in ionization potential between the two arenes involved (the strongest bonds being obtained for the symmetrical complexes) and have described these interactions using the "no bond resonance" picture:

$$A^{\bullet+} \quad B \leftrightarrow A \quad B^{\bullet+} \tag{1}$$

In such a resonance situation, the energy difference between the two resonance structures (i.e., the difference in ionization potential between A and B) is of primary importance in determining the stabilization energy.

Experimental data on dissociation energies for one- and three-electron bonds are remarkably sparse. The noble gas dimer cations and those of the alkali metals lithium and sodium are well characterized, as are the dihalogen radical anions. Meot-Ner and Field[5] have investigated $N_2{\cdots}N_2^{\bullet+}$ and $CO{\cdots}CO^{\bullet+}$ in comparison to $N_2{\cdots}N_2H^+$ and $CO{\cdots}COH^+$. A summary of some of the available data is shown in Table I. Some trends are detectable. The one-electron bond in $H_2^{\bullet+}$ and the three-electron bond in $He_2^{\bullet+}$ both have dissociation energies around 60 kcal mol^{-1} and are the strongest odd-electron bonds in the table. Generally, odd-electron bond strengths decrease on descending the periodic table, but this is not the case for the dihalogen radical anions, where the bond energies in $F_2^{\bullet-}$ and $Cl_2^{\bullet-}$ are very similar. Although a number of three-electron bonded organic radical cations have been observed in solution and even by X-ray crystallography,[7] there are few qualitative data on bond dissociation energies. Bond energies of 11[8] and 14.5[9] kcal mol^{-1} have been deduced for N···N three-electron bonds in polycyclic radical cations, but strain and substituent effects probably influence the bonding strongly in these examples. A number of three-electron bonded radicals and radical ions have been observed by ESR spectroscopy,[10] and some one-electron bonded radical cations in matrices.[11]

Table I. Representative One- and Three-Electron Bond Energies

reaction	bond energy[a] (kcal mol^{-1})
$H_2^{\bullet+} \rightarrow H^+ + H^\bullet$	64.4[b]
$Li_2^{\bullet+} \rightarrow Li^+ + Li^\bullet$	29.4[c]
$Na_2^{\bullet+} \rightarrow Na^+ + Na^\bullet$	22.7[d]
$K_2^{\bullet+} \rightarrow K^+ + K^\bullet$	18.3[e]
$He_2^{\bullet+} \rightarrow He^{+\bullet} + He$	57.4[f]
$Ne_2^{\bullet+} \rightarrow Ne^{+\bullet} + Ne$	31.1[f]
$Ar_2^{\bullet+} \rightarrow Ar^{+\bullet} + Ar$	28.8[f]
$Xe_2^{\bullet+} \rightarrow Xe^{+\bullet} + Xe$	23
$F_2^{\bullet+} \rightarrow F^- + F^\bullet$	29.7[f]
$Cl_2^{\bullet-} \rightarrow Cl^- + Cl^\bullet$	29.1[f]
$Br_2^{\bullet-} \rightarrow Br^- + Br^\bullet$	26.2
$I_2^{\bullet-} \rightarrow I^- + I^\bullet$	24.3
$IBr^{\bullet-} \rightarrow Br^- + I^\bullet$	23.1

[a] Unless otherwise noted, data are $\Delta\Delta H^\circ_f$ values taken from the JANAF Tables (JANAF Thermochemical Tables, 2nd ed., Stull, D. R.; Prophet, H., Eds. *Natl. Stand. Ref. Data Ser. Natl. Bur. Stand.* (*U.S.*) **1971**, *37*) and Rosenstock's compilation of negative ion data (Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Supplement 1). [b] Bates, D. R.; Ledsham, K.; Stewart, A. L. *Philos. Trans. R. Soc. London* **1953**, *A246*, 215. [c] Mathur, B. P.; Rothe, E. W.; Reck, G. P.; Lightman, A. J. *Chem. Phys. Lett.* **1978**, *56*, 336. [d] Carlson, N. W.; Taylor, A. J.; Jones, K. M.; Schawlow, A. L. *Phys. Rev.* **1981**, *A24*, 822. [e] Leytwyler, S.; Herrman, A.; Woeste, L.; Schumacher, E. *Chem. Phys.* **1980**, *48*, 253. [f] Values taken from the compilation given in ref 2.

In contrast to the relative paucity of experimental data, the literature abounds with theoretical studies on odd-electron bonds, even if the many papers on $H_2^{\bullet+}$ are ignored. Thus, the dialkali metal radical cations,[2,12] and di-noble-gas radical cations,[2,13] $F_2^{\bullet-}$,[2]

---

(1) Baird, N. C. *J. Chem. Educ.* **1977**, *54*, 291.

(2) See: Gilbert, T. L.; Wahl, A. C. *J. Chem. Phys.* **1971**, *55*, 5247 and references therein.

(3) Herzberg, G. *Molecular Spectra and Molecular Structure*; 2nd ed.; van Nostrand: Princeton, 1950; Vol. 1, p 355.

(4) Meot-Ner, M.; Hamlet, P.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1978**, *100*, 5466. Meot-Ner, M. *Acc. Chem. Res.* **1984**, *17*, 186.

(5) Meot-Ner, M.; Field, H. *J. Chem. Phys.* **1974**, *61*, 3742.

(6) See, for instance: Alder, R. W. *Acc. Chem. Res.* **1983**, *16*, 321. Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436. Musker, W. K. *Acc. Chem. Res.* **1980**, *13*, 200.

(7) Alder, R. W.; Orpen, A. G.; White, J. M. *J. Chem. Soc., Chem. Commun.* **1985**, 949.

(8) Alder, R. W.; Arrowsmith, R. J.; Casson, A.; Sessions, R. B.; Heilbronner, E.; Kovac, B.; Huber, H.; Taagapera, M. *J. Am. Chem. Soc.* **1981**, *103*, 6137.

(9) Nelsen, S. F.; Alder, R. W.; Sessions, R. B.; Asmus, K.-D.; Hiller, K.-O.; Gobl, M. *J. Am. Chem. Soc.* **1980**, *102*, 1429.

(10) Gilbert, B. C.; Hodgeman, D. K. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1748. Gara, W. B.; Giles, J. R. M.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1979**, 144. Nikishida, K.; Williams, F. *Chem. Phys. Lett.* **1975**, *34*, 302.

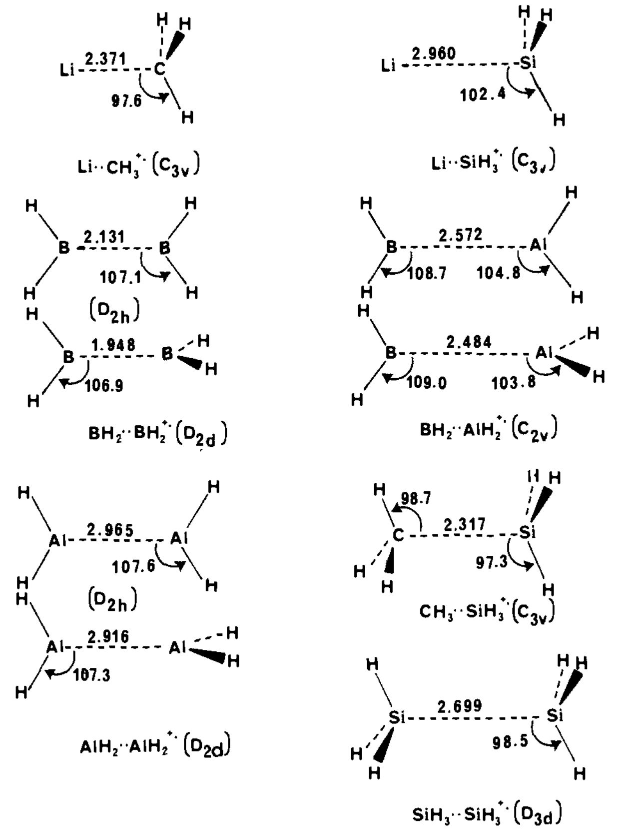
(11) Shida, T.; Kubodera, H.; Egawa, Y. *Chem. Phys. Lett.* **1981**, *79*, 179. Wang, J. T.; Williams, F. *J. Chem. Soc., Chem. Commun.* **1981**, 666.

(12) See, for instance: Flad, J.; Igel, G.; Dolg, M.; Stoll, H.; Preuss, H. *Chem. Phys.* **1983**, *75*, 331. Konowalow, D. D.; Rosenkrantz, M. E. *Chem. Phys. Lett.* **1979**, *61*, 489. Konowalow, D. D.; Stevens, W. J.; Rosenkrantz, M. E. *Chem. Phys. Lett.* **1979**, *66*, 24. Uzer, T.; Dalgarno, A. *Chem. Phys. Lett.* **1979**, *65*, 1. Nemukhin, A. V.; Stepanov, N. F. *Chem. Phys. Lett.* **1979**, *60*, 421. Pakiar, A. H.; Linett, J. W. *Int. J. Quantum Chem.* **1980**, *18*, 661. Car, R.; Meuli, R. A.; Buttet, J. *J. Chem. Phys.* **1980**, *73*, 4511. Henriet, A.; Masnou-Seeuws, F.; *Chem. Phys. Lett.* **1983**, *101*, 535. Bishop, D. M.; Pouchan, C. *Chem. Phys. Lett.* **1983**, *102*, 132. Cardelino, B. H.; Eberhard, W. H.; Borkman, R. F. *J. Chem. Phys.* **1986**, *84*, 3230.

(13) See, for instance: Michels, H. H.; Hobbs, R. H.; Wright, L. A. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1978**, *12*, 257; *J. Chem. Phys.* **1978**, *69*, 5151. Wadt, W. R. *J. Chem. Phys.* **1978**, *68*, 402; **1980**, *73*, 3195. Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1978**, *68*, 3850.

0002-7863/88/1510-1672$01.50/0 © 1988 American Chemical Society

Chart I



$Cl_2^{\bullet -}$,[2,14] $LiH^{\bullet +}$ and $NaH^{\bullet +}$,[15] $ArHe^{\bullet +}$,[16] the water dimer radical cation,[17] and hydrogen fluoride dimer radical cation,[18] $Na_2^{\bullet -}$ and $Li_2^{\bullet -}$,[19] $NH_3 \cdots NH_3^{\bullet +}$,[20,21] and the isoelectronic complexes $NO_2 \cdots NO_2^{\bullet +}$ and $CO_2 \cdots CO_2^{\bullet -}$ [22] have all received theoretical attention. The preceding papers in this series[23-25] dealt with radical cation complexes involving HCl, H_2S, and PH_3 moieties, for which an exponential decline in the three-electron bond energy with increasing difference in ionization potential was found.[26] Finally, Harcourt[27] has pointed out the importance of "Pauling three-electron bonds" in a variety of molecules. This paper reports a comprehensive ab initio molecular orbital study of one- and three-electron bonded radical cation complexes of the elements Li–Ar and their hydrides and attempts to identify the factors affecting odd-electron bond dissociation energies.

Method

All calculations used a CDC version of the GAUSSIAN82[28] program modified from the original VAX code by T. Kovář and A. Sawaryn. The unrestricted Hartree–Fock (UHF) formalism was used for all open-shell species. Spin contamination was neglible in all cases. Optimizations were carried out with use of standard methods with the 6-31G* basis set.[29] Symmetry constraints are given in the tables. Only structures corresponding to one- or three-electron bonded complexes were considered. Thus, the structures reported are often not the global minima and alternative structures, such as $C_2H_6^{\bullet +}$ or hydrogen bonded complexes, may in some cases be more stable. Some of the structures found for weakly bound complexes, especially those involving Ne, collapsed to complexes in which a combination of odd-electron and hydrogen bonding is important, but have been included for completeness. All energy discussions in the text refer to the results of single-point 6-31G* calculations on the Hartree-Fock optimized geometries using a second-order Møller–Plesset (MP2) correction for electron correlation.[30] Post-SCF calculations did not include the non-valence orbitals. The GAUSSIAN82 archive entries for the MP2/6-31G* calculations are available as supplementary material. The nature of some of the more interesting stationary points was determined by diagonalization of the force-constant matrix at UHF/6-31G*.

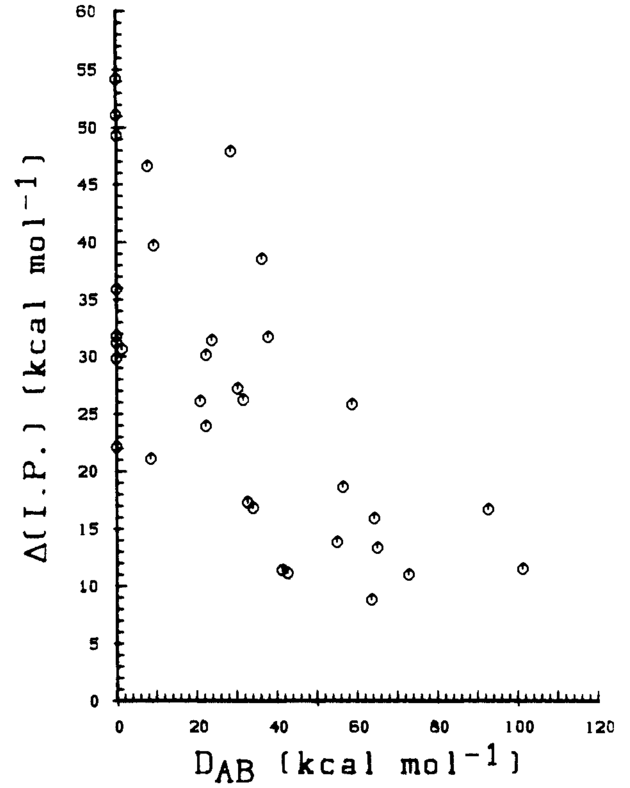


Figure 1. One-electron bond energies, D_{AB}, plotted against Δ_{IP}, the energy for reaction 2.

Results

One-Electron Bonds. The calculated total energies, bond dissociation energies, and ionization potentials for the one-electron bonded complexes formed by the radicals and cations of the groups Li, BeH, BH_2, CH_3, Na, MgH, AlH_2, and SiH_3 are shown in Table II. Some pertinent features of the geometries of selected radical cation complexes are shown in Chart I. The one-electron bond strengths for the alkali metal dimer radical cations, $Li_2^{\bullet +}$ and $Na_2^{\bullet +}$, are calculated to be marginally lower than the experimental values, but the agreement is good. Bond energies for the symmetrical complexes range from 22.1 kcal mol^{-1} for $Na_2^{\bullet +}$ to 54.2 kcal mol^{-1} for $H_2B \cdots BH_2^{\bullet +}$, and the bond energies for the symmetrical complexes are larger for the first row elements than the second. The alkali metals form significantly weaker one-electron bonds than the other elements in the same row. One surprising feature of the $H_2B \cdots BH_2^{\bullet +}$ radical cation is its high rotation barrier, which is caused by hyperconjugation in the

---

(14) Tasker, P. W.; Balint-Kurti, G. G.; Dixon, R. W. *Mol. Phys.* **1976**, *32*, 1651. Jette, A. N.; Gilbert, T. L.; Das, T. P. *Phys. Rev.* **1969**, *184*, 884. Tasker, P. W.; Stoneham, A. M. *J. Phys. Chem. Solids* **1977**, *38*, 1185.

(15) Rosmus, P.; Meyer, W. *J. Chem. Phys.* **1977**, *66*, 13.

(16) Olson, R. E.; Liu, B. *Chem. Phys. Lett.* **1978**, *56*, 537.

(17) Sato, K.; Tomoda, S.; Kimura, K.; Iwata, S. *Chem. Phys. Lett.* **1983**, *95*, 579. Curtiss, L. A. *Chem. Phys. Lett.* **1983**, *96*, 442. Tomoda, S.; Kimura, K. *Chem. Phys.* **1983**, *82*, 215.

(18) Peel, J. B. *Int. J. Quantum Chem.* **1983**, *23*, 653.

(19) Shepard, R.; Jordan, K. D.; Simons, J. *J. Chem. Phys.* **1978**, *69*, 1788.

(20) Cao, H. Z.; Evleth, E. M.; Kassab, E. *J. Chem. Phys.* **1984**, *81*, 1512.

(21) Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1985**, *107*, 345.

(22) Yoshioka, Y.; Jordan, K. D. *J. Am. Chem. Soc.* **1980**, *102*, 2621.

(23) Clark, T. *J. Comput. Chem.* **1981**, *2*, 261.

(24) Clark, T. *J. Comput. Chem.* **1982**, *3*, 112.

(25) Clark, T. *J. Comput. Chem.* **1983**, *4*, 404.

(26) Clark, T. NATO ASI Series C, *Substituent Effects in Radical Reactions*; Viehe, H. G.; Merenyi, R.; Janousek, Z., Eds.; D. Reidel Publishing Co.: Amsterdam, 1986; ACS Petroleum Division Preprints: "Advances in Free Radical Chemistry", Anaheim ACS Meeting, 1986.

(27) Harcourt, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5195.

(28) Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Pople, J. A.; Kahn, L. GAUSSIAN82, Release A, Carnegie-Mellon University, 1982.

(29) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(30) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1976**, *10*, 1.

Table II. One-Electron Bonded Radical Cation Complexes

		HF/6-31G*			MP2/6-31G*		
species	symmetry (NIMAG)[a]	total energy[b]	IP[c]	D_{AB}[d]	total energy[b]	IP[c]	D_{AB}[d]
Li^{+}	K_h	-7.235 54			-7.235 54		
$Li^{\bullet}$	K_h	-7.431 37	122.9		-7.431 37	122.9	
BeH^{+}	$C_{\infty v}$	-14.849 54			-14.869 89		
$BeH^{\bullet}$	$C_{\infty v}$	-15.147 31	186.8		-15.168 05	187.1	
BH_2^{+}	$C_{\infty v}$	-25.470 80			-25.518 50		
$BH_2^{\bullet}$	C_{2v}	-25.749 69	175.0		-25.804 30	179.3	
CH_3^{+}	D_{3h}	-39.230 64			-39.325 14		
$CH_3^{\bullet}$	D_{3h}	-39.558 99	206.0		-39.668 67	215.6	
Na^{+}	K_h	-161.659 29			-161.659 29		
$Na^{\bullet}$	K_h	-161.841 44	114.3		-161.841 44	114.3	
MgH^{+}	$C_{\infty v}$	-199.884 97			-199.904 42		
$MgH^{\bullet}$	$C_{\infty v}$	-200.135 91	157.5		-200.154 44	156.9	
AlH_2^{+}	$D_{\infty h}$	-242.763 60			-242.801 48		
$AlH_2^{\bullet}$	C_{2v}	-243.009 46	154.3		-243.049 35	155.5	
SiH_3^{+}	D_{3h}	-290.328 91			-290.391 21		
$SiH_3^{\bullet}$	D_{3h}	-290.606 12	173.9		-290.674 45	177.8	
			Δ_{IP}[e]			Δ_{IP}[e]	
$Li{\cdot\cdot}Li^{\bullet+}$	$D_{\infty h}$(0)	-14.712 74	0.0	28.8	-14.712 74	0.0	28.8
$Li{\cdot\cdot}BeH^{\bullet+}$	$C_{\infty v}$	-22.407 59	63.9	15.5	-22.428 90	64.2	15.9
$Li{\cdot\cdot}BH_2^{\bullet+}$	C_{2v}	-33.012 66	52.1	17.2	-33.069 46	56.4	18.8
$Li{\cdot\cdot}CH_3^{\bullet+}$	C_{3v}(0)	-46.817 78	83.1	14.6	-46.930 81	92.7	16.7
$Li{\cdot\cdot}Na^{\bullet+}$	$C_{\infty v}$	-169.124 38	8.6	21.2	-169.124 38	8.6	21.2
$Li{\cdot\cdot}MgH^{\bullet+}$	$C_{\infty v}$	-207.396 72	34.6	15.9	-207.416 77	34.0	16.8
$Li{\cdot\cdot}AlH_2^{\bullet+}$	C_{2v}	-250.271 54	31.4	16.7	-250.312 41	32.6	17.3
$Li{\cdot\cdot}SiH_3^{\bullet+}$	C_{3v}(0)	-297.862 05	51.0	12.8	-297.931 99	54.9	13.8
$HBe{\cdot\cdot}BeH^{\bullet+}$	$D_{\infty h}$(0)	-30.073 50	0.0	48.1	-30.116 57	0.0	49.3
$HBe{\cdot\cdot}BH_2^{\bullet+}$	C_{2v}	-40.681 25	11.8	39.6	-40.759 88	7.8	46.0
$HBe{\cdot\cdot}CH_3^{\bullet+}$	C_{3v}(0)	-54.478 90	19.2	44.2	-54.614 86	28.5	47.9
$HBe{\cdot\cdot}Na^{\bullet+}$	$C_{\infty v}$	-176.823 55	72.5	10.6	-176.844 92	72.8	11.0
$HBe{\cdot\cdot}MgH^{\bullet+}$	$C_{\infty v}$	-215.075 02	29.3	26.8	-215.115 86	30.2	27.2
$HBe{\cdot\cdot}AlH_2^{\bullet+}$	C_{2v}	-257.949 17	32.5	24.0	-258.011 36	31.6	26.2
$HBe{\cdot\cdot}SiH_3^{\bullet+}$	C_{3v}(0)	-305.531 40	12.9	34.6	-305.622 44	9.3	39.7
$H_2B{\cdot\cdot}BH_2^{\bullet+}$	D_{2h}(1)	-51.283 15	0.0	39.3	-51.396 18	0.0	46.0
	D_{2d}(0)	-51.293 16	0.0	45.6	-51.409 16	0.0	54.2
$H_2B{\cdot\cdot}CH_3^{\bullet+}$	C_s	-65.077 20	31.0	29.7	-65.248 47	36.3	38.5
$H_2B{\cdot\cdot}Na^{\bullet+}$	C_{2v}	-187.428 66	60.7	12.3	-187.484 80	65.0	13.3
$H_2B{\cdot\cdot}MgH^{\bullet+}$	C_{2v}	-225.680 35	17.5	28.7	-225.756 69	22.4	30.2
$H_2B{\cdot\cdot}AlH_2^{\bullet+}$	C_{2v}[f](1)	-268.553 86	20.7	25.5	-268.651 34	23.8	28.6
	C_{2v}[g](0)	-268.557 76	20.7	27.9	-268.655 79	23.8	31.4
$H_2B{\cdot\cdot}SiH_3^{\bullet+}$	C_s	-316.136 70	1.1	36.5	-316.263 30	9.2	42.5
$H_3C{\cdot\cdot}CH_3^{\bullet+}$	D_{3h}(1)	-78.848 17	0.0	36.7	-79.072 34	0.0	49.3
	D_{3d}(0)	-78.850 54	0.0	38.2	-79.075 27	0.0	51.1
$H_3C{\cdot\cdot}Na^{\bullet+}$	C_{3v}	-201.234 11	91.7	9.9	-201.346 25	101.3	11.5
$H_3C{\cdot\cdot}MgH^{\bullet+}$	C_{3v}(0)	-239.481 01	48.5	23.2	-239.614 17	58.7	25.8
$H_3C{\cdot\cdot}AlH_2^{\bullet+}$	C_s	-282.354 60	51.7	20.1	-282.508 50	60.1	24.1
$H_3C{\cdot\cdot}SiH_3^{\bullet+}$	C_{3v}[h](1)	-329.927 77	32.1	25.0	-330.108 77	37.8	30.6
	C_{3v}[i](0)	-329.928 99	32.1	25.8	-330.110 30	37.8	31.6
$Na{\cdot\cdot}Na^{\bullet+}$	$D_{\infty h}$	-323.535 97	0.0	22.1	-323.535 97	0.0	22.1
$Na{\cdot\cdot}MgH^{\bullet+}$	$C_{\infty v}$	-361.812 34	43.2	10.8	-361.831 48	42.6	11.1
$Na{\cdot\cdot}AlH_2^{\bullet+}$	C_{2v}	-404.686 00	40.0	10.8	-404.726 88	41.2	11.4
$Na{\cdot\cdot}SiH_3^{\bullet+}$	C_{3v}	-452.277 93	59.6	7.9	-452.347 76	63.2	8.8
$HMg{\cdot\cdot}MgH^{\bullet+}$	$D_{\infty h}$(0)	-400.070 85	0.0	31.4	-400.109 61	0.0	31.8
$HMg{\cdot\cdot}AlH_2^{\bullet+}$	C_{2v}	-442.944 42	3.2	28.2	-443.004 73	1.4	32.0
$HMg{\cdot\cdot}SiH_3^{\bullet+}$	C_{3v}	-490.531 00	16.4	25.0	-490.620 41	20.9	26.1
$H_2Al{\cdot\cdot}AlH_2^{\bullet+}$	D_{2h}(1)	-485.815 62	0.0	26.7	-483.896 73	0.0	28.8
	D_{2d}(0)	-485.818 52	0.0	28.5	-485.900 60	0.0	31.2
$H_2Al{\cdot\cdot}SiH_3^{\bullet+}$	C_s	-533.403 03	19.3	20.9	-533.513 95	22.3	23.9
$H_3Si{\cdot\cdot}SiH_3^{\bullet+}$	D_{3h}(1)	-580.982 15	0.0	29.5	-581.121 21	0.0	34.9
	D_{3d}(0)	-580.983 51	0.0	30.4	-581.122 81	0.0	35.9

[a] The number of imaginary frequencies obtained on diagonalization of the force constant matrix. [b] au (= 627.5 kcal mol^{-1}). [c] Adiabatic ionization potential (kcal mol^{-1}) of the radical. [d] Calculated energy (kcal mol^{-1}) for the reaction $A{\cdots}B^{\bullet+} \rightarrow A^{\bullet+} + B$, where A and B are defined as above. [e] Calculated energy (kcal mol^{-1}) for reaction **2**, where A is the fragment with the lower ionization potential. [f] Planar structure. [g] Perpendicular structure. [h] Eclipsed structure. [i] Staggered structure.

perpendicular (D_{2d}) form. The B–B distance in this structure (1.948 Å) is also considerably shorter than that (2.132 Å) in the D_{2h} geometry (See Chart I). These differences are larger than might be expected considering the length of the central bond and suggest that hyperconjugation plays a significant role in determining the bond energies of the radical cation complexes. The rotation barriers and geometry effects in $H_2B{\cdots}AlH_2^{\bullet+}$ and $H_2Al{\cdots}AlH_2^{\bullet+}$ are both low, although the central bond in the former is only 0.3 Å longer than that in $H_2B{\cdots}BH_2^{\bullet+}$.

The unsymmetrical complexes show a general trend that the bond dissociation energies fall off rapidly with increasing Δ_{IP}, the energy for the reaction

$$A^{\bullet+} + B \rightarrow A + B^{\bullet+} \qquad (2)$$

as shown in Figure 1. There is not, however, a usable correlation between the one-electron bond energy, D_{AB}, and Δ_{IP}. An exponential decrease in D_{AB} was found for the three-electron bonded radical cation complexes involving HCl, H_2S, and PH_3,[25] but in

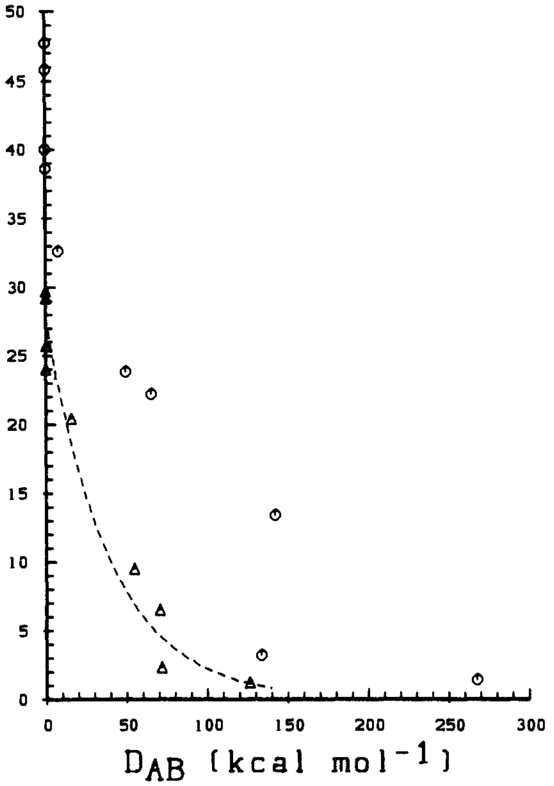


Figure 2. Three-electron bond energies, D_{AB}, plotted against Δ_{IP}, the energy for reaction 2. The triangles are the points for radical cation complexes involving only PH_3, H_2S, and HCl, and the dashed line is the best exponential fit to these points. This correlation is that proposed in ref 25.

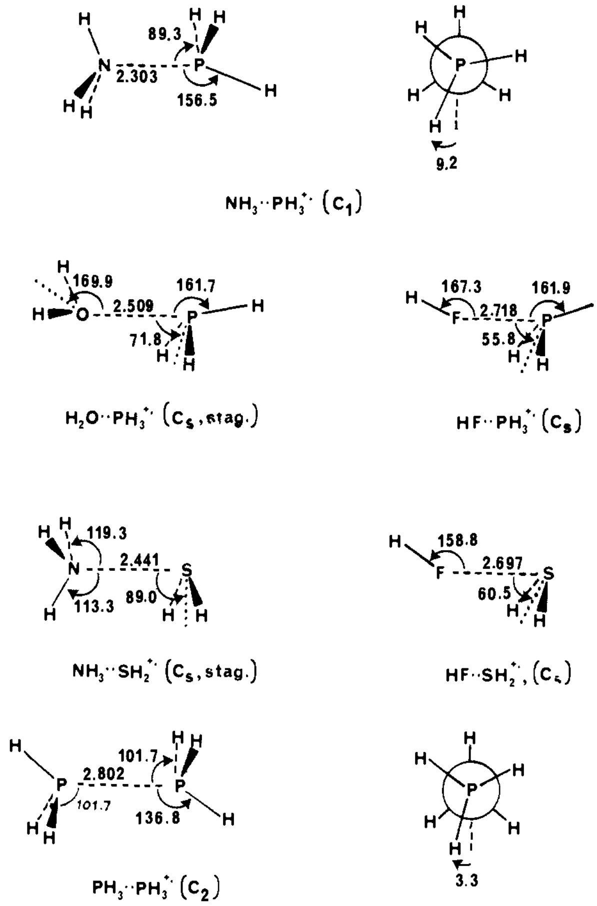
contrast to the data shown in Table II, the bond energies for the complexes $HCl{\cdots}ClH^{\bullet+}$, $H_2S{\cdots}SH_2^{\bullet+}$, and $H_3P{\cdots}PH_3^{\bullet+}$ were all found to be similar.[25] Indeed, closer inspection of Figure 1 suggests that sodium, for instance, consistently forms weak bonds, whereas carbon, boron, and beryllium form stronger bonds than most elements. This suggests that the bond dissociation energies of the symmetrical complexes may be indicative of those to be expected when the element is involved in an unsymmetrical complex. This point will be discussed below.

Three-Electron Bonds. Table III shows the calculated total and bond dissociation energies, ionization potentials, and Δ_{IP} values for the neutral compounds, radical cations, and radical cation complexes of NH_3, H_2O, HF, Ne, PH_3, H_2S, HCl, and Ar. For the noble gas dimer radical cations $Ne_2^{\bullet+}$ and $Ar_2^{\bullet+}$, the bond dissociation energies are calculated to be too high for the former and too low for the latter. This is probably a result of the relatively small basis set used and the inability of the MP2 correction to treat the three-electron bonds adequately for these examples. In all cases, a large increase in the three-electron bond energy is found on going from UHF to MP2. This is especially true for $Ne_2^{\bullet+}$ and $Ar_2^{\bullet+}$ and may explain the discrepancy between the experimental and calculated values. In some cases, especially for the unsymmetrical complexes involving the elements N–F, no three-electron bonded complex radical cation could be optimized because reactions of the type

$$AH_n^{\bullet+} + BH_m \rightarrow AH_{n-1}^{\bullet} + BH_{m+1}^{+} \qquad (3)$$

occur without activation energy. In contrast to the results found for the one-electron bonded radical cation complexes, many of the symmetrical complexes calculated were found not to be local minima on diagonalization of the force constant matrix. Although, for instance, Radom et al.[21] have found D_{3d} $NH_3{\cdots}NH_3^{\bullet+}$ to be a minimum, C_{2h} $H_2O{\cdots}OH_2^{\bullet+}$ is found to be a transition state. The water dimer radical cation has been investigated previously,[19] and we have used the bond dissociation energy of the C_{2h} complex as that of the three-electron bonded structure in order to avoid extra hydrogen bonding effects. Similar considerations apply to the hydrogen fluoride dimer radical cation.[20]

Chart II



The strongest three-electron bond (47.7 kcal mol⁻¹) is found for $HF{\cdots}FH^{\bullet+}$, despite the fact that the complex involved is not a minimum, and the weakest for $Ar_2^{\bullet+}$ (24.0 kcal mol⁻¹). Note that the three-electron bond calculated for $HF{\cdots}FH^{\bullet+}$ is stronger than the two-electron bond is fluorine, an analogous three-electron example of the $Li_2/Li_2^{\bullet+}$ situation, in which $Li_2^{\bullet+}$ is more strongly bound than Li_2.[12] The exponential dependence of D_{AB} on Δ_{IP} found earlier[25] at the MP2/4-31G level for the P, S, and Cl radical cation complexes is retained at MP2/6-31G*, as shown in Figure 2, and in general the calculated bond strengths show only small deviations between the two basis sets. The bond energy found here for $H_3N{\cdots}NH_3^{\bullet+}$ is larger than that found at MP3/6-31G** by Bouma and Radom[21] (40.0 kcal mol⁻¹ compared with an estimated value of 36.8 kcal mol⁻¹ at MP3/6-31G** without zero-point energy correction), but the difference is small and suggests that the MP2/6-31G* numbers may be more reliable than the noble gas dimer radical cation results suggest. As found for the one-electron bonds, the elements of the first row form stronger three-electron bonds than those of the second row. This thermodynamic stability is, however, offset by the kinetic instability of the first row complexes, which either are not minima or undergo extremely facile proton transfer reactions of the type shown in eq 3. $H_3N{\cdots}NH_3^{\bullet+}$ has, for instance, been implicated as an intermediate in the gas phase reaction of $NH_3^{\bullet+}$ with ammonia.[31]

Some of the geometries found for the three-electron bonded complexes are shown in Chart II. The continuum between σ* and trigonal-bipyramidal (TBP) structures found previously[25] for phosphorus-centered radicals is reproduced in the present higher level calculations. The reasons for this behavior have been discussed before[25,32] and need not be repeated here. Surprisingly,

---

(31) Sieck, L. W.; Hellner, L.; Gorden, R., Jr. *Chem. Phys. Lett.* **1971**, *10*, 502.

(32) Clark, T. *J. Chem. Soc., Chem. Commun.* **1981**, 515; *J. Chem. Soc., Perkin Trans. 2* **1982**, 1267. Janssen, R. A. J.; Sonnemans, M. H. W.; Buck, H. M. *J. Am. Chem. Soc.* **1986**, *108*, 6145.

Table III. Three-Electron Bonded Radical Cation Complexes

		HF/6-31G*			MP2/6-31G*		
species	symmetry (NIMAG)[a]	total energy[b]	IP[c]	D_{AB}[d]	total energy[b]	IP[c]	D_{AB}[d]
$NH_3^{\bullet+}$	D_{3h}	-55.873 24			-56.003 44		
NH_3	C_{3v}	-56.184 36	195.2		-56.352 67	219.8	
$H_2O^{\bullet+}$	C_{2v}	-75.615 31			-75.753 87		
H_2O	C_{2v}	-76.010 75	248.1		-76.195 93	277.4	
$HF^{\bullet+}$	$C_{\infty v}$	-99.489 60			-99.616 73		
HF	$C_{\infty v}$	-100.002 91	322.1		-100.181 58	354.4	
$Ne^{\bullet+}$	K_h	-127.751 71			-127.848 07		
Ne	K_h	-128.474 41	453.5		-128.624 72	487.3	
$PH_3^{\bullet+}$	C_{3v}	-342.131 66			-342.213 46		
PH_3	C_{3v}	-342.447 96	198.5		-342.551 50	212.1	
$H_2S^{\bullet+}$	C_{2v}	-398.326 99			-398.425 32		
H_2S	C_{2v}	-398.667 32	213.6		-398.788 21	227.7	
$HCl^{\bullet+}$	$C_{\infty v}$	-459.633 97			-459.742 17		
HCl	$C_{\infty v}$	-460.059 98	267.3		-460.192 24	282.4	
$Ar^{\bullet+}$	K_h	-526.235 04			-526.347 11		
Ar	K_h	-526.773 74	338.0		-526.911 05	353.9	
			Δ_{IP}[e]			Δ_{IP}[e]	
$H_3N{\cdot\cdot}NH_3^{\bullet+}$	$D_{3h}(1)$	-112.095 82	0.0	24.0	-112.420 51	0.0	39.8
	$D_{3d}(0)$	-112.096 13	0.0	24.2	-112.420 86	0.0	40.0
$H_3N{\cdot\cdot}OH_2^{\bullet+}$		proton transfer					
$H_3N{\cdot\cdot}FH^{\bullet+}$		proton transfer					
$H_3N{\cdot\cdot}Ne^{\bullet+}$	$C_{3v}(2)$	-184.348 94	258.3	0.8	-184.630 40	267.5	1.4
	$C_s(0)$	-184.349 52	258.3	1.2	-184.631 15	267.5	1.9
$H_3N{\cdot\cdot}PH_3^{\bullet+}$	C_{3v}[f]	-398.355 94	3.3	21.8	-398.618 94	7.7	32.5
	C_{3v}[g](2)	-398.355 97	3.3	21.8	-398.619 02	7.7	32.6
	$C_s(2)$	-398.356 68	3.3	22.3	-398.619 88	7.7	33.1
	$C_1(0)$	-398.361 82	3.3	25.5	-398.625 46	7.7	36.6
$H_3N{\cdot\cdot}SH_2^{\bullet+}$	C_s[f](1)	-454.562 79	18.4	13.9	-454.844 41	7.9	33.1
	C_s[g](0)	-454.563 04	18.4	14.1	-454.844 70	7.9	33.3
$H_3N{\cdot\cdot}ClH^{\bullet+}$	C_s[f](1)	-515.942 38	72.1	5.7	-516.207 12	62.6	7.2
	C_s[g](1)	-515.942 28	72.1	5.7	-516.206 67	62.6	6.9
$H_3N{\cdot\cdot}Ar^{\bullet+}$	C_s	-582.647 98	142.8	0.6	-582.915 95	134.1	0.9
$H_2O{\cdot\cdot}OH_2^{\bullet+}$	$C_{2v}(2)$	-151.651 95	0.0	16.3	-152.011 44	0.0	38.7
	$C_{2h}(1)$	-151.662 54	0.0	22.9	-152.022 78	0.0	45.8
$H_2O{\cdot\cdot}FH^{\bullet+}$		proton transfer					
$H_2O{\cdot\cdot}Ne^{\bullet+}$		linear H-bonded complex[i]					
$H_2O{\cdot\cdot}PH_3^{\bullet+}$	C_s[f](2)	-418.167 79	49.6	16.0	-418.439 00	65.3	18.6
	C_s[g](0)	-418.172 74	49.6	19.1	-418.444 76	65.3	22.2
$H_2O{\cdot\cdot}SH_2^{\bullet+}$	C_s[h](1)	-474.369 94	34.5	20.2	-474.659 19	49.7	23.8
$H_2O{\cdot\cdot}ClH^{\bullet+}$	C_s[h]	-535.695 20	19.2	12.5	-536.007 14	5.0	38.3
$H_2O{\cdot\cdot}Ar^{\bullet+}$		linear H-bonded complex[i]					
$HF{\cdot\cdot}FH^{\bullet+}$	$C_2(1)$	-199.524 26	0.0	19.9	-199.874 29	0.0	47.7
$HF{\cdot\cdot}Ne^{\bullet+}$		linear H-bonded complex[i]					
$HF{\cdot\cdot}PH_3^{\bullet+}$	$C_s(0)$	-442.153 81	123.6	12.1	-442.416 37	142.3	13.4
$HF{\cdot\cdot}SH_2^{\bullet+}$	$C_s(0)$	-498.350 80	108.5	13.1	-498.630 05	126.7	14.5
$HF{\cdot\cdot}ClH^{\bullet+}$		proton transfer					
$HF{\cdot\cdot}Ar^{\bullet+}$		linear H-bonded complex[i]					
$Ne{\cdot\cdot}Ne^{\bullet+}$	$D_{\infty h}$	-256.240 64	0.0	9.1	-256.534 30	0.0	38.6
$Ne{\cdot\cdot}PH_3^{\bullet+}$		linear H-bonded complex[i]					
$Ne{\cdot\cdot}SH_2^{\bullet+}$	C_s	-526.803 12	239.9	1.1	-527.052 89	259.6	1.8
$Ne{\cdot\cdot}ClH^{\bullet+}$		linear H-bonded complex[i]					
$Ne{\cdot\cdot}Ar^{\bullet+}$	$C_{\infty v}$	-654.712 39	115.5	1.8	-654.977 00	133.4	3.2
$H_3P{\cdot\cdot}PH_3^{\bullet+}$	D_{3h}	-684.609 01	0.0	18.5	-684.805 79	0.0	25.6
	$D_{3d}(2)$	-684.609 06	0.0	18.5	-684.805 87	0.0	25.7
	$C_{2h}(1)$	-684.609 10	0.0	18.5	-684.805 94	0.0	25.7
	$C_2(0)$	-684.610 28	0.0	19.3	-684.807 68	0.0	26.9
$H_3P{\cdot\cdot}SH_2^{\bullet+}$	C_s[f](1)	-740.818 88	15.1	12.5	-741.034 18	15.6	20.4
	C_s[g](0)	-740.819 55	15.1	13.0	-741.034 86	15.6	20.8
$H_3P{\cdot\cdot}ClH^{\bullet+}$	$C_s(0)$	-802.199 91	68.8	5.3	-802.416 09	70.3	6.5
$H_3P{\cdot\cdot}Ar^{\bullet+}$	C_s	-868.906 29	139.5	0.6	-869.126 22	141.8	1.1
$H_2S{\cdot\cdot}SH_2^{\bullet+}$	C_{2v}	-797.023 30	0.0	18.2	-797.257 75	0.0	27.7
	$C_{2h}(0)$	-797.026 11	0.0	20.0	-797.260 94	0.0	29.7
$H_2S{\cdot\cdot}ClH^{\bullet+}$	$C_s(0)$	-858.397 70	53.7	6.7	-858.632 67	54.7	9.5
$H_2S{\cdot\cdot}Ar^{\bullet+}$	$C_s(0)$	-925.101 86	124.4	0.7	-925.338 29	126.2	1.2
$HCl{\cdot\cdot}ClH^{\bullet+}$	$C_2(0)$	-919.721 83	0.0	17.5	-919.981 01	0.0	29.2
$HCl{\cdot\cdot}Ar^{\bullet+}$	C_s	-986.406 92	70.7	1.2	-986.659 61	71.5	2.3
$Ar{\cdot\cdot}Ar^{\bullet+}$	$D_{\infty v}$	-1053.026 82	0.0	11.3	-1053.296 40	0.0	24.0

[a] The number of imaginary frequencies obtained on diagonalization of the force constant matrix. [b] au (= 627.5 kcal mol^{-1}). [c] Adiabatic ionization potential (kcal mol^{-1}) of the neutral molecule. [d] Calculated energy (kcal mol^{-1}) for the reaction $A{\cdots}B^{\bullet+} \rightarrow A^{\bullet+} + B$, where A and B are defined as above. [e] Calculated energy (kcal mol^{-1}) for reaction 2, where A is the fragment with the lower ionization potential. [f] Eclipsed structure. [g] Staggered structure. [h] Anti-structure. [i] The geometry optimized to a structure with a more or less linear hydrogen bond. These structures involve no direct interaction between the heavy atoms and are not included.

the $H_3P\cdots PH_3^{\bullet+}$ radical cation is not a minimum in the D_{3d} geometry calculated previously,[25] but rather distorts to the C_2 structure shown in Chart II. This distortion is caused by a series of effects, including the n → σ^* donation that causes TBP distortions in phosphorus-centered radicals[25,32] and the σ/π mixing that contributes to the strong nonplanarity of $P_2H_4^{\bullet+}$.[33] The complex $H_3N\cdots PH_3^{\bullet+}$ shows a TBP geometry[32] as might be expected for a phosphorus radical cation with a relatively electronegative ligand.[25] The more electronegative first row element nitrogen does not show the same sort of distortion as phosphorus in any of its complexes, in agreement with the predictions of simple qualitative molecular orbital theory.[25] Some weak complexes, such as $H_2S\cdots FH^{\bullet+}$, have structures which suggest that hydrogen bonding is a major contributor to the binding energy, but they are included in Table for completeness. In many cases, the force constant matrix was diagonalized in order to ensure that the structure obtained was a minimum. The numbers of imaginary frequencies are included in the table in these cases.

In general, however, despite the difficulties caused by hydrogen bonding and proton transfer reactions, the rough dependence of D_{AB} on Δ_{IP} and the strengths of the bonds to first row elements compared to those to their second row counterparts are found to be common features of one- and three-electron bonds. The calculated bond strengths for symmetrical complexes, in the range 20–55 kcal mol^{-1}, are also similar for the two types of bond.

Discussion

It is clear from the above results and from the earlier theoretical[25] and experimental[4] work that the strength of odd-electron σ bonds is strongly dependent on Δ_{IP}. The above results also suggest that some elements tend to form stronger or weaker odd-electron bonds than others and that these trends are reflected in the bond energies for unsymmetrical complexes. This factor can be taken into account by expressing the bond energies as a fraction, X_{AB}, of the mean bond energy of the symmetrical complexes for the groups involved

$$X_{AB} = 2D_{AB}/(D_{AA} + D_{BB}) \tag{4}$$

where D_{AA} and D_{BB} are the bond dissociation energies of the complexes $A\cdots A^{\bullet+}$ and $B\cdots B^{\bullet+}$, respectively. Plots of X_{AB} against Δ_{IP} show considerably less scatter than Figures 1 and 2, and, furthermore, the roughly exponential fall off of X_{AB} with increasing Δ_{IP} is very similar for one- and three-electron bonds. This suggests that there may be a common equation that describes the dissociation energies of odd-electron σ bonds. The scatter in the X_{AB} versus Δ_{IP} plot also reveals consistent trends. Bond energies for Li-, Na-, or Ar-containing complexes tend to be lower than expected and those for C-, F-, Si-, and P-containing complexes higher than expected. The pre-exponential factor governing the fall off in bond energy with increasing Δ_{IP} may, therefore, also be dependent on the elements involved. Therefore, a simple equation using the calculated Δ_{IP} and D_{AA} values and using adjustable pre-exponential factors, λ_A, was fitted to the calculated bond energies. This equation took the form

$$D_{AB} = [(D_{AA} + D_{BB})/2] \exp(-\lambda_A\lambda_B\Delta_{IP}) \tag{5}$$

Minimization of the least-squares deviation between the bond energies calculated by eq 5 and the MP2/6-31G* values led to lines of unit slope with intercepts close to zero. The correlation for the most stable complexes of each type shown in Tables I and II (i.e., for one- and three-electron bonds) is shown in Figure 3. The correlation coefficient (R) is 0.9964, and the root-mean-square deviation is 1.4 kcal mol^{-1}. The slope of the least-squares line is 1.0106, and the intercept with the horizontal axis is −0.21 kcal mol^{-1}. The line shown in Figure 3 is the line of unit slope passing through the origin. The fit is naturally improved by the fact that eq 5 gives perfect results for the 16 symmetrical complexes but, nevertheless, the agreement is startling. Table IV shows D_{AA} and optimized λ_A values for the elements. There is a rough correlation between ionization potential and λ_A for the one-electron bonded complexes, but this is not obviously the case for the three-electron bonds. There is little point in speculating on the nature of λ_A at this point because the parameters λ_A and D_{AA} are dependent on each other, so that, for instance, the λ_A value for oxygen or fluorine would change drastically if the D_{AA} value for the most stable form of the dimer radical cation were used.

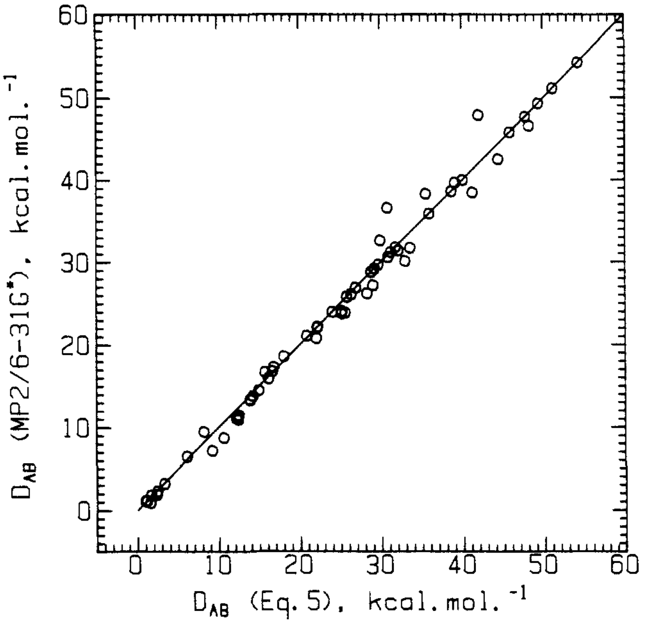


Figure 3. Comparison of the odd-electron bond dissociation energies calculated by eq 5 and the MP2/6-31G* values given in Tables II and III.

Table IV. D_{AA} and λ_A Values for the Hydrides of the Elements Li–Ar

group	D_{AA} (kcal mol^{-1})	λ_A	group	D_{AA} (kcal mol^{-1})	λ_A
Li	28.8	0.137	NH_3	40.0	0.119
BeH	49.3	0.096	H_2O	45.8	0.062
BH_2	54.2	0.111	HF	47.7	0.057
CH_3	51.1	0.066	Ne	38.6	0.089
Na	22.1	0.157	PH_3	26.9	0.122
MgH	31.8	0.125	H_2S	29.7	0.132
AlH_2	31.2	0.131	HCl	29.2	0.177
SiH_3	35.9	0.116	Ar	24.0	0.190

The largest deviations between D_{AB} values predicted by eq 5 and the MP2/6-31G* values occurs in complexes like $CH_3\cdots BeH^{\bullet+}$, in which hyperconjugation certainly provides significant extra stabilization, and $H_3N\cdots PH_3^{\bullet+}$, a TBP radical cation. Strong hyperconjugation often does not result in a failure of eq 5 because a hyperconjugation term is included in the D_{AA} values for most groups. For BeH, however, this is not the case and so bond energies involving this group are often underestimated. Similarly, deviations due to the energy gain on distortion to a TBP structure may not be considered properly by eq 5. In general, however, eq 5 predicts the odd-electron bond dissociation energies reliably and supports the notion that Δ_{IP} is the major controlling factor in this type of bonding. The fact that both the one- and three-electron bonds can be treated in this way is at first surprising, but they can both be treated by the same sort of "no bond resonance" picture shown in eq 1, so that from the resonance point of view they should behave similarly.

The relationship between D_{AB} and Δ_{IP} suggested by eq 5 has a number of consequences. First, as pointed out previously,[24,25] Δ_{IP} can only be small for charged species. Electron transfer from a neutral radical to a neutral Lewis acid or from a neutral Lewis base to a radical always involves separation of charge and is

---

(33) Clark, T. *J. Am. Chem. Soc.* **1985**, *107*, 2597. A quantitative NBO analysis of this and other radical cations and odd-electron bonded species will be presented: Clark, T.; Carpenter, J.; Weinhold, F., manuscript in preparation.

therefore unfavorable in the gas phase. This means that one- or three-electron bonded neutral radicals should be very weakly bound in the gas phase. This has been shown previously,[24,25] but it can also be demonstrated by using the one-electron bonded complex $BH_3{\cdots}CH_3^{\bullet}$ and its three-electron bonded equivalent $NH_3{\cdots}CH_3^{\bullet}$. The former is found to be weakly bound (D_{AB} = 3.0 kcal mol^{-1}, C–B bond length = 2.944 Å) and the latter gives no minimum, but simply dissociates on optimization at UHF/6-31G*. These observations help to explain Baird's[1] contrast between $He_2^{\bullet+}$ and $HeH^{\bullet}$.

However, the above only applies to the gas phase. Reactions of the type

$$A^{\bullet} + B \rightarrow A^{+} + B^{\bullet-}$$

or

$$A^{\bullet} + B \rightarrow A^{-} + B^{\bullet+}$$

are often favorable in solution, so that the solution equivalent of Δ_{IP} may be very small, even for neutral radical complexes. It is tempting to extend eq 5 to solution by substituting the appropriate electrochemical data for Δ_{IP}. Although this is not justified at present, it seems safe to conclude that one- and three-electron bonds in neutral systems will be strongly stabilized in solution relative to the gas phase. Indeed, preliminary calculations using a crude dipole model for the solvent have confirmed this hypothesis.[34] Recent calculations using the SCRF method have demonstrated a similar effect for odd-electron π interactions in neutral radicals.[35]

Summary

Odd-electron σ bond energies fall off exponentially with increasing Δ_{IP}. This behavior can be described accurately by eq 5, both for one- and three-electron bonds.

Neutral odd-electron bonded complexes should all be very weakly bound in the gas phase, but may be strongly stabilized in solution.

Hyperconjugation provides significant extra stabilization for some of the radical cation complexes investigated, despite the long central bonds.

First row elements form stronger odd-electron bonds than their second row equivalents. Hydrogen and helium, which were not investigated here, form the strongest odd-electron bonds. Each group has a characteristic odd-electron bond strength, D_{AA}, found in the symmetrical complexes. Within a given row of the periodic table, the alkali metals and the noble gases form the weakest odd-electron bonds.

Acknowledgment. This work has benefitted from discussions with many colleagues, notably Paul Schleyer, Dieter Asmus, Steve Nelsen, Helmut Schwarz, Tom Kovář, and Elmar Kaufmann. The cooperation of the staff of the Regionales Rechenzentrum Erlangen is gratefully acknowledged.

Supplementary Material Available: The GAUSSIAN82 archive entries for the MP2/6-31G* calculations on the radical cation complexes given in Tables II and III (11 pages). Ordering information is given on any current masthead page.

---

(34) Wilhelm, D.; Clark, T. Poster presented at the Euchem conference on Organic Free Radicals, Assisi, 1986.

(35) Katritzky, A. R.; Zerner, M. C.; Karelson, M. M. *J. Am. Chem. Soc.* **1986**, *108*, 7213.