

Review

# Molecular electron affinities and the calculation of the temperature dependence of the electron-capture detector response

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## Abstract

The use of the electron-capture detector (ECD) to measure molecular electron affinities and kinetic parameters for reactions of thermal electrons is reviewed. The advances of the past decade are emphasized and include the multistate electron-capture detector model and the use of semi-empirical self-consistent field quantum mechanical calculations and half wave reduction potential values to support gas phase experimental results. A procedure for the evaluation of the adiabatic electron affinities of the main group elements and the homonuclear diatomic molecules is presented. Potential excited states are identified for the magnetron (MGN) values for quinones, thermal charge transfer (TCT) values for CS<sub>2</sub>, C<sub>6</sub>F<sub>6</sub>, SF<sub>6</sub> and photoelectron spectroscopy (PES) values for O<sub>2</sub>, NO, nitromethane, and the nucleic acids. Literature electron affinities are then evaluated. The temperature dependence of the electron-capture detector can be calculated using values for kinetic rate constants and electron affinities to optimize response and temperature sensitivity in analytical procedures. The temperature dependence for adenine, guanine, thymine and cytosine are predicted for reactions with thermal electrons. Using the recent advances, the new adiabatic electron affinities are: all in electron volts (eV), 4-F-benzaldehyde (0.57 ± 0.05) and acetophenones (APs) 4-F-AP (0.52 ± 0.05); 2-CF<sub>3</sub>-AP (0.79 ± 0.05); 3-CF<sub>3</sub>-AP (0.79 ± 0.05); 4-CF<sub>3</sub>-AP (0.89 ± 0.05); 3-Cl-AP (0.67 ± 0.05); and 4-Cl-AP (0.64 ± 0.05). The adiabatic electron affinities of chloro and fluorobenzenes range from 0.17 to 1.15 eV and 0.13 to 0.86 eV.

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## 1. Introduction

The electron-capture detector (ECD) is the most sensitive and selective of the traditional gas chromatographic detectors. Absolute electron affinities,  $E_a$  and kinetic parameters for thermal electron attachment, detachment and dissociation reactions can be determined from the temperature dependence of the molar response of the ECD and fundamental constants. The adiabatic electron affinity ( $AE_a$ ) of a molecule is the difference in the energy of the neutral molecule and the negative ion when both are in their most stable states. The excited state  $E_a$  is the difference in energy between the neutral in its most stable state and the ion in an excited electronic state. The lower limit to the  $AE_a$  is zero since the most stable state of any anion is the electron loosely bound by electrostatic forces, including dipole or quadrupole attractions. The valence state  $E_a$  can be negative.

The general methods of measuring  $E_a$  are the equilibrium, the beam, and the photon methods. The electron-capture detector, magnetron (MGN), and swarm equilibrium methods are based on the reaction of thermal electrons with a molecule and provide absolute  $E_a$ . The equilibrium thermal charge transfer (TCT) method based on the electron transfer reactions of molecules and anions gives relative  $E_a$ . The thresholds for reactions with electron or alkali metal beam (AMB) must be combined with bond dissociation energies or ionization potentials to obtain  $E_a$ . The photodetachment (PD), photoelectron spectroscopy (PES), and photoabsorption methods require the photon energies to obtain  $E_a$  from measured thresholds. About 15 years ago, the use of the ECD to measure fundamental kinetic and thermodynamic properties for thermal electron attachment reactions was reviewed [1]. The MGN [2]; TCT [3]; and AMB [4] studies have been reviewed. The photon methods and the  $E_a$  for about 1000 species obtained from the photon methods have been summarized. The majority of these species are not large organic molecules [5].

The  $AE_a$  and bond dissociation energies of molecules can be calculated using a quantum mechanical semi-empirical multiconfiguration configuration interaction (MCCI) procedure, CURES-EC. The acronym stands for "Configuration interaction or Unrestricted orbitals to Relate Experimental quantities to Self-consistent field values by estimating Electron Correlation." It gives a systematic method of varying the number of MCCI orbitals to minimize the difference between the experimental and theoretical values to cure the electron correlation problem. Using the charge densities from these calculations, improved values of the  $E_a$  can be obtained from half wave reduction potentials in aprotic solvents. During the past decade, the  $AE_a$  of adenine, guanine, cytosine, uracil and thymine (AGCUT) have been determined from reduction potentials and verified by CURES-EC. These  $AE_a$  and calculations have then been used to identify excited states of AGCUT in PES [6–13].

This review will systematically identify the  $AE_a$  of the main group atoms and homonuclear diatomic molecules;

summarize the assignment of  $AE_a$  to hydrocarbons; extend the method to other molecular  $E_a$ ; present improved  $AE_a$  and  $D(C-Cl)$  for 3- and 4-Cl-acetophenone and  $AE_a$  of F and Cl-benzenes,  $CF_3$ -acetophenones, F-acetophenones and F-benzaldehydes; establish substitution effects based upon the experimental data; review the measurement of the  $E_a$  of multichlorinated compounds and AGCUT and calculate and contrast their ECD temperature dependence based upon fundamental properties. The evaluation of the  $E_a$  of the main group elements and homonuclear diatomic molecules will serve as a prototype for the assignments of molecular electron affinities to the ground state.

## 2. Evaluation procedure for electron affinities of atoms and homonuclear diatomic molecules

The accuracy of a value is determined by systematic uncertainties. According to Deming "A systematic uncertainty or bias is never discovered, nor has any meaning, unless two or more distinct methods of observation are compared." [14] A list of about 1500 electron affinities including about 500 values for atoms and molecules are tabulated on the internet, without evaluation at NIST (<http://webbook.nist.gov/chemistry>) [15,16]. A NIST search for molecules containing specific elements returns a sequential list of the first entry in the complete list. The complete listing must be consulted to find all the precise values to be averaged or the largest precise value to be assigned to the  $AE_a$ . The majority of the experimental values determined by different methods in the NIST table agree within the random uncertainty. The "best" value is the weighted average of these values. The weighting is important because the uncertainty in the weighted average will never be larger than the smallest uncertainty. In some cases, values differ by more than the uncertainty, for example the MGN values for quinones; AMB values for  $SF_6$  and  $CS_2$ ; TCT values for  $C_6F_6$  and  $CS_2$ , and ECD and PES values for  $CS_2$ ,  $NO$ , and  $O_2$ . Since multiple states have been observed in the same ECD experiment for these compounds, it is clear that any method can give excited state  $E_a$ .

It was once believed that there was only one stable valence state anion. However, more than one valence state  $E_a$  has been measured for even the simplest species. Therefore, it is always necessary to identify the anion state. The electron affinities of atoms are evaluated as follows. If there are two or more values determined by different techniques that agree within the random uncertainty, the average value is the "accurate" value and the precision will be determined by the weighted average of the random uncertainties. In the event that the random uncertainty in a value is much smaller than the others, the average and random uncertainty will be dominated by this value. When a value is significantly lower than the average, it could be for an excited state.

The atomic electron affinities presented in Fig. 1 are plotted against atomic number in Fig. 2. The experimental val-

The Electron Affinities of the Elements (Ea(X) and  
Homonuclear Diatomic Molecules Ea(X<sub>2</sub>) (eV)  
Bond Dissociation Energies BDE (eV)

O	I	II	Ib	IIb	III	IV	V	VI	VII
	1 H 0.7542 [0+] 4.51			Element Ea(X) eV Ea(X <sub>2</sub> ) eV BDE (eV)					
2 He [0+] [0+]	3 Li 0.6180 0.509 1.13	4 Be [0+]	Element Ea(X) eV Ea(X <sub>2</sub> ) eV BDE (eV)		5 B 0.2797 1.30 3.08	6 C 1.2621 3.273 6.3	7 N [0+] [0+] 9.8	8 O 1.4611 1.07 5.16	9 F 3.4012 3.05 1.69
10 Ne [0+] [0+]	11 Na 0.5479 0.430 0.77	12 Mg [0+]	Element Ea(X) eV Ea(X <sub>2</sub> ) eV BDE (eV)		13 Al 0.4328 1.46 1.93	14 Si 1.3895 2.200 3.4	15 P 0.7465(3) 0.61 5.07	16 S 2.0771 1.69 4.42	17 Cl 3.6127 2.45 2.56
18 Ar [0+] [0+]	19 K 0.5015 0.497 0.6	20 Ca 0.0245	29 Cu 1.2358 2.01 1.83	30 Zn [0+]	31 Ga 0.43(3) 1.6 1.43	32 Ge 1.2327 2.035 2.73	33 As 0.814(8) 0.739 3.96	34 Se 2.0207 1.94 3.45	35 Br 3.3636 2.57 1.99
36 Kr [0+] [0+]	37 Rb 0.4859 0.498 0.47	38 Sr 0.0521	47 Ag 1.3045 1.10 1.7	48 Cd [0+]	49 In 0.404(9) 1.27 1.04	50 Sn 1.1121 1.962 2.03	51 Sb 1.0474 3.1	52 Te 1.9709 1.92 2.9	53 I 3.0590 2.524 1.56
54 Xe [0+] [0+]	55 Cs 0.4716 0.469 0.47	56 Ba 0.1446	79 Au 2.3086 1.94 2.34	80 Hg [0+]	81 Tl 0.38(1) 0.95 0.66	82 Pb 1.10(5) 1.366 0.91	83 Bi 0.9424 1.271 2.07	84 Po [1.9(3)]	85 At [2.8(3)]
86 Rn [0+] [0+]	87 Fr 0.491(5)	88 Ra 0.17							

21 Sc 0.19 0.89 1.65(22)	22 Ti 0.08 0.63 1.54(18)	23 V 0.53 0.54 2.753(1)	24 Cr 0.6758 0.51 1.44(5)	25 Mn [0+] 0.68 0.8	26 Fe 0.151(3) 0.9 1.15(9)	27 Co 0.663 1.11 1.69(26)	28 Ni 1.1572 0.95 2.068(1)
39 Y 0.31	40 Zr 0.43	41 Nb 0.89(3)	42 Mo 0.747	43 Tc 0.6(2)	44 Ru 1.046	45 Rh 1.1429	46 Pd 0.5621
57 La 0.47(2)	72 Hf 0.1	73 Ta 0.32(1)	74 W 0.82	75 Re 0.2(2)	76 Os 1.0778	77 Ir 1.5644	78 Pt 2.1251
58 Ce 0.96(3)	59 Pr 0.96(2)	60 Nd 0.05+	61 0+	62-68 0.1+	69 Tm 1.03(3)	70 Yb 0.01+	71 Lu 0.34(1)
89 Ac 0+	90 Th 0.05+	91 Pa 0.05+	92 U 0.05+	93 Np 0+	94 Pu 0.05+		

Fig. 1. Adiabatic electron affinities of atoms and electron affinities and bond dissociation energies of homonuclear diatomic molecules, eV. The values in parentheses are the uncertainty in the last figure. The other values are given with the proper number of significant figures. The 0+ values are a small positive value. The data are taken from [15,23,25].

ues are given with the random error in the last figure in parentheses or with correct significant figures to 0.1 meV, which is accurate and precise enough for chemical purposes. The valence state  $E_a$  of the rare gases and nitrogen are negative. The limiting  $AE_a$  due to long-range interactions are given as “0+.” PES and PD have been used to determine the  $AE_a$  of the main group elements. Some of the photodetachment values have uncertainties in the parts per million

and are the largest precisely measured values. Those of C, H, O, S, Pb, the alkali metals, coinage metal, and halogens halogens, among others have been determined by other techniques [5,15–25]. The ground state electron affinity for lead is assigned to  $1.1 \pm 0.05$  eV determined by photodetachment and electron transfer techniques [15–22]. This agrees with atomic and homonuclear diatomic periodic trends. A lower value,  $0.364 \pm 0.008$  eV is assigned to an excited state

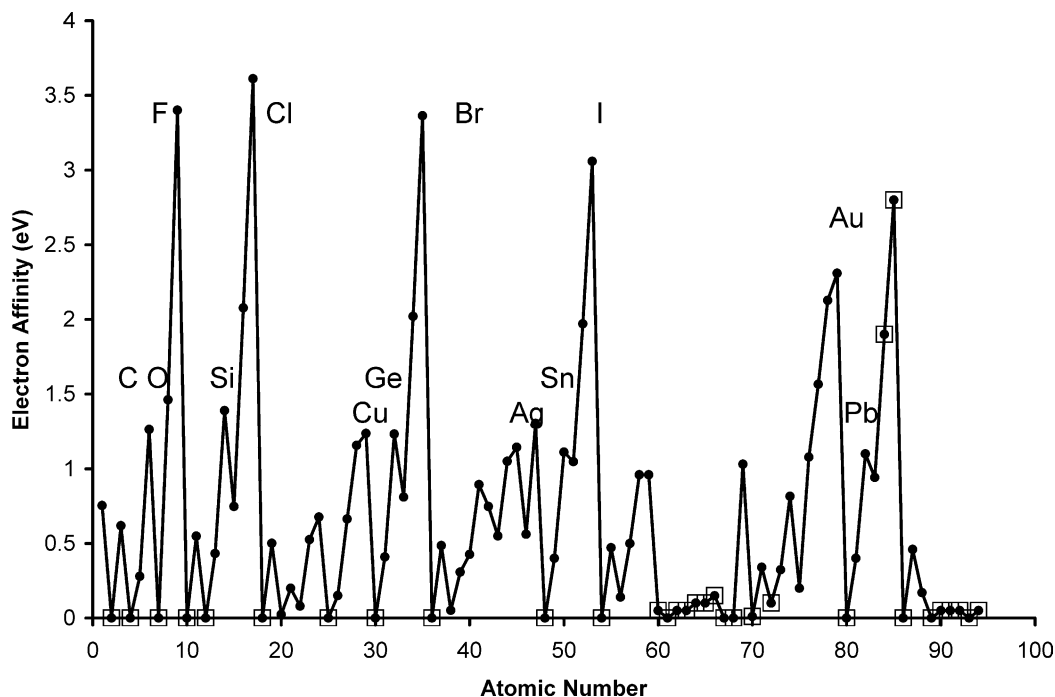


Fig. 2. Electron affinities vs. atomic number. The solid circles are experimental values. The squares are lower limits. The values are found in Fig. 1.

[23–25]. There have been reported values of atomic  $E_a$  which are larger than the selected values, for example, for In and Tl. For In, the 1998 laser PES value is  $0.4040 \pm 0.009$  eV while the 1985 PD value is  $0.3 \pm 0.2$  eV and the 1980 electron impact value is  $0.85 \pm 0.15$  eV. From the original electron impact data, the random uncertainty is at least  $\pm 0.3$  eV. The weighted average ( $A = \sum[a/s^2]/N$ ;  $N = \sum[1/s^2]$ ;  $s^2 = 1/N$ ) is given by  $A = [0.4040/(0.009)^2 + 0.3/(0.2)^2 + 0.85/(0.3)^2]/(N)$  where  $N = 1/(0.009)^2 + 1/(0.2)^2 + 1/(0.3)^2$ .  $A = 0.4042 \pm 0.009$  or 0.404(9). Thus the  $AE_a$  of the main group elements are the largest precisely measured value. The regular patterns shown in Fig. 2 support these assignments. Especially significant is the constancy of the  $E_a$  for C, Si, Ge, Sn and Pb. Values for many of the transition elements have only been determined once so that it is only assumed that the  $E_a$  is for the ground state.

The acquisition of accurate and precise  $E_a$  for molecules is the ultimate goal for experimental and theoretical studies. However, even in the case of the homonuclear diatomic molecules, the majority of the  $E_a$  have only been determined by a single method. Exceptions are the halogens,  $S_2$ ,  $O_2$  and  $C_2$ . The  $E_a$  for the groups IA and B and IIIA–VIIA homonuclear diatomic molecules are shown in Fig. 1 below the values for the atoms. The third entry in the block is the bond dissociation energy of the neutral diatomic molecule. The values for the rare gases are 0+ because they are only due to polarization attractions of the Van Der Waal's dimers. Bound excited states for the halogens have been characterized. The measured  $E_a$  of the main group homonuclear diatomic molecules are consistent with simple molecular orbital theory predictions of the relative bond

order,  $D_e(X_2^-)/D_e(X_2)$  = the net number of bonding electron in the ion divided by that of the neutral as shown in Fig. 3. For the groups I and VII elements, there are two net bonding electrons in the neutral, and one in the anion such that the predicted value for groups I and VII is 0.5. However, the experimental values range from 0.53 to about 1.0. The predicted values for groups III and IV are 1.5 and 1.25 but most of the experimental values also are larger. The change in the bond dissociation energy  $D_e(X_2) - D_e(X_2^-)$  is approximately given by  $E_a(X_2) - E_a(X)$  and is obtained by subtracting the entries in Fig. 1. The largest increase in the dissociation energy is  $3.273 - 1.261 = 2.012$  eV for  $C_2(-)$  while the largest decrease in the dissociation energy is  $2.45 - 3.6127 = -1.2$  eV for  $Cl_2(-)$ . The relative bond order is given by  $1 + \{[D_e(X_2) - D_e(X_2^-)]/D_e(X_2)\} = 1 + \{[E_a(X_2) - E_a(X)]/D_e(X_2)\}$ . For  $C_2$  this is  $1 + 2/6.3 = 1.32$  while for  $Cl_2$  this is  $1 - 1.2/2.56 = 0.53$ . For Pb, this is  $1 + 0.27/0.91 = 1.30$  for  $AE_a$  1.10(5) but it is  $1 + 1/0.9 = 2.11$  for the excited state value of  $0.364 \pm 0.008$  eV. This is larger than any other observed value, supporting the assignment to an excited state. The value for all of the rare gases is one. The values for the groups IA and VIA elements approach one as you go down the table while the values for the groups IIIA and IVA elements are all above unity and generally increase down the table. The group VA elements go from less than one to greater than one from P to Bi. These trends can be easily observed in Fig. 3. The smooth changes across and down the periodic table support the experimental values of the  $AE_a$  of the main group elements and are the major support for the assignment of the experimental  $E_a$  to the  $AE_a$  of the homonuclear diatomic molecules [26,27].

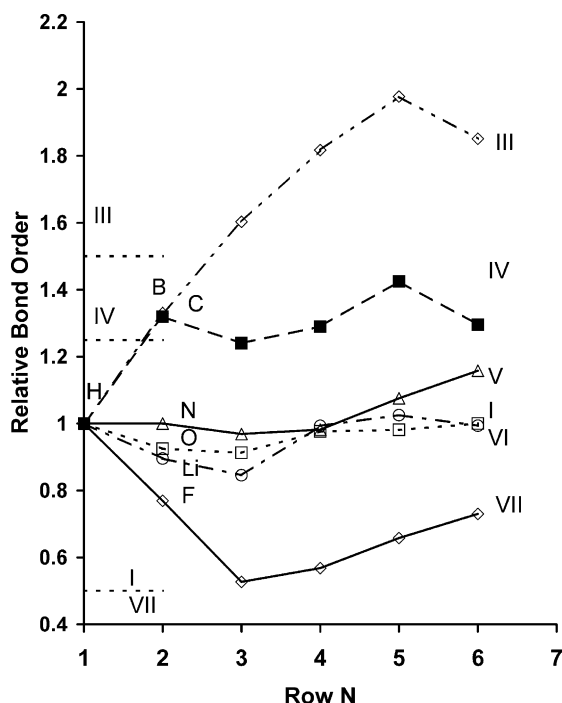
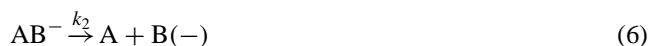
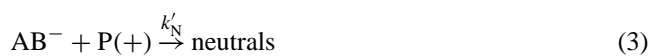


Fig. 3. Relative bond order for the anions of the homonuclear diatomic molecules versus row in the periodic table. This is an update and extension of a figure published in [27].

### 3. The kinetic model of the electron-capture detector and negative ionization mass spectrometer

This review is based on the use of radioactive sources in the ECD but the same kinetic model applies to the pulsed discharge non-radioactive ECD. The development of this type of ionization source has been recently reviewed [28]. The atmospheric pressure and methane chemical ionization negative ionization mass spectrometer (NIMS) sources are analogous to the ECD when thermal electrons are the reactants [28–45]. The reactions in the ECD and in NIMS are electron attachment and detachment, unimolecular dissociative electron attachment and sequential dissociation. These electron molecule reactions are combined with a constant source of electrons, for example from a radioactive foil or discharge and the loss of electrons and ions by recombination in a pseudo-unimolecular process to define the kinetic model. When the standard kinetic expressions are written for these reactions and steady state applied to the negative ions and electrons, the expression for the ECD response can be obtained.



$$K = \frac{k_1(k_N + k_2)}{2(k_{-1} + k_N + k_2)k_D} \quad (7)$$

Some of the rate constants may be small due to energetic considerations. The original model considered only electron attachment to a single negative ion state. The general equation for  $i = 1$  to  $n$  states is:

$$K = \sum_{i=1}^n \frac{(k_{1i})(k_N + k_{2i})}{2(k_D)(k_{-1i} + k_N + k_{2i})} \quad (8)$$

the  $i = 1$  state is the ground state and the rate constants designated as  $k_{1gs}$ ,  $k_{2gs}$ , and  $k_{-1gs}$ . The value of  $k_1$  can refer to either direct dissociation or non-dissociative capture.

Four regions have been observed in the nominal temperature range accessible to NIMS and ECD used as chromatographic detectors. These have been defined based on the relative values of the rate constants. From low (298 K) to high temperatures (600 K), the regions are:

- (1) the  $\beta$  region, where  $(k_N \gg k_{-1} + k_2)$  and  $K = k_1/2k_D$ ;
- (2) the  $\alpha$  region, where  $(k_{-1} \gg k_N + k_2)$  and  $K = [k_N/2k_D][k_1/k_{-1}]$ ;
- (3) the  $\gamma$  region, where  $(k_2 \gg k_N)$ ,  $(k_{-1} \gg k_2)$  and  $K = [k_1k_2/2k_Dk_{-1}]$ ;
- (4) the  $\delta$  region where  $(k_2 \gg k_{-1} + k_N)$  and  $K = k_1/2k_D$ .

Using these approximations, and the single state expression of Eq. (8), the fundamental kinetic and thermodynamic properties of the thermal electron reactions can be obtained from ECD or NIMS data. In the  $\alpha$  region the molecular electron affinity,  $E_a$  and partition function ratios,  $Q_{an}$  can be obtained. In the  $\beta$  region and  $\delta$  region the  $A_1$  and  $E_1$  values can be obtained and in the  $\delta$  region the values of  $A_2$  and  $E_2$  can be obtained. Often temperatures accessible to the ECD give data that overlap these regions so that non-linear least squares procedures must be used to obtain the parameters. From Eq. (8) and the kinetic expressions an equation for least squares analysis can be obtained:

$$k_N = A_N = \text{constant for a given system}$$

$$k_D = A_D = \text{constant for a given system}$$

$$k_1 = A_1 T^{-1/2} \exp\left(\frac{-E_1}{RT}\right)$$

$$k_{-1} = A_{-1} T \exp\left(\frac{-E_{-1}}{RT}\right)$$

and

$$k_2 = A_2 T \exp\left(\frac{-E_2}{RT}\right).$$

In the case of a single state, there are six parameters, two each for the three rate constants  $k_1$ ,  $k_{-1}$ , and  $k_2$ . The least squares equation is:

$$K = k_1(A_N + A_2 T \exp(-E_2/RT)) / [2A_D(A_N + A_{-1} T \exp(-E_{-1}/RT) + A_2 T \exp(-E_2/RT))] \quad (9)$$

These data exhibit  $\alpha$ ,  $\beta$ , and  $\delta$  regions. For two states, there will be 12 parameters, two each for the six rate constants. We have determined at most eight in the two-state case (for example,  $C_6F_6$ ,  $CS_2$ ) or six for the dissociative single state case (for example,  $CH_3NO_2$ ). However by combining data obtained from other experiments, unmeasured quantities can be defined for more than two states from ECD data, as in the case of  $O_2$  [27].

The value of  $k_2$  will be small if  $(D(AB) - E_a(B) > 1.5 \text{ eV})$ , and the data will exhibit an  $\alpha$  and a  $\beta$  region. Four parameters can be involved for a single state. In some cases, only a single positive slope is observed and the absolute  $E_a$  is obtained from the slope in the  $\alpha$  region:

$$K = \left[ \frac{k_N}{2k_D} \right] \left[ \frac{k_1}{k_{-1}} \right] = \left[ \frac{k_N}{2k_D} \right] \left[ \frac{A_1}{A_{-1}} \right] T^{-3/2} \left\{ \exp\left(\frac{E_a}{RT}\right) \right\} \quad (10)$$

$$\ln KT^{3/2} = \ln\left(\frac{A_N}{2A_D}\right) + \ln\left(\frac{A_1}{A_{-1}}\right) + \frac{E_a}{RT} \quad (11)$$

From Eq. (11), the slope in a plot of  $\ln KT^{3/2}$  versus  $1000/T$  is  $E_a/R$ . The intercept is  $\ln(A_N/2A_D) + \ln(A_1/A_{-1})$ . By using the statistical mechanical expression for  $k_1/k_{-1} = K_{eq}$  for the reaction of thermal electrons with molecules:

$$\left(\frac{A_1}{A_{-1}}\right) = \left[\frac{g(A^-)}{g(A)}\right] \frac{h^3}{(2\pi m_e k)^{3/2}} \quad (12)$$

where  $m_e$  is the electron mass,  $k$  and  $h$  are the Boltzmann's and Planck's constants and  $g$  the partition function.

From this equation and the values of the fundamental constants,  $\ln([g(A^-)/g(A)]) = \ln(A_1/A_{-1}) - 12.43 - \ln(A_N/2A_D)$ . This involves the ratio  $(A_N/2A_D)$  so that the concentration of the positive species and the temperature dependence of the intrinsic rate constants will cancel and not affect the value of the slope. With an experimental intercept, the partition function ratio,  $Q_{an} = [g(A^-)/g(A)]$  can be calculated. Originally it was assumed that the  $Q_{an}$  should always be unity and the electron affinity obtained from the "fixed" intercept. Since then, experimental determinations of the electron affinities of  $CS_2$ ,  $CH_3NO_2$ , tetracene, and benz[a]pyrene clearly indicate that the  $Q_{an}$  can be lower than one. The observed  $Q_{an}$  values range from 1 to  $10^{-4}$  [12,29,30].

In the  $\beta$  region, the  $K = k_1/2k_D$  and it is possible to obtain values for  $A_1$  and  $E_1$  from the data. When  $k_{-1} \ll (k_N + k_2)$  the  $A_1$  and  $E_1$  are determined since:

$$\ln KT^{1/2} = \ln\left[\frac{A_1}{k_D}\right] - \frac{E_1}{RT} \quad (13)$$

The maximum  $A_1(\text{max})$  ( $E_1 = 0$ ) is the DeBroglie  $A_1$ , DeBA. The value of  $\ln(\text{DeBA})$  calculated from fundamental constants is about 36. A global plot where the  $Y$ -axis is  $\ln KT^{3/2}$  is usually used even though the actual expression has a different  $T$  dependence. The actual values of  $A_1$  and  $E_1$  can be obtained by using a non-linear least squares procedure.

If dissociation only involves one state, six parameters, two each for the three rate constants  $k_1$ ,  $k_{-1}$ , and  $k_2$  are required. At low temperatures, there will be a  $\beta$  region. At intermediate temperatures there will be an  $\alpha$  region. At higher temperatures, the  $\delta$  region, where  $k_{-1} > k_2 > k_N$  Eq. (8) gives:

$$\ln KT^{3/2} = \ln\left(\frac{A_N}{2A_D}\right) + \ln\left(\frac{A_2 A_1}{A_{-1}}\right) + \frac{(E_a - E_2)}{RT} + \ln T \quad (14)$$

The slope becomes negative since  $E_a < E_2$  and the intercept will become large when  $A_2$  is large. The plot has the slope  $E^* = E_a - E_2 = D(\text{Rad-L}) - E_a(L)$  and intercept  $\ln(A_N/2A_D) + \ln(A_2 A_1/A_{-1})$ . The bond dissociation energy is calculated from:  $D(\text{Rad-L}) = E^* + E_a(L)$ . In order to observe this type of behavior, the pre-exponential term for  $k_2$  must be large. At still higher temperatures, the dissociation will overwhelm the detachment and the expression for  $K$  will be  $k_1/2k_D$  as in the  $\beta$  region. The highest activation energy and pre-exponential term that has been observed is for the dissociation of the anion of  $m$ -fluoronitrobenzene anion,  $\ln[A_2] = 40$ ;  $E_2 = 2 \text{ eV}$ . These values have been verified by RRKM calculations [45,46].

The major emphasis in this paper is on the evaluation of electron affinities. The rate constants for attachment, detachment and dissociation can be obtained from the parameters and the equations:  $k_2 = A_2 T \exp(-E_2/RT)$ ;  $k_1 = A_1 T^{-1/2} \exp(-E_1/RT)$ ;  $k_{-1} = A_{-1} T \exp(-E_{-1}/RT)$ ;  $E_{-1} = E_1 - E_a$ ; and  $\ln(A_1/A_{-1}) = 11.73 + \ln[Q_{an}] + \ln(A_N/A_D)$ . Except for the values of  $k_1$ , there are few other experimental values available for comparison. The  $k_1$  values determined by other methods generally agree with those determined in the ECD. For compounds in which  $E_1$  has been determined to be small such as for  $CCl_4$  and  $SF_6$ , the  $k_1$  will be equal to  $A_1 T^{-1/2}$ , where  $A_1$  is the DeBA.

#### 4. Experimental and calculation procedures

The ECD experimental procedure has been described previously [28–40]. Briefly, known amounts of a compound are

injected into a gas chromatograph and the ECD response measured at different temperatures. The raw data are  $I_b$  is the standing current or baseline of the chromatogram;  $I_e$  the current in the presence of the peak;  $n$  the moles in the 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 chromatographic peaks, the electron-capture coefficient  $K_{EC}$  (l/mol) is given by:

$$K = \left\{ \frac{I_b - I_e}{I_e} \right\}_{\max} \{t_{1/2}\} \frac{V}{n} \quad (15)$$

where  $\{(I_b - I_e)/I_e\}_{\max}$  is the corrected height at the peak maximum and is unitless, and  $t_{1/2}$  the measured peak width at corrected half height. The baseline current,  $I_b$  is nominally temperature independent but if the value changes,  $K$  must be normalized to the maximum value of  $I_b$ . The major problem with the ECD method is the possibility of contamination. If additional ion molecule reactions are to take place other than attachment, detachment and recombination, the concentration of the impurities must be large. These reactions can be observed in NIMS but in the ECD, the net effect will be the reduction in the steady state concentration of the electrons. As a result, the purity of the carrier gases must be high and column bleed must be eliminated for ECD work.

For the  $\alpha$  region, plots of  $\ln KT^{3/2}$  versus  $1000/T$  are linear and a normal least squares procedure can be used to determine the slope and the intercept and their uncertainties. From Eq. (11), the  $E_a$  is the slope multiplied by  $R$ , the gas constant. For dissociative compounds, using Eq. (13), the gas constant times the slope in the  $\gamma$  region is  $E^*$ . The bond dissociation energy  $D(\text{Rad-L})$  is obtained from  $D(\text{Rad-L}) = E^* + E_a(\text{L})$ . With data in more than one region, the non-linear least squares data procedures are used to obtain the parameters. These were done with a custom program in EXCEL. For multiple states, the value of  $A_{1x}$  was set equal to  $A_1$ . For molecules where the low temperature capture is high,  $A_1$  is about equal to the DeBA and  $E_1$ , will be small. The non-linear least squares analysis gives parameters that are consistent with the experimental data.

The theoretical  $AE_a$  of the acetophenones (APs), chlorobenzenes and other compounds and the appropriate  $D(\text{C-L})$  dissociation energies were calculated using HYPERCHEM software. For both calculations the geometry of each molecule, radical, and ion was first annealed by molecular dynamics. Then the quantum mechanical self-consistent field electronic energy of each was calculated. The difference in the energies of the neutral molecule and anion is the adiabatic electron affinity. For  $D(\text{C-Cl})$  calculations the quantity  $E_{\text{neutral}} - (E_{\text{Cl}} + E_{\text{radical}})$  was calculated. For the  $AE_a$  and  $D(\text{C-Cl})$  calculations, the number of filled and unfilled orbitals were selected to minimize the difference between the experimental and theoretical results. The number of filled and unfilled orbitals used in the MCCI is given in parentheses with the product first. Since MCCI always lowers the energy, the use of three filled and unfilled orbitals for the anion or the products of dissociation gives the lowest

energy and RHF(3300) is the maximum value. Likewise, the lowest energy for the neutral and the minimum value is RHF(0033). However, the UHF value for the anion could be larger than the RHF(33) value and yield the maximum value. If the experimental  $E_a$  fits between these extremes, an optimum value can be obtained [7–13]. The experimental values that are smaller than the maximum value could be for excited states. The values for the aromatic hydrocarbons were calculated using MINDO/3; the values for SF<sub>6</sub>, Cl<sub>2</sub>, O<sub>2</sub> and C<sub>6</sub>F<sub>5</sub>NO<sub>2</sub> were calculated using ZINDO while the others were calculated using AM1. With the HYPERCHEM program and a Pentium V computer, the calculations for even the largest molecules could be completed in minutes.

## 5. Results

### 5.1. General results

The evaluated values of electron affinities are given in Tables 1–6. Any original references not specifically cited can be found in the NIST site. In Tables 7–9 are examples of kinetic and thermodynamic parameters determined in the ECD. In Tables 7 and 9 are the new results for acetophenones, fluorobenzenes, and chlorobenzenes to be compared to the previously published values in Table 8 [12,29,30]. In Figs. 4–7 are ECD data for organic compounds and diatomic molecules that illustrate the mechanisms. In Figs. 8 and 9 are plots for the data analysis of the acetophenones and halogenated benzenes. The data in many of these figures have been published but the specific figures have not been published. In the figure captions, the original publications will be cited. The halogens, nitromethane, chlorobenzene to tetrachlorobenzene, and chloroacetophenones undergo both dissociative and non-dissociative capture. The other organic molecules, NO and O<sub>2</sub> undergo non-dissociative capture. The ECD data for C<sub>6</sub>F<sub>5</sub>NO<sub>2</sub>, C<sub>6</sub>F<sub>5</sub>Cl, C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, tetracene, NO and O<sub>2</sub> illustrate inclusion of auxiliary data into the determination of  $E_a$ ,  $Q$ ,  $A_1$  and  $E_1$ . The highest measured  $E_a$  is 1.50 eV for C<sub>6</sub>F<sub>5</sub>NO<sub>2</sub>; the lowest  $0.07 \pm 0.02$  eV for tetramethylbenzene and the most precise  $0.338 \pm 0.002$  eV for acetophenone. For tetracene, naphthalene and C<sub>6</sub>F<sub>5</sub>Cl, C<sub>6</sub>F<sub>6</sub>, C<sub>6</sub>Cl<sub>6</sub>, eight quantities are calculated from the ECD data for two states. More than two states have been observed for aromatic hydrocarbons corresponding to the different C–H bonds [12] (Figs. 4–7).

The  $AE_a$  of tetracene was originally believed to be 0.88, not 1.1 eV because the upturn at higher temperatures was not explained [33]. The two-state model attributes this to  $E_{1g}$ , the activation energy to the ground state. The  $AE_a$  of nitrobenzene and tetracene have been confirmed by PES, TCT, reduction potentials and theoretical calculations. The  $AE_a$  for nitrobenzene, SF<sub>6</sub> and C<sub>6</sub>F<sub>6</sub> have also been confirmed by the temperature dependence of the parent negative ion in negative ion mass spectrometry. Molecular

Table 1  
 Evaluated electron affinities: magnetron, alkali metal beam, thermal charge transfer (eV)

Molecule	AE <sub>a</sub>	NIST	Method(s)	E <sub>a</sub> (E <sub>1/2</sub> )	CURES-EC
Hexacyanobutadiene	3.29(15)	3.291	M	3.30 (10)	3.3
TCNE	2.95(15)	3.166	M, T	2.90 (10)	3.0
TCNQ	2.80(8)	2.800	M, A, T	2.80 (10)	2.8
Hexacyanobenzene	2.54(15)	2.541	M	–	2.7
Bromanil- <i>o</i>	2.60(20)	2.440	A	2.70(10)	2.7
Chloranil- <i>p</i>	2.76(5)	2.775	M*, A, T	2.80(10)	2.8
Fluoranil- <i>p</i>	2.70(10)	2.702	M*, A, T	2.70(10)	2.7
Fluorobenzoquinone	2.20(15)	–	M	–	2.2
Fluorobenzoquinone	2.20(15)	[1.461]	M (NIST)	–	2.2
<i>s</i> -Tetracyanobenzene	2.20(8)	2.203	M	2.2(10)	2.2
<i>s</i> -Tetracyanopyridine	2.17(15)	2.173	M	–	2.5
<i>s</i> -Trinitrobenzene	2.63(15)	2.628	M	2.60(10)	2.6
<i>s</i> -Tricyanobenzene	1.84(10)	1.840	M	–	1.8
<i>p</i> -Benzoquinone	1.860(5)	[1.990]	M*, A, T, P	1.90(5)	1.9
9,10-Anthraquinone	1.59(6)	1.591	M*, T	1.60(10)	1.6
<i>t</i> -Dicyanoethylene	1.02(10)	[1.249]	M, T	–	1.0
Dicyanobenzene- <i>m</i>	0.91(8)	0.911	T	–	0.9
Dicyanobenzene- <i>o</i>	1.03(8)	[0.954]	M, T	1.0(1)	1.0
Dicyanobenzene- <i>p</i>	1.09(8)	1.093	T	–	1.1
Benzonitrile	0.26(5)	0.258	E	0.3(1)	0.3
SF <sub>6</sub>	1.07(5)	1.070	M, T, E, MS	–	1.0
NO	0.86(10)	[0.026]*	See text	–	0.8
CCl <sub>4</sub>	2.04(10)	[0.805]*	A, M, T*	–	2.1
CBr <sub>4</sub>	2.06 (10)	2.060	M	–	2.0
CHCl <sub>3</sub>	1.75(10)	[0.622]*	M, T*	–	1.6
CH <sub>2</sub> Cl <sub>2</sub>	1.30(10)	–	M	–	1.25
C <sub>6</sub> F <sub>6</sub>	0.86(3)	[0.520]*	T, E, P	0.90(10)	0.85
CH <sub>3</sub> NO <sub>2</sub>	0.50 (2)	0.486	A, T, E, MS	–	0.50
F <sub>2</sub>	3.05(2)	3.005	T, A (ISO)	–	3.00
Cl <sub>2</sub>	2.45(2)	2.400	T, A (ISO)	–	2.43
Br <sub>2</sub>	2.57(2)	2.550	T, A (ISO)	–	2.58
I <sub>2</sub>	2.524(5)	2.524	T, P, A (ISO)	–	2.33
O <sub>2</sub>	1.07(10)	[0.450]*	See text	–	1.10
CS <sub>2</sub>	0.88(2)	[0.512]*	A, E, P	–	0.85
NO <sub>2</sub>	2.273(5)	2.273	A, E, P	–	2.25
Nitrobenzene	1.00(1)	1.006	T, E, P, MS	1.00(5)	1.00
Perylene	0.973(5)	0.973	T, E, P	1.01(3)	1.00
Tetracene	1.08(5)	1.067	T, E, P	1.09(3)	1.08
Biacetyl	0.70(5)	0.690	T, E	0.71(3)	0.70
Maleic anhydride	1.44(5)	1.440	A, T	1.45(5)	1.40
Phthalic anhydride	1.25(5)	1.245	A, T	–	1.30

Methods: A, AMB; E, ECD; ISO, isoelectronic principle; M, magnetron; MS, negative ion mass spectrometry; P, PES; T, TCT. (\*) Indicates value is assigned to excited states. Value in square bracket are different from selected value. Value in parenthesis are random uncertainties in the last figures [1–5,15,16,52].

anions of C<sub>6</sub>F<sub>5</sub>NO<sub>2</sub>, C<sub>6</sub>F<sub>5</sub>Cl, C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, tetracene, and O<sub>2</sub> have been observed at the highest ECD temperature [42,47].

In Fig. 5 are the X<sub>2</sub> curves calculated with the two-state model. The data are fit to Eq. (8) with the partition function ratios, *Q*, fixed to unity and the established E<sub>a</sub> (see Table 8). The larger activation energy for the attachment to I<sub>2</sub> is apparent. The A<sub>1</sub> are estimated, and the E<sub>1</sub> values determined from the data [37]. Also in Fig. 6 are ECD data for O<sub>2</sub> [38,42]. The ECD data in the low temperature region and the electron swarm data, shown in Fig. 7, gives an excited state E<sub>a</sub> that coincides with the most precise PES value, 0.430, 0.450 ± 0.002 eV. Besides the initial upturn at higher temperatures, a downturn indicative of

a fourth state is observed. The E<sub>1</sub>, A<sub>1</sub> and some *Q* values are determined from the ECD data for O<sub>2</sub> since the E<sub>a</sub> and their uncertainties are used in the analysis. The ground state curve with E<sub>a</sub> = 1.07 ± 0.07 eV is calculated from estimates of A<sub>1</sub> and *Q* since an E<sub>1</sub> of 1.9 ± 0.2 eV has been measured. The largest E<sub>a</sub> has been measured by multiple techniques [15,16,27,48–51]. Calculated ECD lines for O<sub>2</sub> with E<sub>a</sub> 0.3, 0.2, and 0.05 eV and *Q* = 1 indicate their negligible ECD response. In Fig. 6 are the ECD data for C<sub>6</sub>F<sub>6</sub> and CS<sub>2</sub> that shows two states [29–31]. These have the largest temperature range of the multiple sets of data that have been collected. The four regions are clearly indicated with well-defined limiting slopes where the AE<sub>a</sub> can be determined. In Fig. 7, the calculated curves



Table 2  
List of evaluated molecular electron affinities: hydrocarbons (eV)

Molecule	AE <sub>a</sub>	NIST	E <sub>1/2</sub>	CURES-EC	Methods
Benzene, 1,2,4,5-tetramethyl-	0.07 ± 0.02	0.048	–	0.05	
Styrene	0.10 ± 0.05	–	0.12 ± 0.05	0.10	
Benzene, 1,2,3,5-tetramethyl-	0.11 ± 0.02	0.108	–	0.08	
Benzene, hexamethyl-	0.12 ± 0.02	0.121	–	0.10	
Biphenyl	0.13 ± 0.02	0.130	0.10 ± 0.03	0.14	
Naphthalene, 2-methyl-	0.14 ± 0.02	0.143	–	0.15	
Naphthalene, 1-ethyl-	0.15 ± 0.02	0.147	–	0.16	
Naphthalene	0.16 ± 0.01	–0.200*	0.17 ± 0.03	0.15	PES
Naphthalene, 1-methyl-	0.16 ± 0.02	0.160	–	0.17	
Diphenylmethane	0.16 ± 0.02	0.156	–	0.18	
Naphthalene, 2,6-dimethyl-	0.16 ± 0.02	0.160	–	0.15	
Naphthalene, 2,3-dimethyl-	0.17 ± 0.02	0.173	–	0.18	
Indene	0.17 ± 0.02	0.173	–	0.18	
Benzene, pentamethyl-	0.18 ± 0.02	0.182	–	0.17	
Naphthalene, 2-ethyl	0.19 ± 0.02	0.195	–	0.19	
Naphthalene, 1,4-dimethyl-	0.22 ± 0.02	0.247	–	0.23	
Fluorene	0.24 ± 0.02	0.278	–	0.30	
Triphenylene	0.29 ± 0.02	0.285	0.29 ± 0.03	0.27	
Phenanthrene	0.30 ± 0.02	0.307	0.31 ± 0.03	0.31	
Diphenylethyne	0.32 ± 0.02	0.321	–	0.35	
Ethylene-1,1-diphenyl	0.39 ± 0.02	0.390	–	0.36	
Stillbene	0.39 ± 0.02	0.390	–	0.40	
Biphenylene	0.45 ± 0.05	(0.89)	0.40 ± 0.05	0.45	Collisional dissociation
Chrysene	0.42 ± 0.04	0.397	0.42 ± 0.03	0.43	
Picene	0.50 ± 0.03	0.542	0.49 ± 0.03	0.50	
Benz[e]pyrene	0.55 ± 0.03	0.534	0.56 ± 0.03	0.56	
Benzo[c]phenanthrene	0.58 ± 0.01	0.545	0.58 ± 0.03	0.60	
Pyrene	0.61 ± 0.02*	0.500	0.63 ± 0.03	0.62	
Anthracene, 1-methyl-	0.65 ± 0.02	0.550*	0.65 ± 0.10	0.65	Collisional dissociation
Dibenz[aj]anthracene	0.67 ± 0.03	0.591*	0.65 ± 0.03	0.70	
Dibenz[ac]anthracene	0.69 ± 0.03	–	0.69 ± 0.03	0.68	
Anthracene,	0.69 ± 0.01	0.530*	0.72 ± 0.03	0.70	TCT, PES
Dibenz[ah]anthracene	0.69 ± 0.03	0.595*	0.65 ± 0.03	0.66	
Benz[a]anthracene	0.72 ± 0.01	0.390*	0.72 ± 0.03	0.74	TCT, collisional dissociation
Benz[a]pyrene	0.80 ± 0.03	0.815	0.79 ± 0.03	0.80	TCT
Coronene	0.80 ± 0.10	0.470*	0.74 ± 0.03	0.80	PES, collisional dissociation
1,3,5,7-c-C <sub>8</sub> H <sub>8</sub>	0.80 ± 0.05	0.550*	–	0.8	TCT, PD, PES, collisional dissociation
Acenaphthylene	0.80 ± 0.02	0.403*	0.80 ± 0.10	0.8	
Fluoranthene	0.82 ± 0.04	0.630*	0.83 ± 0.03	0.81	
Azulene	0.84 ± 0.05	0.694*	0.78 ± 0.05	0.78	PES
Benzo[ghi]perylene	0.89 ± 0.10	0.420*	0.90 ± 0.10	0.90	Collisional dissociation
Perylene	0.98 ± 0.01	0.973	1.01 ± 0.03	1.00	TCT, ECD, PES
Tetracene	1.08 ± 0.04	1.067	1.09 ± 0.03	1.08	TCT, ECD, PES
Pentacene	1.39 ± 0.05	1.392	1.37 ± 0.05	1.34	TCT

TCT, thermal electron transfer; ECD, electron-capture detector, PES, photoelectron spectrometry. (\*) Different from selected value [1,15,16,12,36,55–62].

only for O<sub>2</sub>, and C<sub>6</sub>Cl<sub>6</sub>; the electron swarm data for O<sub>2</sub>; the calculated curves and ECD data for NO, C<sub>6</sub>F<sub>6</sub>, nitromethane and chloroacetophenone; and the magnetron data and a calculation for NO with the PES E<sub>a</sub> are shown [2,10,13,15,16,38,39,49]. This gives a clear comparison of the type of data that are obtained from these equilibrium techniques. The higher temperature and smaller 1000/T range for the magnetron data should be noted. The precision of the E<sub>a</sub> determined from magnetron data for NO and the ECD data for CS<sub>2</sub>, nitrobenzene, and C<sub>6</sub>F<sub>6</sub> is increased by multiple determinations. The low E<sub>a</sub> of NO obtained by many techniques could not be measured in the ECD. In

the case of nitromethane, chloronaphthalene, mono to tetrachlorobenzenes and chloroacetophenones, the quantities *D*(C–Cl) and *D*(C–NO<sub>2</sub>) are obtained from the  $\gamma$  region with the established values of the E<sub>a</sub> of NO<sub>2</sub> or Cl. These are shown in Figs. 8 and 9A [10,38,39,41].

## 5.2. Evaluation of the previous electron affinities

In Table 1 are evaluated electron affinities for the molecules studied in the magnetron direct capture method, many of the AMB values, and similar molecules studied

Table 3  
List of evaluated molecular electron affinities (eV) aromatic nitrocompounds

Molecule	AE <sub>a</sub>	NIST	$E_{1/2}$	CURES-EC	Methods
Nitrobenzene	1.00(1)	1.006	1.0 ± 0.05	1.0	2T, E, PES, NIMS
Nitrobenzene-pentafluoro	1.50(10)	1.450	–	1.5	T, E, NMS2
Nitrobenzene- <i>m</i> -F	1.20(5)	1.236	1.20	1.2	2T, E, P, NMS2
Nitrobenzene- <i>o</i> -F	1.08(5)	1.075	1.11	1.1	2T, E, P, NMS2
Nitrobenzene- <i>p</i> -F	1.12(5)	1.119	1.09	1.15	2T, E, P, NMS2
Nitrobenzene- <i>m</i> -methyl	0.98(3)	0.989	0.98	1.0	2T, E, P, NMS2
Nitrobenzene- <i>o</i> -methyl	0.89(3)	0.924	0.89	0.92	2T, E, P, NMS2
Nitrobenzene- <i>p</i> -methyl	0.95(3)	0.954	0.95	0.95	2T, E, P, NMS2
Nitrobenzene- <i>p</i> - <i>t</i> -amyl	1.00(10)	[2.168]	–	0.98	T (scaled wrong)
Nitrobenzene-2,3-dime	0.86(10)	0.854	0.87	0.85	2T, E
Nitrobenzene-3,4-dime	0.92(10)	0.924	0.88	0.93	T
Nitrobenzene-2,4-dime	0.88(10)	0.880	–	0.89	T
Nitrobenzene-2,5-dime	0.85(10)	0.854	–	0.85	T
Nitrobenzene-2,6-dime	0.81(10)	0.811	–	0.78	T
Mitrobenzene-2,4,6-trime	0.73(10)	0.711	–	0.72	T
Nitrobenzene- <i>o</i> -Cl	1.16(10)	1.162	1.20	1.20	2T, E1, NMS2
Nitrobenzene- <i>m</i> -Cl	1.28(10)	1.280	1.26	1.28	2T, E1, NMS2
Nitrobenzene- <i>p</i> -Cl	1.26(10)	1.258	1.28	1.25	T, E1, NMS2
Nitrobenzene-2,3-di-Cl	1.30(10)	1.292	–	1.4	T, NMS2
Nitrobenzene-3,4-di-Cl	1.44(10)	1.444	–	1.5	T, NMS2
Nitrobenzene-3,5-di-Cl	1.52 (8)	1.500	–	1.5	T
Nitrobenzene- <i>o</i> -Br	1.18(10)	1.162	1.20	1.22	T
Nitrobenzene- <i>m</i> -Br	1.32(10)	1.318	1.37	1.35	T, E1
Nitrobenzene- <i>p</i> -Br	1.29(10)	1.292	1.31	1.48	T
Nitrobenzene- <i>o</i> -CF <sub>3</sub>	1.33(10)	1.331	–	1.25	T, NMS2
Nitrobenzene- <i>m</i> -CF <sub>3</sub>	1.41(10)	1.414	1.47	1.45	2T, NMS2
Nitrobenzene- <i>p</i> -CF <sub>3</sub>	1.50(10)	1.500	–	1.55	T, NMS2
Nitrobenzene- <i>m</i> -OCH <sub>3</sub>	1.04(10)	1.040	–	1.0	T, NMS2
Nitrobenzene- <i>p</i> -OCH <sub>3</sub>	0.91(10)	0.911	–	0.89	T
Nitrobenzene- <i>p</i> -NH <sub>2</sub>	0.92(10)	0.915	–	0.90	T
Nitrobenzene- <i>m</i> -NH <sub>2</sub>	0.95(10)	0.945	–	0.92	T, NMS2
Nitrobenzene- <i>m</i> -CN	1.57(10)	1.565	–	1.6	T, NMS2
Dinitrobenzene- <i>m</i>	1.66(10)	1.657	–	1.68	2T, E1, NIMS
Dinitrobenzene- <i>o</i>	1.65(10)	1.652	–	1.68	T, E1, NMS2
Dinitrobenzene- <i>p</i>	2.00(10)	2.003	1.97	2.01	2T, E1, NMS2, PES
<i>s</i> -Trinitrobenzene	2.63(15)	2.628	–	2.70	M
1-Nitronaphthalene	1.23(10)	1.227	1.21	1.3	T, NMS2
1,5-Dinitronaphthalene	1.77(10)	1.765	1.8	–	T

Methods: E, electron-capture detector multiple temperatures; E1, ECD one temperature; M, magnetron; NIMS, negative ion mass spectrometry multiple temperatures; NMS2, only two temperatures; T, thermal charge transfer; ICR and/or HPMS 2T, both ion cyclotron resonance and high-pressure mass spectrometry; ICR, one temperature; HPMS, multiple temperatures; P, electron-capture detector photodetachment threshold; PES, photoelectron spectrometry [1,3,15,16,33–36,47].

with the TCT and ECD methods [1–4,15,16,33–36]. Many of these were evaluated in the 1989 review. At that time, it was concluded that with the exceptions of the ECD (0.86 eV) and TCT (0.52 eV) values for C<sub>6</sub>F<sub>6</sub>, the values for anthraquinone (1.2 eV) and benzoquinone (1.4 eV) determined with the magnetron method, and the alkali metal beam values for SF<sub>6</sub> (0.5–0.8 eV), the experimental  $E_a$  measured in the gas phase agree within the random uncertainty. Rather than disregard the lower values, excited states were postulated. In addition, dramatically different  $E_a$  values for NO (0.86 eV versus 0.02 eV); O<sub>2</sub> (1.07 eV versus 0.46 eV) and CS<sub>2</sub> (0.6 versus 1.0 eV) were reported. These differences have been resolved by interpreting ECD data with multiple states as shown in Figs. 4–7 [1,15,16,27,29–31].

The selected AE<sub>a</sub> and the estimated errors are given in the first column of Table 1. The  $E_a$  were calculated for these

compounds using the CURES-EC method and agree with the evaluated values within the uncertainty. The  $E_{1/2}$  values where available also support the gas phase values. It is now possible to examine values determined only by a single gas phase method by calculating the AE<sub>a</sub>. The sequential NIST values different from the selected values are shown in brackets. Some selected values are averages of reported values. In the case of CCl<sub>4</sub> and CHCl<sub>3</sub>, the NIST values are the most recent but could be for an excited state. The NIST values for NO, O<sub>2</sub>, CS<sub>2</sub>, and C<sub>6</sub>F<sub>6</sub>, have been assigned to excited states [48–51]. More recent  $E_a$  of nitromethane, benzoquinone, tetracene, and perylene have not been included in the NIST table [10,12,52].

The direct capture magnetron values are often considered unreliable because there is no mass identification. However, there are a now a number of magnetron values which

Table 4  
List of evaluated molecular electron affinities (eV) acetophenones and benzaldehydes

Molecule	AE <sub>a</sub>	NIST	CURES-EC	Methods <sup>a</sup>
Acetophenone	0.338(2)	0.334	0.35	E
Acetophenone- <i>o</i> -F	0.49(5)	0.442	0.45	E
Acetophenone- <i>m</i> -F	0.58(5)	0.577	0.55	E
Acetophenone- <i>p</i> -F	0.52(5)	[0.395] <sup>b</sup>	0.50	E
Acetophenone- <i>p</i> -Cl	0.64(5)	0.585	0.62	T, E
Acetophenone- <i>m</i> -Cl	0.67(5)	0.616	0.66	T, E
Acetophenone- <i>o</i> -CF <sub>3</sub>	0.79(5)	[0.642] <sup>b</sup>	0.83	E
Acetophenone- <i>m</i> -OH	0.77(2)	— <sup>c</sup>	0.76	E
Acetophenone- <i>o</i> -OH	0.85(10)	0.850	0.82	T
Acetophenone- <i>m</i> -CF <sub>3</sub>	0.79(5)	0.768	0.80	T, E
Acetophenone- <i>p</i> -CF <sub>3</sub>	0.89(10)	0.898	1.00	T, E
Acetophenone- <i>p</i> -acetyl	1.06(10)	1.062	1.15	T, E
Acetophenone- <i>m</i> -NO <sub>2</sub>	1.33(10)	1.33	1.40	T
Acetophenone- <i>o</i> -NO <sub>2</sub>	1.40(10)	1.40	1.45	T
Acetophenone- <i>p</i> -NO <sub>2</sub>	1.57(10)	1.57	1.50	T
Acetophenone-pentafluoro	0.88(10)	0.876	0.88	T
Acetophenone- <i>p</i> -COOCH <sub>3</sub>	0.96(10)	0.963	1.15	T
Benzaldehyde	0.457(5)	[0.429] <sup>b</sup>	0.45	E
Benzaldehyde- <i>m</i> -F	0.66(4)	0.668	0.64	E
Benzaldehyde- <i>o</i> -F	0.66(4)	0.637	0.62	E
Benzaldehyde- <i>p</i> -F	0.57(5)	[0.486] <sup>b</sup>	0.55	E
Benzaldehyde- <i>m</i> -OCH <sub>3</sub>	0.48(4)	0.429	0.45	E
Benzaldehyde- <i>m</i> -CH <sub>3</sub>	0.43(2)	0.429	0.45	E
Benzaldehyde- <i>p</i> -CH <sub>3</sub>	0.39(2)	0.373	0.40	E
Benzaldehyde-2,4,6-trimethyl	0.44(3)	0.442	0.47	E
Propiophenone	0.36(1)	0.351	0.36	E
Benzaldehyde-pentafluoro	1.10(10)	1.097	1.15	T
Benzaldehyde- <i>m</i> -CN	1.03(10)	0.990	1.08	T
Benzaldehyde- <i>p</i> -CN	1.25(10)	1.250	1.28	T
Benzaldehyde- <i>m</i> -CF <sub>3</sub>	0.85(10)	0.815	0.90	T
Benzaldehyde- <i>p</i> -CF <sub>3</sub>	0.97(10)	0.941	1.05	T
Benzaldehyde-3,5-di-CF <sub>3</sub>	1.26(10)	1.232	[1.54] <sup>d</sup>	T
Benzaldehyde-3,5-di-Cl	1.03(10)	0.989	1.01	T
Benzaldehyde- <i>p</i> -Cl	0.68(10)	0.649	0.72	T
Benzaldehyde- <i>m</i> -Cl	0.70(10)	0.668	0.70	T
Benzaldehyde- <i>p</i> -CHO	1.27(10)	1.236	1.30	T
Benzaldehyde- <i>m</i> -CHO	1.00(10)	0.971	1.06	T
Benzaldehyde- <i>p</i> -NO <sub>2</sub>	1.69(10)	1.691	1.66	T
Benzaldehyde- <i>m</i> -NO <sub>2</sub>	1.43(10)	1.431	1.39	T
Benzaldehyde- <i>o</i> -NO <sub>2</sub>	1.56(10)	1.557	1.50	T

Value in parenthesis are random uncertainty in the last figure [1,3,15,35,63–66].

<sup>a</sup> Methods: E, ECD; T, TCT.

<sup>b</sup> Reference compound or significantly different from selected value.

<sup>c</sup> Not included in the NIST table.

<sup>d</sup> CURES-EC is much larger than the largest experimental value.

have been supported by results from other experimental techniques and the CURES-EC calculations. Excluding the data for anthraquinone, benzoquinone, chloranil, and fluoranil, the deviations of the magnetron values from the selected values is  $\pm 0.15$  eV. The AMB values for the halogens were among the first values to be reported. They are both accurate and precise since they have been confirmed by different methods and also agree with the isoelectronic principle. The selected values for F<sub>2</sub>, Cl<sub>2</sub>, and Br<sub>2</sub> are the more precise values obtained using the isoelectronic principle. The PES value  $2.524 \pm 0.005$  eV for I<sub>2</sub> is the most precise [53]. The quoted uncertainty of alkali metal beam values is  $\pm 0.2$  eV. The values agree with the selected

values within  $\pm 0.1$  eV [4]. However, the *o*-benzoquinone value of 2.44 eV is not supported by the reduction potential or CURES-EC, thus a higher less certain value is selected.

It is important that different values of  $E_a$  have been determined for a given molecule by different investigators using the same experimental technique. In particular, the AMB and TCT methods gave values of 1.0 and 0.6 eV for CS<sub>2</sub> while the TCT method gave values of 0.8 and 0.52 eV for C<sub>6</sub>F<sub>6</sub>. These excited state values were subsequently confirmed by ECD data. There are a number of molecules for which the same value for the  $E_a$  has been obtained by two, three or four methods. All of the assigned values are also ac-

Table 5

List of evaluated molecular electron affinities (eV) anisoles, benzophenones, benzonitriles, and benzoates

Molecule	AE <sub>a</sub>	NIST	$E_{1/2}$	CURES-EC	Methods <sup>a</sup>
Benzophenone	0.68(5)	[0.620] <sup>b</sup>	0.68	0.68	T, E
Benzophenone-4-methoxy	0.61(5)	– <sup>c</sup>	0.61	0.60	E
Benzophenone-4-methyl	0.64(5)	– <sup>c</sup>	0.64	0.64	E
Benzophenone-4-ethyl	0.64(5)	– <sup>c</sup>	–	0.64	E
Benzophenone- <i>p</i> -F	0.70(5)	[0.620] <sup>b</sup>	–	0.70	T, E
Benzophenone-4,4'-di-F	0.78(10)	0.776	–	0.78	T
Benzophenone- <i>p</i> -Cl	0.78(10)	– <sup>c</sup>	0.78	0.81	E
Benzophenone- <i>p</i> -Br	0.90(10)	– <sup>c</sup>	–	0.88	E
Benzophenone- <i>p</i> -I	1.10(20)	– <sup>c</sup>	–	1.10	E
Benzophenone- <i>p</i> -CF <sub>3</sub>	1.08(10)	1.078	–	1.30	T
Benzophenone- <i>p</i> -CN	1.31(10)	1.308	–	1.40	T
Benzophenone- <i>p</i> -NO <sub>2</sub>	1.50(20)	– <sup>c</sup>	–	1.50	E
Benzophenone- <i>m</i> -CF <sub>3</sub>	1.00(10)	1.078	–	1.20	T
Benzophenone- <i>m</i> -NO <sub>2</sub>	1.31(10)	1.308	–	1.40	T
Benzophenone-3,5-di-Cl	1.11(10)	1.106	–	1.15	T
Benzonitrile	0.26(2)	[0.258] <sup>b</sup>	0.25	0.26	E
Benzonitrile- <i>p</i> -NO <sub>2</sub>	1.73(10)	1.726	–	1.72	T
Benzonitrile- <i>m</i> -NO <sub>2</sub>	1.57(10)	1.565	–	1.55	T
Benzonitrile- <i>m</i> -CO <sub>2</sub> CH <sub>3</sub>	0.80(10)	0.798	–	0.79	T
Benzonitrile- <i>p</i> -CO <sub>2</sub> CH <sub>3</sub>	1.00(10)	0.997	–	0.98	T
Benzonitrile-3,5-di-Cl	0.85(10)	[0.798] <sup>b</sup>	–	0.91	T
Benzonitrile-2,6-di-Cl	0.70(10)	0.698	–	0.70	T
Pentafluorobenzonitrile	1.08(10)	1.08	–	1.23	T
1,4-Dicyanobenzene-F <sub>4</sub>	1.89(10)	1.891	1.90	1.90	T
Methyl benzoate	0.20(10)	[0.180] <sup>b</sup>	0.24	0.21	E
Methyl benzoate- <i>p</i> -COOCH <sub>3</sub>	0.82(10)	0.824	0.82	0.80	T
Methyl benzoate- <i>m</i> -COOCH <sub>3</sub>	0.55(10)	0.550	0.58	0.60	E
Dimethyl phthalate	0.60(10)	0.550	0.60	0.61	E
Diethyl phthalate	0.62(10)	0.540	0.65	0.63	E
Methyl benzoate- <i>p</i> -CHO	1.10(10)	1.158	1.15	1.16	T
Methyl benzoate- <i>p</i> -NO <sub>2</sub>	1.48(10)	1.461	1.53	1.45	T
Methyl benzoate- <i>m</i> -NO <sub>2</sub>	1.25(10)	1.227	1.19	1.30	T
Anisole-bentafluoro	0.55(5)	0.542	–	0.60	E
Anisole-tetrafluoro	0.25(5)	0.217	–	0.30	E

Value in parenthesis are random uncertainties in the last figures [1,3,15,33–36].

<sup>a</sup> Methods: E, ECD; T, TCT.<sup>b</sup> Reference compound or significantly different from selected value.<sup>c</sup> Not included in the NIST table.

curate to within the uncertainties: MGN ( $\pm 0.15$  eV), AMB ( $\pm 0.10$  eV), TCT ( $\pm 0.10$  eV), ECD ( $\pm 0.01$ – $0.10$  eV). When these are the largest values, they can be assigned to the AE<sub>a</sub> and be used to test theoretical procedures. Once a theoretical method has been validated for a class of compounds, it can be used to support experimental results as in the case of CURES-EC and the magnetron direct capture values.

### 5.3. Evaluation of electron affinities of hydrocarbons

Electron affinities of hydrocarbon molecules in the NIST table have been assigned to states. The largest precise value is for the ground state. The HC list returned about 140 values. About 90 of these are for radicals [15,54–62]. The largest value is for the C<sub>8</sub>H radical,  $3.97 \pm 0.01$  eV. In many cases, the only measured values for molecules are ECD values. The largest value for a hydrocarbon determined by both ECD and TCT methods listed in NIST is for tetracene. Only the earlier ECD value for an excited state, 0.88 eV and the TCT

value 1.067 eV are listed but the average value from ECD, TCT, and PES is  $1.10 \pm 0.03$  eV [1,33,55]. The largest value for a molecule is  $1.39 \pm 0.10$  eV for pentacene. It was determined by only the TCT method [55]. In the collisional ionization method, the relative electron affinities are determined from the intensity of the ions formed by the dissociation of an electron bound dimer. It is similar to the TCT method. The values for benzo[ghi]perylene, biphenylene and methyl-anthracene were only determined by collisional ionization. The  $E_a$  of coronene was determined by PES and collisional ionization [56–58]. Earlier the CURES-EC and  $E_{1/2}$  values had been reported. Indeed, the  $E_a$  for the polycyclic aromatic hydrocarbons were used to establish a more precise calibration of  $E_{1/2}$  values based on a variable solution energy,  $\text{mddG}[-\Delta\Delta G(\text{sol})]$  for anions. The equation is  $EA = E(\text{ref}) - \text{mddG} + E_{1/2} = 4.18 - 2.20 - n(0.05) + E_{1/2}$ ;  $n = -10$  to 10 where the reference is the Hg pool. Thus  $E_a = 4.18 - 2.20 + 0.20 + E_{1/2} = 2.18 - 1.55 = 0.63$  eV for pyrene with  $n = -4$  and  $E_{1/2} = -1.55$  V versus Hg

Table 6  
List of evaluated electron affinities (eV) aromatic halogen compounds

Molecule	AE <sub>a</sub>	NIST	$E_{1/2}$	CURES-EC	Methods <sup>a</sup>
C <sub>6</sub> F <sub>5</sub> I	1.41(10)	1.410	–	1.40	T
C <sub>6</sub> F <sub>5</sub> Br	1.15(10)	1.150	–	1.34	T
C <sub>6</sub> F <sub>5</sub> Cl	1.01(10)	[0.815] <sup>c</sup>	–	1.15	T, E
C <sub>6</sub> F <sub>6</sub>	0.86(2)	[0.520] <sup>c</sup>	0.85	0.84	T, E
C <sub>6</sub> F <sub>5</sub> H	0.72(5)	[0.434] <sup>c</sup>	0.72	0.77	T, E
1,2,4,5-C <sub>6</sub> F <sub>4</sub> H <sub>2</sub>	– <sub>b</sub>	– <sub>d</sub>	0.50	0.54	–
1,2,3,4-C <sub>6</sub> F <sub>4</sub> H <sub>2</sub>	0.52(5)	– <sub>d</sub>	0.55	0.55	E
1,3,5-C <sub>6</sub> F <sub>3</sub> H <sub>3</sub>	– <sub>b</sub>	– <sub>d</sub>	0.45	–	–
1,3-C <sub>6</sub> F <sub>2</sub> H <sub>4</sub>	– <sub>b</sub>	– <sub>d</sub>	0.26	–	–
1,4-C <sub>6</sub> F <sub>2</sub> H <sub>4</sub>	0.25(5)	– <sub>d</sub>	0.25	0.25	E
C <sub>6</sub> FH <sub>5</sub>	0.13(5)	– <sub>d</sub>	0.10	0.10	E
C <sub>6</sub> Cl <sub>6</sub>	1.15(5)	[0.915] <sup>c</sup>	1.15	1.15	T, E
C <sub>6</sub> Cl <sub>5</sub> H	0.85(10)	[0.729] <sup>c</sup>	0.90	0.90	T, E
1,2,3,4-C <sub>6</sub> Cl <sub>4</sub> H <sub>2</sub>	– <sub>b</sub>	– <sub>d</sub>	0.69	0.71	–
1,2,3,5-C <sub>6</sub> Cl <sub>4</sub> H <sub>2</sub>	– <sub>b</sub>	– <sub>d</sub>	0.68	0.72	–
1,2,4,5-C <sub>6</sub> Cl <sub>4</sub> H <sub>2</sub>	0.65(5)	[0.450] <sup>c</sup>	0.66	0.70	E
1,2,3-C <sub>6</sub> Cl <sub>3</sub> H <sub>3</sub>	– <sub>b</sub>	– <sub>d</sub>	0.49	0.48	–
1,2,4-C <sub>6</sub> Cl <sub>3</sub> H <sub>3</sub>	– <sub>b</sub>	– <sub>d</sub>	0.45	0.45	–
1,3,5-C <sub>6</sub> Cl <sub>3</sub> H <sub>3</sub>	0.48(5)	[0.340] <sup>c</sup>	0.47	0.43	E
1,2-C <sub>6</sub> Cl <sub>2</sub> H <sub>4</sub>	0.30(5)	[0.094] <sup>c</sup>	0.23	0.25	E
1,3-C <sub>6</sub> Cl <sub>2</sub> H <sub>4</sub>	0.29(5)	– <sub>d</sub>	0.25	0.26	E
1,4-C <sub>6</sub> Cl <sub>2</sub> H <sub>4</sub>	0.29(5)	– <sub>d</sub>	0.25	0.25	E
C <sub>6</sub> ClH <sub>5</sub>	0.17(5)	– <sub>d</sub>	0.10	0.13	E
Tetrachloroethylene	0.65(5)	0.640	0.65	0.70	E, NIMS
Trichloroethylene	0.40(5)	0.400	0.40	0.50	E, NIMS
1,1-Dichloroethylene	0.15(5)	0.100	0.15	0.15	E
<i>c</i> -Dichloroethylene	0.10(5)	– <sub>d</sub>	–	0.10	E
<i>t</i> -Dichloroethylene	0.10(5)	– <sub>d</sub>	–	0.10	E
Vinylchloride	0.05(5)	– <sub>d</sub>	–	0.05	E
1-Cl-naphthalene	0.30(5)	0.277	0.30	0.30	E
1-Cl-anthracene	0.83(10)	0.828	0.83	0.82	T, E
2-Cl-anthracene	0.80(10)	0.802	0.73	0.79	T, E
9-Cl-anthracene	0.86(10)	0.859	0.83	0.86	T, E

Value in parenthesis are random uncertainties in the last figures [1,39,41,15].

<sup>a</sup> Methods: E, ECD; T, TCT; NIMS, negative ion mass spectrometry.

<sup>b</sup> Not evaluated.

<sup>c</sup> Significantly different from evaluated value.

<sup>d</sup> Not in the NIST table.

Table 7  
Kinetic and thermodynamic properties for dissociative electron attachment

Species	ln(A <sub>1</sub> )	$E_1$ (eV)	$Q$ (eV)	$E_a$ (eV)	$E_2$ (eV)	ln(A <sub>2</sub> )	$D(C-N \text{ or } C-Cl)$ (eV)
CH <sub>3</sub> NO <sub>2</sub>	36.3(3)	0.20	0.008	0.50(2)	1.00(5)	29.3(3)	2.68(5)
3-Cl-acetophenone	34.9(5)	0.03	0.99	0.67(5)	1.05(5)	28.5(3)	3.96(5)
4-Cl-acetophenone	34.8(3)	0.00	0.60	0.64(5)	1.05(5)	29.4(4)	4.01(5)
C <sub>6</sub> H <sub>5</sub> Cl	35.1(3)	0.07	0.38	0.17(10)	0.73(5)	24.2(3)	4.09(5)
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	35.2(3)	0.03	0.45	0.29(5)	0.72(5)	29.0(3)	4.03(5)
<i>m</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	35.1(3)	0.04	0.81	0.30(5)	0.69(5)	25.7(3)	3.97(5)
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	35.1(3)	0.03	0.70	0.30(5)	0.65(5)	25.7(3)	3.92(5)
<i>s</i> -C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	35.6(3)	0.04	0.64	0.48(5)	0.91(5)	32.9(3)	4.04(5)
<i>s</i> -C <sub>6</sub> H <sub>2</sub> Cl <sub>4</sub>	35.8(3)	0.03	0.94	0.69(5)	1.10(5)	34.2(3)	4.02(5)
1-Cl-naphthalene	35.6(3)	0.14	1.01	0.34(5)	0.82(5)	29.7(2)	3.94(5)

The values in parenthesis are random uncertainties in the last figure. The other figures are given with the proper number of significant figures [39,41].

pool. Using this procedure, reduction potentials and the CURES-EC calculations, the AE<sub>a</sub> were evaluated for 80 hydrocarbon molecules [7,8].

In Table 2 are the gas phase experimental and reduction potential  $E_a$ , for the hydrocarbon molecules in NIST. The

CURES-EC values and the assignments are also included. Asterisks indicate the NIST values which are significantly lower than the selected values. The TCT value for pentacene is confirmed by the  $E_{1/2}$  and the CURES-EC values. The NIST value for coronene was recently determined by

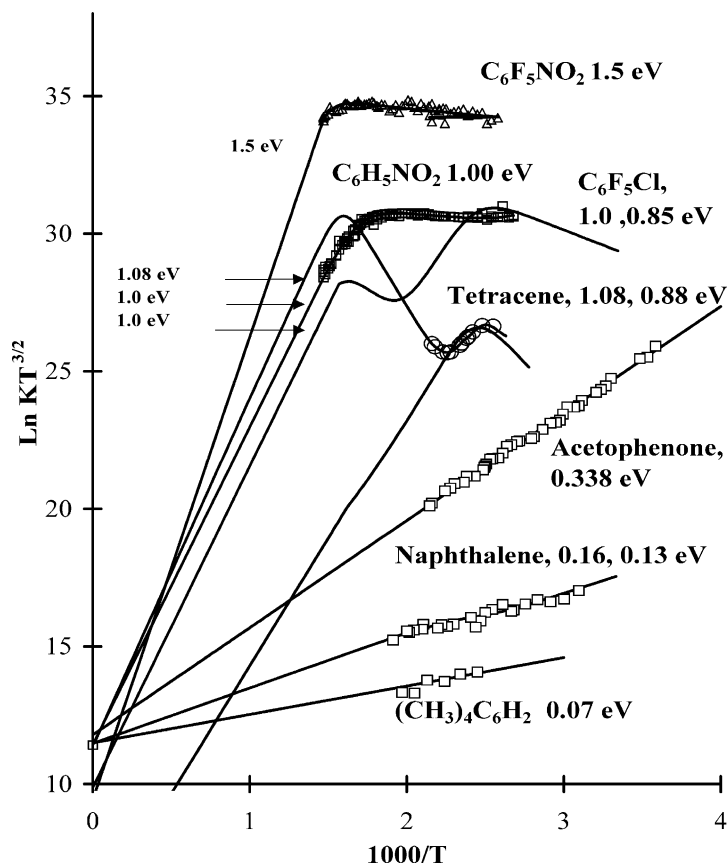


Fig. 4.  $\ln KT^{3/2}$  vs.  $1000/T$  illustrating the range of values determined in the electron-capture detector. The data for the nitrobenzenes were published in [30]. The data for acetophenone was published in [35]. The remaining data were published in [33,36].

assigning the first of two sets of peaks in the PES to the ground state. If the first peak is for an excited state, the second peak at about 0.8 eV can be assigned to the ground state. The higher value is supported by the reduction potential values and has been selected as the  $AE_a$  [7,8]. The value for biphenylene determined by collisional ionization is higher than the selected reduction potential value but could be for the isomer acenaphthylene. The collisional ionization values for benzanthracene, coronene, and benzo[ghi]perylene are assigned to excited states. The ECD value for benzanthracene is selected as the  $AE_a$ . The  $AE_a$  for the others are assigned to the CURES-EC and  $E_{1/2}$  values. The  $E_a$  for cyclooctatetrene is interesting because the photoelectron spectroscopy onset, 1.10 eV is an upper limit that must be corrected for the dramatic geometry difference in the neutral to obtain an  $E_a$  [59–62]. The excited state value of 0.55 eV has been obtained by ECD, TCT and collisional ionization methods. The photodetachment threshold value and the ECD data support a value of 0.8 eV. Some of the other selected  $AE_a$  have been obtained from the multiple state analyses of the ECD data and have not been included in the NIST table. The lower value for acenaphthylene was determined using the constant current ECD that only measured the excited state value [36]. The analysis of data taken earlier in this laboratory using a constant frequency

detector gave the value of 0.8 eV. All of the  $E_a$ , except for naphthalene, determined using the ECD in the linear  $\alpha$  region are the same as listed in the NIST table. The value for naphthalene reported in the NIST table was determined from the extrapolation of photoelectron spectra of hydrated naphthalene anions and by electron transmission spectra. The ECD value is confirmed by the values of the methyl-naphthalenes and the observation of the parent negative ion in negative ion mass spectrometry. The assignments of the hydrocarbon  $E_a$  and the observation of multiple states which are associated with the different types of C–H bonds has been described in more detail in an earlier article [12].

#### 5.4. Evaluation of thermal charge transfer and electron-capture electron affinities

At present the largest number of about 400 organic molecular electron affinities have been determined by the TCT and/or ECD methods [1,3,10–13, 28–41,63–66]. The ECD method has been used to measure electron affinities between 0.05 and 1.5 eV as shown in Fig. 4. The TCT method has been used to measure values between 0.50 eV for nitromethane and 3.2 eV for tetracyanoethylene. Many TCT values were determined by both the ion cyclotron resonance, ICR, and high pressure

Table 8  
Published electron-capture detector parameters

Species	$\ln(A_1)$	$E_1$ (eV)	$Q$	$E_a$ (eV)
C <sub>6</sub> F <sub>5</sub> NO <sub>2</sub>	[36.0]	[0.01]	0.8	1.5 ± 0.1
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	34.6 ± 0.5	0.03 ± 0.01	[1]	1.0 ± 0.01
Acetophenone	–	–	1.0	0.338 ± 0.002
(CH <sub>3</sub> ) <sub>4</sub> C <sub>6</sub> H <sub>2</sub>	–	–	1.0	0.07 ± 0.05
Benzaldehyde	–	–	1.0	0.457 ± 0.005
Methyl benzoate	–	–	1.0	0.20 ± 0.10
Benzonitrile	–	–	1.0	0.26 ± 0.02
Benzophenone	–	–	1.0	0.68 ± 0.05
C <sub>6</sub> F <sub>5</sub> Cl	[36.4]	0.36	[1]	1.01 ± 0.10
C <sub>6</sub> F <sub>5</sub> Cl (ex)	36.4	0.15	0.06	0.82 ± 0.10
C <sub>6</sub> F <sub>6</sub>	34.7	0.04	0.04	0.86 ± 0.02
C <sub>6</sub> F <sub>6</sub> (ex)	34.9	[0.01]	1.0	0.61 ± 0.05
C <sub>6</sub> Cl <sub>6</sub>	[35.4]	0.04	0.03	1.15 ± 0.05
C <sub>6</sub> Cl <sub>6</sub> (ex)	[35.4]	0.02	0.70	0.82 ± 0.10
Tetracene	[37]	0.95 ± 0.05	[1]	1.10 ± 0.05
Tetracene (ex)	[36]	0.80 ± 0.05	1 × 10 <sup>-4</sup>	0.88 ± 0.05
Tetracene (ex2)	[36]	0.65 ± 0.05	[1]	0.53 ± 0.05
Naphthalene	[34.2]	0.2	[1]	0.17 ± 0.05
Naphthalene (ex)	[33.8]	[0.6]	[0.8]	0.13 ± 0.10
CS <sub>2</sub> (bent)	31.2	0.10 ± 0.03	1 × 10 <sup>-3</sup>	0.87 ± 0.03
CS <sub>2</sub> (linear)	32.0	0.03	0.4	0.61 ± 0.04
F <sub>2</sub>	[35.5]	[0.05]	[1]	[3.05]
F <sub>2</sub>	[33]	[0.03]	[1]	[1.7]
Cl <sub>2</sub>	[33]	0.06	[1]	[2.45]
Cl <sub>2</sub>	[35.5]	0.30 ± 0.05	[1]	[1.1]
Br <sub>2</sub>	[35.5]	0.28 ± 0.05	[1]	[2.56]
Br <sub>2</sub>	[33]	0.03	[1]	[1.4]
I <sub>2</sub>	[35.5]	0.45 ± 0.05	[1]	[2.52]
I <sub>2</sub>	[33]	0.05	[1]	[1.5]
O <sub>2</sub>	[24.9]	[0.05]	[1]	0.450 ± 0.002
O <sub>2</sub>	[24.9]	[0.05]	[0.5]	0.430 ± 0.002
O <sub>2</sub>	[24.9]	[0.10]	0.8	0.50 ± 0.05
O <sub>2</sub>	[34.7]	[0.4]	0.01	0.70 ± 0.05
O <sub>2</sub>	[35.2]	[0.8]	0.02	0.75 ± 0.05
O <sub>2</sub>	[35.5]	[0.9]	[0.8]	[0.95]
O <sub>2</sub> (ground state)	[35.5]	[1.9]	[0.8]	[1.07]

The values in square brackets are experimental values from other methods or have been estimated. Values without uncertainties are given to the proper number of significant figures [12,15,27,29,48–51,53].

mass spectrometry HPMS variants [3,63–66]. In the ICR method,  $\Delta G$  values are calculated from measured ion ratios and known concentrations at a single temperature. In the HPMS method, measurements are made as a function of temperature so that  $\Delta H$  and  $\Delta S$  can be obtained ( $\Delta H = \Delta G + T\Delta S$ ). For the ICR single temperature method, a value of  $\Delta S$  is assumed because measurements are made at a single temperature. The combined random and systematic uncertainties in the absolute values due to the direct measurements and the uncertainties in the reference compounds are quoted at  $\pm 0.1$  eV for the HPMS method. The uncertainties in specific values can be lower. At the extremes, the uncertainties in the values can be as large as  $\pm 0.2$  eV. The TCT value in the NIST table for *s*-butyl nitrobenzene should be reduced to  $1.0 \pm 0.1$  eV because it was scaled to an incorrect value of 2.2 eV for the  $E_a$  of SO<sub>2</sub>. In Table 3 are  $E_a$  for nitro compounds determined by either or both the ECD and TCT methods. The CURES-EC and  $E_{1/2}$  values support the ground state assignments. The

values for nitrobenzene, pentafluoronitrobenzene, the nitro-toluenes, and the fluoronitrobenzenes determined by both agree within the random uncertainty specified in column one. Single point ECD data ( $E_1$ ) and the independent observation of the parent negative ions at 373 and 523 K in negative ion mass spectrometry (NMS2) indicate that the chloronitrobenzenes and the bromonitrobenzenes have an electron affinity greater than 1 eV [47]. The CURES-EC and  $E_{1/2}$  values for the dinitrobenzene isomers are especially significant since they support the larger  $E_a$  for the *para*-isomer measured by both the ICR and NIMS procedures.

The  $E_a$  of chloroethylenes, chlorinated and fluorinated benzenes and pentafluorobenzenes have been determined by either or both the TCT and ECD methods. In the ECD data for the fluorobenzenes, two states are observed. The electron affinities of the chlorobenzenes are 0.2–0.3 eV higher than previously reported due to a lower  $Q_{an}$  value for the ground state. In Table 6 are the electron affinities for the halogenated

Table 9  
Electron-capture detector parameters determined in this study

Species	$\ln(A_1)$	$E_1$ (eV)	$Q$	$E_a$ (eV)
2-F-C <sub>6</sub> H <sub>4</sub> COCH <sub>3</sub>	34.5	0.19	1.1	0.49 ± 0.05
4-F-C <sub>6</sub> H <sub>4</sub> COCH <sub>3</sub>	35.5	0.22	0.74	0.52 ± 0.05
3-F-C <sub>6</sub> H <sub>4</sub> COCH <sub>3</sub>	35.6	0.14	0.91	0.58 ± 0.05
<i>p</i> -Diacetyl benzene	[35.2]	0.08	[0.86]	1.01 ± 0.10
<i>p</i> -Diacetyl benzene (ex)	[35.2]	0.08	[1.07]	0.47 ± 0.10
2-F-C <sub>6</sub> H <sub>4</sub> CHO	35.6	0.11	0.54	0.66 ± 0.05
2-F-C <sub>6</sub> H <sub>4</sub> CHO (ex)	35.6	0.02	0.54	0.23 ± 0.04
4-F-C <sub>6</sub> H <sub>4</sub> CHO	35.3	0.11	0.83	0.57 ± 0.07
4-F-C <sub>6</sub> H <sub>4</sub> CHO (ex)	35.6	0.08	1.34	0.48 ± 0.05
3-F-C <sub>6</sub> H <sub>4</sub> CHO	35.2	0.09	0.30	0.66 ± 0.07
2-CF <sub>3</sub> AP	35.6	0.12	0.79	0.79 ± 0.05
2-CF <sub>3</sub> -AP (ex)	35.6	0.04	0.79	0.62 ± 0.04
3-CF <sub>3</sub> -AP	35.6	0.09	0.68	0.79 ± 0.05
3-CF <sub>3</sub> -AP (ex)	35.2	0.03	0.94	0.64 ± 0.04
4-CF <sub>3</sub> -AP	35.2	0.10	0.17	0.89 ± 0.05
4-CF <sub>3</sub> -AP (ex)	35.4	0.04	1.00	0.61 ± 0.04
C <sub>6</sub> H <sub>5</sub> F	35.2	0.63	0.80	0.13 ± 0.05
C <sub>6</sub> H <sub>5</sub> F (ex)	35.2	0.20	0.40	0.07 ± 0.05
<i>p</i> -C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	35.4	0.39	0.22	0.25 ± 0.05
<i>p</i> -C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> (ex)	35.4	0.19	1.00	0.19 ± 0.05
1,2,3,4-C <sub>6</sub> H <sub>2</sub> F <sub>4</sub>	35.5	0.28	0.48	0.52 ± 0.05
1,2,3,4-C <sub>6</sub> H <sub>2</sub> F <sub>4</sub> (ex)	35.8	0.10	0.88	0.40 ± 0.05
C <sub>6</sub> HF <sub>5</sub>	34.9	0.17	0.31	0.72 ± 0.05
C <sub>6</sub> HF <sub>5</sub> (ex)	35.5	0.05	1.04	0.43 ± 0.05
C <sub>6</sub> F <sub>6</sub>	34.7	0.04	0.04	0.86 ± 0.02
C <sub>6</sub> F <sub>6</sub> (ex)	34.9	[0.01]	1.00	0.61 ± 0.05

Value in square bracket are assumed values. The uncertainties in  $\ln[A_1]$  and  $Q$  are less than 10%.

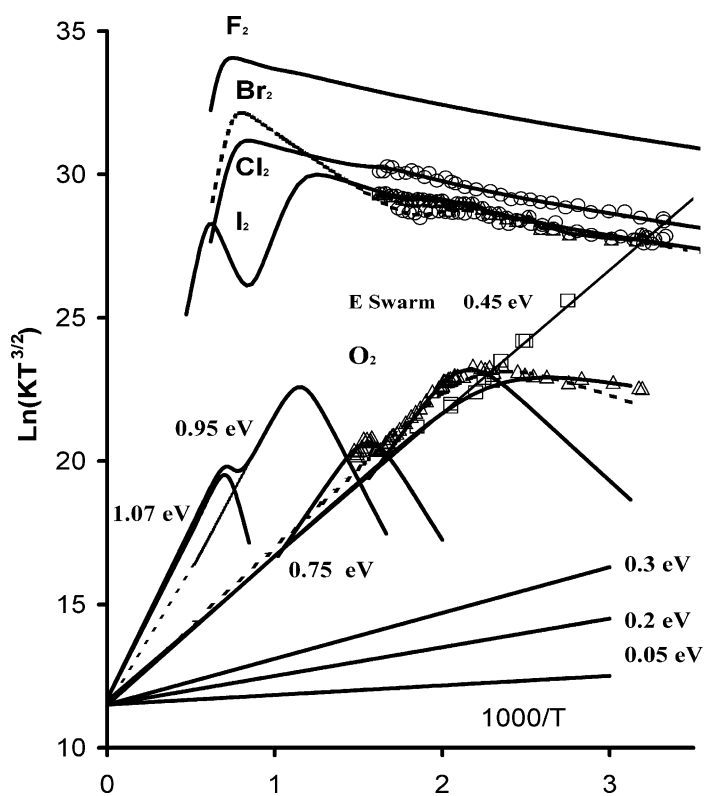


Fig. 5.  $\ln KT^{3/2}$  vs.  $1000/T$  for homonuclear diatomic molecules. The oxygen data were published in [27,49] while the halogen data were published in [37].



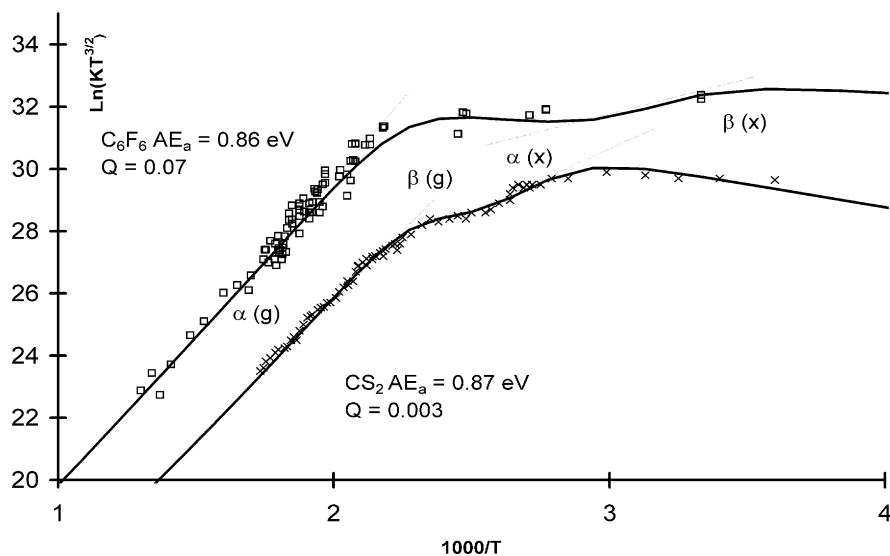


Fig. 6.  $\ln KT^{3/2}$  vs.  $1000/T$  for carbon disulfide and hexafluorobenzene illustrating two states. The data were published in [29–31].

compounds. The ECD values higher than the TCT values are selected as the  $AE_a$ . The CURES-EC values and the reduction potential values support these assignments. The TCT value for  $C_6F_5Br$  is lower than the CURES-EC value and

could be for an excited state. The extension of the methods to larger aromatic systems is demonstrated by the data for the chloronaphthalene and the chloroanthracenes. The general trends for multiple substitutions can be obtained from

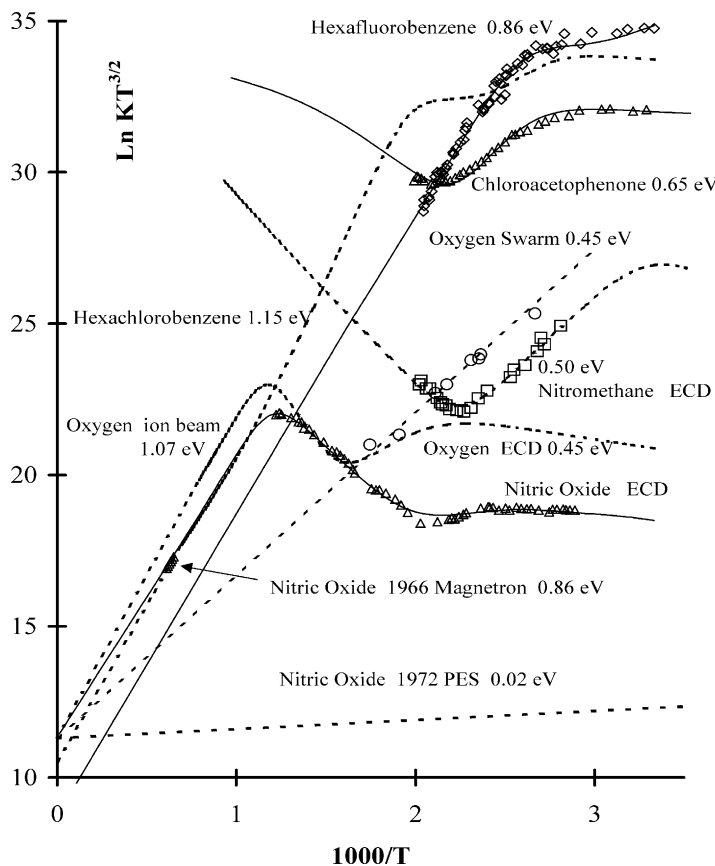


Fig. 7.  $\ln KT^{3/2}$  vs.  $1000/T$  electron-capture detector, magnetron, ion beam and swarm data for multiple states and dissociative and non-dissociative capture. The magnetron data were taken from [2]. The ECD nitromethane, NO and  $O_2$  data were taken from [38,39]. The data have been published in [10,42]. The  $O_2$  ion beam data came from [51].

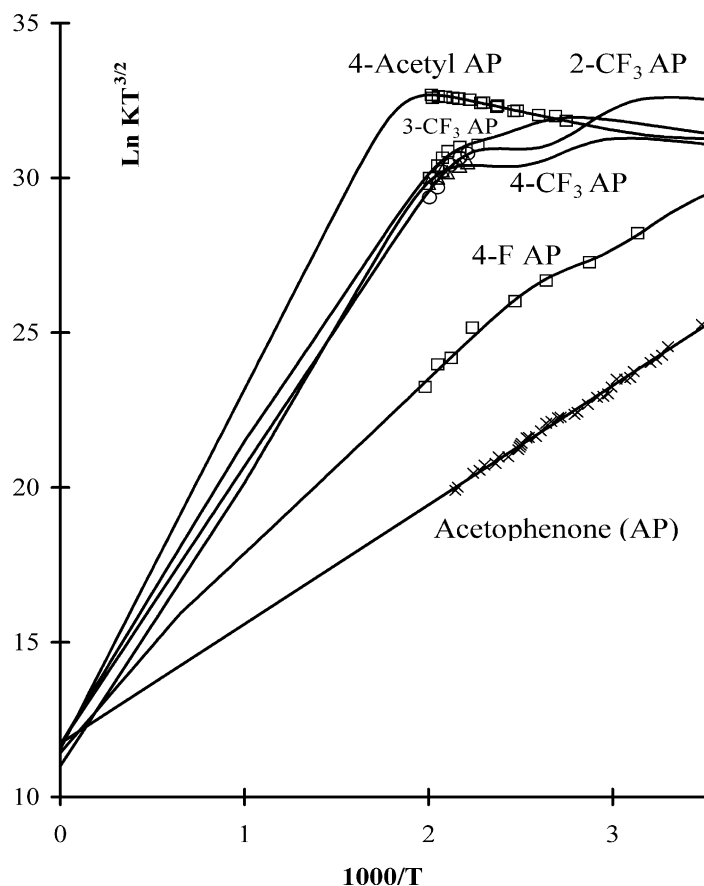


Fig. 8.  $\ln KT^{3/2}$  vs.  $1000/T$  for acetophenones illustrating multiple states and dissociative and non-dissociative capture. The data were taken from [35,39,40].

the compounds with  $E_{1/2}$  data. For the chlorobenzenes data are available for all 12 of the possible isomers. The  $AE_a$  for the fluorobenzenes varies from 0.1 to 0.86 eV. The  $AE_a$  values of chlorobenzenes range from 0.17 to 1.15 eV [41].

In the case of the lower chlorobenzenes and the chloroacetophenones, dissociative electron attachment is observed in the ECD and NIMS data. The experimental bond dissociation energies for 3- and 4-chloroacetophenone, are 3.98 and  $4.01 \pm 0.05$  eV, where  $E_a(\text{Cl}) = 3.613 \pm 0.0001$  eV [15]. By comparison, the CURES-EC AM1 values are both 3.97 eV. This again shows agreement within experimental error and exemplifies the power of computational chemistry programs as a useful analytical tool for making predictions. The predicted temperature dependence for 4-chloroacetophenone is shown in Fig. 7. In addition to the  $\alpha$  and  $\beta$  regions, there is a  $\gamma$  region at higher temperatures with a negative slope, consistent with dissociation where  $E_a < E_2$ . For compounds with similar dissociation energies and  $E_a$ , the temperature dependence will resemble that for the 3- and 4-Cl-acetophenones. The CURES-EC  $AE_a$  for 2-Cl-acetophenone is predicted to be lower than for the 3- and 4-isomers. The relative values are supported by negative ion mass spectrometry data. The NIMS data has a substantially higher abundance of  $\text{Cl}(-)$  and  $(\text{M}-\text{Cl})(-)$  in the spectrum of the *ortho*-isomer [47]. A lower  $E_2$  for the *o*-isomer requires a lower electron affinity

for the molecule based on the equal C–Cl bond dissociation energies. In Table 7 are the kinetic and thermodynamic parameters obtained from the least squares analysis for these compounds. The C–Cl bond dissociation energies are obtained from the data in the  $\gamma$  region. For comparison the values for nitromethane are given [10]. The range of the C–Cl values is small which is anticipated since it is generally assumed that the first aromatic C–Cl bond energies are similar. The chlorobenzenes and 1-Cl-naphthalene also have a C–Cl bond dissociation energy of about 4 eV. In Table 8 are the kinetic and thermodynamic parameters used to calculate the curves in Figs. 4–6. For oxygen six states are assumed and parameters obtained in different experiments used to estimate the parameters from the ECD data. For the halogens, the two activation energies are determined from the ECD data using the estimated parameters and experimental electron affinities.

In Table 9 are parameters for the fluorobenzenes and the acetophenones and benzaldehydes that have been analyzed in this paper. All of the values of  $\ln(A_{1i})$  are 34.5–36.5, within an order of magnitude of  $\ln(\text{DeBA}) = 36$ . All of the  $Q$  values are within the reasonable range of  $10^{-4}$  to 1. For the  $\text{CF}_3$ -isomers, 4-F-acetophenone, 4-F-benzaldehyde and for the Cl-APs the  $E_a$  reported in this study are higher than those previously reported using the single state model

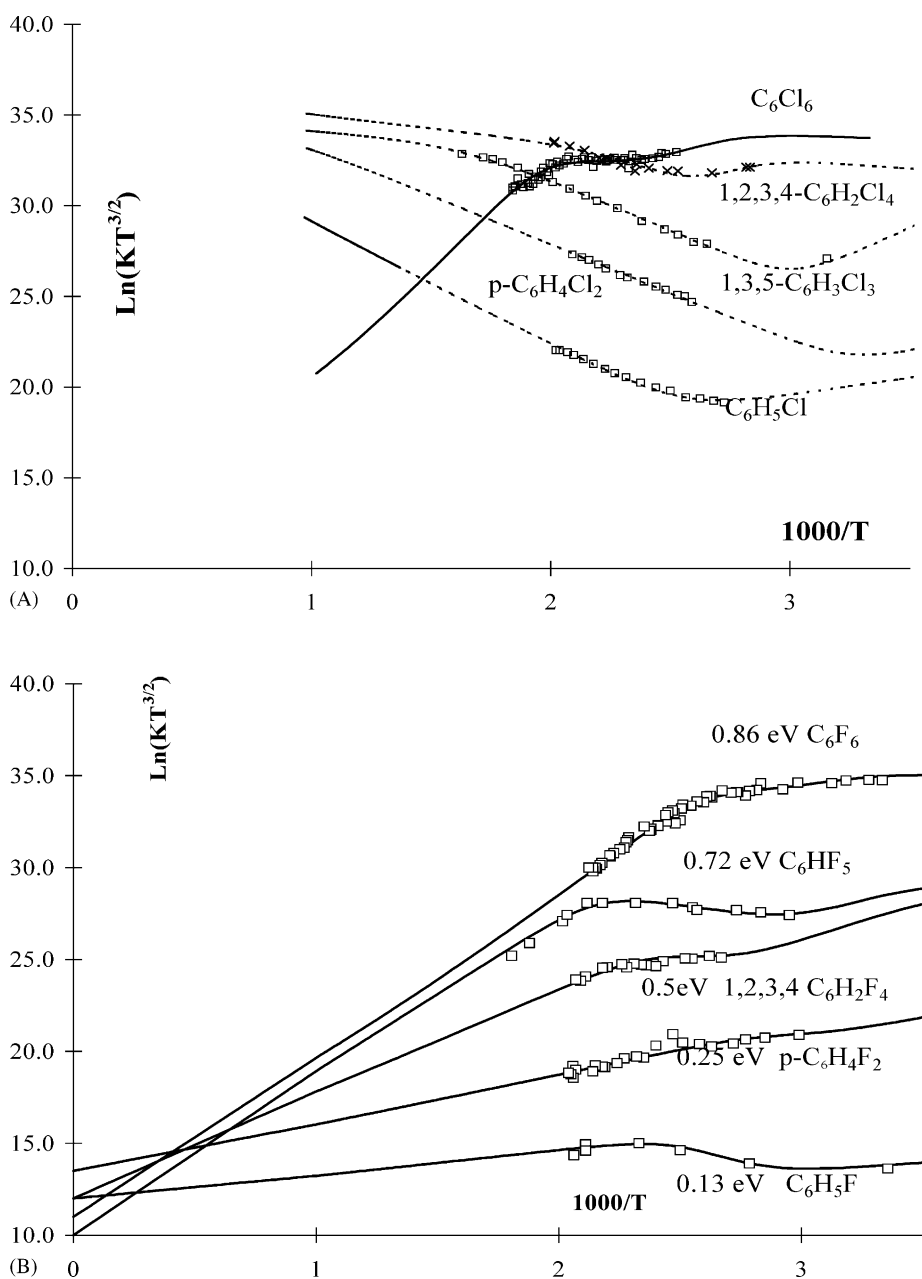


Fig. 9.  $\ln KT^{3/2}$  vs.  $1000/T$  for chlorobenzenes and fluorobenzenes illustrating multiple states and dissociative and non-dissociative capture. The fluorobenzene and chlorobenzene data were taken from [39,41].

[35]. The  $AE_a$  calculated with the two-state model are in agreement with the theoretical calculations.

### 5.5. Substitution effects

Based on the selected values in Tables 1–6, there are now sufficient data to establish general effects for the changes in the electron affinity upon substitutions on benzene. If we consider benzonitrile, methyl benzoate, benzaldehyde, nitrobenzene, and acetophenone as parent molecules, the data demonstrates the order of change in the electron affinities ranging from 1 eV for  $NO_2$  to about zero for the alkyl groups

$NO_2 > CN > CHO > C(CH_3)=O > (COOCH_3) > CF_3 > Cl > F > \text{alkyl}$ . The substitution of a  $CF_3$  group on these compounds increases the  $E_a$  by about 0.4 eV, the substitution of a Cl increases it by 0.20 eV and the substitution of an F increases it by 0.15 eV. However, the effect in the *para* position is much larger than in the *meta* position. The increase for a nitro group ranges from 0.7 to 1.5 eV, that for the CN, CHO,  $C(CH_3)=O$ ,  $COOCH_3$  groups from 0.4 to 0.8 eV and that for the halogens 0.1–0.3 eV. The largest nitro effect is for substitution on benzonitrile in the *para* position, 1.5 eV. For tetramethylbenzene and naphthalene, the alkyl groups increase the  $E_a$  from 0 to 0.1 eV whereas for the quinones

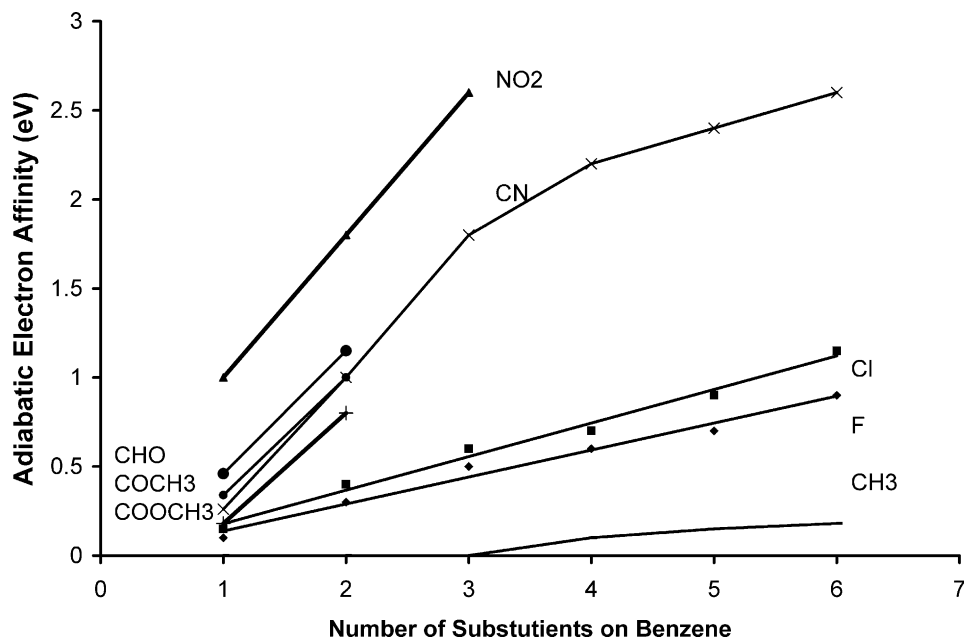


Fig. 10. Adiabatic electron affinity of substituted benzenes vs. number of substituents.

and nitrobenzene, the alkyl groups decrease the  $E_a$  by about the same amount. The  $\text{OCH}_3$  and  $\text{NH}_2$  groups decrease the  $E_a$  by small amounts. These general trends support the measured  $E_a$ . These effects for a single substitution have been correlated with other substitution parameters in TCT and ECD studies [1,3,30,35].

The effect of the available multiple substitutions upon the electron affinities of benzene is shown in Fig. 10. The data available beyond a single substitution are for alkyl, F, Cl, CN, and  $\text{NO}_2$ . The alkyl and halogen substituent effects are linear but those of CN level off at the larger number of substituents. A similar saturation effect should be observed for the  $\text{NO}_2$ , CHO,  $\text{C}(\text{CH}_3)=\text{O}$  and  $\text{COOCH}_3$  groups. The largest effect of fluoro substitution is for *p*-dicyanobenzene and *p*-benzoquinone where four fluoro replacements increases the  $E_a$  by 0.8 eV. The increase in the  $E_a$  is about the same for the CHO,  $\text{C}(\text{CH}_3)=\text{O}$  and  $\text{COOCH}_3$  groups so that in general the absolute  $E_a$  for similarly substituted compounds are in the same order as for the parents, even for mixed substituents.

## 6. Calculation of the electron-capture detector temperature dependence

The ultimate objective of measuring the electron affinities of molecules is to predict the sensitivity and temperature dependence of the electron-capture detector to compounds that might be analyzed. Many of the environmental pollutants have multiple and mixed substituents. In general all of the pesticides are highly chlorinated organic compounds. In addition, chlorinated biphenyls, naphthalenes, and dioxanes are among the most toxic compounds. The ECD has

been used extensively to analyze these compounds. The electron affinities of many of the chlorinated biphenyls and naphthalenes have been estimated from half wave reduction potentials but it was assumed that the solution energy differences were constant. Now that improved  $E_a$  for the chlorobenzenes and CURES-EC calculations are available it is possible to estimate solution energy differences and obtain more accurate  $E_a$ . The temperature dependence of these compounds is very important and has not been extensively studied. As a result, the calculations can offer clues to the best conditions for analysis.

Prior to 1990, there were no estimates of the electron affinities of the biologically significant purines and pyrimidines, adenine, guanine, cytosine, uracil, and thymine AGCUT. At that time we applied substitution and extension of resonance effects to the parent molecules to estimate the electron affinities. Uracil is dihydroxypyrimidine while cytosine is amino-hydroxypyrimidine and guanine is amino and hydroxy-substituted purine. The values for the substituted compounds were found to be 0.5 eV for cytosine, higher for uracil, thymine, and adenine and the highest, 1.3 eV for guanine. The next step was to estimate these quantities by measuring their reduction potential in aprotic solvents and scaling to the measured electron affinities of acridine and anthracene. The values have now been scaled to a larger number of measured electron affinities [9]. The resulting values were (C, 0.56 eV; U, 0.80 eV; T, 0.79 eV; A, 0.94 eV; G, 1.51 eV). These were confirmed by CURES-EC calculations and have been assigned to the  $\text{AE}_a$ . The excited state dipole bound  $E_a$ , which are less than 0.1 eV are listed in the NIST tables. Peaks at the  $\text{AE}_a$  were observed in photoelectron spectra of hydrated uracil and cytosine. The parent negative ions have been

observed for C, U, and T in negative ion mass spectrometry [11,68,69].

### 6.1. Chlorinated naphthalenes, biphenyls, and pesticides

The electron affinity of 1-chloronaphthalene has been measured as 0.30 eV using the ECD. Based on a constant solution energy difference, the  $E_a$  of the octachloronaphthalene is 1.33 eV. The CURES-EC value for the octachloronaphthalene is 1.75 eV. The differences in the calculated and experimental values can be due to solution energy differences so that a value of  $1.55 \pm 0.15$  eV is chosen. In this manner each chlorine atom contributes

less than 0.2 eV to the  $E_a$  in going from naphthalene to the fully chlorinated naphthalene. The curves were drawn with the ECD parameters for the 1-Cl-naphthalene given in Table 7. The electron affinity of the dichloro compound was set to 0.6 eV, the trichloro compound to 0.75 eV and the tetrachloro compound to 0.95 eV. The bond dissociation energies and kinetic parameters were kept the same. The experimental data for *p,p*-DDT, heptachlor, dieldrin and lindane are slightly higher but follow the temperature dependence for perchloronaphthalene [28]. The pesticides undergo dissociative electron-capture as demonstrated by negative ion mass spectrometry at 523 K [47]. The negative ion mass spectrometry of the chloronaphthalenes shows

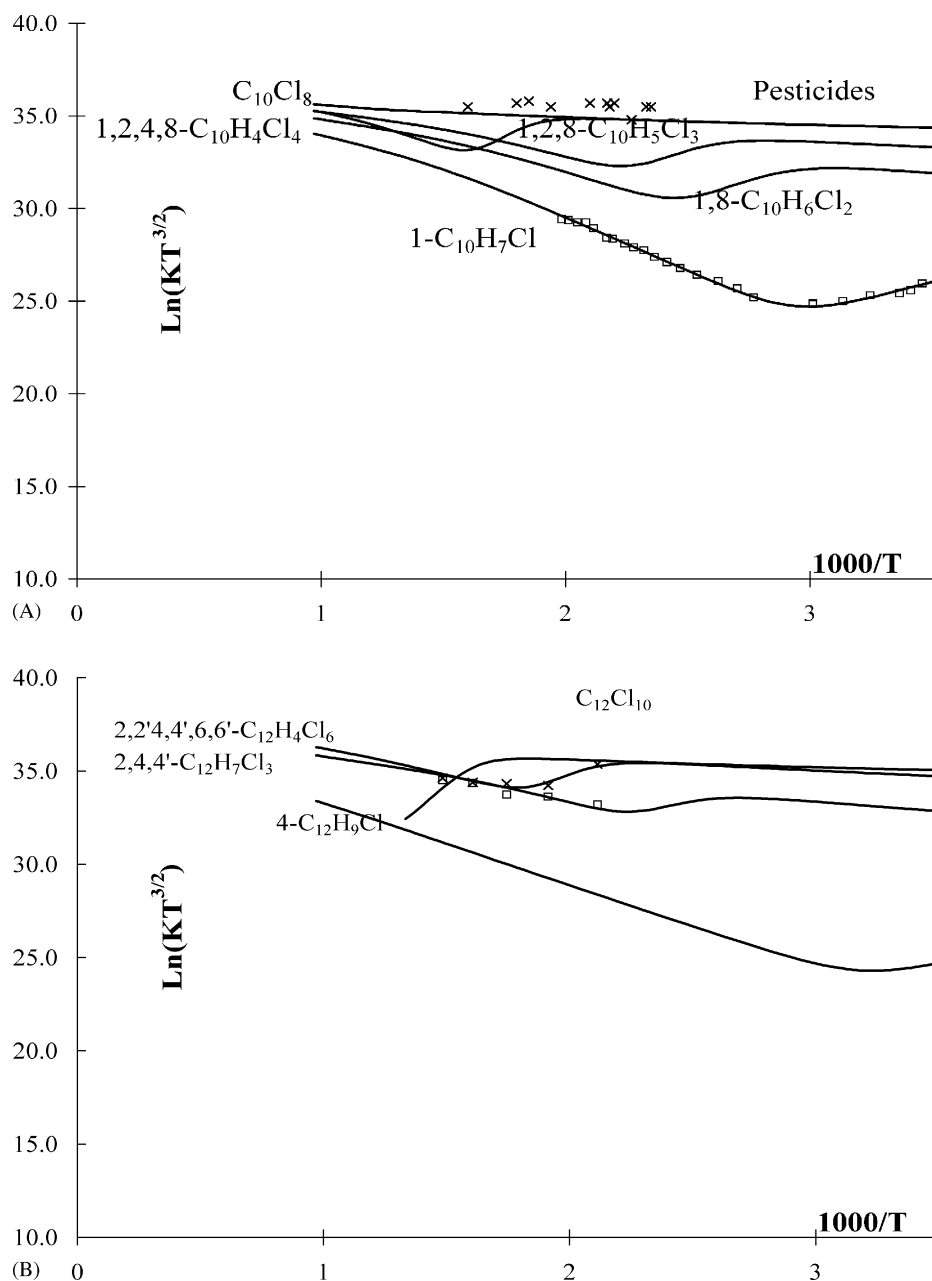


Fig. 11. Calculated  $\ln KT^{3/2}$  vs.  $1000/T$  for chlorinated naphthalenes, biphenyls, and pesticides. The pesticide and biphenyl data were taken from [28] while the chloronaphthalene data were taken from [39].

dissociative electron-capture for the compounds with one to three chlorines at both 273 and 523 K. However, those with four to eight chlorines do not undergo dissociative capture. The ECD curves are clearly in agreement with this information.

The electron affinities of the chlorinated biphenyls are lower than those of the chlorinated naphthalenes. The  $C_{12}H_5Cl_5$  phenylpentachlorobenzene has an electron affinity of about 1.0 eV while that of  $C_{12}Cl_{10}$  is only 0.2 eV higher based on half wave reduction potentials [6]. The first five chlorine atoms raise the electron affinity of biphenyl by about 0.8 eV while the second five only increase the electron affinity by about 0.2 eV. Thus, the substitution on the two rings is somewhat independent. The temperature dependence of the three isomers of the monochloro compound will be similar to the corresponding *m*-, *o*-, and *p*-dichlorobenzene data. Likewise, the temperature depen-

dence of the compounds with two chlorines on the same ring will be similar to the trichlorobenzenes. The fully chlorinated compound will have temperature dependence like that of the hexachlorobenzene. However, the temperature dependence of other chlorinated biphenyls will be difficult to predict. The electron affinities of the compounds with one or two chlorines on one ring and one on the other are about 0.2–0.4 eV based on reduction potentials. In the negative ion mass spectra, dissociative capture is observed at 373 K and increases at 523 K. With two chlorines on each ring, the electron affinities increase to the range of 0.3–0.7 eV and the dissociative capture at 373 K is diminished but at 523 K is still large. With three chlorines on a given ring, the range of the values is 0.5–0.8 eV and the dissociative capture at 523 K is diminished. With four chlorines on one ring and three on the other, the dissociative capture is less than 1%. The isomers with eight and nine chlorines only

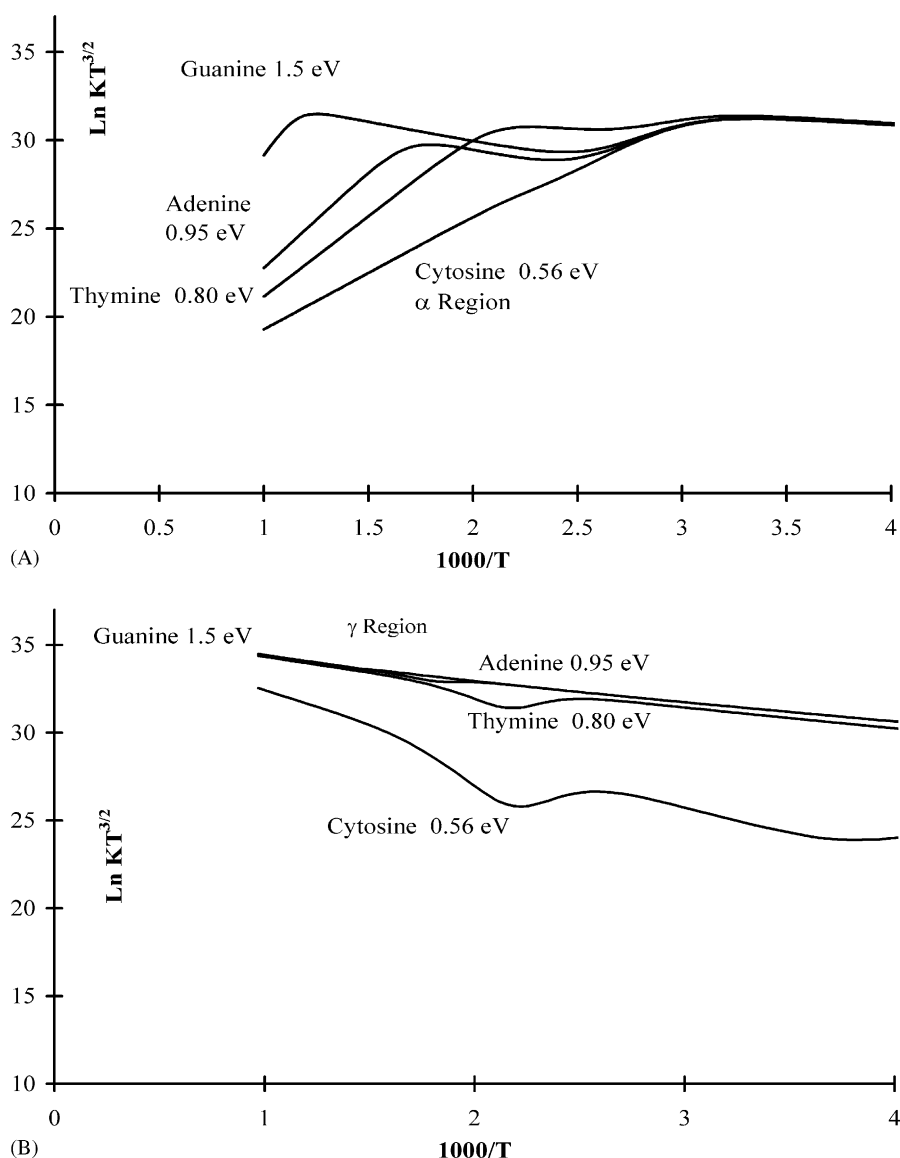


Fig. 12. Calculated  $\ln KT^{3/2}$  vs.  $1000/T$  for adenine, guanine, thymine and cytosine: (A) non-dissociative capture and (B) dissociative capture.

show non-dissociative capture. Approximate curves for the chlorinated biphenyls are shown in Fig. 11B. The data that are shown were obtained using the PDECD [28].

## 6.2. Adenine, guanine, cytosine, thymine and uracil

The electron attachment cross-section for thymine is reported to be as large as that for SF<sub>6</sub> [67–69]. Thus with a value of  $Q = 1$ ;  $A_1 = A_{\max}$ ;  $E_1 < 0.2$  eV and the assumption of an excited state at about 0.5 eV, the curves shown in Fig. 12 are calculated using Eq. (8). Excited state  $E_a$  of C, U, and T have been postulated from electron impact for C and T and PES data for hydrated anions [9,1,68,69]. We have obtained negative ion mass spectra for AGCUT using liquid chromatography and found that at high temperatures, the molecules were deprotonated and formed the anions of the radicals. On this basis, the electron affinities of the radicals formed by losing a hydrogen atom were estimated as  $C_{\min H}$  ( $3.38 \pm 0.05$  eV) and (A, G, U, and T)<sub>minH</sub> ( $3.48 \pm 0.05$  eV) [11,67]. These values were subsequently verified using CURES-EC. With the N–H bond dissociation energy, it is possible to calculate the quantity  $D - E_a$  as about 0.5 eV and to calculate the temperature dependence assuming dissociative electron attachment. The curves are shown in Fig. 12 and indicate a higher ECD response than if non-dissociative capture is assumed. For both cases, the response for cytosine is much smaller (three orders of magnitude at 500 K) than that for the other compounds. The optimum temperatures for the analyses would be at the highest temperature. The response factors for adenine and guanine reach saturation. The response for thymine is not at saturation but will be large. Perhaps the most important part of the calculation is the lower response predicted for cytosine. To our knowledge, there are no routine analyses of these compounds using the ECD. However, by comparison to the pesticides, high-resolution chromatography with high sensitivity should be possible for these compounds.

## 7. Conclusions

The electron affinities of the main group elements, homonuclear diatomic molecules, aromatic hydrocarbons, other organic and small inorganic molecules, nitrocompounds, carbonyl compounds and halogenated aromatic molecules have been systematically evaluated. Three or more experimental procedures have been applied to the determination of electron affinities of nitrobenzene, nitromethane, tetracene, perylene, anthracene, NO, O<sub>2</sub>, I<sub>2</sub>, NO<sub>2</sub>, CS<sub>2</sub>, C<sub>6</sub>F<sub>6</sub>, *p*-benzoquinone, chloranil, fluoranil, and tetracyanquinodimethane. The highest precise value or the weighted average of more than one value is assigned to the adiabatic electron affinity. The values, which differ from the selected values by more than the random uncertainty, are assigned to excited states. The majority of these molecular  $E_a$  have been determined using the TCT

and ECD procedures. The TCT method has been applied to values between 0.5 and 3.0 eV. The ECD procedure has been applied to values between 0 and 1.5 eV. Many of the values reported in this article are the result of the analysis of ECD data in dissertations and theses. These can now be order on line via the internet [70]. Fewer than two-dozen organic molecular  $E_a$  have been determined by the PES, magnetron and AMB methods. The CURES-EC calculations and available half wave reduction potentials support the assignment of the molecular  $AE_a$ . Substitution effects have been calculated and support the assignments of  $AE_a$  for molecules with multiple substitutions. More accurate  $AE_a$  are reported in light of the two-state model: (in eV) 4-F-benzaldehyde ( $0.57 \pm 0.05$ ) and for acetophenones 4-F-AP ( $0.52 \pm 0.05$ ); 2-CF<sub>3</sub>-AP ( $0.79 \pm 0.05$ ); 3-CF<sub>3</sub>-AP ( $0.79 \pm 0.05$ ); 4-CF<sub>3</sub>-AP ( $0.89 \pm 0.05$ ); 3-Cl-AP ( $0.67 \pm 0.05$ ); and 4-Cl-AP ( $0.64 \pm 0.05$ ) and the  $AE_a$  of chloro and fluorobenzenes range from 0.17 to 1.15 eV and 0.13 to 0.86 eV.

A procedure can now be suggested to predict the temperature dependence of the ECD response that can be used by the analytical chemist to determine the temperatures at which to operate the ECD for maximum response and minimum temperature sensitivity. The mechanism for electron attachment must first be postulated to assign nominal rate constants and to determine the thermodynamic equation to be used. The  $AE_a$  and bond dissociation energies can be obtained using quantum mechanical calculations in the MCCI CURES-EC procedure, which can then be used to predict the mechanism for electron attachment. The temperature dependence can also be predicted by analogy to the compounds with measured ECD data. For example, the chlorinated biphenyls and naphthalenes will be like the chlorobenzenes. The nitroacetophenones and compounds with  $AE_a$  greater than 1.1 eV would be like *p*-diacetylbenzene. Those with  $AE_a$  between 0.8 and 1.1 eV would be like the trifluoromethylacetophenones. Those with  $AE_a$  between 0.6 and 0.8 eV would be like tetra and pentafluorobenzene. Those with  $AE_a$  between 0.4 and 0.6 eV would be similar to the fluoroacetophenones or difluorobenzene. The nondissociative molecules with only a single state would have data like AP. Although this procedure may not work for all cases, it is a useful tool for the analytical chemist who has no other information with which to plan an analysis.

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