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## APPLICATION OF A UNIFIED THEORY OF GAS CHROMATOGRAPHIC PHOTOIONIZATION DETECTOR RESPONSE TO A 10.2-eV DETECTOR

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### SUMMARY

The previously poorly understood dependence of gas chromatographic photoionization detector (PID) molar response,  $R$ , on ionization potential, IP, can be explained in terms of the number of ionizable electrons,  $n$ . For hydrocarbons and a 10.2-eV PID, a good approximation is to call  $n$  the number of carbon-carbon  $\pi$ -bonding electrons per molecule.

A critical examination of a previously proposed classification system based on the molar response ratio of a 10.2-eV PID to a flame-ionization detector (FID) is made using the insight into the PID response obtained in this study. A correlation is suggested between this PID/FID response ratio and a classification system of meteorological interest which also extends to paraffins.

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### INTRODUCTION

It has been known for some time that the molar response,  $R$ , of a photoionization detector (PID) in gas chromatography (GC) is dependent on the ionization potential (IP) of the compounds studied<sup>1,2</sup>. However, plots of  $R$  against IP for several compounds and a given PID usually yielded only a scatter of data which vaguely increased as IP decreased<sup>1</sup>. By 1978, an additional influence on  $R$  had been noted. Thus,  $R$  for a given compound appeared to increase roughly as the number of ionizable electrons ( $n$ ) in the compound increased, for a given PID<sup>3</sup>.

The present study presents a unified theory of PID response, which takes into account both IP and  $n$ . This theory may be used to examine the variation in the PID to flame-ionization detector (FID) molar response ratio for different compounds, and is especially interesting in the light of a more empirical study of this ratio done by Driscoll *et al.*<sup>3</sup>. A critical examination of the latter work is made.

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## THEORETICAL

Consider a compound with  $n$  electrons, all of which have identical orbital energies and, thus, identical IPs. Intuitively,  $R$  for this compound is proportional to (1) the number of photons required to ionize an electron in the compound, and (2) the probability that a given photon will find an electron to ionize, which is proportional to  $n$ .

We define a function  $F(\text{IP})$  as the number of photons emitted into the PID ionization chamber which have energies greater than or equal to IP.  $F(\text{IP})$  is thus a "photon-counting function" which counts the number of photons able to ionize an electron of ionization potential IP.

The dependence of  $R$  on the probability of ionization and number of ionizing photons may now be written as

$$R = knF(\text{IP}) \quad (1)$$

where  $k$  is a proportionality constant which varies with the probability that a given type of electron will be ionized, *i.e.*, with the ionization cross-section of an orbital type.

An experimental investigation of eqn. 1 may be made by plotting  $R/n$  against IP for several compounds. If eqn. 1 holds, this plot should also be a plot of  $kF(\text{IP})$  against IP and should thus behave like  $F(\text{IP})$  by decreasing monotonically as IP increases and by becoming zero when IP becomes equal to the highest photon energy emitted into the PID measuring chamber. (In the case of a PID with a window between the lamp and measuring chamber, this photon energy is the UV cut-off of the lamp window.) Furthermore, if compounds with different numbers of ionizable electrons ( $n$ ) are plotted, a plot of  $R/n$  against IP will yield a graph which monotonically decreases to zero at the energy where  $F(\text{IP}) = 0$ , but a plot of  $R$  against IP should give a more scattered, less well behaved, graph which would, in fact, be a plot of  $nkF(\text{IP})$  against IP.

Data for  $n$ -alkanes using a windowless PID with an argon discharge<sup>1</sup> can be plotted in this way. Since this PID reportedly gave no response for methane, the ionizable electrons in  $n$ -alkanes may be taken to be only the carbon-carbon bonding electrons and not the carbon-hydrogen bonding electrons, giving a total of  $n = 2(m-1)$  ionizable electrons for the linear paraffin  $\text{C}_m\text{H}_{2m+2}$ . The plot of  $R/n$  against IP\* in Fig. 1 is a monotonically decreasing function that goes to zero, as expected.

A PID with a light source and a window which will not allow photons of energies greater than about 10.2 eV to enter its ionization chamber offers another opportunity to investigate eqn. 1 (see Experimental). It has been observed that paraffins have relatively small  $R$  values compared to hydrocarbons with carbon-carbon  $\pi$ -bonds when a 10.2-eV PID is used<sup>3</sup>. This behaviour is probably due to the fact that the IPs of paraffins are usually very close to or above the photon-energy limit of 10.2 eV (see Fig. 2), whereas a glance at a table of IPs for hydrocarbons will show that carbon-carbon  $\pi$ -bonded hydrocarbons usually have much lower IPs<sup>4,5</sup>. Thus, to a good approximation, a 10.2-eV PID only ionizes carbon-carbon  $\pi$ -bonding

\* Unless otherwise stated, IPs used in this paper were taken from ref. 4.

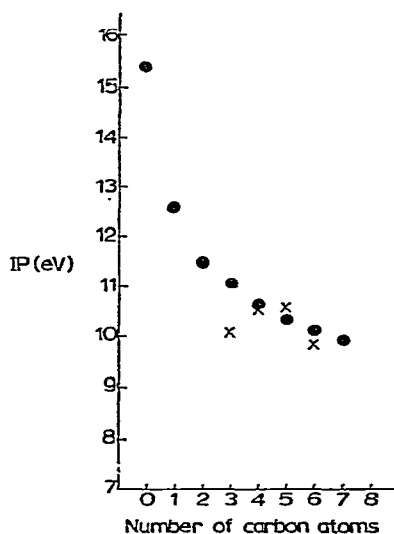
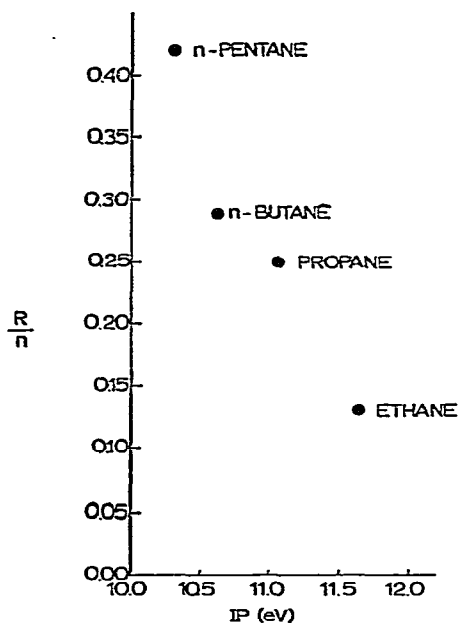


Fig. 1. Plot of  $R/n$  against IP for some  $n$ -alkanes, using data taken with a windowless PID and an argon discharge<sup>1</sup>.  $n$  = Number of carbon-carbon  $\sigma$ -bonding electrons per compound.

Fig. 2. Plot of IP against the number of carbon atoms per compound for  $n$ -alkanes (including hydrogen and methane) (●) and cyclic paraffins (×).

electrons, and, for this PID,  $n$  may be taken as the number of  $\pi$ -bonding electrons in the molecule.  $R/n$  may now be determined and plotted against IP.

Two assumptions are made in applying eqn. 1 to the 10.2-eV PID: (1) only carbon-carbon  $\pi$ -bonding electrons are ionized; (2) orbital-energy splittings of these  $\pi$ -electrons are not significant. These assumptions can be avoided by considering eqn. 1 to give the partial PID response for a given electron-orbital energy and type, and then summing over the partial PID responses to obtain the total PID response,  $R$ . Such an equation could look like

$$R = \sum_i k_i F(\text{IP}_i) + \sum_j k_j F(\text{IP}_j) + \sum_l k_l F(\text{IP}_l) \quad (2)$$

$\begin{array}{ccc} \text{CH}\sigma & \text{CC}\sigma & \text{CC}\pi \\ \text{electrons} & \text{electrons} & \text{electrons} \\ i & j & l \end{array}$

where the subscripts refer to an electron type and the IPs to individual electrons and not to the overall molecule. Eqn. 2 is unfortunately difficult to test since few ionization potentials are tabulated for other than a molecule's most easily ionized electrons. Eqn. 1, on the other hand, is relatively easily investigated and requires only a table of molecular ionization potentials and the determination of PID relative molar responses. This investigation for a 10.2-eV PID constitutes the experimental part of this paper.

## EXPERIMENTAL

Results were obtained using equipment with only a limited choice of GC columns. The principle components used were a Model PI-52-02 PID (HNU Systems, Newton, MA, U.S.A.) equipped with a 10.2-eV lamp, with an HNU Systems electrometer and a Linear chart recorder, and mounted on a Series 460 gas chromatograph (Antek Instruments, Houston, TX, U.S.A.) with nitrogen as the carrier gas. The compounds used and their sources and qualities are shown in Table I.

Because of the limited control of the type of equipment used, we chose to adapt the procedure to the equipment. Thus the following four procedures were used.

TABLE I  
TYPE, SOURCE AND QUALITY OF CHEMICALS USED

<i>Compound</i>	<i>Source</i>	<i>Quality</i>
Nitrobenzene	E. Merck	For synthesis
Cyclohexene	L. Light	
Naphthalene	BDH	For molecular weight determinations
Certified hexanes	Fisher Scientific	Pesticide grade
Toluene	E. Merck	For analysis
Benzene	Kebo AB	Thiophene-free
Ethylbenzene	Kebo AB	B.p. 136–137°C
Mesitylene	Kebo AB	
<i>m</i> -Xylene	Kebo AB	B.p. 138–139°C
<i>p</i> -Xylene	Kebo AB	M.p. 12–13°C
		B.p. 137–138°C
Methylene chloride	E. Merck	For analysis
		Stabilized with <i>ca.</i> 20 ppm pentene
1- $\alpha$ -Pinene	Dr. Theodor Schuchardt GmbH	
Pyridine		

*(a) Solutions in hexane*

Individual solutions with known concentrations near  $10^{-5}$  M of mesitylene, *p*-, *m*-xylene, ethylbenzene and toluene were made up in hexane and 10- $\mu$ l injections were made using a 10- $\mu$ l Terumo MS-10U syringe. A stainless-steel column (2 m  $\times$  2 mm I.D.) was packed with 10% PEG 400 on Chromosorb W (80–100 mesh). The carrier gas head pressure was constant and gave a flow-rate of about 10 ml/min. Only the column oven temperature varied from injection to injection.

*(b) Gas mixtures*

Procedure b differs from a only in the dilution and injection of the compounds. Thus 0.5  $\mu$ l of toluene, benzene and pyridine were injected in various combinations into a 50-ml Becton-Dickinson Yale k7191 glass syringe filled with dry nitrogen at 100°C which was sealed with a glass bead-capped section of flexible PTFE tubing, and the liquid was allowed to evaporate for about 10 min before making three ten-fold dilutions in dry nitrogen. A 0.5-ml volume of the resultant gas mixture was then injected using a 1-ml Hamilton gas-tight syringe. This procedure is well tested in our laboratory and is known to give accurate results for benzene and toluene but not for very much higher boiling compounds.

*(c) Solutions in methylene chloride*

This procedure differs from a in the GC columns and the sample solutions used and is actually two similar procedures. In the first procedure, a stainless-steel column (2 m  $\times$  ca. 2.5 mm I.D.) was packed with 5% SE-30 on Chromosorb W (80–100 mesh). Four injections were made of about 5  $\mu$ l of individual solutions of mesitylene and nitrobenzene of known concentrations near  $10^{-3}$  M in methylene chloride. Adsorption of nitrobenzene on the GC column was noted, but the relative molar response could still be estimated to within  $\pm 20\%$ .

The second similar procedure used a glass column (1.885 m  $\times$  1.6 mm O.D.  $\times$  0.8 mm I.D.), packed with 5% Carbowax 20M on Chromosorb W (80–100 mesh). Carrier gas flow-rates were carefully monitored with each injection and were in general about 4 ml/min. Injections of 0.2  $\mu$ l of individual solutions of mesitylene and isoprene of known concentrations near  $10^{-2}$  M in methylene chloride were made.

*(d) Methylene chloride solutions with mesitylene as internal standard*

Procedure d consisted of injecting solutions containing mesitylene as internal standard and one or more compounds. A 10- $\mu$ l volume of a solution containing known concentrations of  $\alpha$ -pinene and mesitylene near  $10^{-5}$  M was injected onto the SE-30 column previously described. This procedure was also carried out with naphthalene and *p*-xylene instead of  $\alpha$ -pinene. Also 0.4- $\mu$ l volumes of solutions containing known concentrations of mesitylene and one or more of *m*-xylene, ethylbenzene and toluene near  $10^{-3}$  M in methylene chloride were injected onto the Carbowax 20M column previously described.

*General procedures*

Peak-area integration was accomplished by the method of tracing, cutting and weighing.

A Pye Unicam GCD chromatograph equipped with a packed column containing SP 2100 on Chromosorb W and nitrogen as the carrier gas was used along with the Antek gas chromatograph and the Carbowax 20M column in a small investigation of how nitrogen carrier gas flow-rate varies with column temperature.

## RESULTS

Because  $R$  is a function of carrier gas flow-rate,  $f$ , through a PID and because  $f$  varies with temperature, it was in general necessary to take a compound's elution temperature into account in calculating  $R$  for that compound. Through the principle of conservation of energy and the Boltzman law, it can be shown, that, if the carrier gas is an ideal gas and only the column temperature ( $T$  in  $^{\circ}$ K) is varied,

$$f = C_1 T^{-1/2} \quad (3)$$

where  $C_1$  is a constant of proportionality. The behaviour of a real gas, however, involves complicated temperature-dependent intermolecular forces and is expected to deviate from eqn. 3. Experiments with two different gas chromatographs where nitrogen was the carrier gas showed that, to an excellent approximation, the dependence of nitrogen flow-rate on temperature agrees with the equation

$$f = C_R [T^{-1/2} - (784)^{-1/2}] \quad (4)$$

where  $C_R$  is a constant of proportionality. Since  $R$  is proportional to the probability that a compound passing through the PID is ionized, it should also follow that  $R$  is proportional to the time the compound spends in the PID or, simply, that  $R$  is inversely proportional to  $f$ , provided nothing else is varied. Fig. 3 shows that this is in fact the case. Knowledge of the inverse proportionality of  $R$  and  $f$  and eqn. 4

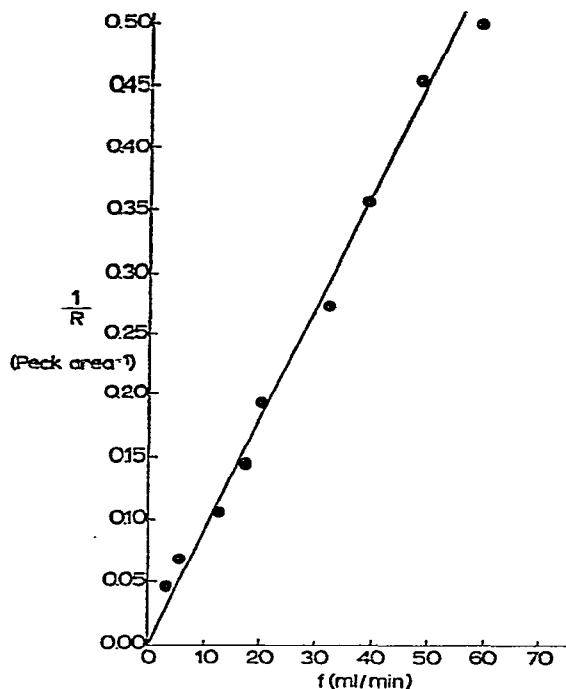


Fig. 3. Plot of  $1/R$  against  $f$ . Data taken from ref. 4.

allows relative responses at "identical" PID conditions to be calculated even when compounds are eluted at greatly different temperatures, if all other conditions are held constant. Fig. 4 is a graph of experimentally determined  $R$  values plotted against IPs relative to a defined value of  $R = 10.0$  for mesitylene, with all the  $R$  values calculated as if constant PID conditions prevailed throughout the experiment. The graph also includes previously published 10.2-eV HNU Systems PID response data<sup>3</sup> which are plotted relative to the present study's experimentally determined  $R$  for benzene. The flow-rate correction to  $R$  for isoprene is exact since the flow-rates were carefully measured during the determination.

Although some of the procedures used to determine  $R$  were expected to be more accurate than others, the spread of  $R$  values for toluene indicates that the experimental points are good to about  $\pm 18\%$  or better. The agreement of data from multiple procedures helps to confirm that the trends in the observed data are real and not just products of a particular experimental procedure.

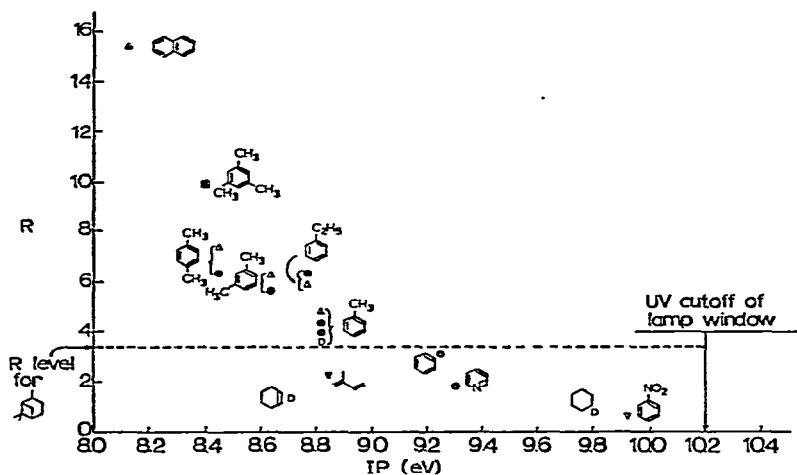


Fig. 4. Plot of  $R$  against IP, for data from procedures a (●), b (⊗), c (▽), d (△ and  $\alpha$ -pinene) and for some previously published data<sup>3</sup> (D) normalized to the present study's  $R$  value for benzene.

## DISCUSSION

The applicability of eqn. 1 to a 10.2-eV PID may be investigated by plotting  $R/n$  against IP. Since, from eqn. 1,  $R/n = kF(\text{IP})$ , such a plot should behave like the "photon-counting function"  $F(\text{IP})$  and decrease monotonically to zero as IP increases to 10.2 eV (the UV cut-off of the lamp window). In addition, compounds with quite different numbers of ionizable electrons ( $n$ ) but similar IPs, and which gave quite distinct points on a graph of  $R$  against IP, should give points located quite close together on a graph of  $R/n$  against IP.

In applying eqn. 1 to a 10.2-eV PID, it is convenient to take  $n$  as the number of carbon-carbon  $\pi$ -bonding electrons per molecule (as previously discussed). If  $6R/n$ , instead of  $R/n$ , is plotted against IP, nothing of theoretical importance is lost and  $R = 6R/n$  for six-electron aromatic compounds may be simply read off from Fig. 4. This allows Fig. 4 to be easily compared with Fig. 5, which is a plot of  $6R/n$  against IP.

In spite of the assumptions made in deriving eqn. 1, Fig. 5 verifies the main points of the theory. The graph does decrease monotonically to zero as IP increases to 10.2 eV, at least within experimental error. Moreover, the points of the compounds for which  $n$  is not equal to 6 (isoprene, cyclohexene and naphthalene), that deviated from the data for the six-electron aromatic compounds in Fig. 4, exhibit no significant deviations in Fig. 5. The essence of eqn. 1 is confirmed.

Two comments should now be made about the assumptions underlying eqn. 1. These assumptions are only approximately valid. Hückel molecular orbital calculations for benzene<sup>7</sup> show that benzene's three  $\pi$ -electron orbitals are not degenerate as assumed. Interestingly, as Fig. 5 shows, this does not cause serious deviations (by benzene-like systems) from the simple graph predicted by eqn. 1.

The other assumption, that only  $\pi$ -electrons are ionized, has some significant exceptions. In particular, Fig. 4 shows that  $\alpha$ -pinene, a compound with no  $\pi$ -electrons,

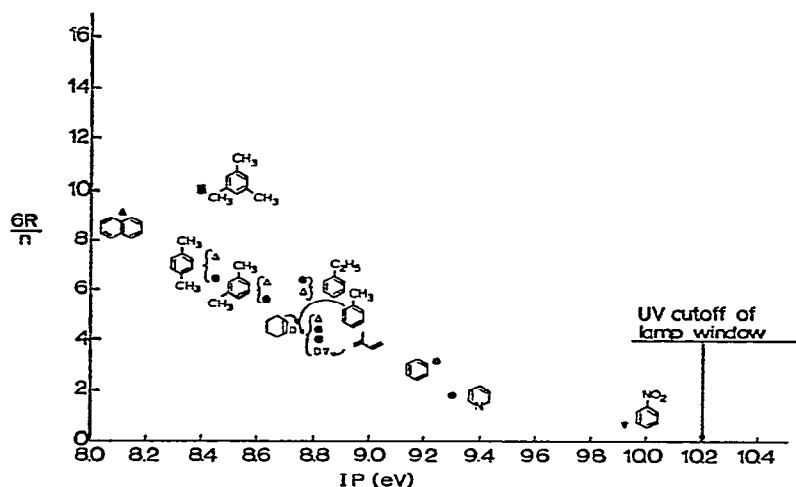


Fig. 5. Plot of  $6R/n$  against IP for data as in Fig. 4.

gives a 10.2-eV PID response as large as that of benzene. It would appear that very ionizable electrons exist in some strained paraffinic systems. It is important to note that eqn. 1 cannot therefore be applied well to strained compounds since a response over and above that due to  $\pi$ -electrons cannot be ruled out. However, many compounds are not appreciably strained, so the general applicability of eqn. 1 is only slightly diminished.

Thus, it appears that eqn. 1 may be used to give insight into a rather interesting hydrocarbon classification scheme proposed by Driscoll *et al.*<sup>3</sup> In their work, advantage was taken of the similarity between the response of the HNU Systems 10.2-eV PID and that of a FID to hydrocarbons. (These two detectors have even been used in series<sup>8</sup>.) The principle number studied was the response ratio (PID/FID) of the PID to the FID at constant flow-rate and lamp intensity. After mostly empirical arguments, it was concluded that, if PID/FID for *n*-octane were assigned the reference value of 1.0, then aromatic hydrocarbons gave PID/FIDs of between 5 and 10, alkenes gave PID/FIDs between 2 and 4 and aliphatic hydrocarbons gave PID/FIDs less than 2.

The general validity of this grouping of PID/FID values may be questionable, but turns out to be consistent with our general understanding of PID response. Combining a knowledge of PID response given by eqn. 1 and the well known proportionality of FID molar response to the number of carbon atoms in a hydrocarbon molecule (*N*) (ref. 9) gives

$$\text{PID/FID} = LnF(\text{IP})/N \quad (5)$$

where *L* is a constant of proportionality and is chosen so that PID/FID = 1.0 for *n*-octane. As a best estimate, *F*(IP) is taken as proportional to the difference between IP and the energy cut-off of the lamp window. Then, PID/FID is roughly proportional to the quotient

$$Q = 10n(10.2 \text{ eV} - \text{IP})/N \quad (6)$$



TABLE II

*Q* VALUES FOR SOME CLASSES OF HYDROCARBON, CALCULATED USING IP VALUES FROM REFERENCE 5

<i>Class</i>	<i>Compound</i>	<i>IP (eV)</i>	<i>Q</i>
<i>Alkyl-substituted naphthalenes</i>			
	Naphthalene	8.12	26.0
	1-Methylnaphthalene	7.96	24.9
	2-Methylnaphthalene	7.955	24.9
<i>Alkyl-substituted benzenes</i>			
	Benzene	9.245	9.6
	Toluene	8.82	11.8
	Ethylbenzene	8.76	10.8
	<i>n</i> -Propylbenzene	8.72	9.6
	Isopropylbenzene	8.69	10.1
	<i>n</i> -Butylbenzene	8.69	9.1
	<i>sec.</i> -Butylbenzene	8.68	9.1
	<i>tert.</i> -Butylbenzene	8.68	9.1
	<i>o</i> -Xylene	8.56	12.3
	<i>m</i> -Xylene	8.56	12.3
	<i>p</i> -Xylene	8.445	13.2
	Mesitylene	8.40	12.0
	Durene	8.025	13.1
<i>Monoynes</i>			
	Acetylene	11.41	0
	Propyne	10.36	0
	1-Butyne	10.18	0.3
<i>Conjugated dienes</i>			
	1,3-Butadiene	9.07	11.3
	Isoprene	8.845	10.8
<i>Monoenes</i>			
	Propylene	9.73	3.1
	Ethylene	10.515	0
	1-Butene	9.58	3.1
	2-Methylpropene	9.23	4.8
	<i>trans</i> -2-Butene	9.13	5.4
	<i>cis</i> -2-Butene	9.13	5.4
	1-Pentene	9.50	2.8
	2-Methyl-1-butene	9.12	4.3
	3-Methyl-1-butene	9.51	2.8
	3-Methyl-2-butene	8.67	6.1
	1-Hexene	9.46	2.5
	Cyclopentene	9.01	4.8
	Cyclohexene	8.945	4.2
	4-Methylcyclohexene	8.91	3.7
<i>Paraffins</i>			
	Methane	12.98	0
	Ethane	11.65	0
	Propane	11.07	0
	<i>n</i> -Butane	10.63	0
	Isobutane	10.57	0
	<i>n</i> -Pentane	10.35	0
	Isopentane	10.32	0
	2,2-Dimethylpropane	10.35	0
	<i>n</i> -Hexane	10.18	0
	2-Methylpentane	10.12	0
	3-Methylpentane	10.08	0
	2,2-Dimethylbutane	10.06	0
	2,3-Dimethylbutane	10.02	0
	<i>n</i> -Heptane	10.08	0
	2,2,4-Trimethylpentane	9.86	0
	Cyclopropane	10.06	0
	Cyclohexane	9.88	0
	Methylcyclohexane	9.85	0

where  $Q$  is defined as zero if IP is greater than 10.2 eV. Table II lists values of  $Q$  for several classes of compounds based on IPs given in ref. 5. It appears that for alkyl-substituted benzenes,  $Q$  is between 9.1 and 13.2. For hydrocarbons with just one double bond, other than ethylene,  $Q$  is between 2.5 and 6.1. Of course, the definition of  $n$  makes  $Q$  equal to zero for both paraffins and ethylene. Thus, a hydrocarbon classification system based on distinct PID/FID values for hydrocarbon classes seems plausible.

The classification system of Driscoll *et al.*<sup>3</sup> is, however, naive. Eqn. 6 forms a basis to look for exceptions to Driscoll *et al.*'s system. PID/FID values may even be calculated for some of these exceptions using the reported<sup>3</sup> value of PID/FID = 8.4 for benzene and the experimental data in the present paper. By increasing the number of double bonds in a compound, an alkene may be made to have a PID/FID value similar to that of an aromatic hydrocarbon (PID/FID = 7.6 for isoprene). Some paraffins give larger than zero PID responses and may be made to behave like an alkene or even an aromatic hydrocarbon (PID/FID = 5.0 for  $\alpha$ -pinene). It is even conceivable that if benzene's IP is sufficiently increased by electron-withdrawing substituents, it may even act like a paraffin (PID/FID = 2 for nitrobenzene if benzene and nitrobenzene are assumed to give the same FID response). This does not mean that PID/FID cannot be helpful in compound classification, but only that the classification system needs to be more sophisticated.

A useful PID/FID classification system could be developed in many ways. Since  $n$  and  $N$  are often roughly proportional to one another in many compounds of GC interest, inspection of eqn. 6 indicates that PID/FID is a rough measurement of average electron ionizability in a compound. It would appear that electrons in carbon-carbon  $\pi$ -bonds are very ionizable and PID/FID values for  $\pi$ -bonded hydrocarbons are thus large. The data for  $\alpha$ -pinene suggest that there are also other types of very ionizable electrons. The real problem is to discover how PID/FID allows a distinction to be made between compounds in a sample of interest. Thus the usefulness of any classification system depends on the nature of the sample to be analyzed. Eqn. 6 is probably a good place to start looking when a classification system is needed for a given sample.

Alternatively, the direct link between PID/FID and a compound's "ionizability" may be of future use. Reaction of hydroxy radicals with hydrocarbons is of interest in ozone formation<sup>10,11</sup>. The ease by which a compound can lose an electron to a hydroxy radical and the ease by which a compound may be ionized are probably similar. Pitts and co-workers<sup>10,11</sup> have collected rate-constant data for the reactions of compounds with hydroxy radicals and have classed compounds by their reactivity. The evidence is hardly definitive, but one can't help but notice that the correlation between reactivity with hydroxy radicals and  $R$  or PID/FID is excellent, even for the paraffin  $\alpha$ -pinene. Thus, PID/FID may someday prove useful for determining in a semiquantitative way the meteorological importance of hydrocarbons in ozone formation.

## CONCLUSION

The assumptions (1) that a 10.2-eV PID only ionizes carbon-carbon  $\pi$ -bonding electrons and (2) that these electrons do not have appreciable orbital splittings allow

the formulation of a semiquantitative model of 10.2-eV PID response for hydrocarbons (eqn. 1). In another form (eqn. 6), this model predicts that the ratio of the 10.2-eV PID response to that of an FID under the same conditions should allow a distinction to be made between some classes of compounds, and also helps to identify some problems with a previously proposed classification scheme based on just such a ratio<sup>3</sup>. Interpretation of eqn. 6 suggested a more natural classification scheme based on a classification method of meteorological interest.

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