

Notes

An Improved IOC- ω Technique: Part V — Ionization Potentials & Heats of Formation of Some Organic Molecules

SURESH C. SHARMA* & BAL KRISHNA

Department of Chemistry, University of Allahabad
Allahabad 211002

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Ionization potentials and heats of formation of some organic molecules have been calculated using an improved IOC- ω technique. The results have been compared with some previously calculated and experimental values.

WE report here the ionization potentials and heats of formation of some organic molecules using an improved IOC- ω technique¹ in which the overlap in the ω -technique has been included. The net charge on atom r has been taken as that resulting when overlap charges are distributed equally over all the atoms involved. The following form the

coulomb integrals has been used for the present work² (Eq. 1):

$$H_{rr} = \alpha_r + \omega \left[(1 - 1/2 \sum_j (p_{rj} S_{rj} + p_{jr} S_{jr})) \right] \quad \dots(1)$$

where all the symbols have their usual significance. Resonance integrals have been calculated using the self-consistent β method³:

$$H_{rs} = \beta_0 \exp(0.55p_{rs} - 0.3666) \quad \dots(2)$$

where H_{rs} is the resonance integral at iteration N and p_{rs} is the bond order at iteration $(N-1)$.

The method of calculation and parameters used have been described in our previous papers¹ of this series. For calculations on heterocyclic molecules, appropriate changes in the α and β parameters have been made using the definition of Wheland and Pauling⁴ and taking $h = 0.5$ and $K = 1.0$ (ref. 5-7). For the calculation of heats of formation we have used the energies of various types of bonds as given by Dewar and Gleicher⁸.

A comparison of the ionization potentials of some alternant hydrocarbons, as calculated by the present method with those calculated using various other

TABLE 1 — IONIZATION POTENTIALS OF SOME ALTERNANT HYDROCARBONS

Molecule	Ionization potential, eV						
	Present work	Dewar <i>et al.</i> ⁹	SCF-MO method ¹⁰	IOC- ω technique ¹¹	Simplified IOC- ω technique ¹²	Experimental	Reference
Dibenz-[1,2:5,6]-anthracene	7.87	7.84	8.070	7.75	7.97	7.42	13
Dibenz-[1,2:7,8]-anthracene	7.93	7.88	8.193	7.92	8.15	7.42	13
Picene	7.61	—	8.157	7.78	7.99	7.62	13
Perylene	7.55	—	7.724	7.35	7.19	7.15	14
Coronene	7.88	—	7.976	7.80	7.95	7.50	13
Hexatriene	8.36	8.43	—	8.43	8.79	8.23	15
Octatetraene	8.02	7.89	—	—	—	7.80	15
Stilbene	8.01	—	—	7.89	7.91	7.95	14
Dibenz-[1,2:3,4]-anthracene	7.94	—	8.098	7.81	8.02	—	—
Benz-[4,5]-pyrene	7.87	7.86	8.024	7.77	7.87	—	—
Benz-[1,2]-pyrene	7.64	7.56	7.747	7.47	7.73	—	—
Dibenz-[1,2:4,5]-pyrene	7.69	—	7.841	—	—	—	—
Pentacene	7.35	—	—	7.17	7.54	—	—
Pentaphene	7.83	—	—	7.72	7.97	—	—
Dibenz-[3,4:5,6]-phenanthrene	7.94	—	—	7.84	8.02	—	—
Hexahelicene	7.93	—	—	7.72	8.00	—	—
Benz-[1,12]-perylene	7.71	—	—	7.57	7.78	—	—
Ovalene	7.51	—	—	7.25	7.51	—	—

TABLE 2 — HEATS OF FORMATION OF SOME NITROGEN CONTAINING HETEROCYCLIC MOLECULES

Molecule	π -Bond energy (eV)	Heat of formation (eV)			
		Present work	Dewar and Harget ¹⁶	Simplified IOC- ω technique ⁷	Expl. values ¹⁷
Pyridine	7.890	51.148	51.88	52.042	51.78
Pyridazine	7.897	45.137	—	—	45.59
Pyrimidine	7.325	44.343	46.86	45.825	46.99
Pyrazine	7.772	44.790	46.32	45.784	46.44
Quinoline	13.829	85.022	85.32	86.049	85.18
Isoquinoline	13.175	84.369	85.32	85.794	—

*Author to whom correspondence should be made at Naval Chemical & Metallurgical Laboratory, Bombay 400023.

methods⁹⁻¹², given in Table 1, shows that the values obtained by us are very close to those obtained by Dewar *et al.*⁹ and using IOC- ω technique¹¹, but generally lower than those obtained using semi-empirical SCF-MO method¹⁰ and simplified version of IOC- ω technique¹². For molecules for which experimental values of vertical ionization potentials are available the first two methods give very encouraging results, while the latter two generally give high values. Since, in the calculations molecular geometry has been assumed to remain unchanged, these values are the so called vertical ionization potentials and therefore, should be essentially higher than the spectroscopic values¹³⁻¹⁵.

Table 2 reports the heats of formation of some nitrogen containing heterocyclic molecules. Our results are in fair agreement with the experimental values¹⁶ although these are not as good as those obtained by Dewar and Harget¹⁷.

References

1. (a) SHARMA, S. C., SRIVASTAVA, A. K. & KRISHNA, B., *J. chem. Soc. Faraday Trans. II*, **71** (1975), 168; 172.
2. KRISHNA, B. & GUPTA, S. P., *J. Am. chem. Soc.*, **92** (1970), 7247.
3. BOYD, G. V. & SINGER, N., *Tetrahedron*, **22** (1966), 3383.
4. WHELAND, G. W. & PAULING, L., *J. Am. chem. Soc.*, **57** (1935), 2086.
5. MURRELL, J. N., *Molec. Phys.*, **1** (1958), 384.
6. BROWN, R. D., *J. chem. Soc.*, (1956), 272.
7. SRIVASTAVA, A. K. & KRISHNA, B., *Indian J. pure appl. Phys.*, **11** (1973), 246.
8. DEWAR, M. J. S. & GLEICHER, G. J., *J. chem. Phys.*, **44** (1966), 759.
9. DEWAR, M. J. S., HASHMALL, J. A. & VERNIER, C. G., *J. Am. chem. Soc.*, **90** (1968), 1953.
10. DEWAR, M. J. S., HASHMALL, J. A. & TRINAJSTIC, N., *J. Am. chem. Soc.*, **92** (1970), 5555.
11. GUPTA, S. P., *Quantum mechanical evaluation of bond parameters in some molecules*, D. Phil. thesis, University of Allahabad, Allahabad, 1970, 34.
12. SRIVASTAVA, A. K., *Studies in theoretical evaluation of some bond parameters of some molecules*, D. Phil. thesis, University of Allahabad, Allahabad, 1973, 50, 52.
13. MASTEN, F. A., *J. chem. Phys.*, **24** (1956), 602.
14. BRIEGLEB, G. & CZEKELLA, Z., *Z. Elektrochem.*, **63** (1959), 6.
15. PRICE, W. C. & WALSH, A. D., *Proc. R. Soc., London A*, **185** (1945), 182.
16. DEWAR, M. J. S., *Molecular orbital theory of organic chemistry* (McGraw-Hill, New York), 1969, 382.
17. DEWAR, M. J. S. & HARGET, A. J., *Proc. R. Soc., London A*, **315** (1970), 457.

An Improved IOC- ω Technique: Oxidation & Reduction Potentials & Charge Transfer Energies of Some Conjugated Hydrocarbons

SURESH C. SHARMA* & BAL KRISHNA

Department of Chemistry, University of Allahabad
Allahabad 211002

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The polarographic half-wave oxidation and reduction potentials of conjugated hydrocarbons and charge transfer energies of their complexes with iodine have been calculated from the values of ionization potentials and electron affinities calculated using a recently described improved IOC- ω technique. The results are compared and found to be in good agreement with the experimental values.

*Present address: Naval Chemical & Metallurgical Laboratory, Bombay 400023.

CORRELATIONS between the polarographic half-wave reduction potentials ($-E_{1/2}$ red.) of conjugated hydrocarbons and the lowest unoccupied HMO energies have been described by various workers¹⁻³. Similar correlations have also been observed⁴⁻⁶ between polarographic half-wave oxidation potentials ($E_{1/2}$ ox.) and energies of highest occupied HMOs. Dewar *et al.*^{7,8} have obtained excellent correlations between reduction potentials and electron affinities and oxidation potentials and ionization potentials using a variable β -semi-empirical SCFMO method for hydrocarbons as well as hetero-molecules. Pysh and Yang⁶ have calculated ionization potentials of some aromatic hydrocarbons from these correlations and measured values of oxidation potentials. The following relations can be derived theoretically between oxidation and reduction potentials and ionization potentials (I) and electron affinities (A)^{6,7}:

$$E_{1/2}(\text{ox.}) = mI + C \quad \dots(1)$$

and

$$-E_{1/2}(\text{red.}) = m'A + C' \quad \dots(2)$$

In a series of charge transfer complexes between a single acceptor and a series of polynuclear hydrocarbons if the interactions between the donor and acceptor are small, the transition energy, ΔE_{CT} for the first charge transfer (CT) band should be given by⁶,

$$\Delta E_{CT} = I - A + \text{const.} \quad \dots(3)$$

I is the ionization potential of hydrocarbon and A , the electron affinity of acceptor molecule. For a given acceptor molecule Eq. (3) becomes:

$$\Delta E_{CT} = I + \text{const.} \quad \dots(4)$$

and a linear plot can be obtained between ΔE_{CT} and I :

$$\Delta E_{CT} = m''I + C'' \quad \dots(5)$$

On the basis of above correlations, we have calculated, in the present paper polarographic half-wave oxidation and reduction potentials of some conjugated molecules and charge transfer transition energies of some iodine-hydrocarbon complexes from the values of ionization potentials and electron affinities, obtained using an improved IOC- ω technique⁹. Method of calculation and some of the results have already been reported^{9,10}. The parameters m and C have been obtained by theoretically calculating the slope and intercept respectively of a plot between $E_{1/2}(\text{ox.})$ (on Y -axis) and I (on X -axis). Similarly parameters m' , C' , m'' and C'' can also be obtained. Here, we have obtained, $m = 0.90$, $C = -5.88$, $m' = -0.86$, $C' = 2.07$, $m'' = 1.032$ and $C'' = -5.098$.

Polarographic half-wave oxidation and reduction potentials of some conjugated hydrocarbons and charge transfer transition energies of some iodine-hydrocarbon complexes have been compared with respective experimental values^{6,11,12} in Table 1. For comparison we have used the values which refer to measurements done under identical experimental conditions for a large number of hydrocarbons, since, although the relative values of oxidation and