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MOLECULAR ELECTRON IONIZATION CROSS - SECTION AND λ_{max} IN THE STUDIES OF ACTIVITIES OF ALKALOIDS

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ABSTRACT

Alkaloids are natural products having an important position in forensic chemistry and medicine due to their pharmacological activities.Not many physical properties of alkaloids have been studied so far excepting UV, IR and NMR studies. This paper deals with the evaluation of Molecular electron ionization cross section (Q) through λ_{max}, a parameter available from UV studies. Electron ionization cross - section was primarily conceived to be of use in radiation chemical data, mass spectrometry and thermo-dynamic studies. But later attempts to correlate Q with structural and related parameters prompted the authors to derive an explicit expression relating λ_{max} and Q. The application of this method to correlate Q and Chemical activity through λ_{max} is a examined and the results are discussed.

KEYWORDS: Alkaloids, molecular polarizability, diamagnetic susceptibility and electron ionization cross-sections.

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INTRODUCTION

Electron ionization cross - section for atoms and molecules are of importance for evaluation of the radiation chemical data, mass spectroscopic studies of ion-molecule reactions and thermodynamic measurements in Plasma and Space Physics. They also constitute one of the fundamental problems concerning electron impact collisions. There has been considerable work on both experimental and theoretical aspects of electron ionization cross sections [1-6]. Electron ionization cross section increase rapidly from threshold energy and reach a flat maximum usually between 50 and 80 eV, and decrease slowly at higher energies. At high electron kinetic energy (71 keV) there is good agreement between the experimental energy dependance of the cross section and simple theory based on the Born approximation[3]. At lower electron energies neither theory nor experiment show good agreement in themselves or with each other [4-6]. Lacking rigorous predictive theory, one has to go through semi - empirical correlations. Otvos and Stevenson[4] suggested that molecular cross sections could be calculated by adding the atomic cross sections. Lampe, Franklin and Field[5] proposed that the additivity postulate does not hold, but a general correlation of cross section with polarizability did exist. The above proposed correlations can be summarized as

1. Additivity of atomic cross sections
2. Linearity with polarizability
3. Linearity with diamagnetic susceptibility

Beran and Kevan[1] have generalized the cross section with the additivity of atomic cross sections for different molecular classes. Subbaiah and Rao et al[7]., have recorded the limitations of these correlations and have suggested modified formula for Q, the molecular electron ionization cross section. In the present investigation, an algebraic relation is developed between the molecular electron ionization cross section (Q) and the wavelength corresponding to the maximum electronic absorption (λ_{max}) based on semi theoretical grounds and is applied to some simple molecular systems. The possibility of a relation between Q and λ_{max} is envisaged on the following concepts. The term ionization cross section does generally refer to the surface area of atom or molecule (assuming it to be spherical) which is susceptible for reaction and the electrons attached to an atom or molecule are in a field different from that when they are isolated. A knowledge of the molecular electron ionizaiton cross sections is useful in estimating the activity of the molecule. Similarly the wavelength at which maximum absorption of energy occurs (λ_{max}) does definitely throw light on the impact of electrons with radiation. Thus an electron, bound to an atom or molecule is responsible for the absorption of radiation as well as its reactivity. Both these molecular electron ionization cross section (Q) and λ_{max} are related to the number of free electrons which are readily responding to the electronic and electromagnetic fields. So a relation between Q and λ_{max} is thought of now.

Present method

The molecular polarizability α_M [8-10] is given by

$$\alpha_M = \frac{N\rho}{4\pi^2 M}\left[\frac{e^2/m}{\upsilon_0^2 - \upsilon^2}\right]$$

$$= \frac{N\rho e^2}{4\pi^2 Mmc^2}\left[\frac{1}{\lambda_0^2} - \frac{1}{\lambda^2}\right]$$

$$= \frac{N\rho e^2}{4\pi^2 Mmc^2}\left[\frac{\lambda^2\lambda_0^2}{\lambda^2 - \lambda_0^2}\right]$$

$$\cong \frac{N\rho e^2}{4\pi^2 Mmc^2}\left[\lambda_0^2\right] \text{------(1)}$$

where λ_0 , the wavelength corresponding to maximum absorption is far separated from λ ,

the wavelength of incident radiation.

N : Avogadro number
e : Charge of the electron
ρ and M refer to the density and Molecular weight of the substance under consideration

C : velocity of light
m : mass of the electron

The diamagnetic susceptibility χ_M Can be given by the relation[10]

$$\chi_M \sigma^{|} \gamma\ m\ \alpha_M \quad \text{------ (2)}$$

where m is a characteristic constant = 0.72 x 10^{19} : γ □ $(0.9)^n$, n reveals the number of unsaturated bonds or rings present in the molecule.

$$\sigma^1 = \left[\sigma_1^{1/n_1}\ \sigma_2^{1/n2} \ldots \sigma_p^{1/n_p}\right]^{1/2} \text{------(3)}$$

Where $\sigma_1, \sigma_2 \ldots\ldots \sigma_p$ are the Pauling percent covalence characters of the bonds.

n_1 , n_2 ,....n_p are the bond orders of the various bonds present in the characteristic group and

$$\sigma_1 = \exp\left[\frac{-(X_{ai} - X_{bi})}{4}\right] \text{-----(4)}$$

Where X_{ai} and X_{bi} are the electro negativities of the bonded atoms a and b of the i^{th} bond.

The modified relation of Beran and Kevan proposed by Rao et al[8-10] can be given by

$$Q = 0.278\,\chi_m$$
$$= 0.278\left[\gamma\, m\sigma^1\, \alpha_M\right] \text{-----(5)}$$

Substituting the value of α_M (1) in the above equation (5)

$$Q = 0.278(0.9)^n \left(0.72 \times 10^{19}\right)\sigma^1 \frac{N\rho e^2}{4\pi^2\, Mmc^2}\left[\lambda_0^2\right]$$

$$= 0.278(0.9)^n \left(0.72 \times 10^{19}\right)\sigma^1(\tau)\frac{\rho}{M}\left(\lambda_0^2\right) \text{-------(6)}$$

$$\text{Where } \tau = \frac{Ne^2}{4\pi^2\, mc^2} = 4.77625 \times 10^{-12} \text{----(7)}$$

If there are multiple wavelengths of absorption, the above equation can be written as

$$Q = 0.95601 \times 10^7 \times (0.9)^n\, \sigma^1 \frac{\rho}{M}\left[\lambda_0^2\right] \text{----(9)}$$

But the equation (9) needs modification in view of the part played by the effective number of electrons (P), which play very important role in the interaction of electromagnetic waves with the free electrons. Equation (9) refer to one electron problem. But there are P electrons which are not taking part in bonding. Also a fraction of P alone need to be considered as they are not in isolated state. Taking the effective role of all these non - bonded electrons, equation (9) gets reduced to

$$Q = (0.1)P\left(0.95601 \times 10^7 \times (0.9)^n\, \sigma^1\left(\frac{\rho}{M}\right)\sum \lambda_{max}^2\right)$$
$$= 0.95601 \times 10^5 \times (0.9)^n\, \sigma^1\left(\frac{\rho}{M}\right)\sum \lambda_{max}^2 \text{----(10)}$$

The order of magnitude in the above equation is so adjusted as yield Q in $_{10}{}^{-16}$ cm^2 .

This equation is applied to a few alkaloids like

Boldine, Berberine, Chelidonine, Papaverine and Noscapine. The necessary data on λ_{max} for these alkaloids are taken from reference (11) and are given in table I and the densities of them are calculated using the empirical relation [12]

$$\rho = \frac{K_{av} M}{N_A \Sigma\, \Delta V_i} \text{------ (11)}$$

Where K_{av} is a constant equal to 0.650; N_A

is a constant equal to 0.60228, M is molecular weight and ΔV_i represents the change in volume of the characteristic group present in the molecule. The values of ΔV_i [12] for different characteristic groups are given in table II. The values of P, the effective number of electrons have been evaluated from the concepts of deMallemann [13,14]. The densities ρ., molecular weight (M), the effective number of electrons (P), the percentage covalency factors (σ^{l}) for these alkaloids are reported in table III. The data on χ , the electronegativities needed for the calculation of σ are taken from the reference (15). The values of molecular electron ionization cross sections (Q) for these alkaloids are reported in table IV. The values of Q reported from susceptibility data as obtained through polarizability (from force field technique[16] and Lippincott - δ -function potential approach[17]) and Pascal's method [18] are also reported in table IV.

The allelopathic activity of the present chosen alkialoids are given in table V.

Table I

λ_{max} Values from UV absorption spectra of alka-

loids (Ref. 11).

Alkaloid	λ_{max} (nm)	$\sum \lambda 2max$ (x 10-9)
Boldine	219, 268, 280, 304, 313	3.8857
Berberine	230, 266, 352, 432	4.3418
Chelidonine	206, 238, 289, 239	2.3972
Papavarine	209, 238, 273, 280, 288, 313	5.4044
Noscapine (Narcotine)	209, 257, 289, 308	2.8506

Table II

Change in the volume of Characteristic group.

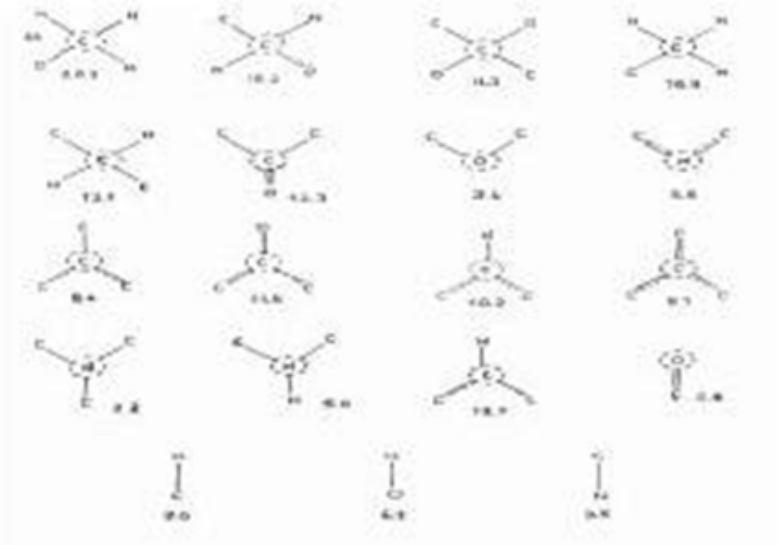

Table III
Parameters

Alkaloid	Molecular Weight (M)	Density Gm/CC(ρ)	Degree of Covalency σ	Effective No. of Electrons (P)
Boldine	327.38	2.382	0.2727	18
Berberine	336.37	2.407	0.3402	18
Chelidonine	353.37	2.970	02353	26
Papaverine	339.39	2.006	0.1908	20
Noscapine (Narcotine)	413.43	3.010	0.3518	30

Table IV
Molecular electron ionization cross-sections Q in AU^2

Alkaloid	Present Method	From χ_M obtained by		
		Force Field Technique	Lippin Cott δ function Model	Pascal's Method
Boldine	10.67	10.38	10.84	11.94
Berberine	13.26	13.57	13.91	14.21
Chelidonine	11.59	11.43	11.77	12.99
Papaverine	8.49	8.71	7.99	8.55
Noscapine (Narcotine)	15.23	15.45	15.73	16.83

Table V
Allelopathic Activity of Alkaloids

Alkaloid	Activity	ED 50%	Ref
Boldine	Toxic for Lemna	0.04	19
Berberine	Reduction of Radical Length in Lepidium	0.01	19
Chelidonine	Reduction of Radical Length in Lepidium	0.1	19
Papaverine	Reduction of Root growth Induction of Poliplody in Allium	-	19
Noscapine (Narcotine)	Inhibition of Germination	-	20

RESULTS AND DISCUSSIONS

The values of Q as reported from λ_{max}

(present approach) and that through χ_M (as obtained from α_M through force field technique and

Lippincott - δ -function potential model) agree fairly well. This method can be claimed to be successful as it provides an easy estimation of electron

ionization cross-section based on the data on λ

This suggests an easy applicability of the present method to various other molecular systems and provide a new venue to use the 'so far unused data' on λ_{max} to get a useful parameter like 'Q', the molecular electron ionization cross section. Thus the present paper opens a new line of approach relating ultraviolet absorption and mass spectroscopic studies.

Activities of alkaloids

From table V it is clear that the activity of chelidonine is seen to be maximum, compared to that of Berberine in the 'reduction of radicle length in Lepidium Loctuca'. Though no formal relationship exist between allelopathic activity of the alkaloids and their structures a plausible explanation for their behaviour could be offered from the calculated molecular electron ionization cross - section values. If the ionized component is less (or molecular electron ionization cross section is less) that means the unionized component will be more and the activity will be more. This can be seen from the molecular electron ionization cross - section (Q) and the degree of covalency $(\sigma^{|})$ values

of Chelidonine and Berberine. While $Q_{Berbeine}$ >

$Q_{Chelidonine}$, the unionized component will be more and hence the activity. In fact the allelopathic activity depends mostly on the unionized component. Thus it can be claimed without ambiguity that molecular electron ionization cross - sections will be helpful in estimating the activity and hence the drug consisting these alkaloids.

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