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PHOTOIONIZATION DETECTOR RESPONSE

ANTHONY N. FREEDMAN

Central Electricity Research Laboratories, Kelvin Avenue, Leatherhead, Surrey KT22 7SE (Great Britain)

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SUMMARY

A number of studies of the factors involved in photoionization detector response are compared, contrasted and tested using published data. It is concluded that ionization potential is the most important single factor and that the relative number of π electrons is not a significant additional factor.

INTRODUCTION

The increasing importance of the photoionization detector (PID), both as a gas chromatography detector and as a selective monitor of the concentration of species of interest in a gas, has resulted in a number of studies of the factors involved in its response¹⁻⁴.

Freedman¹ proposed a mechanism for PID response and from this derived an expression for the PID signal. This treatment was used by Senum² as the basis of a discussion of the effect of using different carrier gases on PID response.

Casida and Casida³ have reported an entirely different intuitive approach to the theory of PID response. In addition, Langhorst⁴ has determined the relative molar response of a large number of compounds using a PID and has drawn empirical conclusions. This paper contrasts, compares and tests these different approaches.

THEORY

Freedman derived the following expression for PID response:

$$i = F\eta\sigma NL [AB] \quad (1)$$

where i is the PID ion current, P is the initial photon flux, F is the Faraday, η is the photoionization efficiency (the probability that a molecule will absorb a photon to give an excited state), σ the absorption cross-section (the probability that the excited state will ionize), N is Avogadro's number, L is the path length and $[AB]$ the concentration of an ionizable substance. Thus for a particular detector and lamp this expression can be simplified to:

$$i/[AB] = k\sigma\eta = R \quad (2)$$

where R is the molar response and k is a proportionality constant. The product $\sigma\eta$ is the photoionization cross-section σ_i .

Casida and Casida's intuitively obtained formula for PID response is:

$$R = kn F(IP) \quad (3)$$

"where k is a proportionality constant which varies (*sic*) with the probability that a given type of electron will be ionized, *i.e.* with the ionization cross-section of an orbital type", n is the number of ionizable electrons and $F(IP)$ the number of photons with energies greater than or equal to the ionization potential (IP). For the 10.2 eV PID n is taken as the number of π bonding electrons only. Carbon-hydrogen bonding electrons are ignored since methane (IP = 12.98 eV) gave no response in an argon discharge ($h\nu = 11.83$ eV) PID⁵. Carbon-carbon σ bond electrons are ignored since "paraffins have relatively small R values compared to hydrocarbons with carbon-carbon π bonds... probably due to the fact that IP's of paraffins are usually very close to or above the photon energy limit of 10.2 eV."

DISCUSSION

The function $F(IP)$ in eqn. 3 must be considered in three separate IP ranges, *viz.* above 10.9 eV, below 10.2 eV and between 10.2 and 10.9 eV. Above 10.9 eV the standard MgF_2 lamp window is opaque hence $F(IP) = 0$. Below 10.2 eV "the number of photons emitted into the PID ionization chamber which have energies greater than or equal to IP" will be I^0 , which is constant for all species. Between 10.2 and 10.9 eV two other factors are important. The energy gap between molecules in excited vibrational states and the ground state of the ion can be up to 0.4 eV less than the IP. In addition, impurities in the lamp may give rise to small side-bands with photon energies between 10.2 and 10.9 eV. These factors will cause species with IP values between 10.2 and 10.9 eV to give a small PID response. The actual response will depend on such factors as temperature and the particular lamp used.

For species with IP < 10.2 eV eqn. 3 can be written as:

$$R \propto Kn \quad (4)$$

where K includes the photoionization cross-section, σ_i , and eqn. 2 can be written:

$$R \propto \sigma_i \quad (5)$$

Thus the difference between the equations of Casida and Casida eqn. 4 and Freedman eqn. 5 is that the former include the number of π electrons.

The theoretical relationship between σ_i and IP is very complex⁷ and includes such factors as molecular geometry and symmetry. This can be seen from Langhorst's data for aromatic hydrocarbons⁴. *o*- and *m*-xylene both have an IP of 8.56 eV and R of 1.14 and 1.15, respectively. The more symmetrical *p*-xylene has IP = 8.445 eV and $R = 1.2$. In contrast, isomeric ethylbenzene has a similar R to *o*- and *m*-xylene of 1.16

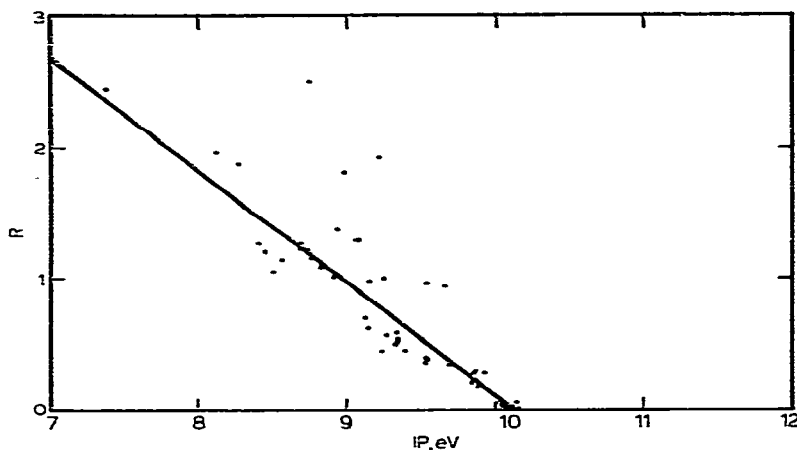


Fig. 1. Response per mole against IP (Langhorst's data).

but a much higher IP of 8.76 eV. The stability of the ion is also important. Aniline, with a very stable ion, has an IP of only 7.7 eV with a relatively low R of 1.13. Freedman suggested that although these other factors were involved, IP was the primary influence on σ_i for most molecules and hence R . The linear regression line for the plot of R against IP using Freedman's data for hydrocarbons gave a correlation coefficient of 93%.

Casida and Casida³ suggest that these plots will be "more scattered" and "less well behaved" than plots of R/n against IP, where n is the number of π electrons. It is not clear why they limit their theory by restricting n to carbon-carbon π -bonded electrons (they only consider hydrocarbons) since this clearly leads to erroneous results. For all alkanes n is zero yet the varying response of the PID to n -alkanes has been reported^{1,4,5}. In addition, if $n = 0$, R/n is infinite which clearly cannot be correct. Freedman's data¹ for eight hydrocarbons which have π electrons gave a

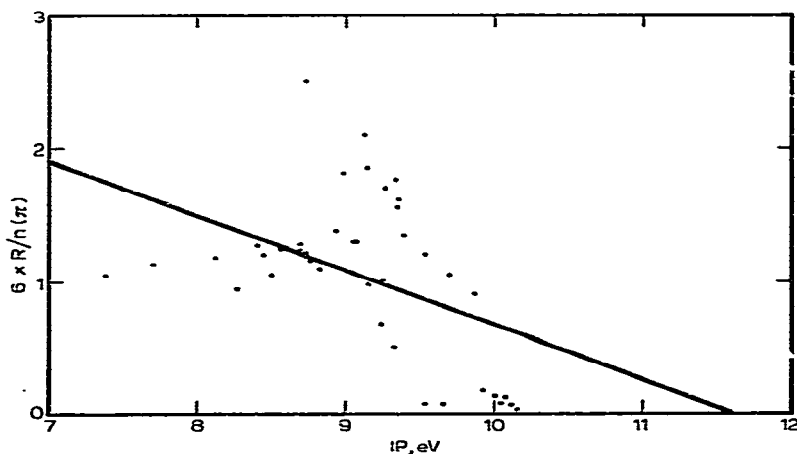


Fig. 2. Response per mole/ $n(\pi)$ against IP (Langhorst's data).

correlation coefficient of 54% for R against IP, which fell to 8% for R/n against IP. The equivalent figures using Langhorst's data⁴ for thirteen hydrocarbons is a correlation coefficient of 82% for R against IP falling to 1% for R/n against IP. Langhorst's data for 50 widely differing compounds, the IPs of which are known, gave a correlation coefficient of 89% for R against IP (Fig. 1). The correlation coefficient for R/n against IP, where n is the number of π electrons from C=O as well as C=C bonds, for the same 50 compounds fell to 25% (Fig. 2). Casida and Casida³ show plots of R against IP and R/n against IP for some compounds and claim that these verify their theory. Unfortunately no data is given.

Casida and Casida state that " α -pinene, a compound with no π -electrons (*sic*), gave a response as large as benzene" and draw some conclusions from this. The compound whose structure is shown on their plot is in fact pinane which indeed has no π electrons. α -Pinene has two π electrons and in addition has a four-carbon strained ring which would result in a further reduction in IP, hence it would not be surprising to obtain a similar response to that of benzene.

Langhorst⁴ draws a number of empirical conclusions regarding the relative sensitivity of the PID to different groups of compounds. In all cases they reflect the changes in IP between the different groups and confirm the proposal that the IP is the most important factor affecting PID response.

Casida and Casida develop their theory further to produce a quotient, Q , for the ratio response of the PID and flame ionization detector (FID) which has been the subject of previous discussion (Freedman¹; Driscoll *et al.*⁶). They give

$$\text{PID/FID} = Ln F(\text{IP})/N \quad (6)$$

where N is the number of carbon atoms and " L is a constant of proportionality and is chosen so that PID/FID = 1.0 for n -octane". This would appear to be a difficulty since according to their theory $n = 0$ for n -octane; however, L is assigned the value 10. $F(\text{IP})$ is taken as "proportional to the difference between IP and the energy cut-off

TABLE I

PID/FID RELATIVE RESPONSE

Compound	Exptl. ratio	Prediction $10n(10.2-IP)/N$	Prediction $(10.2-IP)/N$	Ref.
Toluene	10.0	10.0	10.0	9
Benzene	11.2	8.1	8.1	9
<i>p</i> -Xylene	10.0	11.2	11.2	9
Hexane	2.4	0	0.2	9
Cyclohexane	1.9	0	2.7	1
1-Nonene*	4.6	1.6	4.8	1
<i>n</i> -Decane*	1.3	0	2.0	1
Cyclohexane	2.1	0	2.7	6
<i>n</i> -Octane*	1.0	0	1.8	6
<i>cis</i> -2-Octene*	5.3	2.5	7.6	6
Benzene	8.6	8.1	8.1	6
$\Sigma(x_{\text{exp}} - x_{\text{pred}})^2$		44.6	23.8	

* Estimated IP values used.

of the lamp window" and shown as $(10.2 - IP)$. Since the energy cut-off of the lamp window is 10.9 eV, presumably the photon energy of 10.2 eV is meant. This leads to a formula for the ratio, $Q = 10n(10.2 - IP)/N$. This equation can be tested using previously reported data^{1,6,9} where IPs are known. In addition, it is possible to estimate IPs for higher members of an homologous series by extrapolation of the IPs of the lower members. Table I shows data for PID/FID response. All data have been normalized to toluene = 10. It is clear from Table I that ignoring the number of π electrons gives a much better fit of the data.

Casida and Casida complete their paper by stating that the correlation between reactivity with hydroxyl radicals and R or PID/FID relative response is excellent. No supporting data are provided. We have determined the correlation coefficient for a linear regression of the relative reactivity of hydrocarbons with hydroxyl radicals reported by Darnall *et al.*¹⁰ with: (i) the values of R given by Langhorst⁴; (ii) the IPs, (iii) Casida and Casida's calculated values for PID/FID response. The coefficients are 16%, 27% and 3%, respectively. This lack of any correlation is not surprising since hydroxyl reaction with hydrocarbons is by hydrogen atom abstraction¹¹ and not by ionization.

CONCLUSIONS

- (1) Ionization potential is the most important single factor determining PID response.
- (2) The relative number of π electrons is not a significant additional factor.

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