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Calculations of Electron Affinities Using the MNDO Semiempirical SCF–MO Method

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Abstract: MNDO calculations are reported for the energies and geometries of 65 atoms and molecules and their negative ions. The calculated electron affinities of six atoms were too negative by an average of 1.50 eV, and a similar average error of 1.40 eV was found for ten molecules in which the highest occupied molecular orbital (HOMO) of the negative ion is highly localized on one atom. The mean error in the calculated electron affinities of 26 molecules in which the HOMO is delocalized was 0.43 eV. Koopmans' theorem gave reliable estimates for the vertical ionization potential of these molecules. The most stable isomer of NO_3 was calculated to be peroxynitrite radical, and not nitrate radical, which was calculated to be 1.6 eV higher in energy. This suggests that the previously reported value for the electron affinity of NO_3 may be too low.

Studies of the properties of negative ions have blossomed in the last decade as a result of the introduction of a variety of new instrumental techniques.[1] As a consequence of this renaissance, accurate and reliable values of electron affinities for numerous and widely different molecules are now available. This property, defined as the difference in energy between the lowest rotational–vibrational state of a negative ion and the lowest rotational–vibrational state of the neutral molecule, has been the subject of considerable recent interest.[2] The work of Kebarle and co-workers[3] has shown that knowledge of the electron affinity of a molecule can yield useful thermochemical information about gas-phase ion–molecule reactions. A very wide and related field is the generation of negative ions of organic molecules and their study by negative ion mass spectrometry.[4] A reliable and fast computational method for obtaining electron affinities would obviously be of great aid in such connections.

Current theoretical studies of negative ions have mostly been based on the Hartree–Fock method. Cade[5] was one of the first to show that such calculations cannot lead to reliable estimates of electron affinities. His calculated electron affinity for hydroxyl radical, for example, was −0.1 eV, compared with the experimental value of 1.83 eV.[5] These discrepancies, which can often amount to 2–4 eV, are apparently due to large differences in electron correlation energy between the anions and corresponding radicals.

Cade also demonstrated that the application of Koopmans' theorem could lead to errors in the opposite direction. In the case of hydroxyl radical, for example, he obtained a value of +2.9 eV from the calculated energy of the highest occupied molecular orbital (HOMO) of OH^-. This failure of Koopmans' approximation has been noted frequently,[2] both for ab initio and π SCF methods.[6] It has been suggested that in the case of the ab initio methods, this failure may be partly due to the inadequacy of the basis sets used.[7]

While many significant advances have been made in recent years toward the calculation of electron affinities by ab initio methods,[2,8-10] the large amount of computer time required for the calculations limits them to relatively small systems, even if assumed geometries are used. Since the geometries both of the anion and of the neutral species must be *completely* optimized if adiabatic electron affinities are to be reliably calculated, it seems clear that the only hope of obtaining results of practical value for molecules large enough to be of real chemical interest (cf. ref 4) lies in the use of semiempirical procedures.

Recent work here has led to the development of a semiempirical SCF MO procedure (MNDO[11]) which seemed likely to prove especially effective in this connection. The average error in the heats of formation calculated by it for 254 molecules of many different kinds was only 8.7 kcal/mol and the results for a number of positive ions were of similar accuracy.[11a,b] Since the parameters in MNDO were determined[11] by fitting data only for neutral molecules, there seemed good reason to believe that it would be equally successful in the case of negative ions and we therefore decided to test its potential
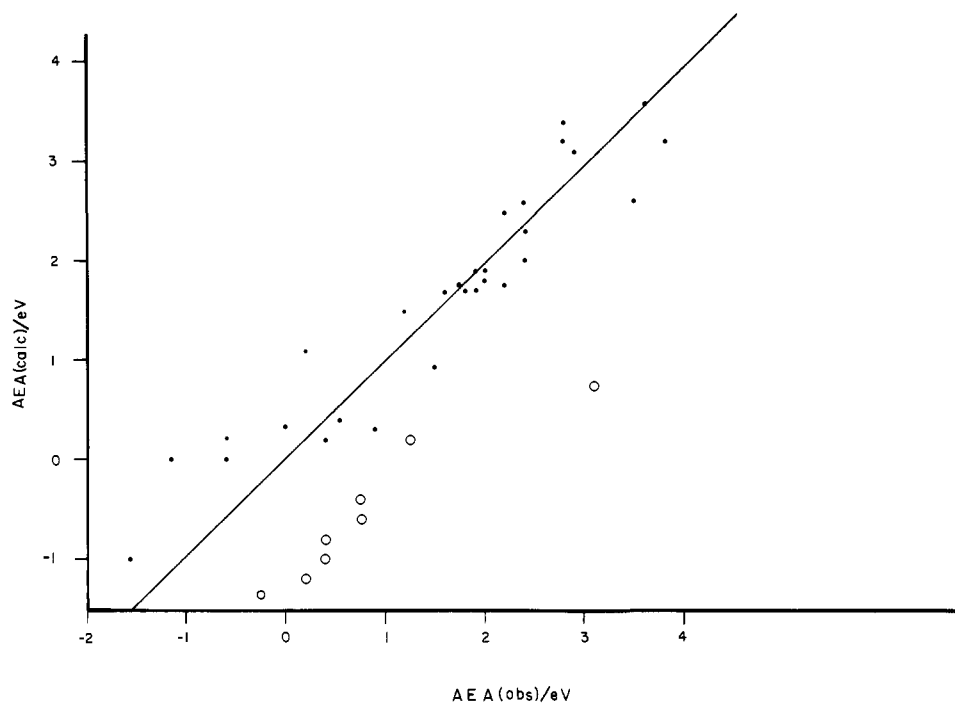
Figure 1. Observed and calculated adiabatic electron affinities (AEAs), showing the line of unit slope. Open points represent "localized" anions (see text).

Table I. MNDO Atomic Electron Affinities

Element	EA_{MNDO}, eV	EA_{obsd},[a] eV
H	−0.942	0.754
Be	−2.876	≤0
B	−1.548	0.28
C	0.256	1.268
N	−1.168	−0.07
O	0.087	1.462
F	1.562	3.399

[a] Reference 17.

in this area. Here we report the results of calculations for a wide variety of such ions, derived from hydrogen and the second period elements, Be–F.

Procedure

Atomic electron affinities were calculated from the one-center atomic integrals reported previously,[11a] with the assumption that the ground state configuration of each negative ion is the same as that of the neutral atom with one more unit of nuclear charge. Molecular geometries were calculated by minimizing the total energy with respect to *all* geometrical variables, using the Davidon–Fletcher–Powell method.[11a] Open shell systems were treated using the half-electron (h-e) approximation.[12] For some large open-shell systems it was found convenient to first optimize the geometry by the spin unrestricted version of MNDO (UMNDO)[11e,13] followed by a final refinement using the h-e method. This technique resulted in a considerable saving in computation time, because UMNDO optimizations are much faster and lead to geometries almost identical with those given by the h-e method. Energies obtained using the h-e method were usually in better agreement with experiment and 2–10 kcal/mol higher than those given by the spin unrestricted approximation. Several diatomic molecules with degenerate electron ground states had to be treated somewhat differently.[14] In these cases, the energy of the ground state was obtained as the lowest (degenerate) root of a 3 × 3 CI based on the h-e orbitals of the open shell singlet.[15]

Adiabatic electron affinities were calculated from the difference in energy between the neutral molecule and its negative ion. For closed shell systems, vertical attachment and detachment energies were estimated by applying Koopmans' theorem[16] to the LUMO and HOMO of the neutral species and the negative ion, respectively.

Results and Discussion

A. Electron Affinities of Atoms. Table I compares the electron affinities calculated by MNDO for hydrogen and the second period elements Be–F with the experimental values recently cited by Lineberger.[17] It will be seen that the MNDO values are uniformly too negative, by ca. 1.5 eV. This error is probably due to the use of inappropriate values for the one-center terms U_{pp}. In MNDO these are treated as parameters and their values are determined from a least-squares fit to the properties of the molecules used as the basis set for the parameterization.[11a] The values obtained in this way are therefore appropriate to calculations for molecules, not atoms. Indeed, if the MNDO value for U_{pp} for fluorine is replaced by that found by Oleari et al.[18] by fitting energies of atomic valence states, the calculated electron affinity of fluorine increases to 3.81 eV (obsd,[17] 3.40 eV). It is interesting to note that Hartree–Fock calculations for fluorine[19] also led to too small a value for its electron affinity (1.36 eV). Here, however, the error is due to a change in correlation energy on passing from neutral fluorine to fluoride anion.

B. Molecular Electron Affinities. Table II shows the calculated heats of formation, and Table III the corresponding molecular geometries, of a variety of molecules and their negative ions (cf. 11a–c). The difference between the heats of formation of a given negative ion and the corresponding neutral species is by definition the adiabatic electron affinity (AEA) of the latter. Table II and Figure 1 compare the calculated AEA with experimental values where these are available. For closed-shell molecules with nondegenerate ground electronic states, the negative orbital energy of the HOMO (in the case of ions) or LUMO (in the case of neutral species) is also given.

These should, according to Koopmans' theorem, be ap-

Table II. Calculated and Observed Molecular Electron Affinities

Molecule	$\Delta H_f(R)^a$	$\Delta H_f(R^-)^a$	EA_{calcd}, eV	EA_{obsd}, eV[b]	$-\epsilon_{HOMO'}$, eV	$-\epsilon_{LUMO'}$, eV	Ref
BeH	60.3	74.5	−0.62	0.74	−0.50		e
BeO	38.2	−2.8	1.78	(1.77)		1.66	f
BO	−1.5	−75.4	3.20	(2.79)	3.26		g
BF$_2$	−136.8	−177.4	1.76	2.21	2.43		h
BF$_3$	−261.1	−271.1	0.43			−1.20	
CH	143.6 ($^2\Pi$)	138.8 ($^3\Sigma^-$)	0.21	1.24			i
		167.4 ($^1\Delta$)	−1.03	0.39			
CF	43.7	32.8 ($^3\Sigma^-$)	0.47	(1.06)			j
		57.9 ($^1\Delta$)	−0.62				
CH$_2$	77.3 ($^3B_1$)	104.7	−1.19	0.21			k
	102.6 ($^1A_1$)		−0.09	1.06			
CH$_3$	25.8	56.8	−1.34	(−0.24)	−1.21		l
CH$_2$F	−33.3	−15.3	−0.78		−0.17		
CHF$_2$	−88.4	−93.7	0.23		1.13		
CF$_3$	−137.2	−178.9	1.81	2.01^c	2.83		m
CF$_4$	−214.2	−197.8	−0.71			−1.61	
C$_2$	232.2 ($^3\Pi_u$)	173.7	2.56	3.5			j
	234.8 ($^1\Sigma_g^-$)		2.65			2.59	
HCC	162.5	104.3	2.52	2.21	2.76		n
Ethylene	15.3	38.8	−1.02	−1.55		−1.32	o
trans-Butadiene	28.9	28.8	0.00	−0.62		−0.39	o
Ethyl	12.8	27.3	−0.63	<0.34	−0.13		p
tert-Butyl	−7.2	−12.0	0.21		0.94		
CF$_3$CH$_2$	−129.8	−151.8	0.95		1.48		
Benzyl	49.6	18.3	1.33	0.88	1.63		q
NCCH$_2$	52.9	31.6	0.92	1.51	1.23		p
Allyl	35.3	26.0	0.40	0.55	0.63		p
Cyclopentadienyl	58.1	18.8	1.70	<1.84	2.14		r
Pyrrole	60.4	14.3	2.00	2.39	2.40		s
Benzene	21.2	22.7	−0.07	−1.15		−0.37	t
Pyridine	28.7	23.7	0.22	−0.62		−0.01	u
CN	128.9	54.9	3.21	3.82	3.27		v
Tetracyanoethene	146.6	76.1	3.06	2.03, 2.88		2.50	w
Tetracyanoquinodimethane	185.7	106.8	3.42	2.80		2.80	x
		116.6 (R^{2-})					
CH$_3$O	−0.1	−39.8	1.72	1.59	2.42		y
CF$_3$O	−152.3	−241.6	3.87		4.96		
C$_2$H$_5$O	−5.7	−45.3	1.72	1.73	2.47		z
tert-Butoxy	−7.1	−47.3	1.74	1.95	2.64		z
PhO	10.0	−42.4	2.27	<2.36	2.53		aa
p-Benzoquinone	−33.1	−76.5	1.88	1.89		1.51	bb
Cyclopent-2-enone	−26.7	−41.5	0.64		0.12		
(γ-methylene-γ-butyrolactone structure)	−72.4	−90.4	0.78		0.22		
CO$_2$	−75.4	−79.5	0.18	−0.60		−0.88	cc
HCO$_2$	−18.0	−101.7	3.63	3.56	3.73		dd
Nitromethane	3.3	−23.8	1.18		0.37		
N$_3$	102.4	52.5	2.16	4.0	2.23		ee
NH	76.4 ($^3\Sigma$)	94.4	−0.78	0.38			ff
	108.5 ($^1\Delta$)		0.61	1.96			
NF	31.6 ($^3\Sigma^-$)	34.3	−0.12				
	56.4 ($^1\Delta$)		0.96				
NF$_3$	−34.1	−42.1	0.35			−0.71	
NH$_2$	37.1	47.3	−0.44	0.75	−0.15		gg
NO	−0.2	−7.9 ($^3\Sigma$)	0.33	0.02			hh
		10.8 ($^1\Delta$)	−0.48				
ONO	−4.6	−63.5	2.55	2.36	3.06		ii
NOO	90.7	35.6	2.38		2.83		
(N—O oxaziridine structure)	74.0	49.4	1.07		1.36		
Nitrate	52.0	−67.0	5.17	3.68	5.41		jj
Peroxynitrite	14.9	−33.2	2.09		2.87		
H$_2$NO	6.2	−3.2	0.41		1.18		
N$_2$O	30.9	5.04	1.12	0.22		−0.34	kk
O$_2$	−15.4 ($^3\Sigma_g^-$)	−19.0	0.16	0.44			ll
O$_3$	29.0^d	−13.6	1.85	2.0			mm
HO	0.5	−5.8	0.27	1.83	0.47		
FO	21.7	−12.4	1.48	(1.20)	1.63		oo
F$_2$	7.3	−10.1	0.75	3.08		−2.01	pp

^{a}kcal/mol calculated using the half-electron method where appropriate. Energies of $^1\Delta$ states were taken as the lowest (degenerate) root of a 3 × 3 CI based on the half-electron orbitals. ^{b} Experimental (adiabatic) electron affinities, eV. ^{c} A vertical value of 2.82 eV has been reported (ref 20). ^{d} Calculated using a 3 × 3 CI. ^{e} Reference 8f. ^{f} Calculated value, ref 8h. ^{g} Calculated value, ref 8g. ^{h} R. D. Srivastava, O. M. Uy, and

Table II (Continued)

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proximately equal to the vertical electron affinity of the neutral species. In cases where the geometries of the negative ion and the neutral molecule do not differ significantly, the adiabatic electron affinity (AEA) and the Koopmans' theorem estimate (KEA) are very similar (i.e., CH_3, BO, CN, HCO_2, N_3). This is in marked contrast to the values given by ab initio calculations[5-9,19] or π SCF methods[7] where large differences between the two quantities have been reported.

In a molecule such as CF_3, where the calculated geometries of the radical and anion do differ appreciably, the KEA value (2.83 eV) is rather larger than the AEA one (1.81 eV), as expected. On the other hand, the KEA value agrees closely with the difference (2.78 eV) between the energies of the anion and the radical when the latter is calculated for the geometry corresponding to the anion. This difference should correspond to the vertical ionization energy of the anion. Brauman et al.[20] have indeed obtained a similar value (2.82 eV) for the vertical ionization energy of CF_3^-.

It has already been shown that the ionization energies obtained from MNDO orbital energies by using Koopmans' theorem agree remarkably well with experiment.[11a-c,f] Thus the ordering of cationic states seems invariably to be correctly predicted, even in cases where the order of the Hartree–Fock orbital energies is different (e.g., N_2, F_2). The success of MNDO in this connection may be partly due to the fact that electron correlation is taken explicitly into account via the parametrization. However, the failure of the Hartree–Fock/ Koopmans' treatment in the case of N_2 and F_2 seems to be due mainly to the neglect of electronic reorganization on ionization and it is difficult to see how this could have been implicitly taken into account in the MNDO oribtal energies.

The results in Table II show that the electron affinities of one class of compounds in particular show large and systematic errors. These are small molecules, mostly diatomics, where the extra electron occupies an orbital which is very largely localized on one atom. Not surprisingly, the errors in the electron affinities of these compounds are similar in magnitude and direction to those previously noted for atoms (cf. BeH, CH, CH_2, CH_3, NH, NH_2, and OH). In contrast, those diatomic molecules where the HOMO of the negative ion is delocalized over both atoms cause no problems (cf. BeO, BO, CN, NO, O_2, and FO).

With the exception of the localized negative ions mentioned above, the calculated electron affinities are generally in very good agreement with experiment. In many cases, we note that the experimental value is intermediate between our calculated adiabatic and vertical values. This may be more than coincidence, since experimental difficulties arise in identifying the transition to the *lowest* vibrational level of the negative ion[21] or neutral molecule.[22,23] Brauman and co-workers[20] have recently suggested that values for electron affinities obtained from photoionization measurements on the negative ion may indeed not always be adiabatic values, but rather an upper bound to them.

Since a number of the systems reported in this paper are of considerable current interest, we will discuss these individually.

1. BeO, BO, and CN. These diatomic molecules have been studied theoretically using the equations-of-motion treatment developed by Simons and co-workers.[8g,h,k] The MNDO results for BO and BeO are in good agreement with the calculations of Simons et al. (Table II), but the MNDO value for CN is less by 0.48 eV than that calculated by Griffing and Simons[8g] and by 0.61 eV than that measured experimentally.[24] Pacansky and Liu[25] have recently recalculated the electron affinity of CN, using a rather larger orbital basis set than Griffing and Simons. They obtained a value of 3.29 eV, close to the MNDO estimate (3.21 eV).

2. CH, CH_2, and NH. These three systems have been studied by the laser photodetachment technique of Lineberger and co-workers.[22,26] This technique is especially important since it can also provide accurate estimates of singlet/triplet energy separations in molecules. In the case of methylene, Lineberger et al. obtained a value for the $^1A_1/^3B_1$ separation of 0.845 eV, much greater than that previously accepted (ca. 0.35 eV[27]. While the individual electron affinities of these systems are not well reproduced by MNDO, since they are all "localized" anions or radicals, the calculated singlet/triplet splittings in CH^- (1.24 eV), CH_2 (1.10 eV), and NH (1.39 eV) are fairly close to the photodetachment values (0.85, 0.85, and 1.58, eV, respectively).

3. Hyperconjugative Stabilization by Methyl Substituents. The calculated MNDO electron affinity of methyl radical (-1.34 eV) is certainly too negative because the HOMO of the carbanion is localized entirely on the carbon $2p_z$ orbital. Cederbaum and von Niessen[9e] have calculated a more reasonable value of -0.24 eV and Marynick and Dixon[9i] estimate $-(0.09-0.35)$ eV, which agrees with our observation that MNDO predicts the electron affinities of "localized" anions to be on average too negative by ca. 1.5 eV (Table II). While the MNDO results for $CH_2F\cdot$ and $CHF_2\cdot$ also seem to be too negative, the electron affinity of $CF_3\cdot$ is reproduced correctly (Table II), since the HOMO becomes progressively less localized along the series $CH_3 < CH_2F < CHF_2 < CF_3$. MNDO predicts a methyl group to be as effective as F in stabilizing a carbanion. For example, the calculated electron affinities of $CH_3CH_2\cdot$ and $FCH_2\cdot$ are similar, and a CF_3 group is correspondingly more effective than a CH_3 group. A similar effect was found for oxygen anions, the calculated electron affinity of $OH\cdot$ being too negative by 1.5 eV, whereas that of $CH_3O\cdot$ was reproduced correctly. The MNDO electron affinity for $CF_3O\cdot$ was much greater than that for methoxyl radical, being indeed one of the largest values calculated. Note (Table III) that MNDO predicts the geometries of both $CH_3O\cdot$ and $CF_3O\cdot$ to be distorted from C_{3v} symmetry, removing the degeneracy of the singly occupied HOMO as required by the Jahn–Teller theorem. Interestingly, the calculated C–O bond lengths in the negative ions CH_3O^- and CF_3O^- were identical (1.287 Å, Table III). The value for the latter is shorter than that calculated by So[28] (1.368 Å) using the 3G basis set. So's value for the CF bond length (1.454 Å) was also longer than the MNDO value of 1.382 Å.

Bartmess and McIver[29] have shown that the gas-phase electron affinities of alkoxy radicals decrease in the sequence

Table III. Calculated Geometrical Parameters for Negative Ions and (in Parentheses) the Neutral Species

Molecule	Point group[a]	Calcd geometry of anion (neutral)[b]
BeO	$C_{\infty v}$	BeO 1.382 (1.335)
BO	$C_{\infty v}$	BO 1.203 (1.170)
BF$_2$	C_{2v}	BF 1.359 (1.291), FBF 105.2 (120.0)
BF$_3$	C_{3v} (D_{3h})	BF 1.370 (1.316), FBF 103.6 (120.0)
CH	$C_{\infty v}$	CH $^3\Sigma^-$ 1.117, $^1\Delta$ 1.117 (1.098)
CF	$C_{\infty v}$	CF $^3\Sigma^-$ 1.309, $^1\Delta$ 1.303 (1.340)
CH$_2$	C_{2v}	CH 1.108 (^{3}B$_1$ 1.051, ^{1}A$_1$ 1.083), HCH 106.8 (^{3}B$_1$ 150.5, ^{1}A$_1$ 116.2)
CH$_3$	D_{3h}	CH 1.077 (1.978), HCH 120 (120)
CH$_2$F	C_s	CH 1.108 (1.086), CF 1.348 (1.305)
CHF$_2$	C_s	CH 1.145 (1.087), CF 1.361 (1.309)
CF$_3$	C_{3v}	CF 1.370 (1.312), FCF 104.0 (115.4)
CF$_4$	C_{2v} (T_d)	CF 1.367, 1.448 (1.347)
C$_2$	$D_{\infty h}$	CC 1.196 ($^3\Pi_u$ 1.275, $^1\Sigma_g^+$ 1.168)
HCC	$C_{\infty v}$	CH 1.052 (1.054), CC 1.217 (1.291)
Ethylene	D_{2h}	CC 1.389 (1.334), CH 1.087 (1.089), CCH 122.9 (123.2)
1,3-Butadiene	C_{2h}	C^{1}C^2 1.381 (1.344), C^{2}C^3 1.414 (1.465), CCC 127.2 (125.7)
C$_2$H$_5$	C_s	CC 1.429 (1.477)
tert-Butyl	C_{3v} (D_{3h})	CC 1.465 (1.494), CCC 119.9 (120)
Benzyl	C_{2v}	CαC^1 1.372 (1.400), C^{1}C^2 1.458 (1.446), C^{2}C^3 1.386 (1.402), C^{3}C^4 1.411 (1.413)
CH$_2$CN	C_{2v}	CC 1.359 (1.401), CN 1.183 (1.164), HCC 121.9 (121.1)
CF$_3$CH$_2$	C_s	CC 1.467 (1.541), CF 1.378, 1.390 (1.358, 1.359)
Allyl	C_{2v}	CC 1.380 (1.383), CCC 130.0 (126.0)
Cyclopentadienyl	D_{5h} (C_{2v})	CH 1.083 (1.081), CC 1.418 (1.446, 1.363, 1.479)
Pyrrolyl	C_{2v}	NC^1 1.373 (1.364), C^{1}C^2 1.416 (1.473), C^{2}C^3 1.417 (1.375)
Benzene	D_{2h} (D_{6h})	CC 1.400, 1.437 (1.407)
Pyridine	C_{2v}	NC 1.373 (1.353), C^{1}C^2 1.386 (1.412), C^{2}C^3 1.429 (1.405)
CN	$C_{\infty v}$	NC 1.178 (1.153)
Tetracyanoethene	D_{2h}	C=C 1.423 (1.373), C–C 1.414 (1.431), CN 1.166 (1.162), CCC 122.1 (122.6)
Tetracyanoquinodimethane(2–)	D_{2h}	NC$^\alpha$ 1.172 (1.162), C$^\alpha$B$^\beta$ 1.402 (1.430), C$^\beta$C^1 1.459 (1.377), C^{1}C^2 1.427 (1.476), C^{2}C^3 1.395 (1.359)
Tetracyanoquinodimethane(1–)	D_{2h}	NC$^\alpha$ 1.163, C$^\alpha$C$^\beta$ 1.413, C$^\beta$C^1 1.416, C^{1}C^2 1.448, C^{2}C^3 1.379
CH$_3$O	C_{3v} (C_s)	CO 1.287 (1.356), CH 1.154 (1.115), HCO 116.2 (112.8, 109.7)
CF$_3$O	C_{3v} (C_s)	CO 1.287 (1.398), CF 1.382 (1.346, 1.348), FCO 114.5 (110.1, 109.2)
C$_2$H$_5$O	C_s	CC 1.572 (1.543), CO 1.294 (1.359), OCC 116.3 (114.6).
tert-Butoxy	C_{3v} (C_s)	CC 1.591 (1.569, 1.565), CO 1.310 (1.373), OCC 112.0 (108.0, 110.2)
Phenoxy	C_{2v}	CO 1.254 (1.232), C^{1}C^2 1.465 (1.490), C^{2}C^3 1.387 (1.381), C^{3}C^4 1.410 (1.418)
p-Benzoquinone	D_{2h}	CO 1.252 (1.226), C^{1}C^2 1.469 (1.501), C^{2}C^3 1.373 (1.349)
Cyclopent-2-enone	C_1	OC 1.250 (1.220), C^{1}C^2 1.432 (1.501), C^{2}C^3 1.404 (1.351), C^{3}C^4 1.497 (1.514), C^{4}C^5 1.552 (1.497), C^{5}C^1 1.547 (1.544)
	C_1	O^{1}C^2 1.401 (1.374), C^{2}C^3 1.438 (1.503), C^{3}C^4 1.501 (1.513), C^{4}C^5 1.555 (1.558), C^{5}O^1 1.400 (1.413), O=C^2 1.240, C=C^3 1.402 (1.343)
CO$_2$	C_{2v} $(D_{\infty h})$	CO 1.236 (1.186), OCC 136.3 (180.0)
HCO$_2$	C_{2v}	CH 1.142 (1.140), CO 1.260 (1.252), OCO 125.6 (128.6)
Nitromethane	C_s	CN 1.537 (1.546), NO 1.247 (1.210), ONC 115.0 (119.3)
N$_3$	$D_{\infty h}$	NN 1.168 (1.174)
NH	$C_{\infty v}$	NH 1.000 ($^3\Sigma^-$ 0.993, $^1\Delta$ 0.993)
NF	$C_{\infty v}$	FN 1.268 ($^3\Sigma^-$ 1.220, $^1\Delta$ 1.215)
NF$_3$	C_{3v}	FN 1.364 (1.315), FNF 113.7 (106.1)
NH$_2$	C_{2v}	NH 1.013 (1.002), HNH 100.9 (104.4)
NO	$C_{\infty v}$	NO $^3\Sigma^-$ 1.178 $^1\Delta$ 1.117 (1.122)
ONO	C_{2v}	NO 1.215 (1.174), ONO 116.5 (133.0)
NOO	C_s	NO 1.192 (1.186), OO 1.254 (1.220), NOO 120.2 (122.3)
O⟍ ⟋ O—N	C_s	NO 1.343 (1.302), OO 1.343 (1.350), OON 58.7 (58.8)
NO$_3$	D_{3h} (C_{2v})	NO 1.235 (1.199, 1.253), ONO 120 (125.4)
Peroxynitrite	C_s	ON 1.194 (1.152), NO′ 1.291 (1.389), O′O″ 1.250 (1.206), ONO′ 112.5 (111.8), NO′O″ 113.9 (112.7)
H$_2$NO	C_s	NH 1.067 (1.023), NO 1.264 (1.223) HNO 109.9 (118.0)
N$_2$O	C_s $(C_{\infty v})$	NN 1.189 (1.128), NO 1.229 (1.181), NNO 131.1 (180)
O$_2$	$D_{\infty h}$	OO 1.193 ($^3\Sigma_g^-$ 1.134)
O$_3$	C_{2v}	OO 1.228 (1.22), OOO 115.8 (115.5)
HO	$C_{\infty v}$	HO 0.939 (0.937)
FO	$C_{\infty v}$	FO 1.268 (1.223)
F$_2$	$D_{\infty h}$	1.707 (1.266)

[a] Symmetry of the anion and (in parentheses) the neutral species if different. [b] Bond lengths A^{i}B^j in angstroms and bond angles A^{i}B^{j}C^k in degrees for the anion and in parentheses the neutral species.

t-BuO· > EtO· > MeO·, although the difference between the first and the last is small (0.22 eV). The MNDO results show an increase of 0.02 eV in the adiabatic and 0.22 eV in the vertical electron affinities.

Our calculations predict a positive electron affinity for *tert*-butyl radical, in contrast to methyl and ethyl radicals. This effect, however, is probably largely due to a decrease in the diffuse nature of the lone pair orbital on the *tert*-butyl carb-

anion. A Slater orbital with an exponent optimized to reproduce the properties of neutral molecules is better able to describe this orbital than a more diffuse orbital as found in CH_3^-.

4. Conjugated Polyenes. Electron scattering experiments[21,30,31] have indicated that the negative ions of ethylene, butadiene, benzene, and pyridine are unstable with respect to electron detachment, and are best described as resonance states. Burrow and Jordan[31] have obtained values of −1.55 and −0.62 eV for the AEA of ethylene and butadiene from their electron transmission spectra. The calculated MNDO AEAs are about 0.5 eV more positive than the experimental ones, although the MNDO KEAs are in closer agreement (Table II). The calculated AEAs of benzene and pyridine were about 0.9 eV more positive than the reported values[21] of −1.15 and −0.62 eV, respectively. In the case of the negative ion of benzene, the ground state is Jahn–Teller distorted, although the difference between the adiabatic (AEA) and vertical (KEA) electron affinity is nevertheless small (0.3 eV, Table II). A number of ab initio calculations on benzene[9g,h,32] have given values for the energy of the LUMO, ranging from 3.24 to 3.78 eV. This indicates again that Koopmans' theorem cannot be used with these methods for estimating electron affinities. A similar error is found for pyridine.[9f] The PPP π SCF calculations of Younkin et al.[6] gave orbital energies for the LUMO which led on average to electron affinities that were 1.9 eV too positive.

Although the errors in the MNDO values for the electron affinities of this class of compounds are rather larger than the average, they nevertheless compare very well with analogous single-configuration calculations by other SCF methods.

5. *p*-Benzoquinone, Tetracyanoethylene, and Tetracyanoquinodimethane. Interest in the properties of these compounds has been recently stimulated by the discovery of the unusual electrical properties of charge transfer compounds involving these species as acceptors.

Cooper et al.[33a] have reported a value for the electron affinity of *p*-benzoquinone which is in very close agreement with the calculated MNDO adiabatic value of 1.88 eV (Table II). The calculated energy of the lowest unoccupied orbital (b_{2g}) corresponds to a vertical electron affinity of 1.51 eV. Cooper et al. also observed resonances at 0.7, 1.35, and 1.9 eV which they assigned to the excited ^2A_u, $^2B_{1u}$, and $^2B_{2g}$ negative ion states. The corresponding MNDO orbital energies (0.02, 0.80, and 1.87 eV), with the exception of the b_{2g} orbital, are in only fair agreement. The identification of the observed resonances as corresponding to these states, however, is by no means certain.

The calculated electron affinity of tetracyanoethylene (3.06 eV) agrees rather poorly with the value (2.03 eV) reported by Lyons and Palmer.[34] More recently, Chen and Wentworth[35] have suggested that a value of 2.9 eV is more reasonable, and this is certainly more consistent with the MNDO value.

Tetracyanoquinodimethane (TCNQ) has been studied by Compton and Cooper.[33b] They obtained a value of 2.8 eV for the electron affinity, compared with the MNDO Koopmans' theorem estimate of 2.8 eV and an adiabatic value of 3.4 eV. This latter value is larger because of a considerable difference between the geometry of the radical anion and the neutral compound (Table III). MNDO quite reasonably predicts a rather larger electron affinity for TCNQ than it does for TCNE, whereas they appear to be equal experimentally. We calculate the species $TCNQ^{2-}$ to be only 9.8 kcal/mol less stable than $TCNQ^-$, and considerably more stable than TCNQ itself. To date, this doubly charged negative ion has not been observed.[33b]

6. CO_2, N_2O, and N_3. There has been considerable controversy concerning the signs of the electron affinities of CO_2 and N_2O (see Massey[1]). There now seems to be agreement that the

AEA of CO_2 is −0.6 eV[36] and that of N_2O is +0.22.[37] These systems are of particular interest, because the addition of an electron is expected to result in a bent species, with a concomitant large difference between the adiabatic and vertical electron affinities. These expectations are borne out by the MNDO calculations, the negative ions being highly nonlinear species (Table III). The electron affinities in both cases are, however, too positive by about 0.8 eV. This may be related to the observation that the linear neutral species are in both cases calculated[11] to be too unstable by about this amount. The azide radical is calculated to have a fairly large AEA, both the radical and the negative ion being predicted to be linear.

7. NO_2 and NO_3. The electron affinity of nitrite (NO_2), although long the subject of uncertainty,[38] now seems to be established as being close to 2.36 eV. There has also been speculation over the existence of an isomer, possibly NOO· or a cyclic form,[38] although recent evidence does not lead to that conclusion.[39] The MNDO calculations do predict three isomers of both NO_2· and NO_2^- to be minima in the potential surface. In each case, however, the most stable isomer had the normal nitrite structure and was at least 3.4 eV lower in energy than the cyclic or peroxy forms. The calculated electron affinity of nitrite was found to be 2.55 eV, in very good agreement with the experimental value, and also with the calculations of Andersen and Simons,[8k] who obtained a value of 2.25 eV for the adiabatic and 2.66 eV for the vertical ionization energy of NO_2^-. The MNDO value for the latter was 3.06 eV.

The electron affinity of nitrate (NO_3) still remains uncertain. Two recent papers[40,41] have reported values of 3.77 and 3.68 eV, respectively. While these agree well, both sets of workers used a value of 17 kcal/mol for the heat of formation of NO_3· in a thermocycle to obtain the electron affinity, with the tacit assumption that this referred to a species with the ONO_2· nitrate structure. We find this assumption *not* to be true. Our calculated heat of formation for the most stable isomer of NO_3· (14.9 kcal/mol) agrees well with the value quoted above, but it refers to a peroxy isomer, ONOO·. Nitrate radical itself is calculated to be much higher in energy (52.3 kcal/mol). The MNDO values for the heats of formation of nitrate and peroxynitrite anions are −67 and −33 kcal/mol, respectively. The former is in very good agreement with the value of −70 kcal/mol determined for nitrate anion by Refaey and Franklin.[40] We predict therefore the existence of two stable forms of NO_3^-, with adiabatic electron detachment energies of 5.17 and 2.09 eV for nitrate and peroxynitrite anions, respectively.

Conclusions

The calculations reported here show that the MNDO semiempirical method reproduces the electron affinities of a wide variety of "delocalized" radicals and molecules with a mean error of ±0.43 eV. Although this error is still undesirably large, the errors tend to be systematic for given types of compound and corresponding corrections can then be applied. There is also uncertainty in many cases concerning the experimental values, due to difficulties in identifying the transition to or from the lowest vibrational state of a negative ion or radical. Since vibrational frequencies can easily be calculated for these species[42-44] it should be possible to calculate Franck-Condon factors for the vibrational transitions, aiding further the interpretation of the experimental results.

We have also demonstrated that application of Koopmans' theorem to the MNDO eigenvalues gives quite good estimates of vertical electron attachment and detachment energies. It would seem that MNDO should prove as useful in the study of reactions of negative ions as it has been for those of neutral molecules.

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