

MASS SPECTROMETRIC DETERMINATION OF THE ELECTRON AFFINITIES OF RADICALS

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ABSTRACT

By mass spectrometric study of the appearance of C_2^- , CH^- and C_2H^- from CH_4 , C_2H_2 , C_2H_4 , C_2H_3X ($X = Cl, F$) the following electronaffinities have been determined: $EA(CH) = (2.6 \pm 0.3)$ eV, $EA(C_2) = (3.3 \pm 0.2)$ eV and $EA(C_2H) = (2.1 \pm 0.3)$ eV. Some evidence is brought to the existence of electronic excited states of these ions. An evaluation of these negative ions dissociation energy in their ground electronic state is given and is found to be of the order of magnitude of the corresponding isoelectronic molecular species dissociation energy.

1. INTRODUCTION

In the last few years theoretical [1-3] and experimental [4-6] work has been devoted to the determination of the atoms and radicals electronaffinity (EA). Very few values, however, are known for radicals [7,8]. We would like to present here the values deduced for EA of CH , C_2 and C_2H from electron impact experiments of both DA (Dissociative Electron Attachment) and IP (Ion-Pair) processes in CH_4 , C_2H_2 , C_2H_4 and C_2H_3X ($X = Cl, F$) and dissociation energies of the corresponding negative ions.

The experimental methods used have been described elsewhere [9,10]. It may be added to these papers dealing with DA processes that the threshold values for ion-pair processes used here have been determined in the same way as for DA but on the deconvoluted first derivative of the IP electron impact efficiency curves [19].

2. ELECTRONAFFINITY OF THE C_2 RADICAL

Previously Honig [11] has given the first values for EA of C_2 as sublimated from graphite: he proposed 3.1 eV and 4.0 eV. Von Trepka [12] gives a mass spectrometric estimate of $EA(C_2) \geq 2.9$ eV from DA in C_2H_2 and C_2H_4 . In table 1 the values of EA (C_2) obtained from measurements of the appearance potentials of C_2^- from C_2H_2 , C_2H_3F and C_2H_3Cl are gathered with the most probable interpretations of the observed thresholds.

Table 1 Appearance potentials, proposed mechanisms and deduced electronaffinities for C_2^-

| Mechanisms | AP(eV) | EA(eV) |
|---|----------------|---------------|
| $C_2H_2 + e^- \rightarrow C_2^- + 2H$ | 7.6 ± 0.2 | 3.3 ± 0.2 |
| $C_2H_3F + e^- \rightarrow C_2^- + H^+ + H + HF$ | 21.8 ± 0.1 | 3.3 ± 0.1 |
| $C_2H_3Cl + e^- \rightarrow C_2^- + H^+ + H + Cl$ | 23.8 ± 0.2 | 3.4 ± 0.2 |

It appears from this table that $EA(C_2) = (3.3 \pm 0.2)$ eV, in good agreement with the lowest value proposed by Honig [11].

Table 2 Appearance potentials, proposed mechanisms and deduced electronaffinities for C_2^-

| Mechanisms | AP(eV) | EA(eV) |
|--|--------------------------|----------------|
| $C_2H_4 + e^- \rightarrow C_2^- + H_2^+ + 2H$ | 28.0 ± 0.1 | 0.04 ± 0.1 |
| $C_2H_3F + e^- \rightarrow C_2^- + H^+ + H + HF$ Max: | 26.6 ± 0.2 (25.0) | 0 |
| $C_2H_3Cl + e^- \rightarrow C_2^- + H^+ + H + Cl$ | 27.3 | 0 |
| $C_2H_3F + e^- \rightarrow C_2^- + H^+ + H + HF$ | 22.9 ± 0.1 | 2.2 ± 0.1 |
| $C_2H_3Cl + e^- \rightarrow C_2^- + H_2 + H + Cl$ Max: | 27.5 ± 0.5 (25.0) | 2.2 |

Max, maximum of the partially resolved peak in the I. E. C. first derivative; (), estimated value of threshold.

In addition, two more values are deducible from other thresholds (table 2).

The lowest values of EA (C2) may be due either to an unknown KE distribution on the fragments or to the formation of C₂⁻ in electronically excited states. Electronic excitation of the neutral fragments is excluded: the energy required should be at least 9 eV above the measured thresholds. It is very unlikely that the same amount of KE should be carried away by C₂⁻ ions formed by different processes from various molecules.

Recently, Herzberg and Lagerqvist [13] discovered a new system of Σ-Σ bands by using a flash discharge in CH₄: this is attributed to the ²Σ_u⁺ - ²Σ_g⁺ transition of C₂⁻. The head of the 0-0 band is at 18487 cm⁻¹ (2.3 eV). No evidence was found for a ²Π-²Σ_g⁺ transition. More recently, the existence of a 541.6 Å band was found by Milligan and Jacox [14] through photolysis of C₂H₂ isolated in an argon matrix; it was attributed to the same transition in C₂⁻.

In the isoelectronic N₂⁺ ion the first three electronic states are X²Σ_g⁺, A² Π at 1.1 eV [15] and B²Σ_u⁺ at 3.15 eV [15]. The three observed values of EA (C₂)(i.e., 3.3 eV, 2.2 eV, and ≈ 0 eV) would be correlated with corresponding states of C₂⁻.

The value of EA (C₂) = 2.2 eV can be attributed to the appearance of C₂⁻ in an electronically excited state corresponding to A² Π. As mentioned above, this transition has not been observed spectroscopically; the Π-Σ transition could be much weaker than the Σ-Σ one if we remember that the corresponding transition in N₂⁺ has a lifetime of about 10⁻⁵ sec [16].

The value EA (C₂) ≈ 0 eV should be attributed to the appearance of C₂⁻ in the B²Σ_u⁺ state. The energy separation of (3.3 ± 0.2) eV between the two Σ states is in agreement with the interval in N₂⁺ and in disagreement with the spectroscopic data. Two interpretations are possible for this value of EA (C₂): (i) the C₂⁻ ion appears vibrationally excited in the B²Σ_u⁺ state or (ii) is formed in a higher excited electronic state ⁴Σ_u⁺ actually not detected spectroscopically, by the forbidden quartet-doublet transitions.

3. ELECTRONAFFINITY OF THE CH RADICAL

Previous electronaffinity experimental values of CH were given by Smith [17] and Von Trepka [12]: they found EA(CH) ≥ 1.4 eV and EA(CH) ≥ 3.1 eV, respectively. In table 3 are listed the thresholds and the most probable mechanisms of formation of CH⁻ from CH₄, C₂H₂ and C₂H₄ by DA and/or IP processes.

Table 3 Appearance potentials, proposed mechanisms and deduced electronaffinities for CH

| Mechanisms | AP(eV) | EA (eV) |
|--|------------|-------------------------|
| CH ₄ + e ⁻ → CH ⁻ + H ⁺ + 2H | 24.4 ± 0.3 | 2.7 ± 0.1 |
| C ₂ H ₂ + e ⁻ → CH ⁻ + C ⁺ + H | 22.1 ± 0.3 | 2.5 ± 0.3 |
| C ₂ H ₄ + e ⁻ → CH ⁻ + CH ₂ + H | 9.0 ± 0.1 | 2.3 ± 0.3 ^{a)} |
| CH ⁻ + CH ₂ + H ⁺ | 23.1 ± 0.1 | 2.7 ± 0.3 ^{a)} |

^{a)} Assuming that D(CH₂=CH₂) = (7.6 ± 0.3) eV [18].

Assuming that no KE is involved in these processes the electronaffinity average value of CH is EA(CH) = (2.6 ± 0.3) eV. This value is 1.0 eV higher than that predicted by Cade [2] and based on Hartree-Fock calculations on CH(X³Σ). Cade's calculated value is EA(CH) = 1.6 eV with an estimated reliability of ± 0.2 eV. Other thresholds and their interpretation are listed in table 4.

Table 4 : Appearance potentials, proposed mechanisms and deduced electronaffinities for CH

| Mechanisms | AP(eV) | EA(eV) |
|---|--------------------------|------------|
| CH ₄ + e ⁻ → CH ⁻ + H + H ₂ | 9.7 ± 0.2 | -0.6 ± 0.2 |
| CH ⁻ + H ⁺ + 2H | 25.4 ± 0.2 27.0 ± 0.2 | 1.7 ± 0.2 |
| | | -0.1 ± 0.2 |
| C ₂ H ₂ + e ⁻ → CH ⁻ + H ⁺ + C | 25.5 ^{a)} | -0.8 ± 0.3 |
| C ₂ H ₄ + e ⁻ → CH ⁻ + CH ₂ + H ⁺ | 25.8 ^{a)} | 0 ± 0.3 |

^{a)} Estimated threshold obtained by extrapolation of insufficiently resolved peaks in the I. E. C. first derivative.

Only one value of the EA(CH) is in agreement with that predicted by Cade [2], namely (1.7 ± 0.2) eV.

The energy-level diagram of the NH molecule, isoelectronic with the CH⁻ ion, shows three electronic states within a range of 3 eV: the ground state X³Σ⁻, whereas a ¹Δ at 1.2 eV [20] and b¹Σ⁺ at 2.27 eV [21] are the first and second electronic excited states, respectively.

The last value EA(CH) = (1.7 ± 0.2) eV can be explained either by electronic excitation or by considering some KE being involved in the mechanism CH₄ + e⁻ → CH⁻ + H⁺ + 2H.

Table 4 also shows four negative values of EA(CH). It is very likely that CH⁻ is formed in an excited electronic state where EA (CH) has a low value. The discrepancy between the four values can be ascribed to the fact that only a part of the excess energy is converted to KE and carried away by the negative ion. Various amounts of KE are involved in the different mechanisms.

4. ELECTRONAFFINITY OF THE C₂H RADICAL

Only one estimated value of EA(C₂H) is given by Von Trepka [12], i.e., EA(C₂H) ≥ 2.8 eV. The C₂H⁻ ion has been detected in the C₂H₂, C₂H₄, C₂H₃F and C₂H₃Cl mass spectra. Table 5 gives the most probable interpretation of the appearance potential of C₂H⁻

Table 5 Appearance potentials, proposed mechanisms and deduced electronaffinities for C₂H⁻

| Mechanisms | AP(eV) | EA(eV) |
|---|--------------------|-----------|
| C ₂ H ₂ + e ⁻ → C ₂ H ⁻ + H | 2.8 ± 0.2 | 2.1 ± 0.2 |
| C ₂ H ₄ + e ⁻ → C ₂ H ⁻ + 3H | 9.9 ± 0.1 | 2.4 ± 0.2 |
| C ₂ H ⁻ + H ⁺ + H ₂ | 18.5 ± 0.3 | 1.9 ± 0.3 |
| C ₂ H ₃ F + e ⁻ → C ₂ H ⁻ + 2H + F | 9.1 ± 0.2 | 2.5 ± 0.1 |
| C ₂ H ⁻ + HF ⁺ + H | 19.9 ± 0.2 | 1.9 ± 0.3 |
| C ₂ H ⁻ + F ⁺ + H ₂ | 22.2 ^{a)} | 2.3 |

^{a)} Estimated value obtained by extrapolation of insufficiently resolved peak in the I. E. C. first derivative.

Except for EA = (2.5 ± 0.1) eV, the values appear to be reproducible within experimental error. From the above data the most probable electronaffinity of C₂H is EA (C₂H) = (2.1 ± 0.3) eV.

From other thresholds listed in table 6 a second value of EA (C₂H) can be obtained.

Table 6 Appearance potentials, proposed mechanisms and deduced electronaffinities for C₂H⁻

| Mechanisms | AP(eV) | EA(eV) |
|---|------------|------------|
| C ₂ H ₂ + e ⁻ → C ₂ H ⁻ + H ⁺ | 18.4 ± 0.1 | 0.09 ± 0.1 |
| C ₂ H ₄ + e ⁻ → C ₂ H ⁻ + H ₂ + H | 6.9 ± 0.1 | 0.07 ± 0.1 |
| C ₂ H ⁻ + H ₂ + H | 21.7 ± 0.3 | 0.5 ± 0.3 |
| C ₂ H ₃ Cl + e ⁻ → C ₂ H ⁻ + H + HCl | 6.2 ± 0.1 | 0.05 ± 0.1 |
| or C ₂ H ⁻ + H ₂ + Cl | | |

An average value of EA(C₂H) is (0.2 ± 0.2) eV, which seems to correspond to an electronically excited state of C₂H⁻.

5. THE DISSOCIATION ENERGIES OF NEGATIVE POLYATOMIC IONS

When the electronaffinity of a radical is known, it is possible to get an idea about the stability of the negative ion in its ground electronic state. A negative ion may dissociate by the process AB⁻ → A⁻+B The relation

$$D_0^\circ(\text{AB}^-) = D_0^\circ(\text{AB}) - \text{EA}(\text{A}) + \text{EA}(\text{AB}) \quad (1)$$

enables us to evaluate the dissociation energy of the AB^- species; $D_0^\circ(\text{AB}^-)$ and $D_0^\circ(\text{AB})$ are the dissociation energies of the negative ion and the neutral species, $\text{EA}(\text{A})$ and $\text{EA}(\text{B})$ are the electron affinities of the fragment and the neutral species, respectively.

5.1. The CH^- ion

If $X^3\Sigma^-$ is the configuration of the ground electronic state of CH^- , the ion dissociates by $\text{CH}(X^3\Sigma^-) \rightarrow \text{C}(^4\text{S}_u) + \text{H}(^2\text{S}_g)$. A second dissociation process is $\text{CH}^- \rightarrow \text{C}(^3\text{P}_u) + \text{H}(^1\text{S}_g)$. The combination of a $^3\text{P}_u$ term with a $^1\text{S}_g$ term gives rise to $^3\Sigma^+$ and $^3\Pi$ states.

Substituting in relation (1) $D_0^\circ(\text{CH}) = 3.47$ eV [21], $\text{EA}(\text{C}) = 1.25$ eV [22] and $\text{EA}(\text{CH}) = (2.6 \pm 0.3)$ eV, it is found that $D_0^\circ(\text{CH}^-) = (4.8 \pm 0.3)$ eV. This is rather close to the dissociation energy of NH , isoelectronic with CH^- , of 4.2 eV [21].

5.2. The C_2^- ion

This ion can dissociate only by $\text{C}_2^-(X^2\Sigma_g^+) \rightarrow \text{C}(^4\text{S}_u) + \text{C}(^3\text{P}_u)$. Using the best value $D_0^\circ(\text{C}_2) = 6.12$ eV [23, 24], $\text{EA}(\text{C}) = 1.25$ eV [22] and $\text{EA}(\text{C}_2) = (3.3 \pm 0.2)$ eV, a $D_0^\circ(\text{C}_2^-) = (8.2 \pm 0.2)$ eV is found, to be compared with 8.7 eV [15] for $D_0^\circ(\text{N}_2^+)$ isoelectronic with C_2^- .

5.3. The C_2H^- ion

The dissociation process of C_2H^- in its ground electronic state is $\text{C}_2\text{H}^-(X^1\Sigma^+) \rightarrow \text{C}_2^-(X^2\Sigma_g^+) + \text{H}(^2\text{S}_g)$. The calculation of $D(\text{C}_2^- \text{-H})$ by relation (1) requires $D(\text{C}_2 \text{-H})$ to be known; this latter value has been found from

$$D(\text{C}_2\text{H}) = \Delta U_f(\text{C}_2) + \Delta U_f(\text{H}) - \Delta U_f(\text{C}_2\text{H}),$$

where ΔU_f is the heat of formation of the radicals. Using $\Delta U(\text{C}_2) = (8.6 \pm 0.2)$ eV [25], $\Delta U(\text{H}) = 2.26$ eV [25] and $\Delta U(\text{C}_2\text{H}) = 5.10$ eV [26], a value of $D(\text{C}_2 \text{-H}) = (5.8 \pm 0.2)$ eV is obtained. Substituting this last value as well as $\text{EA}(\text{C}_2) = (3.3 \pm 0.2)$ eV and $\text{EA}(\text{C}_2\text{H}) = (2.1 \pm 0.3)$ eV in relation (1), $D(\text{C}_2^- \text{-H}) = (4.6 \pm 0.4)$ eV is obtained.

We have shown that a detailed study of the appearance of some negative polyatomic ions in different gases at low pressure, by electron impact, enables us to determine the EA of the corresponding radicals. It has also been possible to bring some evidence to the existence of electronically excited states of the negative polyatomic ions and to give an idea of their stability in terms of the dissociation energy in their ground electronic state.

It should be desirable that these last points be confirmed by other independent methods such as spectroscopic ones; such measurements are now in progress for the Cp^- ion [13].

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