Short communication

Determination of multiple electron affinities of carbon disulfide using electron-capture detection

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Abstract

The electron affinities (EAs) for carbon disulfide in the literature cluster around two values, 0.895 ± 0.02 eV and 0.55 ± 0.06 eV. Two negative ion states are observed in the temperature dependence of the electron-capture detector. The EAs obtained from these data are 0.61 ± 0.04 eV for the linear anion and 0.873 ± 0.025 eV for the bent anion. The theoretical semi-empirical MINDO/3 EAs are 0.582 eV and 0.891 eV. These support the literature values for the two states and establish the most appropriate values. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The electron affinities (EAs) for carbon disulfide in the literature cluster around two values which differ by more than the experimental error, 0.895 ± 0.06 eV and 0.55 ± 0.1 eV [1–8]. We show that thermal electron attachment to CS_2 measured in electron-capture detection (ECD) leads to two negative ion states. The EAs are 0.61 ± 0.04 eV for the linear anion and 0.873 ± 0.025 eV for the bent anion. Semi-empirical MINDO/3 calculations support these values. A non-linear least squares procedure is given for analyzing ECD data.

The 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.

Before 1960, few accurate molecular EAs had been determined in the gas phase [9–11]. Subsequently, experimental gas phase EA values have been primarily determined by five techniques; the ion molecule reaction bracketing (IMRB) or titration technique; the ECD method; the photoelectron spectroscopy (PES) technique, the alkali metal beam (AMB) method; and the ion molecule reaction energy (IMRE) technique. The IMRB and ECD methods were introduced in the 1960s, the AMB and PES methods in the 1970s, and the IMRE technique in the 1980s. The IMRB and IMRE methods use the kinetics or thermodynamics of the direction of electron transfer in ion molecule reactions to determine EAs. The PES method is based on the determination of the threshold for laser photodetachment. The AMB method uses the threshold for ion pair formation. In the ECD method, the equilibrium

constant for the reaction of a molecule with thermal electrons, K_{eq} (M,e) is measured at different temperatures [4,9,11–15].

All of the experimental EAs for CS_2 are listed in Table 1. In 1961, the first value of the EA of CS_2 was determined by kinetic bracketing between NH_2 and SO_2 [1]. Based on current EAs, this is 0.9 ± 0.2 eV [9]. Photoelectron spectra were reported in 1985 and 1997 [6,7]. The most precise EA is the 1986 PES value of 0.895 ± 0.02 eV [6]. The ECD data were first collected in 1966 but the electron affinity obtained from these data was not published until 1981 [4]. We could not reconcile the value with the IMRB value, and did not understand the unusual fine structure in the data. Later the structure was attributed to excitation of a bending vibration implying a transition to another state [14]. The weighted average literature values are 0.895 ± 0.02 eV or 0.55 ± 0.06 eV. Which of these is the true electron affinity of CS_2? More importantly, which one should be used for bracketing experiments? The answer is that both are valid and the state of the anion must be considered in the bracketing experiment. By fitting the ECD data to an expanded kinetic model, two states are observed. The photoelectron spectra, Rydberg alkali metal studies, and semi-empirical calculations show two states [6–8,16]. Finally simple Walsh diagrams predict two states, a linear and a bent one. We present the values of the rate constants and activation energies for the attachment and detachment of electrons to these two states.

2. Kinetic model of ECD

The ECD reactions are kinetically controlled but in some cases, the equilibrium constant can be measured. For molecules in which the lowest dissociative pathway are endothermic, the ECD 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 react with positive ions with rate constants k_D' and k_N' (e^- or $AB^- + P^+ =$ 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. If an excited state is formed then the rate constants must be given a specific subscript for the state, either x or g. If steady state or equilibrium is assumed between the excited and ground states, the electron-capture expressions are simply additive. Under pulsed conditions, the positive ion, electron and negative ion concentrations are assumed to attain a steady state.

$$\frac{I_b^2 - I_{e-}^2}{I_{e-}I_b} = K[AB] \tag{1}$$

Table 1
Electron affinities of carbon disulfide (eV)

State	This work		Literature			Weighted average	MINDO/3[a]
Bent	0.873 ± 0.025	ECD	>0.8	PES	7–97	0.89 ± 0.01	0.891
	0.90 ± 0.02	PES[b]	0.895 ± 0.02	PES	6–86		
			1.0 ± 0.2	AMB	2–75		
			0.9 ± 0.2	IMRB	1–61		
Linear	0.61 ± 0.04	ECD	<0.8	PES	7–97	0.58 ± 0.03	0.582
	0.60 ± 0.1	PES[b]	0.51 ± 0.10	IMRE	10–87		
			0.53 ± 0.11	IMRB	5–85		
			0.58 ± 0.1	ECD	4–81		
			0.62 ± 0.2	AMB	3–75		
			0.5 ± 0.2	ECT[c]	2–73		

[a] Bent angle = 160.84; bent-r = 160.2 pm; r-linear = 159.6 pm; r-neutral = 154.4 pm.
[b] Interpretation of data from Ref. [7].
[c] Endothermic charge transfer.

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. Since $[(I_b + I_{e^-})/I_b]$ is approximately 2 at low fractional capture, K can be approximated as [14]:

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

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 state specific subscripts x and g,

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

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.

3. Experimental

The ECD experimental procedure has been described previously [4,11–15]. The kinetic parameters are independent of the specific equipment. The equipment used for these determinations was also used to study the fluoronitrobenzenes and has been described [15]. We have obtained similar results with a commercial detector operated in the constant current mode.

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:

$$K_{EC} = [(I_b - I_e)/I_e]_{max} t_{1/2} V/n \quad (4)$$

where $[(I_b - I_e)/I_e]_{max}$ 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 semi-empirical MINDO/3 calculations were carried out using the Hyperchem software and the Cures-EC procedure for minimizing the difference between the theoretical and experimental values of EAs [16].

The non-linear least squares data fits were obtained using a custom program in Excel. The values of A_{1x} and E_{1x} were determined from the limiting low temperature data. The other six kinetic parameters were determined in a non-linear least squares fit of the data to Eq. (3). In this manner, data in which there was no low temperature data could be related to data where low temperature data were available. We do not report the values from the commercial detector but simply mention that similar results were obtained.

4. Results and discussion

In Fig. 1, the ECD data are presented as $\ln KT^{3/2}$ versus $1/T$. The data are a combination of four runs determined on different days. Another set of three runs taken at a different reaction time were combined to get independent estimates of the rate constants and energetics. The curve is the least squares fit to the data. The parameters determined directly were: A_{1g}, E_{1g}, A_{-1g}, E_{-1g}, A_{-1x} and E_{-1x}. These are given in Table 2. By combining these values with estimates for A_{1x} and E_{1x} we obtain: $\ln (A_{1x}/A_{-1x}) = 11.44 \pm 0.7$; $\ln (A_{1g}/A_{-1g}) = 6.08 \pm 0.7$ and the EA values of 0.61 ± 0.04 eV (linear) and 0.873 ± 0.025 eV (bent) shown in Table 2. The units used in A are mol/l, seconds and degrees Kelvin.

The values of $\ln (A_{1i}) = 31-32$ are about two-orders of magnitude lower than the maximum value estimated from the DeBroglie wavelength of an electron, $\ln (A_{max}) = 36$. The rate constants for thermal electron attachment to CS_2 obtained from the parameters agree with values from alkali metal electron transfer to CS_2 [8].

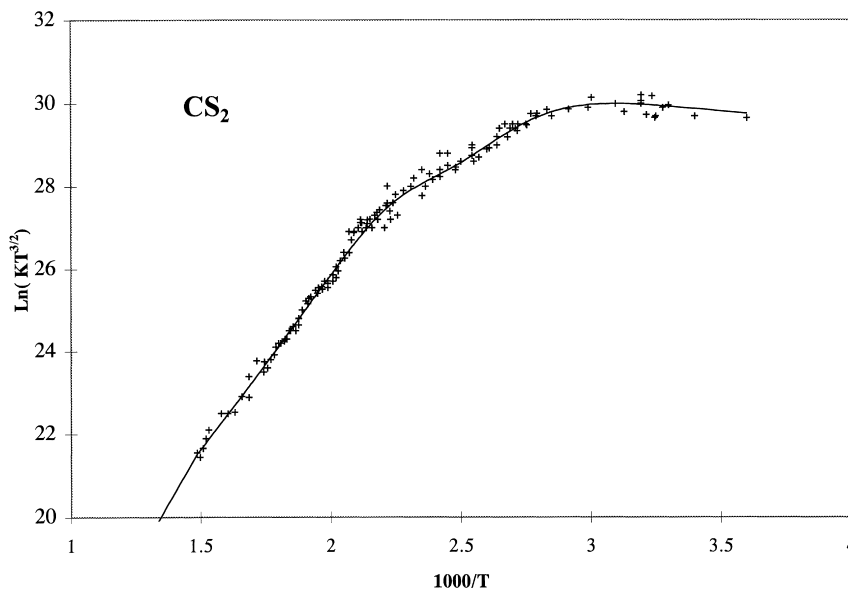For $\ln (A_1/A_{-1})$, ECD values typically fall in the

Fig. 1. ECD data as $\ln KT^{3/2}$ vs. $1/T$ for CS_2.

range of 10–13. The value of $\ln (A_{1x}/A_{-1x})$ falls in this range, but the value of $\ln (A_{1g}/A_{-1g})$ does not. From the statistical mechanical expression for K_{eq} for the reaction of thermal electrons with molecules:

$$A_1/A_{-1} = [g(A^-)/g(A)]h^3/(2\pi m_e k)^{3/2} \qquad (5)$$

where m_e is the electron mass and k and h are the Boltzmann's and Planck's constants and the g values are partition functions and $\ln (A_1/A_{-1}) = 12.43 + \ln \{[g(A^-)/g(A)]\}$. With a value of the experimental ratio of A_1/A_{-1}, the partition function ratio can be calculated. In the case of the excited state this is 0.4 and in the case of the ground state, this is 10^{-3}. The geometry of the linear anion is close to that of the neutral and the ratio of the partition functions is close to 1.

The lower value for the ground state reflects the bent geometry of the anion. We have observed low intercepts for C_6F_6 (ground state), CH_3NO_2, naphthaldehyde and tetracene.

By combining the data from multiple ECD determinations in a rigorous non-linear least squares analysis more precise and accurate values for the two states are obtained. The current ECD and the PES ground state values agree within the error and support the inherent assumptions made in the data analysis. The very recent photoelectron spectra of CS_2 was used to obtain an upper limit for the EA of 0.8 eV. We interpret this as a minimum value for the ground state and a maximum value for the excited state. Both photoelectron spectra show transitions to the linear form at lower energies [6,7]. The threshold for the lower energy process is 0.6 ± 0.1 eV from the recent data. If the onset for the ground state is taken two peaks higher, then the EA is 0.9 eV [7]. The MINDO/3 calculated vertical transition is 0.84 eV. Both PES spectra show a peak at this energy This corresponds to the 0–5 transition for the linear anion to the linear neutral. By assuming two states, and assigning the lower value to the excited state, all of

Table 2
Kinetic parameters for thermal electron attachment to carbon disulfide

State	$\ln A_1$	E_1 (eV)	$\ln A_{-1}$	E_{-1}	$\ln A_1/A_{-1}$	(g_A/g_N)
Bent	31.20 ± 0.42	0.100 ± 0.01	20.51 ± 0.42	0.970 ± 0.015	6.08 ± 0.07	10^{-3}
Linear	31.94 ± 0.2	0.026 ± 0.02	24.41 ± 0.50	0.636 ± 0.03	11.47 ± 0.7	0.4

the literature values agree within the error. The alternative is to assume either large errors or a systematic error.

The MINDO/3 EAs are 0.891 eV for the bent anion and 0.582 eV for the linear anion [16]. These values were optimized to agree with the literature values of the EAs of the two states, not the average values reported in this paper. The weighted averages of the experimental values are 0.89 ± 0.01 eV (bent) and 0.58 ± 0.03 eV (linear). The agreement of these predictions for both states is rewarding. It also support the use of Cures-EC to optimize and predict theoretical values of EAs.

We would like to address two concerns brought up by others about thermal electron reactions studied in ECD. These are: (1) the possible reaction of the anions with impurities in the carrier gas such as oxygen, water or CO_2, and (2) the need to identify the products of the reaction in ECD by mass spectrometry. We have considered and dismissed these. Our only concerns about ECD data are the possibility of hyperthermal electrons and the identification of the state of the negative ions. The first can be tested by measuring the absolute rate constants for molecules such as CCl_4 or SF_6 or the temperature dependence for molecules such as CH_2Cl_2. The second point is of concern in all experiments. We can address this problem by seeking the highest slope as has been done for CS_2. The comparison of gas phase EAs with values obtained by half wave reductions potentials and theoretical EAs are other ways to address this problem.

We dismiss ion molecule reactions by noting the concentrations of the negative ions in the ECD are exceedingly small. Thus large concentrations of an impurity would be required to compete with attachment, detachment, dissociation or recombination. Also the cross section for reaction with thermal electrons is much greater than for ions and the impurities would react with the electrons before they would react with the ions. The ECD is one of the most sensitive detection devices known, and in order to observe negative ions in a mass spectrometer, higher concentrations of the analyte are required. Reactions with impurities may be observed in the mass spectrometer but not in the ECD because of the differences in concentrations.

The mass spectrometric identification of the prod-

ucts is useful but not necessary. In many cases energetics of reactions involving intermediates are interpreted on the basis of chemical logic. Besides, isomers and excited states give exactly the same mass as the ground state so they can not be distinguished with mass spectrometry. As noted above, the problem of identifying the state of the product ions is common to all experimental techniques. For example, in the case of thermal electron reactions of C_6F_6 in high-pressure mass spectrometry or swarm experiments, the product might be an excited state. The EAs from these data, 0.5 ± 0.1 eV [7,8] are considerably lower than the ECD value, 0.86 ± 0.02 eV [17] and the photoelectron spectroscopy and negative ion chemical ionization mass spectrometry value, 0.8 ± 0.1 eV [17–19]. The semi-empirical calculations support two low lying electronic states, one with an electron affinity of 0.83 eV [16]. Rydberg electron transfer studies indicate two different forms of the anion of both CS_2 and C_6F_6 [8].

In conclusion, the ECD data for CS_2 is a good example of the observation of multiple negative ion states, even at atmospheric pressure. Also, without citing specific examples, dipole bound and valence states of anions have recently been observed. Taken together, these observations dispel the myth that only one bound negative ion state can exist at the same time.

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References

[1] K. Kraus, W. Muller-Duysing, H.J. Neuert, Z. Naturforsch. A 16 (1961) 1385.

[2] B.M. Hughes, C. Lifschitz, T.O. Tiernan, J. Chem. Phys. 59 (1973) 3162.

[3] R.N. Compton, P.W. Reinhardt, C.D. Cooper, J. Chem. Phys. 63 (1975) 3821.

[4] E.C.M. Chen, W.E. Wentworth, J. Chromatogr. 217 (1981) 151.

[5] E.P. Grimsrud, G. Caldwell, S. Chowhury, P. Kebarle, J. Am. Chem. Soc. 107 (1985) 4627.

[6] J.M. Oakes, G.B. Ellison, Tetrahedron 42 (1986) 6263.

[7] J. Schiedt, R. Weinkauf, Chem. Phys. Lett. 274 (1997) 18.

[8] A. Kalamarides, C.W. Walter, K.A. Smith, F.B. Dunning, J. Chem. Phys. 89 (1988) 7226.

[9] G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data., 17 (1988) Suppl. 1.

[10] P. Kebarle, S. Chowhury, Chem. Rev. 87 (1987) 513.

[11] E.C.M. Chen, Doctoral Dissertation, University of Houston, Houston, TX, 1966.

[12] W.E. Wentworth, E.C.M. Chen, J.E. Lovelock, J. Phys. Chem. 70 (1966) 445.

[13] E.C.M. Chen, W.E. Wentworth, Mol. Cryst. Liq. Cryst. 171 (1989) 271.

[14] W.E. Wentworth, E.C.M. Chen, in: A. Zlatkis, C.F. Poole (Eds.), Electron Capture – Theory and Practice in Chromatography (Journal of Chromatography Library, Vol. 20), Elsevier, Amsterdam, 1981, p. 27.

[15] E.C.M. Chen, E.S.D. Chen, W.E. Wentworth, J. Phys. Chem. 95 (1991) 520.

[16] E.C.M. Chen, E.S.D. Chen, J. Chem. Phys., in press.

[17] E.C.M. Chen, E.S.D. Chen, W.E. Wentworth, J. Chem. Phys 100 (1994) 6981.

[18] A. Nakajima, T. Taguwa, K. Hoshino, T. Sugioka, T. Naganuma, F. Ono, K. Watanabe, K. Knakao, Y. Konishi, R. Kishi, K. Kaya, Chem Phys. Lett. 214 (1993) 88.

[19] E.C.M. Chen, J.R. Wiley, C.F. Batten, W.E. Wentworth, J. Phys. Chem. 98 (1994) 88.