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## CORRELATION AND PREDICTION OF ELECTRON-CAPTURE RESPONSE FROM MOLECULAR PARAMETERS

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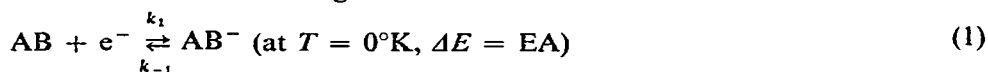
### SUMMARY

The kinetic model of the electron-capture detector (ECD) relates the response to the fundamental properties of the capturing species. In the case of molecules which undergo reversible reactions, the important properties are the electron affinity, the rate constant for thermal electron attachment and the rate constant for ionic recombination. The direct calculation of the response has not been carried out because of the limited number of experimental values. In this paper, the available molecular electron affinities are correlated with the reversible half wave reduction potentials in aprotic solvents for these compounds in order to provide additional electron affinities to calculate ECD response factors. Examples of this procedure are given for data on aromatic hydrocarbons, aldehydes and ketones determined in this laboratory; and data on substituted benzophenones, aromatic hydrocarbons and heterocyclic compounds taken from the literature. Both the magnitude and the temperature dependence are predicted. The success with these compounds suggests that the effect of substituents on half wave reduction potentials can be extended to the prediction of electron affinities and in some cases, the ECD response from the structure of these molecules.

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### INTRODUCTION

The analytical significance of the electron-capture detector (ECD) is based upon its sensitivity and selectivity, so that it is important to be able to estimate the response of a compound from its chemical structure. Early efforts to accomplish this were empirical, but the kinetic model of the ECD<sup>1</sup> relates the response and its temperature dependence to kinetic and thermodynamic properties of the molecule. The exact equations are determined by the type of electron capture reaction. In the case of reversible (non-dissociative) capture, the important parameters are the electron affinity of the molecule (EA), the rate constant for thermal electron attachment,  $k_1$ , and its activation energy ( $E^*$ ), and the rate constant for ionic recombination,  $k'_{N1}$ . These parameters refer to the following reactions





The dissociative reactions



have been considered in the kinetic model but will not be discussed in detail in this article.

Despite the existence of these theoretical relationships, the calculation of the ECD response from the fundamental parameters has not been carried out because of the absence of reliable independent experimental values. Consequently, the ECD results have been used to obtain values of the above properties. Recently, we have found good agreement with about ten values of electron affinities obtained with the ECD and those obtained with other experimental techniques<sup>2</sup>. In addition, there is reasonably good agreement between  $k_1$  values using the ECD and those reported in the literature. This essentially supports both procedures and suggests that ECD responses and temperature dependencies can be calculated from fundamental parameters.

However, a major problem still exists, since other than the values obtained from the ECD, there are only about 40 molecular electron affinities in the literature and most of these are above 1 eV and are thus outside the experimental range of the ECD<sup>1-9</sup>. In addition, no single technique has been applied to the full range of measured values so that the relationship between the electron affinity and molecular structure has not been accurately investigated. However, relative molecular electron affinities can be obtained from either the measurement of the reversible half-wave reduction potentials in aprotic solvents or the determination of the absorption maxima for charge transfer complexes. In addition, relative electron affinities can be obtained from the Hückel coefficients by empirical correlations.

In some cases, the first step in the polarographic reduction of a compound is the reversible formation of the molecular negative ion and the half-wave reduction potential can be related to the electron affinity. Since the reduction is carried out in solution, the effect of the solvent must be taken into account. If the change in solvation energy is constant or is proportional to the electron affinity, then the polarographic half-wave reduction potentials,  $E_{\frac{1}{2}}$ , can be used to estimate relative electron affinities. By correlation with known experimental gas phase electron affinities, absolute values can be obtained from half-wave reduction potentials. Assuming that the change in solvation energy is constant, the relationship for the correlation is simply

$$EA = E_{\frac{1}{2}} + K \quad (4)$$

Where  $E_{\frac{1}{2}}$  is the reversible potential in an aprotic solvent, referenced to the standard calomel electrode (SCE). Szwarc<sup>10</sup> and Chen and Wentworth<sup>9</sup> examined this relationship for aromatic hydrocarbons and charge transfer acceptors, respectively, but fewer than twelve data points were available. At present, both electron affinity<sup>1-9</sup> and half-

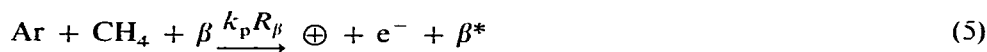
wave reduction potential data<sup>10-16</sup> are available for more than fifty compounds so that the correlation should be examined with the extended data. This has been done and the results will be reported in this article. Briefly, a good correlation is observed so that the electron affinities obtained from  $E_{\frac{1}{2}}$  values can be used to predict ECD responses. The electron affinities obtained from charge transfer complex absorption maxima and Hückel coefficients generally agree with those obtained from  $E_{\frac{1}{2}}$  values so that if reduction potentials are not available, then these other quantities can be used. Furthermore, these results can be used to establish relationships between electron affinities and structure which can then be used to relate ECD response to structure.

To illustrate these points, the results from the kinetic model will first be briefly described, the  $E_{\frac{1}{2}}$  correlation will be presented, and finally, the ECD response for several compounds will be calculated and compared with experimental data from this laboratory and from the literature. In particular, aromatic hydrocarbons, aldehydes, ketones and substituted benzophenones will be considered. Then the electron affinities will be related to the structure of the molecules and estimates for the response for several compounds will be made and compared with experimental results recently reported in the literature.

#### KINETIC MODEL

The ECD is essentially a gas phase reaction vessel in which thermal electrons are a reactant. The number of thermal electrons is measured by the application of a brief pulse after a given reaction time, which removes essentially all of the free electrons and initiates a new cycle. If the rate constants for all of the reactions taking place are known or can be measured and if the build up and removal of the various species can be properly taken into account, then the electron concentration in the presence of capturing species can be calculated and hence the response of the detector. In order to do this, a kinetic model for the ECD has been proposed and supported by experimentation<sup>1,2</sup>.

The pertinent chemical reactions in the model for a molecule which does not dissociate upon electron attachment are given in eqns. 1 and 2. In the absence of a capturing species, the reactions are:



These reactions lead to a set of differential equations which have been solved numerically under certain restrictions, and give the expression<sup>17</sup>

$$\left[ \frac{b - [e^-]}{[e^-]} \right]_{a \rightarrow 0} = \frac{1}{2} \frac{k'_{N1} [\oplus] k_1 a}{k'_D [\oplus_0] (k'_{N1} [\oplus] + k_{-1})} = K'a \quad (7)$$

where  $a$  is the concentration of AB,  $b$  is the electron concentration in the absence of AB and  $[e^-]$  is the electron concentration in the presence of AB;  $[\oplus]$  and  $[\oplus_0]$  are the

corresponding positive ion concentrations. It is assumed that the fraction of capture is less than 10%, a condition usually met under analytical conditions and that the ratio  $e^-/[⊕] = f$ , a constant. The constancy of  $f$  was empirically established in the solution to the set of differential equations for the specific case where a constant fraction of the positive ions are removed at the end of the reaction sequence.

At high temperatures, (designated the alpha region), the equation for  $K'$  becomes

$$K' = \frac{1}{2} \frac{k_{N1}'}{k_D'} \frac{k_1 a}{k_{-1}} \quad (8)$$

or using the statistical mechanical expression for  $K_{\text{eq}}$ ,

$$\ln K' T^{3/2} = \ln A + \ln \frac{1}{2} \frac{k_{N1}'}{k_D'} + \frac{EA}{RT} \quad (9)$$

where  $EA$  is the electron affinity and  $A$  is determined from fundamental constants, and  $k_{N1}'/k_D'$  can be assumed to be approximately constant. Thus eqn. 9 gives the temperature dependence of the ECD response and relates it to the electron affinity of the molecule and hence the half wave reduction potential via eqn. 4.

At low temperatures, designated the beta region,

$$K' = \frac{1}{2} \frac{k_1}{k_D' [⊕_0]} \quad (10)$$

so that the ECD response is determined by  $k_1$  which is essentially independent of temperature and is independent of the electron affinity of the molecule.

If there are no exothermic or slightly endothermic dissociative processes, then the molecule will capture electrons reversibly and an estimate of the electron affinity will define the temperature dependence and potentially the magnitude. If the electron affinity is greater than 0.8 eV, the data will be in the beta region and will be temperature independent. The magnitude of the response will be governed by the rate constant for thermal electron attachment which is generally large ( $10^{-7}$ – $10^{-9}$   $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ) for most organic compounds. If the electron affinity is between 0.4 and 0.8 eV, then the data will exhibit both a beta and an alpha region. At higher temperatures, the response will decrease with increasing temperature and the slope will be governed by the electron affinity. The intercept in the high temperature region at  $1/T = 0$  will be  $14.7 \pm 2.0$ . This assumes an average value for the ratio  $k_{N1}'/k_D' \approx 16$ . If the electron affinity is less than 0.5 eV, then the data will be in the alpha region and will decrease with increasing temperature. The only exceptions to this latter point are molecules such as  $\text{O}_2$ ,  $\text{NO}$ ,  $\text{COS}$  and  $\text{NO}_2$ , which are in the beta region because of low rate constants,  $k_1$ . In the alpha region, the higher the electron affinity, the higher the response. In the beta region the response depends on the magnitude of the rate constant which cannot be predicted precisely.

## CORRELATION

The available data for the EA's and  $E_{1/2}$  values are plotted in Fig. 1 and are tabulated in Table I. The line is drawn for the least squares estimate,  $K = 2.49 \pm 0.20$  eV. The larger symbols are used to represent data with only a single  $E_{1/2}$  value. The smaller symbols represent the average of multiple  $E_{1/2}$  values, but all  $E_{1/2}$  values were used to determine  $K$  in eqn. 3. Also shown in Table I are the deviations from the correlation where it appears that the last four values, which are electron transmission results, are consistently low, however, the other data show no apparent bias error. The standard deviation in  $K$  is consistent with the errors in the electron affinity and the  $E_{1/2}$  values considering that different solvents and data sources are used.

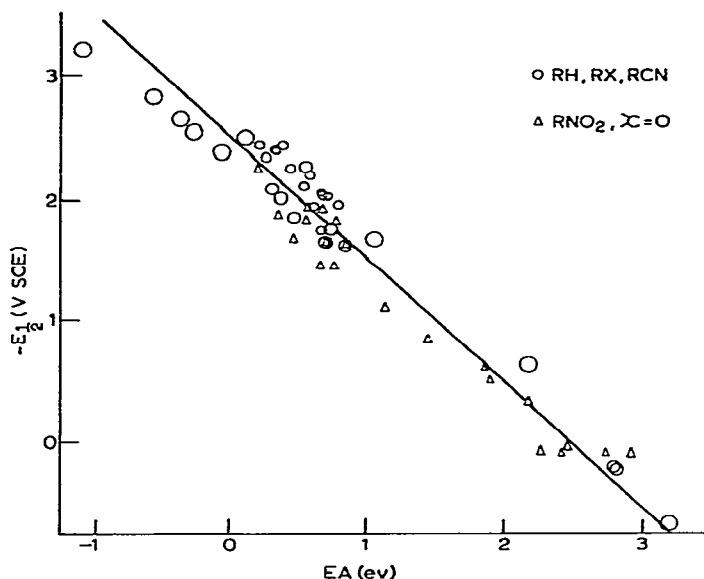


Fig. 1. Half-wave reduction potentials versus SCE ( $E_{1/2}$ ) plotted against the gas phase electron affinity. The negative values of the electron affinities are vertical electron affinities.

Coincidentally, a value of  $2.49 \pm 0.26$  eV was obtained for the pi charge transfer complex acceptors alone<sup>9</sup>. The electron affinities from half-wave reduction potentials generally agree quite well with values obtained from charge transfer complex absorption spectra data<sup>9</sup>.

## EXPERIMENTAL

The procedure and equipment used in this study have been described earlier<sup>1</sup>. A plane parallel plate tritium ECD was used. The compounds were all reagent grade and were used without further purification since a gas chromatographic column was used. All solvents were nanograde.

The electrochemical data and the data for the substituted benzophenones were

TABLE I  
ELECTRON AFFINITIES AND HALF-WAVE REDUCTION POTENTIALS

<i>Compound</i>	<i>Electron affinity (refs. 1-9)</i>	$-(\bar{E}_\frac{1}{2})$ (refs. 10-16) <i>V vs. SCE</i>	<i>Deviation (eV) EA - (<math>\bar{E}_\frac{1}{2} + 2.49</math>)</i>
Hexacyanobutadiene	3.24	-0.60	0.15
<i>p</i> -Fluoranil	2.92, 2.27	-0.04	0.38, -0.26
Tetracyanoethylene	2.88, 2.80	-0.20	0.22, 0.11
Tetracyanoquinodimethane	2.83, 2.80	-0.16	0.18, 0.15
<i>p</i> -Chloranil	2.76, 2.40	-0.02	0.25, -0.11
<i>p</i> -Bromanil	2.44	0.00	-0.05
Fluorobenzoquinone	2.16	0.37	0.04
<i>s</i> -Tetracyanobenzene	2.15	0.66	0.32
<i>p</i> -Benzoquinone	1.89	0.53	-0.07
Naphthoquinone	1.86	0.63	0.0
Maleic anhydride	1.40	0.87	-0.22
Nitrobenzene	1.10	1.12	-0.27
<i>o</i> -Dicyanobenzene	1.04	1.68	0.23
Acenaphthylene	0.80	1.65	-0.04
Cinnamaldehyde	0.80	1.64	-0.02
1,2-Benzpyrene	0.67	2.06	0.25
1-Naphthaldehyde	0.73	1.64	-0.02
1,2-Benzanthracene	0.67	2.06	0.25
Azulene	0.66	1.64	-0.19
Benzophenone	0.64	1.76	-0.09
<i>p</i> -Methylbenzophenone	0.64	1.86	0.11
Dibenz[ <i>a,j</i> ]anthracene	0.64	2.07	0.22
Dibenz[ <i>a,h</i> ]anthracene	0.64	2.05	0.23
2-Naphthaldehyde	0.63	1.50	-0.36
Fluoranthene	0.63	1.77	-0.09
Biacetyl	0.63	1.71	-0.15
Cyclooctatetraene	0.60	1.61	-0.28
Pyrene	0.59	2.10	0.20
Anthracene	0.56	1.95	0.02
4-Methoxybenzophenone	0.56	1.88	-0.05
Benzo[ <i>c</i> ]phenanthrene	0.54	2.22	0.27
Diethyl phthalate	0.52	1.87	-0.10
Picene	0.52	2.29	0.22
3,4-Benzpyrene	0.51	2.13	0.15
Benzaldehyde	0.50	1.81	-0.18
<i>s</i> -Tetrachlorobenzene	0.45	1.85	-0.19
Nitromethane	0.44	1.68	-0.37
Chrysene	0.41	2.25	0.19
Acetophenone	0.34	1.91	-0.24
<i>s</i> -Trichlorobenzene	0.34	1.99	-0.16
<i>p</i> -Dichlorobenzene	0.34	2.49	0.34
Phenanthrene	0.31	2.43	0.25
Triphenylene	0.29	2.44	0.24
1-Chloronaphthalene	0.28	2.15	-0.11
Benzonitrile	0.24	2.32	0.07
Methyl benzoate	0.20	2.23	-0.06
Naphthalene	0.15	2.48	0.14
<i>o</i> -Dichlorobenzene	0.09	2.51	0.11
Styrene	-0.25	2.46	-0.25
Biphenyl	-0.37	2.63	-0.23
Pyridine	-0.62	2.71	-0.40
Benzene	-1.15	3.31	-0.33

obtained from the literature so that the original references should be consulted for the experimental details.

## RESULTS AND DISCUSSION

The capture coefficients are plotted as  $\ln K'T^{3/2}$  vs.  $1/T$  in Fig. 2 for the carbonyl compounds and in Fig. 3 for the non-benzenoid hydrocarbons. All of the compounds have a beta region while fluoranthene, benzo[*g,h,i*]fluoranthene, acenaphthylene and acetophenone have an alpha region. The pertinent half-wave reduction potentials and the electron affinities calculated from eqn. 1 are given in Table II along with the electron affinities and the rate constants for thermal electron attachment obtained from the ECD data. From the  $E_{1/2}$  data, it is predicted that the ECD response for terephthalaldehyde and diacetylbenzene will be high and temperature independent up to a temperature of about 900°K for diacetylbenzene and 700°K for terephthalaldehyde when the response will drop sharply as shown by the dotted lines in Fig. 2. The ECD data for acetophenone-1 predicts that this compound can be reduced polarographically with a half wave reduction potential of about  $-1.88 \pm 0.2$  V vs. SCE.

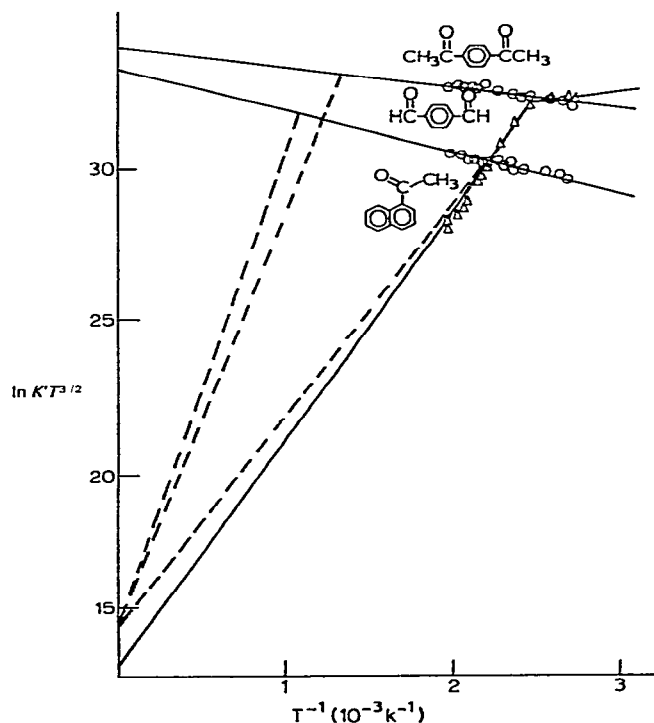


Fig. 2.  $\ln K'T^{3/2}$  versus  $1/T$  for aromatic carbonyl compounds.

The  $E_{1/2}$  data for fluoranthene and acenaphthylene indicate that the response for fluoranthene should be less than that for acenaphthylene at high temperatures and that the response for both should increase with decreasing temperatures and level off

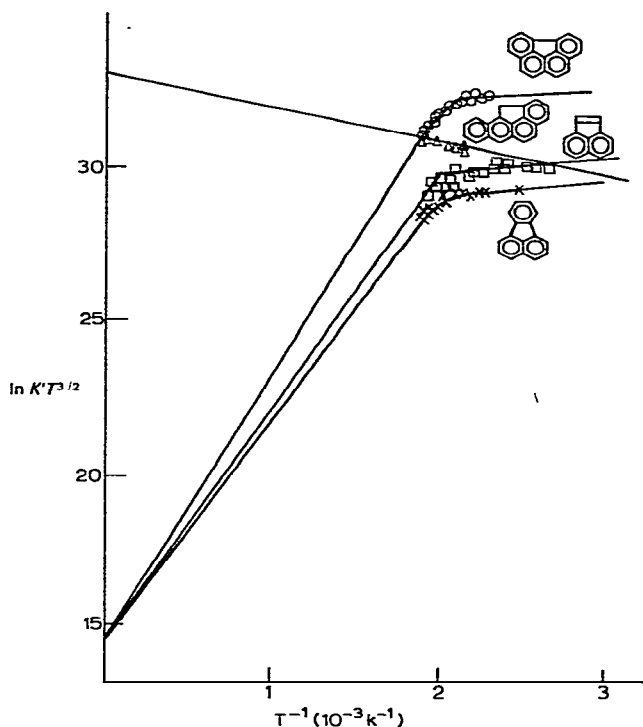


Fig. 3.  $\ln K'T^{3/2}$  versus  $1/T$  for aromatic hydrocarbons.

at a high value at low temperatures. On the basis of the ECD data, we predict that cholanthrene and benzo[*g,h,i*]fluoranthene could be reduced polarographically with half-wave reduction potentials,  $-1.69 \pm 0.2$  and  $-1.79 \pm 0.2$  vs. SCE. The general agreement between the predictions and the data for the ECD results can be seen in Figs. 2 and 3.

Eqn. 1 can also be used to evaluate the consistency of the electron affinity and half wave reduction potential data in the literature. Vessman and Hartvig<sup>18</sup> presented ECD data as a function of temperature for a series of substituted benzophenones. Their primary purpose was to use the ECD for the analysis of these compounds and hence response factors as a function of temperature were obtained at low fractional capture. A tritium source was used in a commercial detector and low pulse intervals were used to minimize the noise level. The results are shown in Figs. 4 and 5. The general features are the same as in Figs. 2 and 3. Electrochemical data is available for some of these and the corresponding data are shown in Table II. The predictions from the  $E_{1/2}$  data are all in agreement with the ECD results within the experimental error. This is especially important in the case of the bromo and iodo compounds where the agreement supports the basic assignment of the primary step to the formation of a negative ion intermediate in the polarographic studies.

The ECD data for the chloro and bromo derivatives curve upward at high temperatures, indicating that a dissociative process occurs. This combination of a dissociative and a non-dissociative mechanism has been observed previously<sup>19</sup>. A



TABLE II  
ELECTRON AFFINITIES AND RATE CONSTANTS

Compound	$-E_1$ (refs. 10-16) V vs. SCE	$EA_{cal}^*$ (eV)	$EA$ (ECD) (eV)	$k_1$ (ECD) (approximate) ( $cm^3 molecule^{-1} sec^{-1}$ )
Acetonaphthone-1			$0.61 \pm 0.1$	$1 \times 10^{-7}$
<i>p</i> -Diacylbenzene	1.41	1.08	$0.8 \pm 0.2$	$1 \times 10^{-7}$
Terephthalaldehyde	1.16	1.33	$\geq 0.8 \pm 0.2$	$3 \times 10^{-8}$
Fluoranthene	1.77	0.72	$\geq 0.63 \pm 0.2$	$3 \times 10^{-8}$
Benzof[ <i>g,h,i</i> ]fluoranthene			$0.68 \pm 0.1$	$1 \times 10^{-7}$
Cholanthrene			$0.8 \pm 0.2$	$5 \times 10^{-8}$
Acenaphthylene	1.65	0.84	$\geq 0.7 \pm 0.2$	$3 \times 10^{-8}$
Benzophenone	1.75	0.73	$0.64 \pm 0.1$	
4-CH <sub>3</sub>	1.79	0.64	$0.64 \pm 0.1$	
4-C <sub>2</sub> H <sub>5</sub>			$0.64 \pm 0.1$	
4-CH <sub>3</sub> O	1.86	0.61	$0.56 \pm 0.1$	
4-CF <sub>3</sub>			$0.8 \pm 0.2$	$7 \times 10^{-8}$
4-NO <sub>2</sub>			$> 1.0 \pm 0.2$	$2 \times 10^{-7}$
4-F	1.74	0.75	$0.66 \pm 0.1$	$5 \times 10^{-8}$
4-Cl	1.62	0.78	$0.8 \pm 0.2$	$2 \times 10^{-8}$
4-Br	1.60	0.89	$0.9 \pm 0.2$	$7 \times 10^{-8}$
4-I	1.49	1.00	$1.0 \pm 0.2$	$3 \times 10^{-7}$
3-F	1.61	0.88		
3-Cl	1.59	0.9		
3-Br	1.59	0.93		

\* The values of  $EA_{cal}$  are obtained from  $EA = E_1 + 2.49 \pm 0.2$  eV.

similar change in mechanism is observed for 4Cl, 4Br and 3Br-benzophenone in the polarographic experiments at low sweep rates when an irreversible process occurs at a lower potential.

#### Relationship between the ECD response and molecular structure

The response for compounds which undergo reversible capture in the alpha region can be predicted from the molecular electron affinities, based on (1) the results presented in this article, (2) the earlier study of charge transfer complex acceptors and (3) the kinetic model for the ECD. Thus if the EA is (1) less than 0.4 eV, (2) between 0.4 and 0.8 eV or (3) greater than 0.8 eV, then the general magnitude and temperature dependence in the alpha region can be estimated. The magnitude of the response in the beta region cannot be predicted at present but the response should be relatively temperature independent.

Two extreme approaches have been taken towards predicting electron affinities from molecular structure, one strictly empirical, and the other involving the use of semi-empirical parameters. Examples of the latter are the Hückel model used by Wentworth *et al.*<sup>20</sup> in the study of several substituted aromatic carbonyl compounds, the electrostatic model presented by Page and Goode<sup>3</sup> and the variable beta modification of the PPP approximation to the Hartree Fock equation as presented by Younkin *et al.*<sup>21</sup>. The early empirical studies related ECD response to

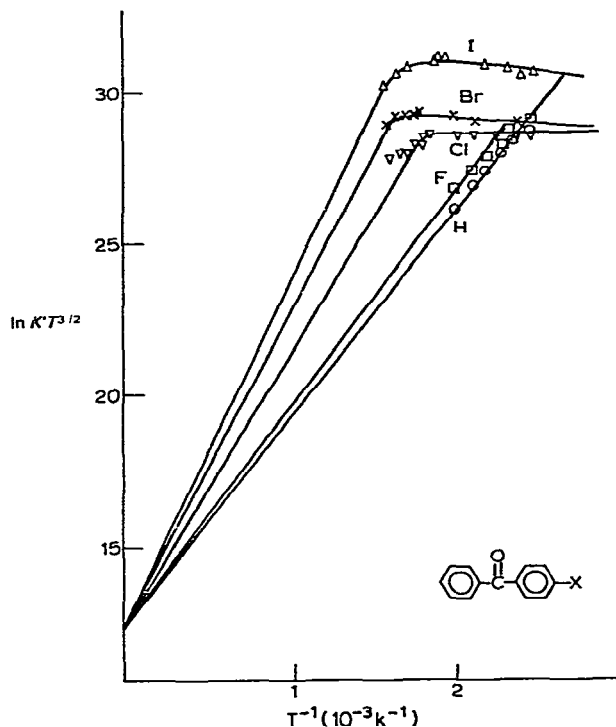


Fig. 4.  $\ln K'T^{3/2}$  versus  $1/T$  for benzophenone and halogen substituted benzophenones (ref. 18).

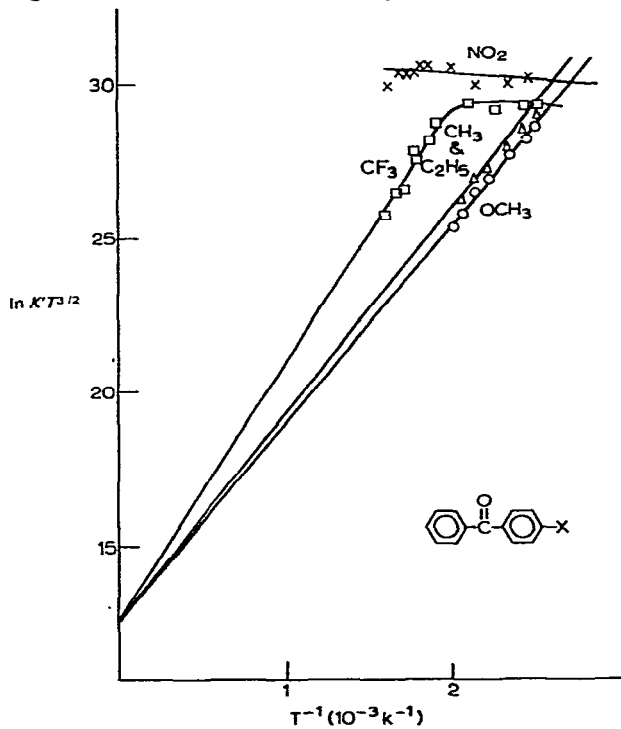


Fig. 5.  $\ln K'T^{3/2}$  versus  $1/T$  for substituted benzophenones (ref. 18).

structure without regard to reversibility or the particular temperature region<sup>22-24</sup>. More recent empirical studies by Zlatkis and coworkers<sup>25,26</sup>, Hattori *et al.*<sup>27</sup>, Wojnárovits and Földiák<sup>28</sup>, and Vessman and Hartvig<sup>17</sup> include both magnitude and temperature data.

The approach taken in this article is an intermediate one. The general effect of the various substituents on the electron affinities of alkanes, olefins, benzene and aromatic hydrocarbons will be investigated. In addition, the possibility of dissociative capture will be considered. The functional groups which increase the electron affinity

are in the order  $\text{NO}_2 > \overset{\text{O}}{\parallel} \text{CH} > \overset{\text{O}}{\parallel} \text{CCH}_3 > \overset{\text{O}}{\parallel} \text{COR} > \text{CN} > \text{CF}_3 > \text{X}$ . Alkyl and methoxy groups generally lower the electron affinity. The exact magnitude of the change depends upon the magnitude of the electron affinity of the basic compound. In general, the lower the electron affinity of the basic compound, the greater the change upon substitution. This can be somewhat understood on the basis of a greater perturbation. This trend is also evidenced in the  $E_{\frac{1}{2}}$  and the charge transfer estimates of electron affinities.

The electron affinities of the alkanes are negative by more than 2 eV. For example, the onset of  $\text{H}^-$  from methane occurs at 7 eV<sup>29</sup>. A single nitro group raises the electron affinity to the 0.4 eV range but dissociation occurs at higher temperatures. Even  $\text{CF}_4$  does not have a positive electron affinity. The only other group to increase the electron affinity of alkanes above 0.2 eV is the conjugated acetyl group such as seen in biacetyl. The substitution of Cl, Br and I on alkanes generally leads to dissociative capture.

The electron affinity of ethylene is  $-1.78$  eV<sup>30</sup>. The effects of the substituents on ethylene can be seen in Fig. 6. Chloro, bromo and iodo ethylenes will probably dissociate upon electron capture. The effect of the alkyl groups has been taken from

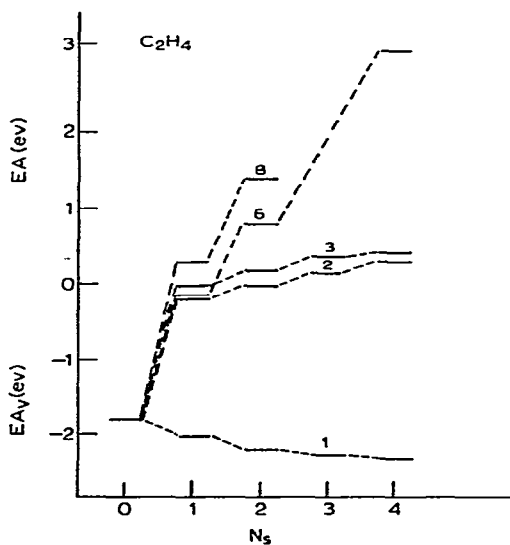


Fig. 6. Electron affinities of substituted ethylene *versus* number of substituents. 1,  $\text{CH}_3$ ; 2,  $-\text{CH}=\text{CH}_2$ ; 3,  $\text{C}_6\text{H}_5$ ; 6,  $-\text{CN}$ ; 8,  $-\text{CO}(\text{CH}_3)$ .

electron transmission studies. The leveling effect for the CN group is less than for other groups (see also the leveling effect in benzene)<sup>30</sup>.

The electron affinity of benzene is  $-1.13$  to  $-1.35$  eV from electron transmission results. The effects of the substituents on the electron affinity of benzene can be seen in Fig. 7. It must be emphasized that both vertical and adiabatic electron affinities are shown. The bromo and iodo benzenes will undergo dissociative capture over the total range of temperatures. The mono- and dichlorobenzenes also undergo dissociative capture at all temperatures but the other chlorobenzenes will capture electrons reversibly at low temperatures. The aromatic esters will also undergo dissociative capture at high temperature.

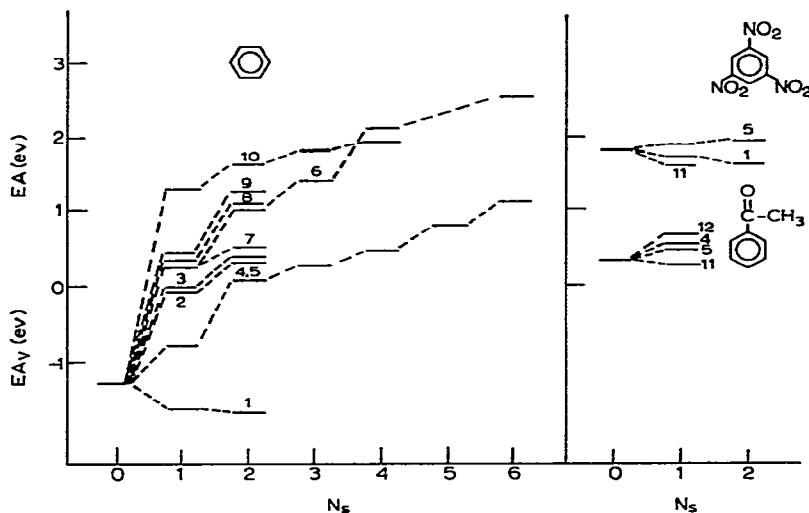


Fig. 7. Electron affinities of substituted benzenes versus number of substituents. 1,  $-\text{CH}_3$ ; 2,  $-\text{CH}=\text{CH}_2$ ; 3,  $\text{C}_6\text{H}_5$ ; 4,  $-\text{Cl}$ ; 5,  $-\text{F}$ ; 6,  $-\text{CN}$ ; 7,  $-\text{COOR}$ ; 8,  $-\text{CO}(\text{CH}_3)$ ; 9,  $-\text{COH}$ ; 10,  $-\text{NO}_2$ ; 11,  $\text{OCH}_3$ ; 12,  $-\text{CF}_3$ .

The electron affinities of the polycyclic aromatic hydrocarbons are all greater than that of benzene. A number of values have been reported from ECD data and can be used as a starting point and the general direction of the substituent effect can be obtained from Figs. 6 and 7. The substitution of a nitrogen atom for a CH group in an aromatic hydrocarbon will increase the electron affinity. For example, the vertical electron affinities of pyridine and benzene are  $-0.8$  eV and  $-1.25$  eV, respectively<sup>30</sup>. In addition, there are some basic structural groups which imply high electron affinities such as the quinone group, and conjugated dicarbonyls. Thus a general procedure for establishing electron capture responses can be given as follows.

First, examine the molecule and determine the basic hydrocarbon structure and estimate the electron affinity of this group. Next, consider the most effective electron withdrawing substituent in the molecule and adjust the electron affinity accordingly. Consider the possibility of dissociative capture and terminate if the capture is not reversible. Next, look for other substituents which may either increase or decrease the electron affinity and adjust accordingly. The leveling effect must be taken into account when making these estimates.

If the electron affinity of the molecule is greater than 0.8 eV, then the data will certainly be in the beta region and the magnitude of the ECD response will be determined by the rate constant,  $k_1$ . Two attempts have been made to relate the  $k_1$  value to the structure, one through the electron polarizability of the molecule and the other through the electron affinity of the molecule. Neither of these present an adequate correlation of the results.

Sullivan<sup>32</sup> has applied the polarization model to electron attachment reactions and obtained the relationship

$$k_1 = \left( \frac{4\pi q^2 \alpha_E}{m} \right)^{\frac{1}{2}} \quad (11)$$

where  $q$  is the electron charge,  $m$  the mass of the electron and  $\alpha_E$  the electronic polarizability. This was successfully applied to a number of pesticides and chlorinated biphenyls and the experimental rate constants were between 50 to 85 % of the theoretical values. Note that on the basis of this theory, there is an upper limit to the rate constant which is defined by the maximum value of the polarizability. However, eqn. 11 does not explain all of the variation in  $k_1$  since experimental values cover six orders of magnitude while the square root of the polarizability only covers a single order of magnitude. Of course, an empirical probability term can be added to the rate constant expression but the magnitude of this term is then unpredictable at present. If the probability term is assumed to be unity, then the early empirical studies of the relative responses for 17 Cl, Br, F and nitro substituted nitrobenzene can be used to test eqn. 11 (refs. 33 and 34). The electron affinities of all of these compounds should all be greater than 1 eV and, based on the ECD response, the  $k_1$  values are in the range  $10^{-7}$  to  $10^{-8}$  cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup>. The magnitudes of  $k_1$  have been related to the number and location of the substituents.

The other approach postulates that the value of  $k_1$  depends on the electron affinity of the molecule for the polycyclic aromatic hydrocarbons. This may be valid for certain related molecules but is not true in general. This can be seen by noting that the  $k_1$  values of NO<sub>2</sub>, SO<sub>2</sub> and O<sub>2</sub> are in the range  $10^{-12}$  to  $10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup> while the electron affinities are about 2.2, 1.1 and 0.45 eV, respectively, and the  $k_1$  values for naphthoquinone, nitrobenzene and acetophenone are in the range of  $10^{-7}$  to  $10^{-8}$  cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup> while the electron affinities are about 1.8 and 1.2 and 0.3 eV, respectively<sup>2,35</sup>.

These response considerations have been based upon the plane parallel plate detector using a tritium source and a fixed frequency pulsed mode of electron collection. Thus in comparing these predictions with actual responses, deviations from these conditions must be noted. In fact, these general predictions can be used to identify actual differences in the response for different operational modes. Three recent articles reporting ECD responses will now be discussed in order to illustrate the use of these predictions.

Miller *et al.*<sup>36</sup> have recently reported the ECD response for a number of aromatic hydrocarbons and heterocyclic, methyl and chloro substituted aromatic hydrocarbons. The measurements were made at a single temperature as a part of a study of oxygen enhancement of ECD responses. Wojnárovitz and Földiák<sup>28</sup> have reported the response of a series of hydrocarbons and alkyl substituted hydrocarbons

as a function of temperature and have obtained electron affinity values. Both studies used a nickel-63 source in a concentric geometry and used the constant current mode. Hattori *et al.*<sup>27</sup> report ECD responses, temperature dependencies, and electron affinities for a series of chloro, bromo and methyl substituted nitrobenzenes and several chlorobenzenes using a concentric geometry with a nickel source and a d.c. field for electron collection.

Most of the aromatic hydrocarbons examined by Miller *et al.*<sup>36</sup> have been studied in this laboratory and the relative order reported for these compounds is in agreement with our results on electron affinities. Results are given for nitrogen heterocyclic analogs of anthracene and phenanthrene and the response increases as expected in the heterocyclic compounds. The substitution of chlorine on phenanthrene and anthracene results in an increase in the response as expected. The effect of substitution of a methyl group on anthracene and benzanthracene is in the opposite direction from that which is expected. The greatest increase in the response is for 7,12-dimethylbenanthracene (8500) as compared to the parent compound (130). This implies an increase in the electron affinity of about 0.2 eV.

A similar effect was noted in the results of Wojnárovits and Földiák<sup>28</sup> who report that methyl and ethyl substitution on naphthalene increase the electron affinity by as much as 0.1 eV for 1,4-dimethylnaphthalene. They also report that tetra-, penta- and hexamethylbenzene and biphenyl have electron affinities in the range of 0.1 to 0.2 eV in contrast with the half-wave reduction potentials and Hückel calculations which indicate that these compounds have negative electron affinities. The results for azulene, anthracene, phenanthrene and naphthalene agree with results from this laboratory<sup>1</sup>. An estimate of the electron affinity of acenaphthylene (0.46 eV) is not in agreement with the result reported in this article. There are two possible explanations for these discrepancies. The obvious one is that the constant current response is not always equivalent to the constant frequency response. This is supported by the fact that certain compounds exhibit non-linear responses with concentration in the constant current mode. The other possibility is that the results pertain to a non-thermal process in the ECD which is not related to the Hückel calculation and the  $E_{\pm}$  measurements. This point can be clarified by determining the temperature dependence for these compounds in a fixed frequency, tritium, parallel plate detector.

The electron affinities of the nitrobenzenes and the penta- and hexachlorobenzenes are predicted to be greater than 1 eV and hence the ECD data should be in the beta region. The results of Hattori *et al.*<sup>27</sup> agree with this at low temperatures but at high temperatures, the slope of the plot of  $\ln KT^{3/2}$  vs.  $1/T$  becomes positive indicating an alpha region for nitrobenzene, nitrotoluene and the penta- and hexachlorobenzenes. The alpha region for the nitrotoluenes is larger and is better defined for the nitrotoluenes than for nitrobenzene indicating that the electron affinities of the nitrotoluenes are less than the electron affinity of nitrobenzene, as anticipated. The authors report values of EA' which are actually determined from the positive slopes in the limited alpha regions but a better procedure would be to assume a fixed intercept and to calculate the slope from this value and the last data point in the alpha region (see Figs. 2 and 3). The unexpected appearance of an alpha region for these compounds could be due to the d.c. collection mode or could be a real result. The answer to this question also resides in the collection of data in a "standard" system.

## CONCLUSIONS

(1) The half-wave reduction potential in aprotic solvents ( $E_{\frac{1}{2}}$ ) has been related to experimental gas phase electron affinities by the relationship  $EA = E_{\frac{1}{2}} + 2.49 \pm 0.20$  eV over the range of electron affinities of  $-1.0$  to  $3.2$  eV. The relationship is satisfied within the experimental uncertainty and  $E_{\frac{1}{2}}$  values can be used to estimate electron affinities of molecules. If  $E_{\frac{1}{2}}$  data are not available, electron affinities can be estimated from charge transfer complex absorption maxima based upon earlier correlations with electron affinities obtained from  $E_{\frac{1}{2}}$  values<sup>9</sup>.

(2) The ECD data for several aromatic hydrocarbons, carbonyl compounds and substituted benzophenones has been interpreted with the aid of the above correlation and previously unreported electron affinities are given.

(3) A procedure for predicting electron affinities of compounds from their structure has been presented and hence the magnitude and temperature dependence of the response can be predicted for data in the alpha region. If the electron affinity is greater than  $0.8$  eV, or if the data is in the beta region, the magnitude of the response depends upon the rate constant,  $k_1$ , which is presently not predictable, in general. The polarizability theory may be useful in predicting  $k_1$  from molecular structure if the probability of reaction is unity.

(4) The experimental responses and their temperature dependence has been examined in light of the above method and some agreements and some disagreements were noted. The major discrepancies occur in the range of electron affinities of  $0$  to  $0.2$  eV and the effect of alkyl substitution on electron affinities. These studies used a fixed frequency and/or a d.c. mode of electron collection and a nickel-63 source with a concentric electrode. Thus, the validity and source of these discrepancies can be clarified by obtaining ECD response and temperature dependence data with a plane parallel plate detector with a tritium source operated in the constant frequency mode.

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