NOTES

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Ionization Potentials of Radicals as Determined by the Unrestricted MINDO/2 Method[1]

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Synopsis. The parametrization in the MINDO/2 theory has been applied to the unrestricted Hartree-Fock method to give the appropriate ionization potentials of various radicals.

A knowledge of the ionization potentials (IP's) of radicals is of importance when considering the various theories of molecular structures. This knowledge, for example, when combined with the electron-impact appearance potentials, yields useful information on the heats of formation of free radicals. In order to interpret the mass spectra of organic compounds it is necessary to know the IP's of various radicals, since, in the fragmentation of a molecular ion such as $[P\text{–}Q]^{\cdot+} \rightarrow P\cdot + Q^+$ or $[P\text{–}Q]^{\cdot+} \rightarrow P^+ + \cdot Q$, the positive charge is indicated by Stevenson's rule[2] as remaining predominantly on the fragment with the lower IP.

From both the kinetic and mass spectroscopic methods it is difficult to get all the values of the IP's of the individual fragments.[3] Alternatively several molecular orbital (MO) theories can predict those values. As will be discussed, the CNDO/2[4] and INDO[5] theories provide unrealistic values. Therefore, the MINDO/2 theory,[6] which gives IP's for the closed-shell molecules close to those found experimentally, has been adopted in this study. However, the formal extension of the semi-empirical MO theory for closed-shell systems to open-shell systems involves a fundamental problem. The parameters in the original MO theory have been so adjusted as to give appropriate results for the closed-shell systems. This paper will discuss the adaptability of the unrestricted MINDO/2 method in the calculation of IP's, comparing those obtained by the CNDO/2, INDO, and experimental methods.

Method of Calculation

The calculations here are based on the unrestricted INDO methods of Pople *et al.*[5,7] The one-center integrals, the two-center repulsion integrals, the core-electron attractions, the one-electron resonance integrals, and the core-core repulsions were estimated as in the original MINDO/2 method,[6] where none of parameters were changed. Further details will not be repeated here. The bond-lengths (in Å) of the fragments are assumed to be as follows: $C(sp^3)$–$C(sp^3)$, 1.54; $C(sp^3)$-$C(sp^2, sp)$, 1.50; C–C, 1.35; C–O, C=N, 1.25; C=C(conj.), 1.40; C(sp)=O, 1.15; C–H,

Table 1. Ionization potentials[a] of fragments by means of CNDO/2, INDO, and MINDO/2 methods

Fragments[b]	CNDO/2		INDO		MINDO/2		Experiment[e]
	KIP[c]	DIP[d]	KIP	DIP	DIP	DIP	
CH_3	13.19(3.24)[f]	12.19(2.24)	13.13(3.18)	12.38(2.43)	10.51(0.56)	10.19(0.24)	9.95(0.03)[g]
CH_3CH_2	11.30(2.52)	10.10(1.32)	11.24(2.46)	10.20(1.42)	9.68(0.90)	9.05(0.27)	8.78(0.03)
$CH_3CH_2CH_2$	11.35(2.66)	9.97(1.28)	11.30(2.61)	10.11(1.42)	9.64(0.95)	8.87(0.18)	8.69(0.05)
$(CH_3)_2CH$	10.17(2.27)	8.82(0.92)	10.13(2.23)	8.92(1.02)	9.16(1.26)	8.30(0.40)	7.90(0.05)
$CH_3CH_2CH_2CH_2$	11.34(2.70)	9.87(1.23)	11.28(2.64)	10.01(1.37)	9.64(1.00)	8.76(0.12)	8.64(0.05)
$CH_3CH_2(CH_3)CH$	10.30(2.37)	8.80(0.87)	10.27(2.34)	8.93(1.00)	9.22(1.29)	8.22(0.29)	7.93(0.05)
$(CH_3)_3C$	9.39(1.97)	7.94(0.52)	9.38(1.96)	8.07(0.65)	8.77(1.35)	7.75(0.33)	7.42(0.05)
CH_2-CH=CH_2	10.81(2.65)	9.74(1.58)	10.61(2.45)	9.65(1.49)	9.65(1.49)	8.91(0.75)	8.16(0.03)
CH_2=$C(CH_3)$-CH_2	10.88(2.85)	9.68(1.65)	10.69(2.66)	9.59(1.56)	9.63(1.60)	8.77(0.74)	8.03(0.05)
$C_6H_5CH_2$	9.84(2.08)	8.75(0.99)	9.56(1.80)	8.54(0.78)	9.30(1.54)	8.52(0.76)	7.76(0.08)
$CH\equiv C$-CH_2	11.10(2.85)	10.18(1.93)	10.82(2.57)	10.03(1.78)	9.59(1.34)	9.01(0.76)	8.25(0.08)
$CH_3(CN)CH$	10.92(1.16)	9.89(0.13)	10.89(1.13)	9.95(0.19)	10.20(0.44)	9.52(−0.24)	9.76(0.1)
$NCCH_2CH_2$	11.83(1.98)	10.44(0.59)	11.77(1.92)	10.56(0.71)	10.36(0.51)	9.44(−0.41)	9.85(0.1)
$NC(CH_3)_2C$	10.08(0.93)	8.90(−0.25)	10.13(0.98)	9.05(−0.10)	9.76(0.61)	8.88(−0.27)	9.15(0.1)
$NCCH_2$	12.13(1.26)	11.24(0.37)	12.12(1.25)	11.34(0.47)	10.99(0.12)	10.41(−0.46)	10.87(0.1)
CHO	11.68(1.80)	11.45(1.57)	11.18(1.30)	11.00(1.12)	9.91(0.03)	9.80(−0.08)	9.88(0.05)
CH_3CHO	8.17(0.12)	7.26(−0.79)	7.63(−0.42)	6.85(−1.20)	8.14(0.09)	7.69(−0.45)	8.05(0.17)

a) In units of eV. b) The conformations were all set to be staggered. c) Koopmans' IP. d) Difference of the total energies between the ion and radical ($E_{\mathrm{ion}} - E_{\mathrm{radical}}$). e) Picked up from the data compiled by A. G. Harrison.[3] f) Difference between the calculated and experimental values. g) Experimental error.

1.09; O–H, 1.00; N–H, 1.02. The unpaired electron in each radical was assumed to occupy a 2p atomic orbital.

Results

Calculations were carried out for specific radicals (by the unrestricted methods) and ions (by the restricted methods). Table I shows the differences in total energies (DIP's) between the ion and the radical, the values of $-\varepsilon^{ho}$'s (KIP's) (where the ε^{ho}'s are the energies of the highest occupied MO's), and, in the last columns, the experimental values determined by the electron-impact method (with an error of *ca.* 0.1 eV). From Koopmans' theorem, the KIP value should be approximately equal to the IP value. It can be seen that the KIP values determined by the unrestricted CNDO/2 and INDO include an inconstant error of more than 3 eV in comparison with the experimentally-determined values. In the present method, the error is kept within 1.5 eV.

The CNDO/2 and INDO methods also yield DIP values with an inconstant error, though this error is considerably less than in the KIP values determined by the same methods. It is interesting that the difference between the DIP values and the corresponding experimental values becomes smaller as the number of substituents of the carbon atom of the radical center decreases.

Although the bond-lengths and the bond-angles have not been optimized, the DIP values obtained by the MINDO/2 method are far closer to the experimentally-determined values than those calculated by any other method. The difference between the DIP and the experimental values is relatively constant according as the type of radical, *i.e.*, *ca.* 0.25, 0.75, and −0.3 eV for alkyl radicals, unsaturated radicals, and radicals with an N or O atom respectively. This suggests that such a difference must be brought about by the inappropriate molecular geometries.

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8) The program of the restricted and unrestricted MINDO/2 method with the subprogram of energy-partition may be sent on request to one of the authors (H. I.).