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Electron Affinities and Ionization Potentials of Aromatic Hydrocarbons

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Molecular electronegativities have been established and these appear to be constant. With this assumption some electron affinities and ionization potentials are predicted. The predicted ionization potentials agree well with values estimated from charge transfer spectra. Estimations of electron affinity values are made for a large number of aromatic hydrocarbons based on graphical data utilizing experimental electron affinities and absorption frequency data. Estimations of heats of solution have been made and these appear to be a complex function of several parameters. The data have been extrapolated to $h\nu = 0$, which gives a value of the electron affinity for graphite considerably below the work function of the crystal. The extrapolation of the curve based on experimental ionization potentials to $h\nu = 0$ yields an intercept above the work function of graphite. These are interpreted in terms of the difference in graphite solid and vapor. The unequal splittings of electron affinities and ionization potentials around the work function for solid graphite are interpreted. The question of whether the ionization potential and electron affinity are equal for both solid and vapor graphite is considered.

Introduction

There has always been considerable interest in the electron affinities and ionization potentials of atoms and molecules. Considerable data exist on ionization potentials of molecules obtained from both experimental and theoretical sources.¹⁻⁸ Despite this, there is a considerable scatter in the experimental values depending upon the method employed. There is less scatter among the theoretically calculated values although some notable discrepancies exist. The agreement between experimental and theoretical results in general is reasonably good, but again some exceptions are to be found.

The information available on molecular electron affinities is decidedly more scarce and inconsistent. Until recently, there existed no experimental values for large molecules. However, Wentworth and Becker have very recently interpreted some electron capture phenomena in terms of electron affinities.⁹ Values are given for seven aromatic hydrocarbons. Earlier work principally by Matsen¹⁰ and co-workers utilized half-wave reduction potential data to establish trends of the electron affinities of aromatic hydrocarbons. The lack of information on solvation energies precluded actual evaluation of the electron affinities. There have been several theoretical attempts made with varying degrees of sophistication.^{8,11-13} Using the ω -technique with $\omega = 3.8$, Ehrenson⁸ was limited in correlating his values with the existing values of others. The calculated electron affinities of several hydrocarbons by Hoyland and Goodman¹³ agree quite well with the experimental values of Wentworth and Becker. Very recently, Scott and Becker,¹⁴ employing the closed form equation from the ω -technique suggested by Ehrenson, calculated a large number of electron affinities for hydrocarbons. One value of ω (3.8) gave generally good results for those compounds for which experimental and theoretical data

existed. For two or three compounds, $\omega = 3.73$ improved the correlation with experiment.

This investigation has several purposes: (1) establishment of molecular electronegativities, (2) to provide a more meaningful evaluation of the electron affinities of a large number of aromatic hydrocarbons, (3) evaluate and interpret the meaning of extrapolation of the ionization potential and the electron affinity data to $h\nu = 0$, (4) discuss the comparative energy difference in the solvation of negative ions and molecules, and (5) comparison of data based on pure theory and experiment.

Results and Discussion

Molecular Electronegativities.—Of first importance is the possibility of establishing molecular electronegativities based on the Mulliken definition. For certain aromatic hydrocarbons, both electron affinity (*EA*) and ionization potential (*IP*) data are available. The former of these is based on the experimental values determined by Wentworth and Becker⁹ while the latter are experimental values obtained from the sources noted in Table I. There are four hydrocarbons for which both data are available and the values of the electronegativity are given in Table I. It is indeed salient to point out how constant the electronegativity is for these cases, 4.07 ± 0.05 (maximum deviation). Hush and Pople¹² suggested from their theoretical approach that the sum of the *EA* and *IP* should be a constant for alternate hydrocarbons. In addition, Hedges and Matsen^{10,11} noted that both the Hückel and ASMOH theories suggested that the *IP* and *EA* as a function of energy of the lowest transition should be symmetrical about the work function for graphite. The data reported herein provide a striking confirmation in particular of the proposal of Hush and Pople.¹²

In view of this observed constancy in molecular electronegativity for the hydrocarbons, it should be possible to use the mean value to calculate *EA* or *IP* when one or the other is known. This has been done and is shown in Table I. The value of -1.1 e.v. for the *EA* of benzene from Table I is near several of the theoretically calculated values. In the case of naphthalene, the *EA* values of -0.12 , $+0.02$ exist depending upon the source of the *IP* data. The *EA* prediction for naphthalene is also given. In three cases, triphenylene, chrysene and benz(a)anthracene, there exist *EA* data but no *IP* data. The predictions for these are given in Table I. Estimates of the *IP* for these same three compounds have been made by Briegleb and Czekalla¹⁵ based on charge transfer spectra. Table I shows there is excellent agreement between the predictions based on this investigation and that of Briegleb and Czekalla.

(1) F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

(2) M. E. Wacks and V. H. Dibeler, *ibid.*, **31**, 1557 (1959).

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(4) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

(5) A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron*, **5**, 149 (1959); *J. Am. Chem. Soc.*, **82**, 4123 (1960).

(6) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(7) J. R. Hoyland and L. Goodman, *J. Chem. Phys.*, **36**, 12 (1962).

(8) S. Ehrenson, *J. Phys. Chem.*, **66**, 706 (1962).

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(10) F. A. Matsen, "Proceedings of 1957 Conference on Carbon," Pergamon Press, New York, N. Y., 1957, p. 21, and references therein.

(11) R. M. Hedges and F. A. Matsen, *J. Chem. Phys.*, **28**, 950 (1958).

(12) N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

(13) J. R. Hoyland and L. Goodman, *J. Chem. Phys.*, **36**, 21 (1962).

(14) D. R. Scott and R. S. Becker, *J. Phys. Chem.*, **66**, 2713 (1962).

(15) G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **63**, 6 (1959).

TABLE I

ELECTRONEGATIVITIES OF HYDROCARBONS^a

Compd.	IP, ^{a,b} e.v.	IP, ^c e.v.	-EA, ^b e.v.	x
Benzene	9.24 PI	(-1.1)	(4.07)	
Naphthalene	8.26 W	(-0.12)	(4.07)	
	8.12 PI	(.02)		
Anthracene	7.55 W		.42	3.99
	7.66 S			4.04
Phenanthrene	8.03 W		.20	4.12
	8.06 S			4.13
Triphenylene	(8.00)	8.0	.14	(4.07)
Benzo(c)phenanthrene	7.84 S		.33	4.09
Chrysene	(7.80)	7.8	.33	(4.07)
Benz(a)anthracene	(7.68)	7.6	.46	(4.07)
Pyrene	7.72 W		.39	4.06
Naphthacene	7.15 S		(.98)	(4.07)

^a PI \equiv photoionization: benzene and naphthalene from H. Watanabe, *J. Chem. Phys.*, **22**, 1565 (1954); **26**, 542 (1957). W \equiv from M. E. Wacks and V. H. Dibeler, *ibid.*, **31**, 1557 (1959). S \equiv Stevenson values less 0.56 e.v., private communication to Matsen.¹⁰ ^b Values in parentheses calculated on basis of mean value of 4.07 for molecular electronegativity. ^c Experimental estimates of ionization potentials from charge transfer spectra.¹⁵

Electron Affinities.—Figures 1 and 2 contain curves utilizing the 0-0 frequency of the lowest energy transition¹⁶ and electron affinity and ionization potential data. Of first importance is the plot of electron affinity data based on the work of Wentworth and Becker.⁹ Both the curves based on solution and vapor frequencies have nearly the same slope, approximately -0.76 , and intercepts at zero frequency of approximately 2.9. Only the solution frequencies are shown in Fig. 1 and 2 since this information was available for more compounds. Figure 1 has an expanded scale in order to show better the fit of the data to a straight line. Figure 2 contains the same information, but is intended to show better the slopes and the intercepts of the two sets of data with respect to the work function of graphite. Matsen,^{10,17} using apparent electron affinity data obtained from half-wave reduction potential data, found a slope of -0.54 and an intercept of 4.8. The intercept was interpreted in terms of the work function of graphite, since in the limit of Hückel theory the difference in energy between the highest filled and lowest unfilled orbitals goes to zero for graphite. In addition, within the limits of Hückel theory for alternate hydrocarbons, both the highest electron affinity and lowest ionization potential energies are proportional to $h\nu$ where $h\nu$ is the difference in energy between the lowest unfilled and highest filled orbitals. The proportionality constant = ± 0.5 since the orbitals referred to above are symmetrically arranged about a mid-point α (equal to 4.39, the work function for graphite¹⁸). Matsen noted the fact that in view of the close similarity of the actual and Hückel predicted slopes, the Hückel error was probably being cancelled by solvation energy.

The first area of discussion shall concern the regions of Fig. 1 and 2 in which actual data exist. The approach of Hush and Pople¹² notes that $EA = IP$ is equal to a constant and moreover that for graphite sheet $EA = IP$. Since graphite sheet presumably refers to an infinite two-dimensional molecule, this would correspond to graphite vapor. Moreover, since their calculated values were compared to the work function, this would refer to the solid. Thus, it must be inferred that $EA = IP$ for graphite vapor and solid. Hückel theory predicts $IP = EA$ for graphite. Presumably this would refer to the molecule and thus the vapor state. How-

(16) R. S. Becker, I. Sen Singh, and E. A. Jackson, *J. Chem. Phys.*, May, 1963.

(17) F. A. Matsen, *ibid.*, **24**, 602 (1956).

(18) A. Braun and G. Busch, *Helv. Phys. Acta*, **20**, 33 (1947).

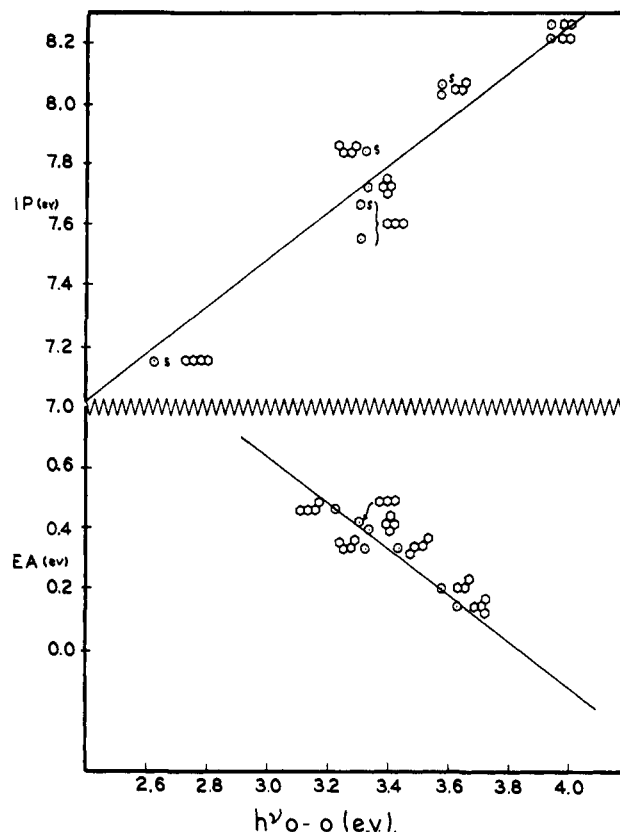


Fig. 1.—Graph of experimental IP and EA vs. $h\nu_{0-0}$ of the lowest energy electronic transition.

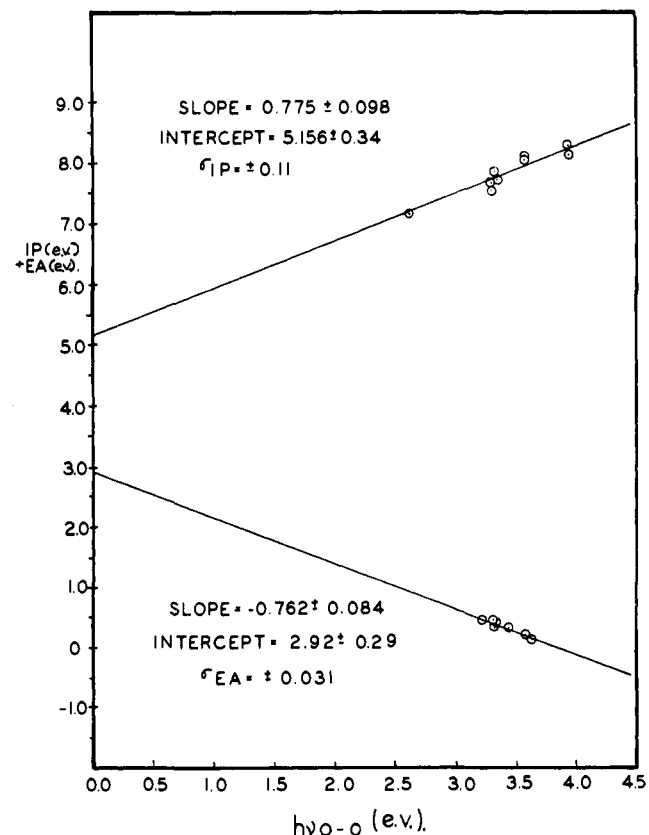


Fig. 2.—Graph of experimental IP and EA vs. $h\nu_{0-0}$ showing extrapolation to $h\nu_{0-0} = 0$. Values quoted are the least squares estimates of the slope and intercept for the IP (upper) and EA (lower) curves.

ever, Matsen¹⁰ used Hückel theory to infer a symmetrical arrangement of IP and EA curves about a mid-point

whose value is 4.39, the work function for graphite solid.¹⁹ Also, it was assumed that $IP = EA$ for graphite solid. However, if the work function for graphite is 4.39 e.v. in solid and vapor, then the present investigation shows an unsymmetrical splitting of the EA and IP curves (see Fig. 1 and 2) in contradiction to the predictions. This can be accounted for in several ways, of which the following are most likely: (1) the work function for graphite in the vapor state is not 4.39 e.v., but approximately 4.07 e.v. as determined from the electronegativity as previously discussed and the mean value from Fig. 2; (2) the additional electron repulsion term in the radical (negative ion) compared to that in the radical resulting from ionization would actually lower the EA relative to what would be expected, giving the disproportionate splitting about 4.39. More will be said concerning this following the next consideration.

Pertinent to the above discussion, but of partial independent consideration, is the problem of the slope and the extrapolation of the data. It is noteworthy that over the range considered the curves of EA and IP have nearly the same slope and are remarkably linear, especially the EA curve. Also, in an attempt to compare our results with those of Matsen, we have extrapolated to $h\nu = 0$. It is noteworthy that there is considerable discrepancy between this work and that of Matsen¹⁷ regarding the EA data. Despite the fact that our plots contain fewer data points, it is not conceivable that additional data would give an intercept as large as 4.8. Moreover, our slope is greater (-0.76 vs. -0.54) and a decrease in our slope would further increase the discrepancy in the intercept values. The disagreement in slope with that predicted by Hückel theory simply implies that Hückel theory is not capable of predicting the proper value because of inherent limitations. If it is assumed that the molecule at $h\nu = 0$ is graphite, then the intercept values for the IP (5.16 ± 0.34) and EA (2.92 ± 0.29) curves infer that the EA and IP for graphite are different. The justification for the linear relationship is based on Hückel theory and on assumed linear character of the Q -term in the equations of Hush and Pople with ν . The true significance of this result has several implications: (1) it may not in fact be proper to assume a linear extrapolation to $h\nu = 0$, (2) the extrapolation actually refers to graphite vapor (an infinite two dimensional molecule). It has not been demonstrated in fact whether $IP = EA$ for solid graphite. Assuming a linear extrapolation and that $IP = EA = 4.39$ for graphite solid, then our intercept would best be interpreted as the electron affinity of graphite vapor. Thus the EA value is some 1.47 e.v. below that of graphite (solid). If, in fact, the linear extrapolation is valid, the predictions of Hückel theory, Matsen,^{10,19} and Hush and Pople¹² that $IP = EA$ for graphite vapor (sheets) is incorrect.

Our approach is consistent in concept with the recent proposal of Kearns and Calvin,²⁰ who presume that the vapor state electron affinity of several aromatic hydrocarbons is considerably below the work function of the crystal. This supposition was based on ionization potential data for large molecules in the solid state which were on the average 1.28 e.v. lower than the ionization potentials of the gaseous state. The difference in IP of these two states was attributed to the increased stabilization of the positive ion through polarization forces in the crystal. By the same token the vapor state electron affinity would be lower than in the crystal state as a result of a corresponding stabilization of the nega-

tive ion in the crystal. If the stabilization of the negative ion equals that of the positive ion, then it would be expected that the extrapolation to $h\nu = 0$ would be approximately 1.28 e.v. lower than the electron affinity of graphite in the solid state.

Despite the previous consideration, there still remains a disproportionate splitting around the work function for the solid (4.39). This can be accounted for on the basis of a difference in the repulsion terms in the respective molecular ions. The only other escape from this dilemma is to consider the work function for graphite solid is approximately 4.07 which would then result in a symmetrical splitting of the IP and EA curves at graphite and in the region of the experimental data. Finally, it is possible that the linear extrapolation to $h\nu = 0$ is not valid. If this is true, then it is possible that $IP = EA$ for solid and vapor graphite. The most likely values would appear to be 4.39 or 4.07 depending upon whether a symmetrical splitting need exist in fact.

Matsen^{10,17} found the slope for the ionization potential curve to be greater than that of the electron affinity curve. Since the ionization potential data were free of solvent interaction problems, this curve was reflected about $4.8 = \alpha$ and the difference between the reflected curve and the apparent electron affinity curve was taken as the difference in the heat of solution of the neutral molecules and negative ions.²¹ It was noted that this was related to $h\nu$ simply by $\Delta E = 0.357h\nu$. Table II gives the values of ΔE of solution for some hydrocarbon ions in ethylene glycol monomethyl ether as solvent based on experimental EA data⁹ and on EA data estimated from the extrapolation in Fig. 1 using frequency data given by Matsen.¹⁷ It is assumed that a linear extrapolation is valid to at least a value slightly below $h\nu = 2$ e.v. The half-wave reduction potentials in ethylene glycol monomethyl ether were measured by Bergman.²² The frequency data of Matsen are based on the maxima of the lowest energy transitions and not the 0-0 frequencies as is ours. Since the lowest energy and true electronic energy is deduced from the 0-0 frequency data, this would be preferred. Although not all the molecules considered by Matsen are included, a broad selection is given. It is interesting to note that a maximum variation of 0.5 e.v. exists for ΔE no matter what data are chosen. This is true despite a wide variation in EA , frequency of absorption, number of condensed benzene rings and shape of the molecules. Also, there is considerable inconsistency in ΔE as a function of the number of condensed benzene rings and size in contradiction to what was expected by Matsen.^{10,17}

Table III compares some EA values of some hydrocarbons obtained in a variety of investigations. The data of Hoyland and Goodman if plotted in Fig. 1 would result in a slope of approximately -1.2 and an intercept of 5 e.v. If the EA value calculated for benzene were included, the value of the slope would increase to -1.5 and the intercept to 5.6 e.v. These are considerably greater than those found in the present investigation. The data from this work are based both on extrapolation and an average value of the electronegativity. The value for benzene is based on calculation from the electronegativity because of questionable linear extrapolation to this extreme end point. The value for naphthalene is the same from extrapolation and the average value obtained from the electronegativity approach.

(21) It appears as if the reflection of the IP curve is incorrect in Matsen's graph.¹⁰ The true reflection lies between the A' and A curves. Also, in Table I, columns 3 and 6 should be anthracene and benzo(c)phenanthrene, respectively.

(22) S. Bergman, *Trans. Faraday Soc.*, **50**, 829 (1954).

(19) Matsen has recently reinterpreted his extrapolation as molecular graphite (vapor); private communication to Ralph S. Becker, 1963.

(20) D. R. Kearns and M. Calvin, *J. Chem. Phys.*, **34**, 2026 (1961).

In the case of naphthacene, two values EA for naphthacene exist, 0.91 and 0.98. In view of the singular IP value, we tend to favor the lower value obtained from extrapolation, 0.91 e.v. Finally, we favor the experimental EA values of Wentworth and Becker⁹ over those obtained by Matsen. As has been previously mentioned, data to be obtained from extrapolation would best involve the 0-0 frequency of the lowest transition rather than the maximum. Ideally of course the vapor data should be used (not shown in Fig. 1). However, as previously mentioned, the difference in slope between the two curves is almost insignificant although there is a slight difference in intercept value. The values obtained from 0-0 data would generally not agree with those obtained from maxima since these usually do not coincide (naphthacene is an exception, for example). Also, some of the maxima used¹⁷ may not correspond to the first transition but, instead, the second. The differences in values can be seen by comparing columns 3 and 6 of Table II. Nevertheless, the use of such data gives an approximation and such is shown for a number of examples in Table II. It is anticipated that better spectroscopic data will be available in the near future to improve the estimates.

It is interesting that the suggestion of $\epsilon = 3.8$ by Ehrenson⁸ does provide an improvement in the calculated values compared to the experimental ones for the few cases given. Use of $\omega = 3.8$ by Scott and Becker¹⁴ generally gives good agreement with experiment. Another value, $\omega = 3.73$, provided further improvement in two or three cases. The values of Hoyland and Goodman⁷ are in generally good agreement with experiment and values calculated assuming χ constant. The limited data of Pople⁶ give the wrong sign for phenanthrene and the data of Hedges and Matsen¹¹ give the wrong sign in three cases and varying agreement in magnitude elsewhere.

Ionization Potentials.—The present authors have made no experimental determination of IP 's. Figures 1 and 2 show plots of existing experimental ionization potential data vs. the lowest energy 0-0 frequency from the absorption spectra. As can be seen, the slope of the experimental data is quite close to that obtained from the electron affinity data. This extremely good agreement is somewhat fortuitous if one considers the errors in the slopes which are quoted in Fig. 2. The standard deviations are on the order of magnitude of ± 0.1 . The IP intercept is at 5.16 e.v., considerably above the work function of graphite. The experimental

TABLE II continued






























Compd.	Matsen EA'	ν (Matsen)	EA_2 from Matsen frequencies ^c	ΔE_{s01} ^d
	3.38	2.74	0.83	2.55
	3.71	2.15	1.28	2.43
	3.62	2.25	1.19	2.43
	3.03	3.55	0.22	2.81
	3.36	2.81	0.78	2.58
	3.64	2.30	1.17	2.47
	3.02	3.53	0.23	2.79
	3.32	2.83	0.72	2.60
	3.72	2.37	1.11	2.61
	3.00	3.53	0.23	2.77
	2.92	3.71	.09	2.83
	3.00	3.59	.18	2.82
	3.32	2.85	.75	2.57
	3.04	3.45	.29	2.75
	3.08	3.20	.48	2.60
	2.93	3.63	.15	2.78
	3.29	2.86	.74	2.55
	3.87	1.97	1.42	2.45
	2.90	3.74	0.07	2.83
	2.90	3.77	.05	2.85
	3.06	3.59	.11	2.95
	3.38	2.86	.77	2.61
	3.69	2.27	1.19	2.50
	3.08	3.20	0.48	2.60
	3.89	1.93	1.45	2.44
	3.79	2.15	1.28	2.51
	3.42	2.74	0.83	2.59
	3.23	3.24	0.45	2.78
	3.77	2.10	1.32	2.45

TABLE II
ESTIMATION OF ΔE_{s01} AND EA OF NEUTRAL MOLECULES AND IONS

Compd.	Matsen EA'	Exptl. $-EA_1$	ΔE_{s01} ^b	ν (Matsen)	EA_2 from Matsen ¹⁷ frequencies ^c	ΔE_{s01} ^d
Benzene	2.19	(-1.1) ^a (-0.57)	3.29 2.76
Naphthalene	2.59	(- .05) ^a (- .05)	2.64 2.64	4.35	-0.40	2.99
Anthracene	3.11	.42	2.69	3.31	.50	2.61
Phenanthrene	2.63	.20	2.43	4.24	-.31	2.94
Benz(a)-anthracene	3.04	.46	2.58	3.45	.29	2.75
Benzo(c)phenanthrene	2.82	.33	2.49	3.93	-.07	2.89
Chrysene	2.76	.33	2.43	3.88	-.04	2.80
Triphenylene	2.60	.14	2.46	4.36	-.41	3.01
Pyrene	2.96	.39	2.57	3.72	.09	2.87
Naphthacene	3.43	(.98) ^a (.91)	2.45 2.52	2.63	.92	2.51

^a First values (in parentheses) are estimated from the assumed constancy of the electronegativity and the second value was estimated from the linear extrapolation in Fig. 1 and 0-0 frequency data. ^b $\Delta E_{s01} = EA' - EA_1$. ^c Estimated from the linear extrapolation in Fig. 1 and Matsen's frequencies. ^d $\Delta E_{s01} = EA' - EA_2$.

value for benzene was not included in this graph. If the data of Hoyland and Goodman were plotted,¹⁷ a substantially greater slope would exist (~ 1.4) and a significantly lower value for the intercept (~ 2.3 e.v.) would be obtained. Moreover, their slope is also greater than that resulting from their EA data.

As mentioned previously, Matsen¹⁰ assumed the EA curve should be a reflection of the IP curve. This is

TABLE III
 COMPARATIVE ELECTRON AFFINITY VALUES OF SOME HYDROCARBONS

Compd.	Wentworth and Becker* and this study	Scott and Becker ^{14b}	Hoyland and Goodman ⁷	Ehrenson ^{8c}	Pople ⁹	Hedges and Matsen ¹¹
Benzene	-1.10 ^a	-1.59	-1.40	-1.62	-1.40	-1.63
Naphthalene	-0.05 ^a	-.25	-0.21	-0.25	-0.14	-0.38
Anthracene	.42	.42	.61	.43	.64	.49
Phenanthrene	.20	.17	.25	.0	-.06	-.20
Benz(a)anthracene	.46	.4662
Chrysene	.33	.3104
Benzo(c)phenanthrene	.33	.37	-.14
Triphenylene	.14	.12	-.28
Naphthacene	.91 ^a	.7982
Pyrene	.39	.42	0.5568

^a This study, assumed best estimate. ^b Using $\omega = 3.73$ for phenanthrene, benzo(c)phenanthrene, triphenylene and $\omega = 3.8$ for the remainder. ^c Using $\omega = 3.8$ since $\omega = 1.4$ as used in ionization potential data gave absurdly high values.

approximately borne out in this work except that the reflection would be about 4.04 e.v. rather than the experimentally determined work function of graphite, 4.39 e.v. If the line of reflection is considered to be $\alpha =$ work function of graphite, this suggests the possibility that the experimental work function may be slightly high. Also, of course, the existence of a disproportionate splitting about 4.39 is possible as previously discussed. Further, if the data actually refer to vapor, then the reflection line would represent the work function for the vapor, 4.07, as noted earlier. There are no estimates of error quoted for the work function so it is difficult to establish what reliability should be put on this value. Earlier experimental values of the work function for graphite were lower than 4.39 e.v.^{23,24} On the other hand, the true IP intercept at $h\nu = 0$ could conceivably pass through the work function of graphite (4.39).

Conclusions

The interpretation in part is complicated by consideration of the state of graphite; that is, whether molecular graphite (vapor) or solid graphite is involved. Also, the problem of linear extrapolation to $h\nu = 0$ and the assumption of $IP = EA$ for solid graphite pose additional major obstacles.

Certain definite conclusions can be made: (1) The most significant is the fact that the electronegativities of the hydrocarbons studied appear to be constant. This is equivalent to the prediction of Hush and Pople that $IP = EA$ for such molecules. This result allows for prediction of one or the other of the parameters. (2) The slopes of the EA and IP curves as a function of the energy of the lowest transition are nearly the same. Moreover, the EA curve in particular is remarkably linear over the range investigated. From these curves, a modest extrapolation permits the evaluation of EA for a large number of hydrocarbons. (3) ΔE is not a simple function of the energy of the lowest transition. Moreover, there is only a small variation of ΔE over a

broad range of energies of absorption, number of condensed rings, and geometry of the molecules. (4) Finally, there is variable agreement of our experimental EA values and those predicted by theories and other experiments.

The remaining conclusions are complicated by the problems noted in the above opening paragraph. Nevertheless, these must be considered because of their significance for theoretical consideration and their intrinsic importance. The EA and IP data indicate an unsymmetrical split about the work function for solid graphite (4.39). This indicates that the work function for vapor graphite is not 4.39 but approximately 4.07 or that there is an unsymmetrical splitting about 4.39 caused by the difference in the number of repulsion terms in the two ions. Assuming a linear extrapolation of the EA and IP curves to $h\nu = 0$, a similar conclusion results based on the intercept data. Assuming the extrapolation is valid and that $EA = IP = 4.39$ for solid graphite, the lower EA and higher IP must be interpreted in terms of the difference expected in stabilization energy between solid and vapor graphite. Despite this, a disproportionate splitting remains and only the difference in repulsion terms can account for the result. The actual fact that $IP = EA$ for vapor graphite is not in agreement with several theories that assume $IP = EA$ for solid and vapor graphite. One of the obvious ways out of the dilemma is to assume that approximately $4.07 = IP = EA$ is the correct value for solid graphite. Also, if the extrapolation is not linear to $h\nu = 0$, then it is possible for $IP = EA$ for solid and vapor graphite. The most likely values would appear to be 4.39 or 4.07.

Despite whether the linear extrapolation to $h\nu = 0$ is valid, the problem of the unsymmetrical splitting about $4.39 = \alpha$ is real and not hypothetical. The considerations above offer the only obvious alternative explanations.

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