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Journal of Chromatography A, 827 (1998) 91–104

JOURNAL OF  
CHROMATOGRAPHY A

# Modified kinetic model of the electron-capture detector Molecular electron affinities and electron collection modes

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Received 18 June 1998; received in revised form 15 September 1998; accepted 15 September 1998

## Abstract

The kinetic model for electron-capture detection (ECD) has recently been expanded to include excited states. Multiple electron affinities for  $C_6F_6$ , anthracene and tetracene have been reported in the literature. The temperature dependence of the ECD response is calculated using these values and the expanded two state model. Activation energies and pre-exponential terms for kinetic rate constants are determined. The pre-exponential terms for thermal electron attachment are compared with the maximum value calculated from the DeBroglie wavelength of the electron and the probability for stabilization. Temperature data from different methods of electron collection are compared. A general procedure for the determination of electron affinities from ECD data is presented. The following ECD electron affinities are reported:  $C_6Cl_6$ ,  $1.17 \pm 0.02$  and  $0.71 \pm 0.02$ ;  $C_6F_5Cl$ ,  $0.96 \pm 0.03$  and  $0.82 \pm 0.02$ ;  $C_6F_5NO_2$ ,  $1.52 \pm 0.02$ ;  $C_6H_5NO_2$ ,  $1.00 \pm 0.01$  and *m*-hydroxyacetophenone,  $0.74 \pm 0.02$  (all values in electron volts, eV). © 1998 Published by Elsevier Science B.V. All rights reserved.

**Keywords:** Detection, GC; Electron-capture detection; Kinetic studies; Electron affinity; Hydrocarbons, aromatic; Polynuclear aromatic hydrocarbons

## 1. Introduction

The year 1998 marks the fiftieth anniversary of electron-capture detection (ECD) according to its inventor, J.E. Lovelock [1]. It also marks the passage of a scientist who happened to be a pioneer in the field of chromatography and was personally responsible for the unique role of the ECD in chromatography and physical chemistry, Albert Zlatkis.

Lovelock is the father of ECD but Zlatkis was its salesman. This article is written as a tribute to the man who introduced the ECD to us and the world. Indeed, Lovelock began the description of his personal odyssey with the electron-capture detector as follows. “When I first came to Houston in 1958 and felt the touch of its warm humid air on my skin it seemed like a place where interesting things might happen....I was met at the airport by Al Zlatkis and taken directly to his laboratory at the University of Houston. There we set it (the ECD) up and in no time were running samples of products from the Houston Petrochemical Industry; mixtures called “platformates” and “reformates” which I had never heard spoken of before. They gave the most glorious

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and unbelievably excellent chromatograms resolving components hitherto only suspected to be present. It was not pure science but it surely was one of those days when everything goes right technically and life as a scientist seems to be very worthwhile....

In 1961, I came to Houston again...This provided at last an opportunity to spend full time in discovering how the electron-capture detector really worked. In this I was fortunate to have nearby both Dr. Zlatkis who by then had become a close friend and colleague and Drs. Wentworth and Chen of the University of Houston. This fruitful collaboration led to the first plausible kinetic model of the electron-capture detector [2].”

The model has remained basically unchanged for thirty years and has provided much fundamental data on the kinetics and thermodynamics of reactions of thermal electrons with molecules. The first accurate electron affinities of molecules were determined using the electron-capture detector [3]. Quite appropriately, the data used to obtain these electron affinities were collected by Lovelock, Zlatkis and Becker [4]. The electron affinity (EA) of a molecule is defined as the difference in the energy of the neutral molecule and the negative ion when both are in their most stable state. The excited state EA is the difference in energy between the neutral in its most stable state and the ion in an excited electronic state. In 1998, the kinetic model was expanded to include an excited state, as in the case of CS<sub>2</sub> [5]. This was done to explain the structure in the temperature dependence of the response of ECD when plotted as  $\ln KT^{3/2}$  vs.  $1000/T$  where  $K$  is the molar response of the ECD system and  $T$  is the absolute temperature.

This paper illustrates the effect of the mode of electron collection and the presence of two states on ECD temperature dependence. This will be accomplished by first comparing the calculated and experimental ECD responses for C<sub>6</sub>F<sub>6</sub>, anthracene and tetracene. Ground state and excited state electron affinities have been measured for these molecules by other techniques [6–18]. New ECD data for acetophenone, benzaldehyde, naphthalene, C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, C<sub>6</sub>F<sub>5</sub>NO<sub>2</sub>, C<sub>6</sub>Cl<sub>6</sub>, C<sub>6</sub>F<sub>5</sub>Cl and *m*-hydroxyacetophenone, C<sub>8</sub>H<sub>8</sub>O<sub>2</sub> taken under the constant-current- variable frequency mode or at constant frequency, 50 μs reaction time, will be presented.

These data more precisely define the effect of temperature upon response factors. Previously unreported ECD electron affinities will be given. A modified procedure for obtaining fundamental properties from ECD data will be presented and applied to a number of aromatic hydrocarbons. Half wave reduction potential data and semi-empirical calculations will be used to support the ECD electron affinities [6,7].

The alternative gas phase methods used to determine the electron affinities of the test molecules are based on: (1) the measurement of the equilibrium constant of the electron molecule reaction using ECD or negative ion mass spectrometry (MS); (2) the interaction of photons with molecules, the photoelectron spectroscopy (PES) method and (3) the kinetics and/or thermodynamics of thermal charge transfer (TCT) reactions. A more complete discussion of these methods and a comprehensive listing of electron affinities is available and should be consulted for detailed references [12]. The literature values of the ground state and excited state electron affinities (in eV) are: tetracene 1.04±0.05 (TCT) and 0.88±0.05 (ECD); anthracene, 0.69±0.01 (ECD) and 0.530±0.005 (PES); C<sub>6</sub>F<sub>6</sub> 0.86 ±0.02 (ECD, PES, MS) and 0.52±0.1 (TCT) [6–18]. Other electron affinities reported by both the ECD and TCT methods respectively in eV are: C<sub>6</sub>Cl<sub>6</sub> (1.1, 1), C<sub>6</sub>F<sub>5</sub>Cl, (>0.7, 0.85), C<sub>6</sub>F<sub>5</sub>NO<sub>2</sub> (1.5, 1.5) [11,13,17–19]. A TCT electron affinity of 0.85±0.05 eV for *o*-hydroxyacetophenone has been reported [20]. The ECD value for C<sub>6</sub>F<sub>5</sub>Cl is a lower limit. The electron affinity of C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> has been measured to be 1.00±0.015 eV by many techniques and verified by half wave reduction potentials [11,12,18].

Structure was clearly observed in the ECD temperature dependence of carbon disulfide. In the ECD data for tetracene, structure is also observed. In the case of C<sub>6</sub>F<sub>6</sub>, minor structure is observed. In the case of anthracene, three different sets of ECD data in the literature are consistent with an excited state [2,14,16]. For C<sub>6</sub>F<sub>5</sub>Cl there is definite structure in the data, while that for C<sub>6</sub>F<sub>5</sub>NO<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, C<sub>6</sub>Cl<sub>6</sub> and C<sub>8</sub>H<sub>5</sub>O<sub>2</sub> have little or no structure. Since structure has been the exception rather than the rule for ECD data, multiple negative ion states have not been necessary to explain the majority of the temperature data.

## 2. Kinetic model of the ECD system

ECD reactions are kinetically controlled but in some cases, the equilibrium constant can be measured. For molecules in which the lowest pathway for dissociation by thermal electron attachment are endothermic, the reactions are the formation of a molecular negative ion,  $AB^-$ , and the subsequent electron detachment with rate constants  $k_1$  and  $k_{-1}$  ( $AB + e^- = AB^-$ ). The electrons and negative ions are neutralized by reaction with positive ions with rate constants  $k'_D$  and  $k'_N$  ( $e^-$  or  $AB^- + P^+ = \text{neutrals}$ ). Assuming low fractional capture or constant positive ion concentrations,  $[P^+]$  these bimolecular rate constants can be replaced with pseudo unimolecular rate constants  $k_D$  and  $k_N$ . When the positive ion, electron and negative ion concentrations are assumed to attain a steady state.

$$\frac{I_b - I_{e^-}}{I_{e^-}} = K[AB]/2 \quad (1)$$

where  $I_{e^-}$  is the electron current in the presence of a sample molecule, AB, and  $I_b$  is the electron current in the absence of the capturing species and  $[(I_b + I_{e^-})/I_b]$  is approximately two at low fractional capture, the limiting value of  $K$  can be approximated as: [5,21]

$$K = \frac{k_{1x}k_N}{2(k_D)(k_{-1x} + k_N)} + \frac{k_1k_N}{2(k_D)(k_{-1} + k_N)} \quad (2)$$

substituting into Eq. (2) the kinetic expressions;  $k_N = A_N$ ;  $k_D = A_D$ ;  $k_1 = A_1 T^{-1/2} \exp(-E_1/RT)$ ; and  $k_{-1} = A_{-1} T \exp(-E_{-1}/RT)$  with the excited state specific subscript  $x$ ,

$$K = \frac{A_N A_1 T^{-1/2} \exp(-E_1/RT)}{2A_D [A_N + A_{-1} T \exp(-E_{-1}/RT)]} + \frac{A_N A_{1x} T^{-1/2} \exp(-E_{1x}/RT)}{2A_D [A_N + A_{-1x} T \exp(-E_{-1x}/RT)]} \quad (3)$$

Assuming equal values of  $A_N$  for the ground and excited state, there are eight parameters to be determined, two each for the four rate constants. The values of  $A_N$  and  $A_D$  depend upon the specific detector since they involve the positive ion concentrations. The form of the rate constants has been chosen to reflect the temperature dependence for

unimolecular dissociation so that the  $A_{-1}$  term has a  $T$  dependence. Consequently, the  $A_1$  term has a  $T^{-1/2}$  dependence. This is different from the original assumption where  $A_1$  was arbitrarily assigned a  $T^{-3/2}$  dependence.

At temperatures high enough to populate only the ground state, called the  $\alpha_g$  region, the value of  $K$  becomes

$$K = (A_N/2A_D)(A_1 T^{-3/2}/A_{-1}) \exp(EA/RT) \quad (4)$$

and

$$\ln KT^{3/2} = \ln(A_N/2A_D) + \ln(A_1/A_{-1}) + EA/RT \quad (5)$$

using the statistical mechanical expression for  $K_{eq}$  for the reaction of thermal electrons with molecules

$$(A_1/A_{-1}) = [g(A^-)/g(A)]h^3/(2\pi m_e k)^{3/2} \quad (6)$$

where  $m_e$  is the electron mass and  $k$  and  $h$  are the Boltzmann's and Planck's constants and the  $g$ 's are partition functions and  $\ln(A_1/A_{-1}) = 12.43 + \ln(A_N/2A_D) + \ln\{[g(A^-)/g(A)]\}$ . With experimental  $A_1/A_{-1}$  and  $\ln(A_N/2A_D)$ , a value of  $[g(A^-)/g(A)]$ , the partition function ratio, PFR, can be calculated. Note that in this region, it is the ratio of  $(A_N/2A_D)$  that is involved so that changes in the concentration of the positive species and the temperature dependence of the intrinsic rate constants will not affect the value of the slope since they cancel in the ratio. However, the magnitude of this ratio and the experimental  $A_1/A_{-1}$  will depend upon the specific compound and detector design and conditions.

If the activation energy for the attachment to the ground state is sufficiently large, greater than about 0.1 eV, there will be structure in the data. At lower temperatures or larger  $1000/T$ , there will be an apparent plateau, called the  $\beta_G$  temperature region, followed by a rise with a slope corresponding to the excited state electron affinity, the  $\alpha_x$  temperature region. At still lower temperatures, another plateau region, called the  $\beta_x$  temperature region, is observed where  $K = (k_1 + k_{1x})/(2A_D)$ . In this region the response will be relatively temperature independent when  $k_{1x}$  is larger than  $k_1$ . In the event that more than one temperature independent attachment process is possible, the ECD response could have multiple  $k_{1i}$  values with low activation energies so that the

apparent  $A_1$  can be larger than the DeBA. An important example of this could be the maximum capture pesticides.

The rate constants for electron attachment as a function of energy are often compared with a maximum value which is called the Langevin rate constant. It is  $\pi\lambda^2$  where  $\lambda$  is the DeBroglie wavelength of the electron with a thermal distribution. The DeBroglie wavelength of the electron can be calculated from fundamental constants. The term “Langevin cross section” can be applied to both thermal and hyperthermal electrons. In the following discussion, the maximum value of the pre-exponential term for the reactions with thermal electrons will be called the DeBroglie  $A_1$  value (DeBA).

The different values of the  $A_1/A_{-1}$  are due to the fact that electron attachment is a two-step process which requires stabilization to the ground state. Thus at sufficiently high pressures or third body concentrations,  $A_1$  will approach a maximum value when the stabilization occurs on every collision. The stabilization term is analogous to the  $Z$  factor in traditional collisional theories of kinetic rate constants and can be designated as the  $Z$  (electron-capture stabilization),  $Z_{\text{ecs}}$ . There are well established cases where the experimental  $A_1$  is less than the DeBA in the ECD, most notably for oxygen and  $\text{CS}_2$  [5,22]. This is due to the low value of  $Z_{\text{ecs}}$ .

Equilibrium is assumed for the transfer between the excited state and the ground state. If this is not the case, then rate constants for these processes can be added to the numerator of the ground state term and the denominator of the excited state term. This would allow a better fit in the transition region for tetracene and  $\text{C}_6\text{F}_5\text{Cl}$ .

The above kinetic model has been restricted to molecules which do not dissociate upon thermal electron attachment. However, the general model has also been applied to molecules which dissociate. The effect of the multiple states upon the dissociative model has not been considered in detail. By analogy to the single state model, the expression for  $K$  could be modified to include a dissociative rate constant in the numerator and denominator for the two terms in Eq. (2). In the case of the unimolecular dissociation, there will generally be only one process so that  $K = k_1/2A_D$ .

### 3. Experimental and calculation procedures

The ECD experimental procedure has been described previously [2,5,18,21–23]. The kinetic parameters are independent of the specific equipment. The specific equipment used for  $\text{C}_6\text{Cl}_6$ ,  $\text{C}_6\text{F}_5\text{Cl}$ , and  $\text{C}_8\text{H}_8\text{O}_2$  has been described [18]. A standard Hewlett-Packard constant-current ECD system and chromatograph was used for the  $\text{C}_6\text{F}_5\text{NO}_2$  and  $\text{C}_6\text{H}_5\text{NO}_2$  data. These data were taken at low fractional capture using the standard integration software. The chromatographic conditions were adjusted to obtain baseline resolution of the three fluoronitrobenzene, nitrobenzene and pentafluoronitrobenzene at isothermal conditions. The samples were injected repeatedly and the temperature of the detector dropped slowly. The equipment and procedures for the other compounds are given in the original articles. Briefly, known amounts of a compound are injected into a gas chromatograph and the ECD response measured at different temperatures. The raw data are  $I_b$ , the standing current or baseline of the chromatogram;  $I_e$  the current in the presence of the peak;  $n$  the moles injected;  $V$  (l/s); the total flow-rate in the detector corrected to temperature by the ideal gas law and the temperature. Using triangulation for the area of symmetrical chromatographic peaks, the electron-capture coefficient  $K$  (l/mol) is given by:

$$K_{\text{EC}} = ([I_b - I_e]/I_e)_{\text{max}}\{t_{1/2}\}V/n \quad (7)$$

where  $([I_b - I_e]/I_e)_{\text{max}}$  is the corrected height at the peak maximum and is unitless, and  $t_{1/2}$  is the measured peak width (s) at corrected half height. The baseline current,  $I_b$  is nominally temperature independent but if the value changes due to a change in the concentration of impurities,  $K$  must be normalized to the maximum value of  $I_b$ .

The non-linear least-squares data fits were obtained using a custom program in EXCEL. The value of  $A_{1x}$  was set equal to  $A_1$  and was initially estimated as DeBA or as determined by the data in the low temperature region. The experimental EA values were used with their respective errors in the least-squares. The ratio of  $A_1$ ,  $A_{-1}$ ,  $E_1$  and  $E_{-1}$  were determined from the high temperature ECD data.

The value of  $E_{1x}$  was estimated and  $E_{-1x}$  was obtained from the literature values of the EA. For molecules where the  $A_{1x}$  is about equal to DeBA, the activation energy,  $E_{1x}$  will be small. The values of  $A_{1x}$ ,  $A_{-1x}$ ,  $E_{1x}$  and  $E_{-1x}$  for tetracene and  $C_6F_5Cl$ , were determined from the ECD data in the intermediate region while the value of  $E_1$  was determined from the upward turn leading to the ground state [14]. The temperature dependence can be calculated from electron affinities in the literature if the PFR and  $Z_{ecs}$  are known. The least-squares analysis of the ECD data improves the accuracy of the parameters.

For the data in the equilibrium region, the plots of  $\ln KT^{3/2}$  vs.  $1000/T$  are linear so that any data reduction procedure can be used to determine the slope and the intercept. The electron affinity is obtained by multiplying the slope by  $R$ , the gas constant. The high-temperature intercept can be obtained by using a calibration compound. A good compound for this purpose is acetophenone because  $Z_{ecs}$ ,  $A_N/A_D$  and the PFR are about one, based upon extensive data obtained over a wide temperature range. For other compounds, this will be an upper limit to the intercept. In the case of constant-current or 50  $\mu s$  fixed frequency data, the actual intercept can be compared with the value calculated from fundamental constants which is 11.74. Other potential reference compounds are naphthalene, phenanthrene and benzaldehyde.

If  $k_1$  and its temperature dependence has been reliably measured, then  $A_D$  can be calculated for a specific detector and condition of cleanliness. In other words, the instrumental factor can be calibrated. A good compound for this purpose is  $CCl_4$ . The rate constant,  $k_1$ , is almost equal to the DeBA and the activation energy is essentially zero. To determine if structure can be observed in ECD data,  $C_6F_6$ ,  $CS_2$  and  $C_6F_5Cl$  can be used. All of these compounds have the advantage of being volatile so that a wide temperature range in ECD can be examined.

The semi-empirical calculations with multiconfiguration configuration interaction (MCCI) were carried out using the HYPERCHEM software and the CURES-EC procedure for minimizing the difference between the theoretical and experimental values of

electron affinities [7]. The specific semi-empirical procedure and number of orbitals used in the multiconfiguration configuration interaction, MCCI, are designated by  $M/3$  (3300). The term  $M/3$  stands for the MINDO/3 Hamiltonian and parameters and the numbers in parentheses are the number of filled and unfilled orbitals used in the semi empirical calculation. The AM1 and PM3 methods are standard semi-empirical procedures and the addition of configuration interaction to the calculations is an extant procedure in HYPERCHEM.

#### 4. Results and discussion

In Figs. 1–6, the ECD data are presented as  $\ln KT^{3/2}$  vs.  $1/T$ . The lines are the least-squares fit to the data subject to the assumptions given in Section 3. The temperature dependence for the determination of the highest ECD EA ( $C_6F_5NO_2$ , 1.5 eV) and a

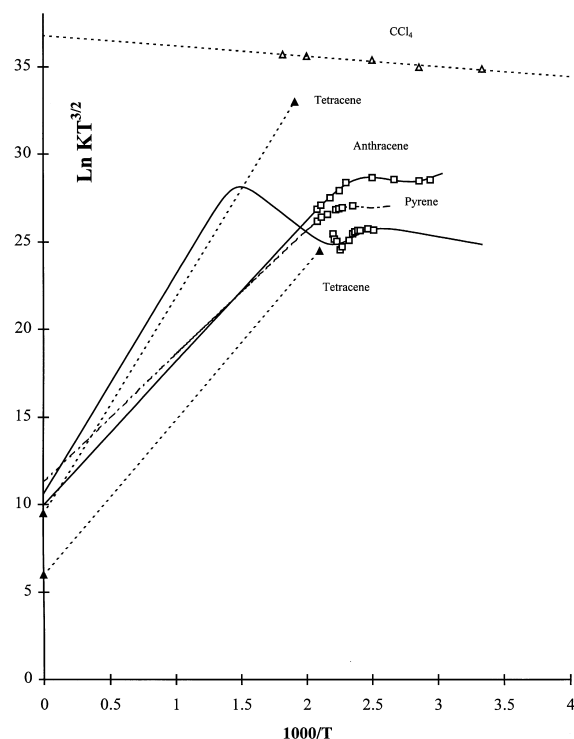


Fig. 1. ECD data as  $\ln KT^{3/2}$  vs.  $1/T$  for  $CCl_4$ , anthracene, pyrene and tetracene [4,14,24].

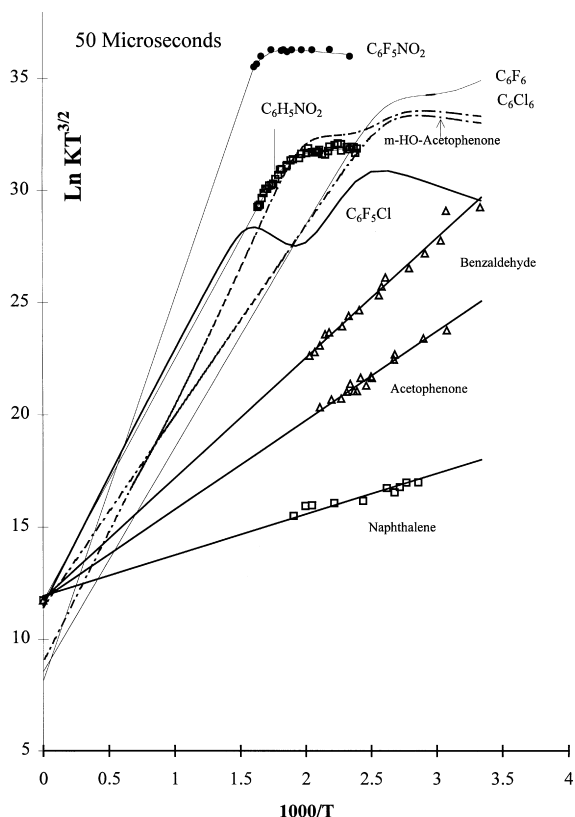


Fig. 2. ECD data as  $\ln KT^{3/2}$  vs.  $1/T$  data taken at 50  $\mu\text{s}$  fixed frequency.

low EA (naphthalene, 0.14 eV) are shown. These represent approximate boundaries for the ECD temperature dependence for the determination of molecular electron affinities. In Fig. 1, data for  $\text{CCl}_4$  are shown to provide an illustration of an upper calibration compound even though dissociative electron-capture is known to occur. The anthracene, tetracene, and pyrene data shown in Fig. 1 were collected by Lyons et al. in 1968 using ethylene rather than methane as a dopant gas. The studies did not use a chromatograph for separation [14]. The two other data points for tetracene in Fig. 1 were taken from the literature [4,24].

The data in Fig. 2 were taken at 50  $\mu\text{s}$  in this laboratory. The data and the differences between the calculated and experimental data and the calculated curves for  $\text{C}_6\text{F}_6$ ,  $\text{C}_6\text{Cl}_6$ ,  $\text{C}_6\text{F}_5\text{Cl}$  and *m*-hydroxyacetophenone are shown in Figs. 3 and 4. The data for acetophenone, benzaldehyde and naphthalene in

Fig. 2 were collected in the 1960s to investigate the effect of reaction time on the temperature dependence [22].

The constant-current data in Fig. 5 are included to show that the constant-current mode can be used to obtain fundamental properties. The data for  $\text{C}_6\text{F}_5\text{NO}_2$  and  $\text{C}_6\text{H}_5\text{NO}_2$  have not been published while the data for anthracene and naphthalene were published by Wojnarovits and Foldiak [16]. The anthracene data are extended to higher temperatures and better define the ground state electron affinity. The naphthalene data define the intercept and were used as a reference compound in the original studies. The data for  $\text{C}_6\text{H}_5\text{NO}_2$  may have a slight change in slope at lower temperatures which could indicate an excited state.

The calculated curves for the constant-current and 50  $\mu\text{s}$  data are compared in Fig. 6. The differences are due to instrumental and/or carrier gas differences. The lower response of the constant-current detector in the plateau region indicates a larger value of  $A_D$ . This illustrates the importance of calibration of the detector, especially in the constant-current mode. The previously published 1000  $\mu\text{s}$  data are compared with the 50  $\mu\text{s}$  and constant-current data in Fig. 6 [22]. The extensive data for acetophenone are shown since they can be used for calibration.

The parameters used to obtain the curves are given in Table 1. Except for nitrobenzene and the excited state of tetracene, the values of  $\ln(A_{ij})$  are 34–37, within an order of magnitude of  $\ln(\text{DeBA})=36$ . The units of  $A$  are mol/l, s and K. The  $Z_{\text{ecs}}$  values are about 1 for the majority of the compounds. For the excited state of tetracene, the  $Z_{\text{ecs}}$  value is  $10^{-2}$  and partially accounts for the lower PFR value. For nitrobenzene, the  $Z_{\text{ecs}}$  value is 0.03 but the PFR is about unity. On the other hand, for the excited state of  $\text{C}_6\text{F}_6$  the  $Z_{\text{ecs}}$  value is one but the PFR value is about 0.03. Other approximate PFR ratios are given in Tables 1 and 2.

It must be emphasized that estimates of parameters from other experiments are included in the data reduction procedures with the appropriate errors. For example, in the case of  $\text{C}_6\text{F}_6$  the excited state electron affinity, rate constant for thermal electron attachment, and the high-temperature intercept values obtained from other experimental procedures and the ground state electron affinities from the other

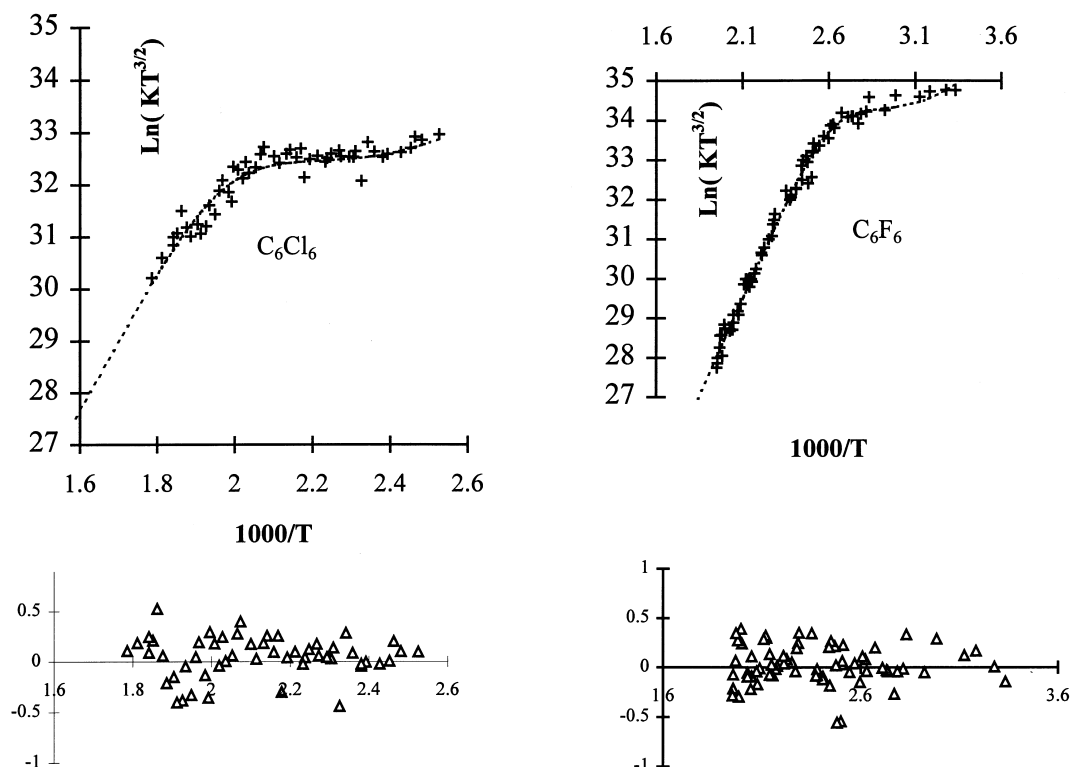


Fig. 3. ECD data as  $\ln KT^{3/2}$  vs.  $1/T$  data taken at 50  $\mu$ s fixed frequency for  $C_6F_6$  and  $C_6Cl_6$ . The lower graphs are the deviations between the experimental and calculated values.

ECD experiments are included in the data reduction procedure. Thus the values in Table 1 must be at least as accurate as these input values and errors.

In Table 2, the electron affinities of the aromatic hydrocarbons obtained from the ECD data are given and compared with the literature values. These should now be used as the most appropriate ECD electron affinities of these compounds. The  $M/3$  (2300) value for the ground state electron affinity of tetracene is 1.04 eV. The  $M/3$ (0000) value is 0.91 eV which agrees with the excited state value. The  $M/3$ (3100) value for anthracene is 0.702 eV while the  $M/3$ (2100) value is 0.540 eV. The AM1 (0033) EA of  $C_6F_6$  is 0.83 eV, while the PM3 UHF value is 0.39 eV. These support the experimental values shown in Tables 1 and 2. Other ground state EA values are confirmed by half wave reduction potential measurements and CURES EC MCCI calculations as shown in Table 2.

In the single temperature method of obtaining

electron affinities, the ECD response of a compound with a known electron affinity and that for a compound with an unknown EA are measured. If the partition function ratios are equal,  $EA(unk) = EA(ref) - RT \ln(K_{ref}/K_{unk})$ . In order to obtain absolute values, the value of  $EA(ref)$  must be known. The EA of anthracene used to obtain absolute values was 250 meV too low. [3] The values in Table 3 should replace those electron affinities since they are independent from the values in Table 2 which are based upon different data. The assumption of a constant PFR ratio for anthracene and the excited state of tetracene is not valid as illustrated in Fig. 1. In this case, the single point determination using anthracene as a reference point only gives a lower limit to the excited state electron affinity of about 0.6 eV. In Tables 2 and 3 are the electron affinities of dibenz[*a,c*]anthracene and perylene and determined from literature ECD data using the single point procedure [24,25]. The parent negative ions of many

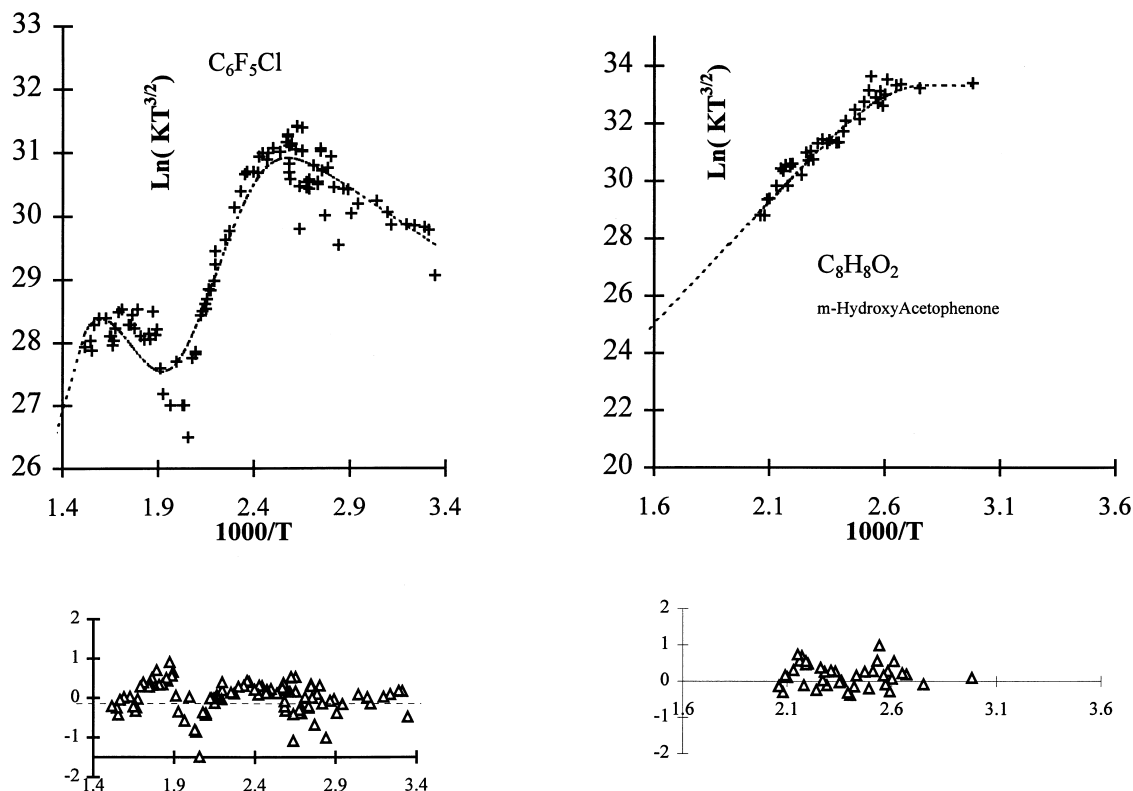


Fig. 4. ECD data as  $\ln KT^{3/2}$  vs.  $1/T$  data taken at  $50 \mu\text{s}$  fixed frequency for  $\text{C}_6\text{F}_5\text{Cl}$  and  $\text{C}_8\text{H}_8\text{O}_2$ . The lower graphs are the deviations between the experimental and calculated values.

of these aromatic hydrocarbons have been observed in the gas phase in negative ion mass spectrometry [26–28]. Of particular importance is the observation of the anion of naphthalene which clearly suggests a positive electron affinity [26,27].

#### 4.1. Acetophenone, benzaldehyde, naphthalene $\text{C}_6\text{H}_5\text{NO}_2$ , $\text{C}_6\text{F}_5\text{NO}_2$ , *m*-hydroxyacetophenone

The ECD data for these compounds are all typical of the single state ECD model which is in the literature. The first three exhibit only an  $\alpha$  temperature region where the electron affinity is equal to the slope times  $R$  and the intercept should be 11.74 if the PFR ratio and the  $A_N/A_D$  ratios are one. The other three exhibit both  $\alpha$  and  $\beta$  regions. Except for  $\text{C}_6\text{F}_5\text{NO}_2$  there are sufficient data in both regions to define a slope and an intercept.

The  $50 \mu\text{s}$  ECD data for acetophenone, benzal-

dehyde and naphthalene, obtained in the 1960s, are given to show that the slopes are independent of the reaction time in Fig. 6. The ECD EA values in Table 1 are a weighted average of at least four determinations. The intercept values for all three compounds in both the fixed frequency and the constant-current mode are about 11.74. Therefore, these compounds can be used to calibrate an instrument and to establish an upper limit for the intercept. The ECD response at a single temperature in the equilibrium region and an assumption of a PFR value can lead to a lower limit for the EA.

The data for *m*-hydroxyacetophenone (m-HAP),  $\text{C}_6\text{F}_5\text{NO}_2$  and  $\text{C}_6\text{H}_5\text{NO}_2$  are typical of other ECD data. The  $A_1$  values for m-HAP and  $\text{C}_6\text{F}_5\text{NO}_2$  are about equal to the DeBA. Thus the  $E_1$  is approximately zero. Since there is no indication of an excited state in these data, the data reduction with only four parameters is carried out. The m-HAP and



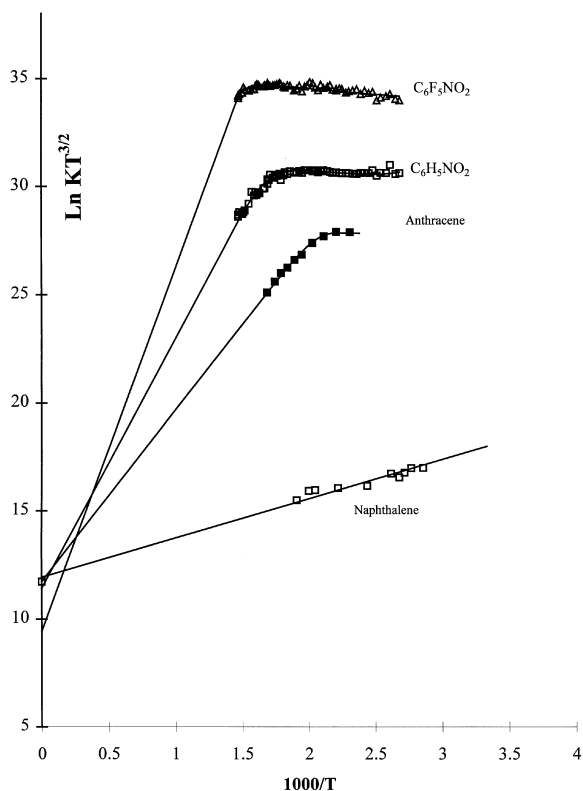


Fig. 5. ECD data as  $\ln KT^{3/2}$  vs.  $1/T$  constant-current data (this work and Ref. [16]).

$C_6H_5NO_2$  have a unit PFR while the PFR for  $C_6F_5NO_2$  is 0.08. The electron affinity of *m*-HAP is  $0.74 \pm 0.04$  eV, comparable to the TCT value for the *ortho* isomer,  $0.85 \pm 0.05$  eV. Based upon the electron affinity of  $0.339 \pm 0.002$  eV for the parent compound, the OH substitution increases the electron affinity by about 0.4 eV.

The data for  $C_6H_5NO_2$  and  $C_6F_5NO_2$  in Fig. 2 have been published previously. The data for  $C_6H_5NO_2$  are representative of about 15 independent ECD determinations. The EA for  $C_6H_5NO_2$  is  $1.00 \pm 0.015$  eV. The PFR ratio and the  $A_1$  value for nitrobenzene have been determined in other experiments [10,18,23]. Thus the ECD temperature dependence of  $C_6H_5NO_2$  can be calculated from literature data. The more extensive constant-current data in Fig. 5 were collected in a series of chromatograms also containing *m*-, *o*-, and *p*- $FC_6H_4NO_2$ . The ECD EA values are more precise than the literature values

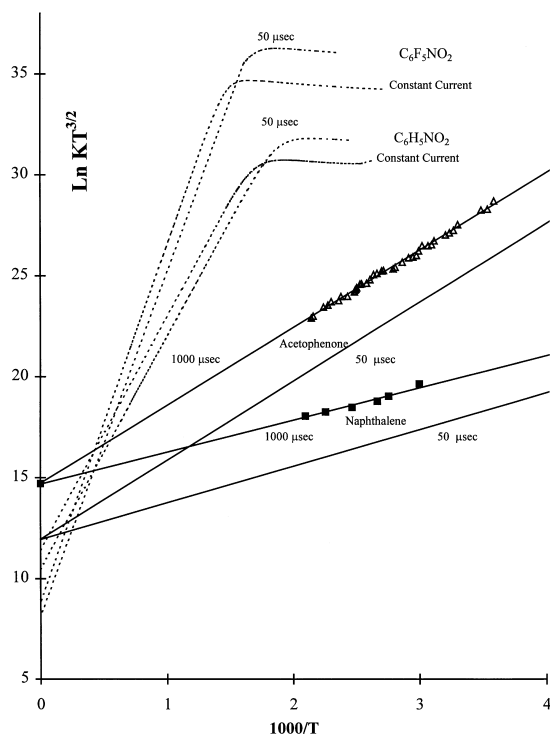


Fig. 6. ECD data as  $\ln KT^{3/2}$  vs.  $1/T$  curves from Figs. 2 and 5 (data at 1000  $\mu$ s, [2]).

due to the extensive ECD data. For example, the  $E_1$  and  $A_1$  values are well defined from the ECD data. There may be a slight upturn in the constant-current ECD data for  $C_6H_5NO_2$  indicating structure. Excited states are expected since the dissociation in the C–N dimension could lead to either the  $NO_2^-$  radical or the aromatic radical anion. In the case of  $C_6H_5NO_2$  the lowest limit leads to  $NO_2^-$  while for  $C_6F_5NO_2$  the opposite is the case. The dissociation limits are separated by about 1 eV so that separations of 0.4–1.0 eV are reasonable.

#### 4.2. Anthracene, pyrene, tetracene, $C_6F_6$ , $C_6F_5Cl$ and $C_6Cl_6$

The electron affinity of anthracene was established from the three sets of ECD data and used to determine the other parameters. The values in Table 1 are the weighted average of the values from the three determinations. The activation energy for the rate constant for attachment to the ground state of anthracene is relatively large,  $0.18 \pm 0.01$  eV. This is

Table 1  
Kinetic parameters for the ECD data

Compound	$\ln [A_1]$	$E_1$ (eV)	$\ln [A_{-1}]$	$E_{-1}$ (eV)	$EA = -E_1 + E_{-1}$ (eV)	$\ln [A_1/A_{-1}]$	PFR
Acetophenone					0.339±0.002	11.74	1
Benzaldehyde					0.457±0.005	11.74	1
Naphthalene					0.140±0.008	11.74	1
<i>m</i> -HO-Acetophenone	35.54±0.20	0.05±0.01	24.30±0.01	0.79±0.04	0.74±0.04	11.24±0.21	0.6
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	32.56±0.03	0.00±0.01	21.03±0.05	1.00±0.02	1.00±0.01	11.54±0.06	1
C <sub>6</sub> F <sub>5</sub> NO <sub>2</sub>	36.54±0.11	0.01±0.01	27.33±0.16	1.52±0.02	1.51±0.02	9.21±0.20	0.08
Anthracene	35.26±0.05	0.18±0.01	23.59±0.15	0.87±0.004	0.69±0.01	11.67±0.19	1
Pyrene	34.01±0.09	0.17±0.01	22.37±0.33	0.79±0.01	0.61±0.01	11.65±0.34	1
Tetracene (gs)	36.15±0.04	0.44±0.03	24.64±0.6	1.50±0.06	1.11±0.05	11.51±0.4	1
Tetracene (xs)	33.15±0.58	0.17±0.03	30.10±0.63	1.03±0.04	0.86±0.05	3.05±0.63	(10 <sup>-4</sup> )
C <sub>6</sub> F <sub>6</sub> (gs)	34.65±0.01	0.04±0.01	26.14±0.01	0.87±0.02	0.86±0.02	8.61±0.01	0.04
C <sub>6</sub> F <sub>6</sub> (xs)	[34.94±0.2]	[0.01±0.01]	22.96±0.27	0.62±0.05	0.61±0.05	11.98±0.5	1
C <sub>6</sub> F <sub>5</sub> Cl (gs)	36.43±0.01	0.39±0.01	25.62±0.1	1.35±0.02	0.96±0.03	11.80±0.1	1
C <sub>6</sub> F <sub>5</sub> Cl (xs)	36.43±0.01	[0.15]	27.98±0.12	0.96±0.05	0.82±0.05	8.46±0.2	0.04
C <sub>6</sub> Cl <sub>6</sub> (gs)	34.30±0.36	0.02±0.02	28.26±0.28	1.19±0.01	1.17±0.02	6.04±0.46	6·10 <sup>-3</sup>
C <sub>6</sub> Cl <sub>6</sub> (xs)	[35.63]	[0.02]	24.21±0.88	0.71±0.02	0.71±0.02	11.79±0.88	1

The parameters in parentheses have been assumed.

Table 2  
Electron affinities of aromatic hydrocarbons (eV)

Compounds	ECD-MT <sup>a</sup>	PES <sup>b</sup>	TCT <sup>b</sup>	EA ( $E_{1/2}$ ) <sup>c</sup>	$M/3$ <sup>d</sup>	PFR
Benzene				-0.72±0.05	-0.74	
Naphthalene	0.14±0.01			0.14±0.05	0.15	1
Anthracene (xs)		0.53±0.005				
Anthracene	0.69±0.01	0.68±0.02	0.60±0.1	0.66±0.03	0.65	1
Tetracene (xs)	0.85±0.02				0.05	
Tetracene	1.11±0.05		1.04±0.1	1.11±0.05	1.04	1
Pentacene			1.35±0.1	1.35±0.05	1.34	
Phenanthrene	0.31±0.01			0.31±0.05	0.35	1
Triphenylene	0.29±0.01			0.23±0.05	0.28	1
Benzenanthracene	0.73±0.01			0.70±0.04	0.76	1
Dibenz[ <i>a,c</i> ]anthracene <sup>e</sup>	0.68±0.10			0.64±0.05	0.65	0.1
Chrysene	0.42±0.04			0.41±0.04	0.42	0.5
Benz[ <i>c</i> ]phenanthrene	0.59±0.01			0.58±0.05	0.61	1
Picene	0.54±0.01			0.57±0.05	0.57	1
Dibenz[ <i>a,h</i> ]anthracene	0.69±0.05			0.72±0.05	0.72	0.1
Dibenz[ <i>a,j</i> ]anthracene	0.68±0.05			0.66±0.05	0.68	0.1
Perylene <sup>e</sup>	1.00±0.10	0.98±0.005	0.98±0.1	1.00±0.05	1.00	1
Pyrene	0.61±0.01			0.58±0.05	0.59	1
Benz[ <i>e</i> ]pyrene	0.54±0.05			0.57±0.05	0.57	1
Benz[ <i>a</i> ]pyrene	0.78±0.02		0.75±0.1	0.80±0.05	0.80	0.05
Fluoranthene	0.78±0.02			0.83±0.05	0.81	0.1
Biphenyl	0.13±0.02			0.14±0.05	0.12	1
Styrene	0.10±0.05			0.10±0.05	0.10	1

<sup>a</sup> The experimental values are obtained from ECD measurements in this article. Data Refs. [2,21–23].

<sup>b</sup> TCT, Ref. [13]; PES, Refs. [15,25].

<sup>c</sup> The half wave reduction potential values were obtained by using  $EA = C + E_{1/2}$ . The  $E_{1/2}$  values are averages of the values tabulated in Ref. [30] by N. Kozaneki. MS project UHCL 1994 see Refs. [3,6,17,18,21–23] for the procedures.

<sup>d</sup> MINDO/3, Multiconfiguration configuration interaction M/3 MCCI CURES EC Ref. [7].

<sup>e</sup> Single point data from Ref. [24].

Table 3  
ECD electron affinities (eV)

	Multiple point	Single point <sup>c</sup>
Anthracene <sup>a</sup>	0.69±0.01	Reference compound
Benanthracene <sup>a</sup>	0.73±0.01	0.73±0.03
Pyrene <sup>a</sup>	0.61±0.01	0.65±0.03
Benz[ <i>c</i> ]phenanthrene <sup>a</sup>	0.59±0.01	0.59±0.03
Phenanthrene <sup>b</sup>	0.308±0.008	Reference compound
Chrysene <sup>c</sup>	0.419±0.036	0.44±0.04
Triphenylene <sup>b</sup>	0.285±0.008	0.26±0.03
Tetracene (gs)	1.11±0.05	Reference compound
Perylene <sup>d</sup>		1.0±0.1
Dibenz[ <i>a,h</i> ]anthracene	0.69±0.05	Reference compound
Dibenz[ <i>a,c</i> ]anthracene <sup>d</sup>		0.68±0.1

<sup>a</sup> Non-linear least squares.

<sup>b</sup> Fixed intercept – this is chosen unless the variable intercept value is higher as with chrysene, Ref. [2].

<sup>c</sup> Determined intercept and determined error, Ref. [2].

<sup>d</sup> Data taken from Ref. [24].

<sup>e</sup> The nominal error in the revised single temperature values is 30 meV, the average deviation between the current best and the revised values is 25 meV.

in contrast to the earlier single state activation energy which was assumed to be about zero and gave an  $A_1$  value a factor of 30 lower than the DeBA. The present values of  $A_1$  and  $E_1$  are consistent with values obtained using an independent procedure [29]. The partition function ratio for the ground state is about one. The only indication of an excited state is a slight upward turn of the data at low temperatures in Fig. 1. No obvious structure is observed in the other ECD data. The excited state electron affinity was included in the model to obtain the overall temperature dependence and to determine the EA. The electron affinity is  $0.69\pm 0.01$  eV. The improved precision is due to the use of the multiple determinations, especially the higher temperature constant-current data. The parameters and data reported for pyrene are similar to those for anthracene except that only one other set of temperature data is combined in the data analysis procedure.

The ECD EA in the literature for tetracene is for an excited state. These data are quite different from the others because the value of  $A_{1x}$  is less than DeBA. This is partially due to the lower  $Z_{ecs}$ . The

two literature points were obtained with a fixed frequency (reaction time of 10–20  $\mu$ s) detector, in 1962 (lower temperature) and with a constant-current detector (higher temperature) in the 1980s [4,24]. The earlier value is lower than that for anthracene, consistent with the multi temperature data reported by Lyons [14]. The more recent data point is about a factor of three lower than that for carbon tetrachloride, a maximum capture species [24]. This can be rationalized by assuming a lower stabilization factor and a consequently lower intercept for the excited state. This could be due to the lower pressure in the older ECD systems. The constant-current experiments were carried out as a part of studies using oxygen as a dopant which could affect the  $Z_{ecs}$ . The fixed frequency point is for the excited state while the more recent point is for the ground state. This is illustrated by drawing a line with the proper slope through the respective experimental data points in Fig. 1. The multiple temperature data indicated a change in slope at the higher temperatures [14]. This was unexplained but can now be considered as structure indicating a higher electron affinity for the ground state. The partition function ratio is about  $10^{-4}$  for the excited state, approximately the same as for the ground state of  $CS_2$  [5]. It is the lowest PFR that has been observed. The ground state EA of tetracene is  $1.11\pm 0.05$  eV reflecting the half wave reduction potential value as it should.

The ground state ECD electron affinity for  $C_6F_6$  has been determined in independent ECD and PES experiments. Only one set of data out of multiple ECD determinations are shown in Fig. 3. The rate constant for thermal electron attachment to  $C_6F_6$  has been determined to be  $1\cdot 10^{-7}$  ml/molecule s or  $6\cdot 10^{13}$  l/mol s at room temperature [8]. This value and its error are used in the least-squares data reduction procedure. Since this is only slightly lower than the value for  $CCl_4$  which has a zero activation energy, the values of  $E_1$  and  $E_{1x}$  for  $C_6F_6$  can be assumed to be small. When the single state model is used,  $A_1$  is low,  $E_1$  is negative and  $k_1$  at 298 K is too large. This is an indication of multiple states. A ground state PFR value of 0.1 has been measured by negative ion mass spectrometry [10]. Since the excited state electron affinity has also been measured, the temperature dependence of the ECD response can be calculated from the literature data.

The ECD data gives more precise values for the PFR and activation energies.

The electron affinities of  $C_6Cl_6$  and  $C_6F_5Cl$  have been measured with the TCT technique [11,19]. The ground state ECD value of  $C_6Cl_6$  is  $1.17 \pm 0.02$  eV. The AM1(0033) value is 1.18 eV. The excited state EA of  $0.72 \pm 0.05$  eV has not been reported previously. The separation between the states is about 0.4 eV which is slightly larger than for  $C_6F_6$ . The data for  $C_6F_5Cl$  clearly shows structure indicative of two states. The electron affinity of the lower state ( $0.82 \pm 0.02$  eV) agrees with the value obtained from TCT measurements. Thus the higher electron affinity ( $0.96 \pm 0.02$  eV) is attributed to the ground state. The PM3(0012) value is 0.94 eV. The separation is slightly less than that for  $C_6F_6$ . Parent negative ion of all three halobenzenes is observed at both 373 K and 525 K in negative ion mass spectrometry [28].

#### 4.3. The determination of electron affinities from ECD temperature dependence

Based on the above data analysis a procedure for determining electron affinities from ECD data for molecules which only form a molecular anion can be described. If it is assumed that no dissociative capture occurs, such as in the case of the aromatic hydrocarbons, then the determination of the electron affinity merely requires that the electron-capture detector response be measured as a function of temperature and that it be established that the data is in the equilibrium region (previously designated the  $\alpha$  region). If there are sufficient data in the equilibrium region then the electron affinity can be obtained from the slope of the  $\ln KT^{3/2}$  vs.  $1000/T$  plot by simply multiplying by  $R$  as in the case of acetophenone, benzaldehyde and naphthalene. If there are not sufficient data in the equilibrium region, then a “fixed” intercept can be assumed and the limiting slope will give a lower limit to the electron affinity. In some cases, there are sufficient data in the equilibrium region, but the intercept is lower. Previously, it was assumed that the “fixed” intercept value was more precise and should be used as the appropriate ECD EA. Based on the current knowledge of the PFR values, it is clear that the lower intercepts and the higher EA values are more appropriate. The fixed upper limit intercept EA and its

precision is then recognized as only a lower limit to the electron affinity.

In the earlier data reduction procedure the data in the linear region is selected and the EA determined by fitting the data to a straight line. With modern computers, it is possible to rapidly carry out rigorous non-linear least-squares operations. For compounds with data in more than one region, a more precise electron affinity can be obtained by using all of the data. The use of combined data to obtain a self consistent set of values is now also possible as in the case of the two nitrobenzenes and anthracene.

A procedure for establishing the most appropriate published ECD EA can now be given. If the determined intercept is greater than the fixed intercept value, use the determined intercept value and the corresponding errors. If the determined intercept value is lower than the fixed intercept value, assume that there are insufficient data in the equilibrium region and use the “fixed” intercept value as a lower limit to the EA. The precision of the value refers to the precision of the lower limit. An upper limit to the EA can be obtained if the PFR is set equal to  $10^{-4}$ . If a nominal PFR value of 0.05 is assumed, then a possibly more accurate but less precise value of the electron affinity can be obtained. This is based on the fact that for every order of magnitude change in the PFR value, there is about a 0.1 eV change in the electron affinity at 500 K. Using this procedure the single temperature excited state electron affinity of tetracene is  $0.8 \pm 0.15$  eV. The ground state electron affinity from the constant-current point is  $1.2 \pm 0.15$  eV. If there are absolutely no data in the equilibrium region, then this range will apply to the lower limit for the EA. For example in the case of the pesticides, the lower limit to the electron affinity would be  $1.5 \pm 0.15$  eV. The values can be verified by half wave reduction potentials or theoretical calculations. Finally, if there are sufficient data in the equilibrium region and in the plateau region, use a four parameter non-linear least-square procedure to obtain the kinetic parameters and the EA.

The procedure described above was used to obtain the electron affinities for the molecules in Table 2. Note that only a single EA value is given with the appropriate errors. Although the original ECD data were only obtained at a few temperatures, a concentration dependence was carried out at each tem-

perature so that multiple points were obtained. This is in contrast to the recent ECD data shown in Figs. 3–6 and the acetophenone data where the temperature of the detector was dropped continuously and only a single injection made at each temperature. In these cases, the temperature must be lowered slowly so that the temperature measurements are accurate. Consequently, it is best to make as many injections as can be eluted in the time necessary to lower the temperature so that the curves can be better defined.

It is now possible to describe a procedure for obtaining electron affinities for other molecules using modern detectors which normally operate at constant-current or are non-radioactive detectors. The first step in the procedure should be the calibration of the detector using a maximum capture, temperature independent species such as  $\text{CCl}_4$ . This will establish a value of  $A_D$  for the specific detector and electron energy. A large value of  $A_D$  or low response might indicate a contaminated detector or hyperthermal electrons. The next step should be the determination of the intercept for a compound with a known PFR value such as naphthalene, acetophenone or benzaldehyde. This will establish a nominal value of the maximum intercept. For these compounds, it should be about 11.74. If these results are attained, data for other compounds can be obtained and the data analyzed as described above. It is especially important to note structure in the data. It is also important to verify the electron affinities by either half wave reduction potentials or theoretical calculations.

The kinetic model can also be used to predict the temperature dependence of molecules if the electron affinities are estimated by some other technique. If the electron affinity is greater than about 1.5 eV and the determination of the electron-capture response at a single temperature indicates that the PFR and  $Z_{\text{ecs}}$  are unity then the temperature dependence should be like that for  $\text{C}_6\text{F}_5\text{NO}_2$ . Examples are the dinitrobenzenes. For molecules with electron affinities in the range 0.7–1.5 eV, the response should decline at higher temperatures as in the case of nitrobenzene, pyrene, or *m*-hydroxyacetophenone. For these compounds, the maximum response will be at the lowest temperature and careful temperature control is essential for analytical determinations. For molecules with electron affinities less than 0.7 eV, the response will

decline with increasing temperature over the complete range of temperatures and the absolute response will be lower for compounds with lower electron affinities. Thus for different molecules, the ECD response for a fixed temperature can vary over five to six-orders of magnitude depending upon the electron affinity of the molecule.

If it is suspected that multiple states or dissociative electron-capture is possible, then structure may be observed in the ECD temperature dependence. In the event that dissociative electron-capture does not take place, the temperature dependence could be like that for tetracene or  $\text{C}_6\text{F}_5\text{Cl}$ . However, if conditions could be altered to stabilize the negative ion to the ground state, then the effect of the multiple states can be minimized. One possibility would be to use higher pressures in the ECD. Another would be to use alternate dopants. The use of higher pressures in the ECD might have an additional benefit since it has been demonstrated that the intrinsic recombination coefficients for electrons and positive ions decrease at higher pressures. Thus the value of  $A_D$  would be lower and the ECD sensitivity higher.

## 5. Conclusions

The effect of multiple states on the ECD temperature dependence of anthracene, tetracene and  $\text{C}_6\text{F}_6$ , can be calculated using electron affinities in the literature. The ECD electron affinity of *m*-hydroxyacetophenone,  $\text{C}_8\text{H}_8\text{O}_2$  is reported. Excited state and ground state electron affinities are reported for  $\text{C}_6\text{Cl}_6$ , and  $\text{C}_6\text{F}_5\text{Cl}$  based on the observation of structure in the ECD data. The constant-current ECD data for nitrobenzene indicates a slight upturn at lower temperatures which might indicate an excited state. Approximate values of the partition function ratios are obtained. The majority of these are about 1 but the value for the excited state of tetracene is about  $10^{-4}$ . This is one of the lowest values measured to date and defines a nominal range for PFR values.

A procedure for obtaining electron affinities from ECD data at multiple temperatures is given. Thus for the values in the literature, the fixed intercept value should be used if it is larger than the determined intercept value. If the intercept is significantly lower

than the nominal value, then the determined intercept value should be used since this indicates a lower PFR. Finally if data are available in at least two regions, then the non-linear least-square procedure should be used to determine the electron affinity. The electron affinities of a number of aromatic hydrocarbons are reported using this data reduction procedure.

The only instrumental parameters which are determined are the values of  $k_D$  and  $k_N$ . The other parameters are determined from the temperature dependence. Thus collection modes and cleanliness influence the temperature range and hence the accuracy of the other parameters. The constant-current mode and the lower  $t_p$  modes offer a larger temperature range. The only precautions which must be observed are the energy of the electrons and the collection of the data in the linear region.

## Acknowledgements

The authors thank the Robert A. Welch Foundation, Grant E-0095, and the UH-Clear Lake, Grant BC-0022 for support of this work.

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