

The Dependence of the Thermal Electron Attachment Rate Constant in Gases and Liquids on the Energy Position of the Electron Attaching State

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Dedicated to Prof. Dr. H. Baumgärtel on the occasion of his 60th birthday

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Thermal electron attachment rate constants for halocarbons in the gaseous phase, $(k_a)_{th}$, and thermal electron attachment rate constants for a number of molecules in liquid cyclohexane, $(k_a)_L$, are summarized in an effort to discern the dependence of the thermal electron attachment rate constant for molecules embedded in gases and in liquids on the energy position, E_{NIS} , of the electron attaching state. For these molecules the $(k_a)_{th}$ varies only slightly with E_{NIS} as long as E_{NIS} is < 0.0 eV (i.e., as long as the electron affinity of the molecule is positive), but it decreases precipitously with increasing E_{NIS} when $E_{NIS} > 0.0$ eV (i.e., when the electron affinity of the molecule becomes negative). The $(k_a)_L$ exhibits a similar behavior except that it remains virtually constant well above 0.0 eV, up to $E_{NIS} \approx 0.9$ eV, and thereafter decreases precipitously. This energy shift between the gaseous and the liquid phase correlations is consistent with the magnitude of the polarization energy of the anions in liquid cyclohexane and its effect on E_{NIS} . It indicates that in the liquid phase the rate constant $(k_a)_L$ for these molecules is essentially constant (and very large; often equal to diffusion-controlled values) as long as the energy E_{NIS} of the electron attaching state in the liquid is < 0 eV, that is, as long as the molecule has negative ion state(s) which are lowered below 0.0 eV in the liquid. This conclusion may be of wider validity.

Thermische Elektronenanlagerungsratenkonstanten von gasförmigen Halogenkohlenwasserstoffen $(k_a)_{th}$ wie von Molekülen, die in flüssigem Cyclohexan gelöst sind $(k_a)_L$, werden

mit dem Ziel untersucht, einen Zusammenhang zwischen der thermischen Elektronenanlagerungsratenkonstante und der Energie der elektronenanlagernden Zustände (E_{NIS}) in Abhängigkeit von der Umgebung der Moleküle zu beschreiben. Es zeigt sich, daß $(k_a)_{\text{th}}$ sich nur wenig in Abhängigkeit von E_{NIS} verändert, wenn $E_{\text{NIS}} < 0.0$ eV, d.h. für Moleküle mit positiver Elektronenaffinität. Im Fall von Molekülen mit $E_{\text{NIS}} > 0.0$ eV (Moleküle mit negativer Elektronenaffinität) fällt jedoch $(k_a)_{\text{th}}$ mit steigendem E_{NIS} stark ab. Für $(k_a)_{\text{L}}$ wird ein sehr ähnliches Verhalten gefunden, allerdings bleibt E_{NIS} bis zu ≈ 0.9 eV konstant um dann auch bei höherem E_{NIS} stark abzufallen. Diese energetische Verschiebung zwischen der Gasphase und der flüssigen Phase läßt sich in konsistenter Weise mit der Größe der Polarisationsenergie von Anionen, die in Cyclohexan gelöst sind, und ihrem Einfluß auf E_{NIS} erklären. Dies zeigt, daß $(k_a)_{\text{L}}$ für die untersuchten Moleküle weitgehend konstant ist und große Werte annimmt, die häufig den diffusionskontrollierten Werten entsprechen, solange die Energie des elektronenanlagernden Zustandes E_{NIS} in der flüssigen Phase < 0 eV beträgt, bzw. solange das Molekül negative Ionenzustände aufweist, die in der Flüssigkeit unter Werte < 0.0 eV erniedrigt werden. Diese Schlußfolgerung ist möglicherweise von weitreichender Bedeutung.

I. Introduction

Extensive recent studies (e.g., Refs. [1–5]) on electron attachment to molecules in gases and in liquids have shown that the rate constant, k_a , of electron attachment to a molecule depends strongly on the nature of the molecule itself, the internal energy of the molecule, the energy of the captured electron, and the medium in which the reaction occurs. The effect of the medium on the magnitude of the electron attachment rate constant can be profound; it depends strongly on the “state” of the electron (whether the excess electron is quasi-free or localized) in the medium, and the mode (dissociative or nondissociative) of electron attachment. The energetics of the electron attachment process are medium dependent also. In dense matter, excess electrons are normally in thermal equilibrium with the medium and consequently their energies can be represented by a Maxwellian distribution function characteristic of the medium’s temperature. Hence, in dense matter the quantity of primary interest is the value of the thermal electron attachment rate constant $(k_a)_{\text{th}}$. Within the scope of the present work, it is those resonant electron attachment processes which are located at or below ~ 1 eV which are of primary interest. For these, the rate constant k_a can be very large since k_a is generally larger the lower the energy position, E_{NIS} , of the electron attachment resonance [1, 3]. It is, thus, essential to know how much the molecular (gaseous) values of E_{NIS} are lowered in the liquid and how this lowering affects the magnitude of $(k_a)_{\text{th}}$.

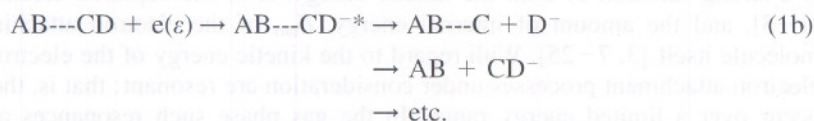
This work is focused on halocarbons and on compounds for which the thermal electron attachment rate constant has been measured in dielectric liquids (liquid cyclohexane).

II. Electron attachment to molecules in the gaseous and in the condensed phases of matter

A. Basic electron attachment mechanisms

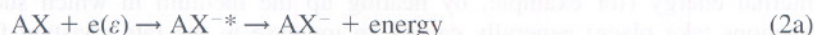
In both the gaseous and the condensed phases of matter, electron attachment to molecules leading to the formation of negative ions occurs via two fundamental reactions:

(i) dissociative electron attachment



and

(ii) nondissociative electron attachment



The electron attachment reactions (1a) and (1b) lead to the formation of fragment negative ions and free radicals, whereas the reactions (2a) and (2b) lead to the formation of parent negative ions. In the above reactions, $e(\varepsilon)$ represents an electron with kinetic energy ε , AX represents a diatomic molecule, $AB\cdots CD$ represents a polyatomic molecule, and AX^{-*} and $AB\cdots CD^{-*}$ represent transient negative ions formed with a capture cross section $\sigma_0(\varepsilon)$; A , $AB\cdots C$, and AB are radicals, and X^{-} , D^{-} , and CD^{-} are stable anions formed with an attachment cross section

$$\sigma_a(\varepsilon) = \sigma_0(\varepsilon)p \quad (3)$$

where p is the probability that the transient negative ion AX^{-*} or $AB\cdots CD^{-*}$ will lead to a stable negative ion as opposed to decaying via other processes (e.g., elastic and inelastic electron scattering). The transient anion intermediates have lifetimes which vary from femtoseconds to milliseconds depending on the negative ion state, the kinetic energy of the captured electron, the internal energy of the capturing molecule, and other factors [1–3, 6–8]. Reaction (1b) can lead to multiple fragmentation of the polyatomic molecule $AB\cdots CD$.

In reactions (2), the formation of the parent anions AX^{-} and $AB\cdots CD^{-}$ requires that the electron affinities of the AX and $AB\cdots CD$ molecules are positive and that the excess energy of the transient anions (symbolized by the asterisk*) is removed quickly; this latter requirement is easily satisfied in a dense medium due to the fast interaction of the transient anion with its surroundings. For many polyatomic molecules, reactions (1) and (2) occur

concomitantly even with thermal electrons. A distinction between the two is, however, essential since the products of the two types of reactions are different and, hence, the physical parameters which determine their reaction (or reactions) with their surroundings are different.

B. Dependence of electron attachment to molecules on the captured electron's kinetic energy and the molecule's internal energy

In both the dissociative and the nondissociative electron attachment processes, the rate constant k_a (or the cross section σ_a) for negative ion formation is a strong function of both the kinetic energy, ε , of the captured electron [1–3], and the amount of internal energy, E_{int} , of the electron attaching molecule itself [3, 7–25]. With regard to the kinetic energy of the electron, electron attachment processes under consideration are resonant; that is, they occur over a limited energy range. In the gas phase such resonances are located in the energy range from about 0.0 eV to about 15 eV [1–3]. With regard to the internal energy of the molecule, an increase in the molecule's internal energy (for example, by heating up the medium in which such reactions take place) generally causes an increase in the rate constant for dissociative electron attachment (due to increased autodissociation of the transient anion) when the reaction is endothermic and an activation energy is required. Parent anions will autodestruct with higher probability as their internal energy is increased due to increased autoejection (autodetachment) of the attached electron.

C. Effect of the nature, density, and state of the medium on electron attachment

The effect of the nature, density, and state of the medium on electron attachment processes has been the subject of many recent studies [5, 26, 27]. It is manifested principally in two ways: (i) via its effect on the "state" of the electron which is being captured, and (ii) via its effect on the negative ion state (or states) of the electron attaching species.

With regard to (i), excess electrons in nonpolar, high-mobility liquids are quasi-free and they usually attach very efficiently to molecules embedded in the liquid when the electron affinity of the molecules in the liquid is positive [26–31]. In such liquids, while the energies of the electrons obey a Maxwellian distribution function, the actual energy which is available for the electron attachment reactions can be in excess of thermal depending on the energy V_0 of the quasi-free electron at the bottom of the conduction band of the liquid. A negative V_0 value — with respect to the vacuum level at 0.0 eV — would signify that the "electron affinity of the bulk medium" is negative and, therefore, that $|V_0|$ energy is available for the reaction. Values of V_0 for a number of liquids and dense fluids have been measured and have been summarized by a number of authors [26, 27, 32–34].

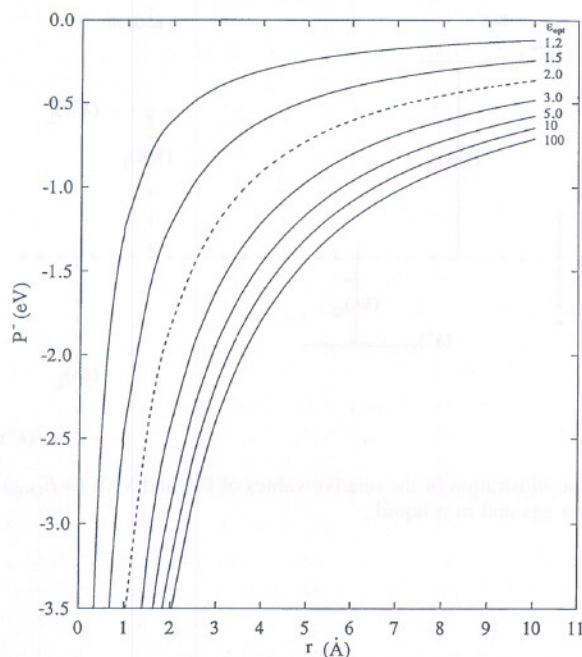


Fig. 1. Polarization energy P^- as a function of the radius r of the anion for various values of the optical dielectric constant ϵ_{opt} of the liquid, as predicted by the Born equation (see the text).

With regard to (ii), the medium influences the lifetime of the anionic state, the dissipation of its excess energy, and its energy position [5, 26, 27, 35]. The energy position of the anionic states leading to stable negative ions is lowered in the liquid compared to its gaseous value often by over 1 eV, depending on the size of the anionic state and the medium. A rough estimate of this lowering can be obtained from the value of the polarization energy P^- of the anion in the dense medium as given by the Born equation, viz.,

$$P^- = (-e^2/2r)(1 - 1/\epsilon_{\text{opt}}) = (-7.2/r)(1 - 1/\epsilon_{\text{opt}}). \quad (4)$$

In Eq. (4) P^- is in eV, r is the effective radius of the anion in Å, and ϵ_{opt} is the optical dielectric constant of the nonpolar fluid. The dependence of P^- on r and ϵ_{opt} is shown in Fig. 1. For a typical nonpolar liquid $\epsilon_{\text{opt}} \approx 2$ (Refs. [27, 33]), and $P^- \approx -1.2$ eV for $r \approx 3$ Å. For higher values of ϵ_{opt} and smaller anions (e.g., Cl^-), P^- can be much larger. Independent of the magnitude of P^- , it is clear that the positions of the resonant negative ion states which lead to stable negative ions are shifted to lower energies, and as a

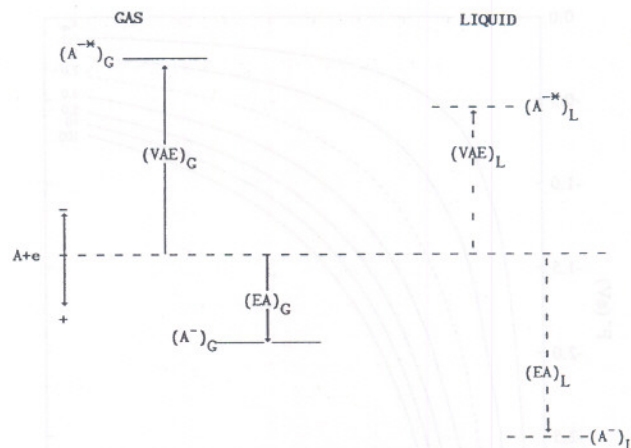


Fig. 2. Schematic illustration of the relative values of EA and VAE ($\equiv E_{LNIS}$) for a species A embedded in a gas and in a liquid.

result the electron affinities of molecules increase in going from the gas to the liquid. A general simple relationship between the electron affinity of a molecule in the gaseous phase, $(EA)_G$, and in the liquid phase, $(EA)_L$, is

$$(EA)_L = (EA)_G + V_0 + P^- \quad (5)$$

i.e., $(EA)_L$ exceeds $(EA)_G$ by an amount equal to the sum, $V_0 + P^-$, of the polarization energies of the electron and the negative ion in the liquid (see Refs. [27, 35]).

A consequence of the lowering of the energy of the electron attachment resonances in dense matter compared to low-pressure gases is that molecules which do not attach slow electrons ($\varepsilon \leq 1$ eV) in the gaseous phase may do so in dense fluids (e.g., liquids), and those which attach slow electrons in the gaseous phase via resonances lying at energies less than ~ 1 eV may attach electrons more efficiently in liquids because of the lowering of their negative ion states down to or below 0.0 eV. This is significant for nondissociative and for dissociative electron attachment processes; in the latter case anionic dissociations which are not energetically possible in the gas phase can actually become exoergic in the liquid phase. Furthermore, the higher value of $(EA)_L$ compared to $(EA)_G$ would make the removal of the extra electron from the anion embedded in the liquid energetically more

demanding than for the same anion in a low-pressure gas [35].

III. Thermal electron attachment rate constants for halocarbons in the gaseous phase and their dependence on the energy of the electron attaching state

In this section measurements of the thermal electron attachment rate constants $(k_a)_{th}$ for halocarbon molecules in the gaseous phase are summarized along with the electron affinity, EA, and the vertical attachment energy, VAE, of the electron attaching molecule. We taken the values of the VAE to be given by the energy, E_{LNIS} , of the lowest negative ion state of the molecule which lies energetically above the lowest ($v = 0$) vibrational level of the molecule, which is itself taken to be located at the vacuum level, i.e., at 0.0 eV. This is represented by the broken horizontal line (denoted by $A + e$) in Fig. 2 where we illustrate the relative positions of the EA and VAE ($\equiv E_{LNIS}$) for a species A embedded in the gas and in the liquid. The vertical attachment energy is defined [1] as the difference in energy between the neutral molecule in its ground electronic, vibrational and rotational states plus an electron at rest at infinity, and the molecular negative ion formed by the addition of the electron to the neutral molecule without change in the internuclear separations of the constituent nuclei. The energy ε_{max} of the lowest maximum in the electron attachment cross section function $\sigma_a(\varepsilon)$ (ε is the captured electron's kinetic energy) as determined in electron attachment studies in the gas phase is also of interest, since in the absence of a measurement of E_{LNIS} , ε_{max} can be used as an approximate value of the VAE of the molecule. It must be kept in mind, however, that the absolute value of the VAE is larger than ε_{max} due to the effect of autodetachment on the latter [1, 3].

In Table 1 are listed available data on $(k_a)_{th}$, EA [$\equiv (EA)_G$], VAE ($\equiv E_{LNIS}$), and ε_{max} for 46 halocarbons. These data have been obtained from a variety of sources and in some instances they are uncertain. However, in their totality they constitute a reliable set of fundamental data, on the basis of which certain correlations can be attempted. We, thus, have plotted in Fig. 3 the values of $(k_a)_{th}$ given in Table 1 as a function of the corresponding values of EA or $-E_{LNIS}$. When more than one value of these quantities is listed, the bracketed values (see Table 1) are the ones used in the plots. From Fig. 3 it is clearly seen that $(k_a)_{th}$ is a function of the energy position of the negative ion state which is responsible for electron capture. The values of $(k_a)_{th}$ are very large (equal to or close to their maximum s-wave values) as long as EA is positive (< 0.0 eV), and in spite of their large spread they show a slight increase with increasing value of EA. The values of $(k_a)_{th}$ decrease precipitously with decreasing EA or $-E_{LNIS}$ when the EA becomes progressively more negative (i.e., when the values of E_{LNIS} increase). Actually, there seems to be a break in the functional dependence of $(k_a)_{th}$ on $EA/-E_{LNIS}$ that occurs at ≈ 0.0 eV; for $EA = 0.0$ eV, $(k_a)_{th} \geq 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

Table 1. Halocarbons (predominantly dissociative electron attachment).

Molecule	$(k_a)_m^{a,b}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	EA (eV)	E_{LNIS}^c ($\equiv$ VAE) (eV)	e_{max}^d (eV)
1. CH_3Cl	$<1.9 \times 10^{-15}$ [36, 37] $<5 \times 10^{-15}$ [36, 38] $<10^{-14}$ [16, 39] $<10^{-13}$ [36, 40] $[<10^{-13}]$	$>-3.4^e$	3.45 [41, 42] 3.3 [43]	0.8? [43]
2. CH_3Br	10.8×10^{-12} [44] 7.0×10^{-12} [37] 6.7×10^{-12} [45] 6.0×10^{-12} [19, 46] 5.3×10^{-12} [47] 3.6×10^{-12} [48] $[6.5 \times 10^{-12}]$	$>-0.46^e$	-0.46 [41, 49]	0.3 [19] ^f 0.38 [44]
3. CH_3I	12×10^{-8} [19, 46] 9.5×10^{-8} [50] 8.6×10^{-8} [51] 7.0×10^{-8} [52] $[9.3 \times 10^{-8}]$	0.24, 0.29 0.39 [41] [0.31]		<0.05 [50] 0.025 [19] ^f 0.026 [53] 0.048 [51] ^f
4. CH_2Cl_2	0.65×10^{-12} [36, 54] 4.6×10^{-12} [36, 55] 4.7×10^{-12} [36, 56] 4.8×10^{-12} [36, 40] $[4.7 \times 10^{-12}]$	$>-1.23^e$	1.23 [41, 42]	
5. CH_2Br_2	10.6×10^{-8} [57] 9.3×10^{-8} [19, 46] 9.0×10^{-8} [50] $[9.6 \times 10^{-8}]$	$>-0.05^e$		0.05 [19] ^f ~ 0.08 [50] ^f
6. CHCl_3	4.4×10^{-9} [46, 58] 4.0×10^{-9} [52] 3.8×10^{-9} [59, 60, 61, 62] 3.6×10^{-9} [63] 2.6×10^{-9} [40, 52] 2.3×10^{-9} [54] 2.2×10^{-9} [40] 2.0×10^{-9} [64] 1.3×10^{-9} [36, 57] $[3.1 \times 10^{-9}]$	0.57, 1.76 [41] [>-3.5] ^e	0.35 [42]	0.35 [65] 0.12 [46, 64] ^f
7. CHF_3	3.6×10^{-14} [36, 65] 4.6×10^{-14} [36, 56] $<6.2 \times 10^{-14}$ [36, 66] $[4.8 \times 10^{-14}]$	$>-5.4^e$	5.4? [67]	
8. CHF_2Cl	$<1.6 \times 10^{-13}$ [36, 66] $<3.3 \times 10^{-13}$ [36, 65] $[<3.3 \times 10^{-13}]$	$>-1.9^e$	1.9[?] [67]	

Table 1. (continued).

Molecule	$(k_a)_{th}^{a,b}$ ($cm^3 \text{ molecule}^{-1} s^{-1}$)	EA (eV)	E_{LNIS}^c ($\equiv VAE$) (eV)	ε_{max}^d (eV)
9. CH_2Cl_2	1.5×10^{-12} [36, 65]	$> -0.96^e$	0.96 [41, 42]	
10. CCl_4	4.4×10^{-7} [36, 51, 54] 4.2×10^{-7} [68] 4.1×10^{-7} [36, 48, 69] 4.0×10^{-7} [64, 70] 3.9×10^{-7} [46, 58] 3.8×10^{-7} [71] 3.7×10^{-7} [62] 3.5×10^{-7} [66] 3.3×10^{-7} [63] 2.9×10^{-7} [59, 72] 2.8×10^{-7} [73] 2.5×10^{-7} [56] 2.4×10^{-4} [61] 1.6×10^{-7} [54] 1.3×10^{-7} [54] $[3.4 \times 10^{-7}]$	2.12, 2.0 [41] [2.06]	< 0.0 [42]	< 0.01 [36, 64]
11. CF_4	$< 10^{-16}$ [56, 74, 75] $< 10^{-13}$ [76] $< 3.1 \times 10^{-13}$ [66] $[< 10^{-16}]$	$> -6.7^e$		6.7 [77]
12. CF_3Cl	5.2×10^{-14} [56] 7×10^{-14} [74] 2×10^{-13} [78, 79] $< 3.1 \times 10^{-13}$ [66] $[1.5 \times 10^{-13}]$	$> -1.4^e$		1.5 [13] 1.35 [78] 1.3 [79]
13. CF_3Br	0.9×10^{-8} [64] 1.4×10^{-8} [59, 60] 1.5×10^{-8} [62, 80] 1.6×10^{-8} [19, 46] $[1.4 \times 10^{-8}]$	0.91 [41]		< 0.01 [64] 0.08 [18] ^f
14. CF_3I	1.7×10^{-7} [51] 1.9×10^{-7} [81] 2.0×10^{-7} [64] $[1.9 \times 10^{-7}]$	1.4, 1.6, 2.2 [41] 1.6 [82] [1.7]		0.027 [51] ^f
15. CF_2Cl_2	0.7×10^{-9} [74] 0.8×10^{-9} [48] 1.2×10^{-9} [61, 78] 1.3×10^{-9} [83] 1.8×10^{-9} [62] 1.9×10^{-9} [52] 2.2×10^{-9} [84] 3.2×10^{-9} [46, 58] $[1.6 \times 10^{-9}]$	0.4 ± 0.3 [41, 82] 1.29, 1.49 [41] [0.4]	0.98 [42]	0.15 [46, 64] 0.55 [79] 0.63 [78]

Table 1. (continued).

Molecule	$(k_a)_{th}^{a,b}$ (cm^3 molecule $^{-1}$ s $^{-1}$)	EA (eV)	E_{LNIS}^c ($\equiv$ VAE) (eV)	ε_{max}^d (eV)
16. CF ₂ Br ₂	$\sim 0.6 \times 10^{-7}$ [80] 2.6×10^{-7} [59, 60] 3.0×10^{-7} [46, 57, 85, 86] $[2.6 \times 10^{-7}]$	$> -0.04^e$		< 0.04 [59]
17. CFCI ₃	3.1×10^{-7} [62] 2.6×10^{-7} [46, 58] 2.4×10^{-7} [61, 71, 86, 87, 88] 1.8×10^{-7} [64] 1.2×10^{-7} [52, 59, 60] 1.0×10^{-7} [74] $[2.1 \times 10^{-7}]$	1.1, 1.5 [41, 82] [1.3]		< 0.02 [64] 0.00 ± 0.05 [79, 87]
18. CFBBr ₃	4.8×10^{-9} [46, 86]	$> -0.05^e$		$0.05[85]^f$
19. CCl ₃ Br	4.9×10^{-8} [57] 8.2×10^{-8} [46, 89]			
20. C ₂ H ₅ Cl	$< 1.6 \times 10^{-15}$ [37] $\sim 10^{-13}$ [39] $[< 10^{-13}]$	$> -1.4^e$		~ 1.4 [39]
21. C ₂ H ₅ Br	2.8×10^{-13} [38] 9.0×10^{-11} [73] 1.4×10^{-10} [?] ^g $[< 1.4 \times 10^{-10}]$	$> -0.76^e$		0.72 [73] 0.76 [90]
22. C ₂ H ₅ I	5.2×10^{-9} [51] 5.8×10^{-9} [57] $[5.5 \times 10^{-9}]$	$> -0.07^e$		0.07 [51] ^f
23. 1,1-C ₂ H ₄ Cl ₂	2.1×10^{-11} [36, 61, 91]	$> -1.08^e$		1.08 [92]
24. 1,2-C ₂ H ₄ Cl ₂	3.2×10^{-11} [36, 61, 91]	$> -0.53^e$		0.53 [92]
25. 1,2-C ₂ H ₄ ClBr	1×10^{-9} [46, 85]	$> -0.16^e$		0.16 [85]
26. 1,1-C ₂ H ₄ Br ₂	1.5×10^{-8} [46, 85]	$> -0.07^e$		0.07 [46, 85] ^h
27. 1,1,1-C ₂ H ₃ Cl ₃	1.6×10^{-8} [36, 59] 1.5×10^{-8} [36, 46, 53, 61, 73, 91, 93] 1.1×10^{-8} [64] $[1.5 \times 10^{-8}]$	$> -0.13^e$		$0.13?$ [46, 92]
28. 1,1,2-C ₂ H ₃ Cl ₃	3.1×10^{-10} [46, 93] 1.8×10^{-10} [36, 53, 61, 91] 1.5×10^{-10} [36, 59] $[2.1 \times 10^{-10}]$	$> -0.4^e$		0.2 [46] ^f ~ 0.4 [92]

Table 1. (continued).

Molecule	$(k_a)_{th}^{a,b}$ (cm^3 molecule $^{-1}$ s $^{-1}$)	EA (eV)	E_{LNIS}^c ($\equiv$ VAE) (eV)	ε_{max}^d (eV)
29. 1,1,1-C ₂ F ₃ Cl ₃	1.4×10^{-7} [64] 2.3×10^{-71} 2.4×10^{-7} [46, 93, 94] 2.8×10^{-7} [53, 61, 91] $[2.3 \times 10^{-7}]$	$> -0.05^e$		< 0.05 [53, 64]
30. 1,1,2-C ₂ F ₃ Cl ₃	1.1×10^{-8} [46, 53, 61, 91, 93, 94] 1.2×10^{-8} [62] $[1.1 \times 10^{-8}]$	$> -0.05^e$		< 0.05 [53] 0.11 [46]
31. 1,1-C ₂ F ₄ Cl ₂	4.8×10^{-9} [53, 61, 89, 91]	$> -0.05^e$		< 0.05 [53]
32. 1,2-C ₂ F ₄ Cl ₂	7×10^{-10} [53, 61, 89, 91]	$> -0.05^e$		< 0.05 [53]
33. 1,1-C ₂ F ₄ Br ₂	1.6×10^{-7} [46, 85]	$> -0.04^e$		< 0.04 [46, 85] ^f
34. C ₂ F ₆	$< 1.0 \times 10^{-16}$ [56, 75] $< 1.0 \times 10^{-13}$ [77] $< 1.6 \times 10^{-13}$ [66, 94, 95, 97] $[< 10^{-16}]$	$> -3.9^e$		3.9 [77]
35. C ₃ F ₈	$< 1.0 \times 10^{-18}$ [56] $< 3 \times 10^{-13}$ [75] $< 1.2 \times 10^{-12}$ [66] 1.8×10^{-12} [76] $[< 3 \times 10^{-13}]$	$> -2.9^e$		2.9 [77]
36. cis-1,2-CHCl=CHCl	$< 10^{-10}$ [61]	$> -1.3^e$		1.3 [92]
37. C ₂ HCl ₃	1.9×10^{-9} [59] 2.4×10^{-9} [52] 2.8×10^{-9} [61] $[2.6 \times 10^{-9}]$	0.3 [82] 0.4 [98, 99] [0.35]		0.19 [92]
38. C ₂ F ₃ Cl	6.6×10^{-12} [100]			
39. C ₂ Cl ₄	1.04×10^{-7} [61, 91]	0.5 [90] 0.64 [99] [0.57]		< 0.1 [74] ^j 0.18 [92]
40. 1-C ₃ H ₃ I	1.2×10^{-8} [81]	$> -0.057^e$		0.057 [81] ^j
41. 2-C ₃ H ₃ I	1.1×10^{-9} [81]	$> -0.076^e$		0.076 [81] ^j
42. C ₆ H ₅ F	$< 10^{-13}$ [95, 96]		0.65, 0.82 0.89, 0.90 [41] ^k 0.9 [41] ^l $> -0.82^e$ [0.82] ^m	
43. C ₆ H ₅ Cl	3×10^{-14} [95, 96]		0.30, 0.75, 0.70 [41] ^k 0.75 ⁿ $> -0.73^e$ [0.73] ^m	

Table 1. (continued).

Molecule	$(k_a)_{th}^{a,b}$ (cm ³ molecule ⁻¹ s ⁻¹)	EA (eV)	E_{LNIS}^c ($\equiv VAE$) (eV)	ϵ_{max}^d (eV)
44. C ₆ H ₅ Br	6.5 × 10 ⁻¹² [95, 96]	> -0.67 ^e	0.7, 0.67 [41] ^k 0.7 [41] ^l [0.67] ^m	
45. C ₆ H ₅ I	1 × 10 ⁻⁸ [95, 96]	0.11 [41] ^{l,o}		
46. C ₆ HF ₅	7 × 10 ⁻¹² [95, 96] <10 ⁻¹⁰ [97] 10 ⁻¹⁰ [98] [<10 ⁻¹⁰]	> -0.15 ^e	<0.15 [101] ^k	

^a $T = 295-300$ K.
^b When more than one value is listed, the value in the brackets is the one used in the discussion and the comparisons throughout this paper.
^c E_{LNIS} = Energy position of the lowest negative ion state detected in electron scattering experiments as given by the energy position of the resonance cross section maximum; these energy positions are the “vertical attachment energies” [1, 3] and represent a lower limit to the (negative) electron affinity (EA) of the molecule.
^d ϵ_{max} = Energy at which the cross section due to the lowest dissociative electron attachment resonance peaks.
^e Based on the respective values in either column 4 or 5.
^f Activation energy for dissociative electron attachment.
^g Obtained by integrating a Maxwellian distribution function ($T = 300$ K) over the cross section reported for C₂H₅Br in Ref. [90].
^h Activation energy; at $T = 298$ K the relative yields of Br⁻ and Br₂⁻ are, respectively, 97% and 3%.
ⁱ K. Kondo and R. W. Crompton quoted in Ref. [64].
^j Parent negative ions are also found at ~ 0.0 eV.
^k Onset of the lowest negative ion resonance or position of the lowest vibrational peak of the lowest negative ion resonance observed.
^l Average of all values in Ref. [41].
^m Average of onset values of the lowest negative ion resonance listed or average of the position of the first vibrational peak of the lowest negative ion resonance listed.
ⁿ Average of all negative values in Ref. [41].
^o There is a very large spread in the values listed.

A similar behavior is exhibited by other molecules which attach electrons dissociatively (like the halocarbons in Table 1) or nondissociatively (e.g., aromatic molecules, perfluorocarbons, oxygen-containing molecules) [112]. To indicate this we give in Table 2 relevant data for benzene and six of its derivatives which attach electrons nondissociatively. These data are shown in Fig. 3 as open circles.

IV. Thermal electron attachment rate constants for molecules in liquid cyclohexane

In this section, measurements of the rate constant, $(k_a)_L$, for thermal electron attachment to molecules in room-temperature liquid cyclohexane are sum-

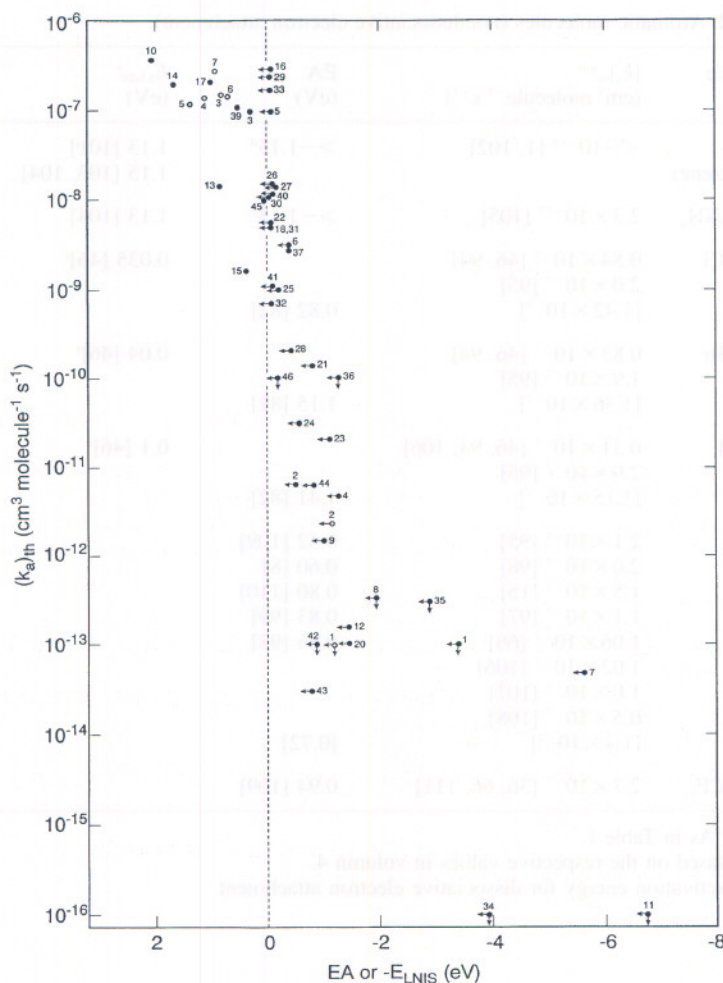


Fig. 3. $(k_a)_{th}$ as a function of $EA/-E_{LNIS}$ for halocarbons (●) (numbers identify molecules as in Table 1) and some aromatics (○) (numbers identify molecules as in Table 2).

marized (Table 3); the rate constants are given in the units given by the authors, namely in $M^{-1} s^{-1}$ ($1 M^{-1} s^{-1} = 1.66 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$). The rate constants $(k_a)_L$ refer almost exclusively to the attachment of quasi-free electrons ($T \approx 295 \text{ K}$; at this temperature the V_0 of liquid cyclohexane is 0.01 eV [26]). An effort has been made to find gaseous values of EA and/or E_{LNIS} for these molecules so that a plot of $(k_a)_L$ versus EA or $-E_{LNIS}$ can be made in a manner similar to that for gases. The data found in the literature are given in Table 3 and are plotted in Fig. 4.

Table 2. Aromatic molecules (nondissociative electron attachment).

Molecule	$[k_a]_{th}^{a,b}$ ($cm^3 \text{ molecule}^{-1} s^{-1}$)	EA (eV)	E_{LNIS}^c (eV)
1. C ₆ H ₆ (Benzene)	$< \sim 10^{-13}$ [1, 102]	$> -1.15^d$	1.13 [101] 1.15 [103, 104]
2. C ₆ H ₅ NH ₂	2.3×10^{-12} [105]	$> -1.13^d$	1.13 [104]
3. C ₆ F ₅ Cl	0.84×10^{-7} [46, 94] 2.0×10^{-7} [95] $[1.42 \times 10^{-7}]$	0.82 [82]	0.035 [46] ^e
4. C ₆ F ₅ Br	0.83×10^{-7} [46, 94] 1.9×10^{-7} [95] $[1.36 \times 10^{-7}]$	1.15 [82]	0.04 [46] ^e
5. C ₆ F ₅ I	0.31×10^{-7} [46, 94, 106] 2.0×10^{-7} [95] $[1.15 \times 10^{-7}]$	1.41 [82]	0.1 [46] ^e
6. C ₆ F ₆	2.1×10^{-7} [95] 2.0×10^{-7} [98] 1.5×10^{-7} [15] 1.1×10^{-7} [97] 1.06×10^{-7} [66] 1.02×10^{-7} [106] 1.0×10^{-7} [107] 0.5×10^{-7} [108] $[1.4 \times 10^{-7}]$	0.52 [109] 0.60 [8] 0.80 [110] 0.83 [99] 0.86 [98] [0.72]	
7. C ₆ F ₅ CF ₃	2.7×10^{-7} [36, 66, 111]	0.94 [109]	

^{a,b,c} As in Table 1.^d Based on the respective values in column 4.^e Activation energy for dissociative electron attachment.

It is seen from Fig. 4 that $(k_a)_L$ depends on EA or $-E_{LNIS}$ in a manner similar to the dependence of $(k_a)_{th}$ on EA or $-E_{LNIS}$. However, the data in Fig. 4 show that $(k_a)_L$ is very large for values of EA or $-E_{LNIS}$ up to about -0.9 eV [$(k_a)_L \geq 2 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ for those molecules with $EA \geq -0.8$ eV and $(k_a)_L \geq 3.3 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ for those molecules with $EA \geq -0.4$ eV], i.e., up to about 0.9 eV lower values of EA than the corresponding gaseous phase data (Fig. 3). This indicates a downward shift of ~ 0.9 eV in the values of E_{LNIS} , i.e., negative ion states with $E_{LNIS} \leq 0.9$ eV shift to ≤ 0.0 eV in liquid room-temperature cyclohexane and, consequently, make the electron attachment process energetically more favorable and the $(k_a)_L$ larger. Once $(EA)_L \geq 0.0$ eV, the $(k_a)_L$ is likely to attain diffusion-controlled or nearly diffusion-controlled values as the data in Table 2 and data on other

Table 3. Thermal electron attachment rate constants (k_a)_L for a number of molecules in liquid cyclohexane and their respective gaseous values of the electron affinity (EA)_G (= EA).

Molecule	(k_a) _L ^{a,b,c} (M ⁻¹ s ⁻¹)	(EA) _G (= EA)
1. CH ₃ I	2 × 10 ¹² [113] 4.3 × 10 ¹² [114]	0.31 [41] ^{d,e}
2. CH ₂ Br ₂	3.6 × 10 ¹² [115]	> -0.05 ^e
3. CCl ₄	1.8 × 10 ¹² [113] 2.7 × 10 ¹² [116] 2.9 × 10 ¹² [114] 4.3 × 10 ¹² [117] 3.0 × 10 ¹² [31] [3.3 × 10 ¹²] ^f	2.06 ^e
4. CHClBr ₂	3.2 × 10 ¹² [115]	
5. C ₂ H ₅ Br	2 × 10 ¹² [116]	> -0.76 ^e
6. 1,2-C ₂ H ₄ Cl ₂	5.1 × 10 ¹² [115]	> -0.53 ^e
7. 1,1,2-C ₂ H ₃ Cl ₃	3.3 × 10 ¹² [118]	> -0.4 ^e
8. 1,1,2,2-C ₂ H ₂ Cl ₄	4.2 × 10 ¹² [114, 118]	
9. 1,1,1,2-C ₂ H ₂ Cl ₄	4.5 × 10 ¹² [114, 118]	
10. C ₂ HCl ₅	3.4 × 10 ¹² [114, 118]	
11. C ₂ Cl ₆	4.4 × 10 ¹² [114, 118]	
12. C ₂ HCl ₃	4.0 × 10 ¹² [114, 118]	0.35 ^e
13. C ₂ Cl ₄	5.0 × 10 ¹² [114, 118]	0.57 ^e
14. C ₆ H ₅ CH ₂ Cl	4.4 × 10 ¹² [114]	
15. o-C ₆ H ₄ Cl ₂	3.8 × 10 ¹² [115]	-0.4, -0.36, 0.09 [41] [-0.22]
16. SF ₆	4 × 10 ¹² [116]	1.05 [119] 1.07 [99] [1.06]
17. Benzene	< 2 × 10 ¹⁰ [114]	> -1.13 ^g [101, 103]
18. Toluene	0? [114] < 1 × 10 ⁸ [120]	> -1.11 ^g [104]
19. Phenol	1 × 10 ¹⁰ [115]	> -1.01 [104]
20. Aniline	0? [114] < 1 × 10 ⁸ [118] < 3 × 10 ⁹ [28] [< 3 × 10 ⁹]	> -1.13 [104]
21. Benzoic acid	1.9 × 10 ¹² [114]	> -0.4 [121]

V. Conclusions

The observed correlations $(k_a)_{th}$ vs. EA or $-E_{LNIS}$ and $(k_a)_L$ vs. EA or $-E_{LNIS}$ indicate that for the molecules considered in this paper the same negative ion states are involved in the attachment of thermal electrons to molecules in both the gaseous and the liquid phase of matter. In the latter environment, however, the electron attaching states are shifted to lower energies due to the polarization energy, which for room temperature liquid cyclohexane is indicated to be about -0.9 eV. The values of $(k_a)_{th}$ and $(k_a)_L$ are large (close to their maximum) and change only slightly with the target molecule and its electron affinity as long as EA [$\equiv (EA)_G$] or $(EA)_L$ are positive. Once EA or $(EA)_L$ becomes negative, $(k_a)_{th}$ and $(k_a)_L$ decrease precipitously with decreasing electron affinity i.e. with increasing energy position (E_{LNIS}) of the electron attaching state. These findings are significant in efforts to explore possible mechanisms of toxic action of molecules via "electron capture reactions" [112].

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