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Vertical Ionization Potentials of Radicals by the MINDO/3 Method*

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Several methods are used to estimate the ionization potentials of radicals by the MINDO/3 procedure. The results are in quite good agreement with each other and with experiment.

Key words: Radicals, ionization potentials of ~

The various MINDO [1 – 3] approximations have given quite good estimates of ionization potentials of closed shell molecules using Koopmans' theorem. This in particular is true of the most recent version (MINDO/3 [3]). In the case of radicals, however, MINDO calculations are generally carried out using the "half-electron" approximation [4]. Here the energy of the singly occupied MO cannot be directly related to the corresponding ionization potential. As can easily be shown, making the usual assumption that the MOs remain unchanged during the ionization process, the ionization potential (I_1) of the radical is given by:

$$I^1 = -E_0 + \tfrac{1}{2}J_{00} \tag{1}$$

where E_0 is the orbital energy of the singly occupied MO and J_{00} is the corresponding Coulomb integral. Ionization potentials calculated in this way for a number of radicals, using Eq. (1) and MINDO/3, are shown in the Table, together with experimental values. The agreement is about as good as for closed shell molecules [3]. The Table also shows how important is the last term in Eq. (1). In the case of alkyl radicals the orbital energies (E_0) are almost the same, the decrease in ionization potential with increase in the size of the radical being due almost entirely to the decrease in J_{00}. This reflects the increasing delocalization of the unpaired electron as the size of the molecule increases. Indeed, the same argument applies in the case of methyl and allyl, the "half-electron" orbital energies of which are almost identical.

Vertical ionization potentials can also be estimated from the relation:

$$I^2 = \Delta H_f(\mathrm{R}^+) - \Delta H_f(\mathrm{R}\cdot) \tag{2}$$

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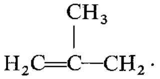
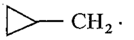
Table 1. Ionization potentials (eV) of radicals

Compound	I(obs)[a]	I^1	I^2	I^3	$\frac{1}{2}(I^1+I^3)$	$-E_i$	$\frac{1}{2}J_{00}$
$CH_3\cdot$	9.84	9.52	9.42	9.33	9.43	3.98	5.54
$CH_3CH_2\cdot$	8.38	8.77	8.39	8.00	8.38	3.87	4.90
$(CH_3)_2CH\cdot$	7.55	8.35	7.79	7.23	7.79	3.84	4.51
$(CH_3)_3C\cdot$	6.93	8.18	7.50	6.83	7.50	3.88	4.30
$CH_3CH_2CH_2\cdot$	8.10	8.80	8.27	7.74	8.27	3.86	4.94
$H_2C{=}CH\cdot$	8.95	8.24	8.01	7.78	8.01	3.67	4.57
$HC{\equiv}C{-}CH_2\cdot$	—	8.08	7.85	7.61	7.85	3.90	4.18
$H_2C{=}CH{-}CH_2\cdot$	8.07	7.97	7.73	7.49	7.73	3.92	4.05
$H_2C{=}CH{-}\dot{C}H{-}CH_3$	7.71	7.73	7.34	6.94	7.34	3.87	3.86
 $H_2C{=}C(CH_3){-}CH_2\cdot$	8.01	7.96	7.62	7.28	7.62	3.88	4.08
	8.05	8.40	7.95	7.50	7.95	3.84	4.56
	—	7.87	7.41	6.95	7.41	3.56	4.31
$ClCH_2\cdot$	9.32	8.89	8.62	8.35	8.62	3.56	5.13
H_2N	11.4	11.17	10.92	10.68	10.92	4.68	6.49
$H_2N{-}NH\cdot$	7.9	7.56	7.22	6.86	7.21	2.28	5.29
$HO\cdot$	13.17	13.69	13.49	13.30	13.49	6.43	7.26
$OCH\cdot$	9.8	8.39	8.35	8.29	8.34	3.38	5.01
$ON\cdot$	9.25	8.23	8.22	8.22	8.22	2.54	5.68
$O_2N\cdot$	9.8	8.62	8.54	8.46	8.54	3.40	5.22

[a] Experimental values, unless otherwise indicated.

where $\Delta H_f(R\cdot)$ is the heat of formation calculated for the radical and $\Delta H_f(R^+)$ that for the cation calculated with the same geometry[1]. These values are also shown in the Table. The differences between them and the I^1 values reflect the change in energy due to orbital reorganization where the radical loses its odd electron. As expected, the I^2 values are systematically lower, by 0.2–0.5 eV.

The ionization potential of the radical R · is equal, by definition, to the electron affinity of the corresponding cation R^+. Thus a third way of estimating the ionization potential of a radical R · is to use Koopmans' theorem to estimate this electron affinity; i.e.

$$I^3 = -E_{n+1} \tag{3}$$

where the cation contains n pairs of electrons so that E_{n+1} is the energy of the lowest unoccupied (virtual) MO in R^+. Here again the calculations are to be carried out with the same geometry as for the radical. The corresponding values are also shown in the Table. Here orbital reorganization during conversion of the cation to the radical will lower the energy of the latter; the I^2 values therefore should be – and are – greater than the I^3 ones.

Since the energies of reorganization should both involve mainly the electrons occupying filled MOs of R · or R^+, one might expect the differences between I^1 and I^2 and between I^2 and I^3 to be similar. If so, the mean of I^1 and I^3, i.e. $\frac{1}{2}(I^1 + I^3)$,

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[1] All the geometries were calculated by minimising the total energy with respect to all geometrical variables (see [3]), no assumptions of any kind being made.

should be close to I^2. These values are also listed in the Table; it will be seen that the difference between I^2 and $\frac{1}{2}(I^1 + I^3)$ is usually less than 0.01 eV and only in one case is as much as 0.02 eV.

The Fock operators for $R\cdot$ and R^+ differ in our formulation by the term $\frac{1}{2}(J_0 - K_0)$. The energy of reorganization (ΔE) of the paired electrons on passing from $R\cdot$ to R^+ is then given approximately by second order perturbation theory as

$$\Delta E \simeq \frac{1}{2} \sum_{i=1}^{n} \sum_{j=n+1}^{N} \frac{\langle \Psi_i | 2J_0 - K_0 | \Psi_j \rangle^2}{E_j - E_i} \tag{5}$$

where there are n filled MOs ($\Psi_1 - \Psi_n$) and N MOs all together. In order to analyse ΔE, it is convenient to replace the MOs in Eq. (5) by localized occupied and virtual orbitals. The expression in Eq. (5) is invariant to this transformation since $|2J_0 - K_0|\Psi_i\rangle\langle\Psi_i|2J_0 - K_0|$ is a hermitean operator. We can now estimate the contributions of various types of reorganization to ΔE.

Current theories would lead one to expect the main contribution to come from hyperconjugation, this being much more important in R^+ than in $R\cdot$. The corresponding terms in Eq. (5) are those where Ψ_i is an occupied CH bond orbital while Ψ_j is the lowest virtual orbital (i.e. that singly occupied in $R\cdot$). Calculations for several alkyl radicals show, however, that these terms in fact account for less than 20% of ΔE. The main contributions arise from terms whose Ψ_i is a filled bond orbital and Ψ_j the corresponding virtual (antibonding) orbital, representing polarization of the corresponding σ bond by the positive charge in R^+. Since this effect is not included in the I^1 values, these underestimate the decrease in ionization potential of $CH_3\cdot$ with increasing alkylation. On the other hand ΔE is relatively insensitive to structural changes. Thus the values of ΔE for *n*-Pr and *i*-Pr are similar. It will be seen that the difference (0.45 eV) between the corresponding I^1 values is indeed close to that (0.55 eV) between the observed ionization potentials. As expected, this parallel does not hold for radicals of different size. Thus the difference in I^1 between ethyl and isopropyl (0.42 eV) is much less than that (0.83 eV) between the observed ionization potentials.

The ΔE values should also be less in cases where the charge in the cation is delocalized. This is seen rather nicely in a comparison of allyl and its two monomethyl derivates where the I^1 values reproduce the ionization potentials closely.

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