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MASTER

INTERMEDIATE PHASE STUDIES FOR UNDERSTANDING RADIATION INTERACTION
WITH CONDENSED MEDIA: THE ELECTRON ATTACHMENT PROCESS*

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Intermediate phase studies, namely studies of radiation processes and effects as well as physicochemical reactions at densities between those corresponding to low pressure gases and liquids, are fundamentally necessary for the development of a coherent understanding of radiation interaction with matter. There is need for uniting, linking together of our knowledge on radiation processes occurring in low pressure gases with that in the condensed phase.

In this paper I wish to elaborate briefly on one aspect of this problem, namely on the efforts currently underway at our laboratory to bridge the gap in our existing knowledge on electron attachment processes in gases and liquids. I wish to report (A) the conclusions of a comprehensive study where gaseous data on electron attachment have been related to hydrated electron-molecule reaction rates and (B) the first information on electron attachment to molecules in very high pressure gases, with special reference to O_2 . The latter studies are being performed with gas pressures between 0.5 to ~80 Atms and will be accompanied by direct physical studies on liquids about which I will defer discussion.

A. Relevance of quantities describing electron attachment processes in gases to hydrated electron reaction rates, $R_{e\text{aq}}$

The following physical quantities describing electron attachment processes in gases have been found¹⁻³ to be of interest in this study: parent negative ion lifetime τ_a , molecular electron affinity $(EA)_G$, cross section maximum, i.e., the resonance energy ϵ_{max} .

The following conclusions have been reached.^{1,2}

1. When $(EA)_G < 0$ eV or $\tau_a < 10^{-12}$ sec, $R_{e_{aq}}$ is much less than $10^{10} M^{-1} \text{sec}^{-1}$ (10^4 to $\sim 10^7 M^{-1} \text{sec}^{-1}$). This suggests that for these molecules the electron affinity, $(EA)_L$, in the liquid environment is $\leq 3/2 kT$. However, when $(EA)_G \geq -0.5$ eV, $R_{e_{aq}}$ is large (10^9 to $\sim 10^{10} M^{-1} \text{sec}^{-1}$) indicating that $(EA)_L > \frac{3}{2} kT$ (but small). This is due to the effect of solvation on the negative ion which increases its stability.

2. When $(EA)_G > \frac{3}{2} kT$ (and independent of the value of τ_a) and/or $\tau_a > 10^{-6}$ sec (i.e., when a long-lived parent negative ion is formed in the field of the ground electronic state) and/or $\epsilon_{\text{max}} \leq 3/2 kT$ (i.e., the cross section for the attachment process — dissociative or non-dissociative — increases sharply at thermal energies with a possible maximum below $\frac{3}{2} kT$)^{1,2}, $R_{e_{aq}}$ is large, $\sim 3 \times 10^{10} M^{-1} \text{sec}^{-1}$, and most probably diffusion-controlled. It appears that either of the above conditions [$(EA)_G > \frac{3}{2} kT$; $\tau_a > 10^{-6}$ sec; $\epsilon_{\text{max}} \leq \frac{3}{2} kT$] is sufficient for $R_{e_{aq}}$ to attain diffusion-controlled values.

3. The magnitude of $R_{e_{aq}}$ appears to be independent of $(EA)_G$ when $(EA)_G > 0$ eV (see Fig. 1).

4. On the basis of conclusion 2 above, values of $R_{e_{aq}}$ can be predicted for a number of organic molecules for which gaseous data is available. Such predictions have been made^{1,2} for 35 organic molecules.

B. Electron attachment to molecules in very high pressure gases: O_2

The O_2^{-*} ion belongs to the group of transient molecular negative ions referred to as moderately short-lived ($10^{-12} \leq \tau_G < 10^{-6}$ sec)⁴ and hence it can easily be stabilized collisionally in a high pressure (swarm) experiment. In Fig. 2 the rate of electron attachment to O_2 in O_2 , N_2 mixtures is plotted as a function

of the mean electron energy, $\langle \epsilon \rangle$, for O_2 pressures $P_{O_2} \rightarrow 0$ and for N_2 pressures, P_{N_2} , as indicated in the figure. The attachment rates are seen to increase constantly with increasing P_{N_2} . For each P_{N_2} the maximum value of the attachment rate is attained at $\langle \epsilon \rangle \approx 0.05$ eV. Using the actual experimental data points (solid circles in Fig. 2) or the smoothed-out data (broken curves in Fig. 2) the attachment cross sections shown in Figs. 3 and 4 as closed and open circles, respectively, were obtained⁵ by making use of the analytical methods we have described recently.⁶ These methods^{5,6} allow the determination of absolute electron attachment cross sections as a function of electron energy from electron attachment rate data obtained from very high pressure (swarm) experiments. They constitute a fundamental advancement in electron attachment studies.

The main features of the data in Figs. 2 to 4 are: (i) their absolute basis; (ii) the distinct structure in the cross section functions for $P_{N_2} < 1000$ torr; and (iii) the gradual shift of the cross section functions towards thermal energies with the increasing of N_2 density. In Table 1 the energy integrated cross section, $\int_0^\infty \sigma_a(\epsilon) d\epsilon$, the maximum value of the attachment rate, $\alpha w(\langle \epsilon \rangle_{\max})$, the values, $\langle \epsilon_{\max} \rangle$, of the electron energy at which $\sigma_a(\epsilon)$ shows maxima or shoulders, and the energy separation, $\Delta\epsilon$, of the observed maxima or shoulders are given for various total pressures which are essentially those of N_2 . Throughout this paper these total pressures will be referred to as N_2 pressures, P_{N_2} , since the percentage of O_2 is very small (in almost all measurements $5 \times 10^{-7} < \frac{P_{O_2}}{P_{N_2}} < 3 \times 10^{-3}$).

The two distinct peaks in the cross section function observed for the two lowest values of P_{N_2} (300 and 500 torr) at 0.05 and 0.24 eV are interpreted, respectively, as being due to the processes

and

i.e., capture of the electron into the fourth and fifth vibrational levels of O_2^- from the $v = 0$ vibrational level of O_2 , with a subsequent stabilization of O_2^{-*} by an N_2 molecule, viz.

where the N_2 molecule acts simply as an agent for removing excess energy. At low N_2 pressures instead of the sequential two-step process [reactions (1) or (2) followed by (3)], the electron attachment process to O_2 can be viewed as a one-step three-body electron attachment reaction

in which the N_2 molecule acts as a third body removing energy in what may be called a "distant" collision, without perturbing the potential energy curves of O_2^- during capture. The continuous and gradual shift of the cross section functions

towards thermal energies and the pronounced increase in their sharpness at near zero energies seen in Figs. 3 and 4, however, suggest that as the N_2 density increases, electron attachment to O_2 cannot be described solely in this fashion, and that N_2 does not act simply as a stabilizing third body in "distant" collisions. The observed consistent changes in $\sigma_a(\epsilon)$ seem to suggest that N_2 seriously perturbs the O_2^- potential energy curves during capture with a net downward shift in what may be called "hard" or "sticky" collisions, the effect becoming more dominant the higher the N_2 density. This brings in mind the familiar effect of solvation which apparently seems to be important from these densities.

On the basis of the trend exhibited by the cross section functions shown in Figs. 3 and 4 one would expect the capture cross section to become a very sharp resonance at near zero energies in the limit of very high densities (efforts are currently in progress to investigate this for P_{N_2} up to ~ 80 Atms). This would certainly be consistent with the conclusions in section (A), namely that $R_{e_{aq}}$ attains diffusion-controlled values when $\sigma_a(\epsilon)$ is sharply peaking at thermal or subthermal energies.

Let us now assume that electron attachment to O_2 in O_2, N_2 mixtures proceeds via the following two mechanisms:

and

The main difference between mechanisms (i) and (ii) is this: in mechanism (i) N_2 is assumed to act simply as a stabilizing third body in "distant" collisions, not affecting the O_2^- potential energy curves, while in mechanism (ii) N_2 is assumed to be involved in "hard", "sticky" collisions which result in a serious perturbation of the O_2^- potential energy curves during capture, with a possible formation of a transient complex $[O_2^{-*} - N_2]$ which can be destroyed by autoionization (or collision) or lead to O_2^- upon collision with a second N_2 molecule. At low pressures mechanism (i) could, of course, be viewed as a one-step three-body attachment process involving "distant" collisions. In mechanism (i) the reaction $O_2^{-*} \rightarrow O_2^- + h\nu$ has been neglected as it is insignificant.⁴ Similarly, the reaction $[O_2^{-*} - N_2] \rightarrow O_2^- + N_2 + h\nu$ has been neglected. In both mechanisms (i) and (ii), the effect of O_2 as a stabilizing third body has been neglected since we are considering $(\alpha w)_0$, i.e., the attachment rates for $P_{O_2} \rightarrow 0$. We shall, further, restrict our discussion to values of $(\alpha w)_0$ at ~ 0.05 eV (see Fig. 2), i.e., to rates due to capture into the lowest vibrational level of O_2^- which lies above the level $v = 0$ of O_2 .

If mechanisms (i) and (ii) are taken to be plausible, the rate of change of the electron density due to electron capture by O_2 can be expressed as

$$\frac{\partial n_e}{\partial t} = -v_a n_e = -k_1 n_{O_2} n_e \frac{k_3 n_{N_2}}{(k_3 + k_4) n_{N_2} + k_2} - k_5 n_{O_2} n_{N_2} n_e \frac{k_7 n_{N_2}}{(k_7 + k_8) n_{N_2} + k_6} \quad (5)$$

In Eq. (5) v_a is the overall attachment frequency, n_e , n_{O_2} , and n_{N_2} are the number densities for electrons, oxygen, and nitrogen molecules, respectively, and $k_1 \dots k_6$ are the rate constants for the processes considered in (i) and (ii). From Eq. (5) we have

$$\frac{(\alpha w)_0}{n_{N_2}} = \frac{k_1 k_3}{(k_3 + k_4) n_{N_2} + k_2} + \frac{k_5 k_7 n_{N_2}}{(k_7 + k_8) n_{N_2} + k_6} \quad (6)$$

If we now turn our attention to Fig. 5 where $\frac{(\alpha w)_0}{P_{N_2}}$ is plotted as a function of P_{N_2} we see that the experimental data can be represented by

$$\frac{(\alpha w)_0}{P_{N_2}} = A + B P_{N_2} \quad (7)$$

where A and B are constants.

Considering that $n_{N_2} \propto P_{N_2}$, Eq. (7) is consistent with Eq. (6) when

$$(k_3 + k_4) n_{N_2} \ll k_2 \text{ and } (k_7 + k_8) n_{N_2} \ll k_6 \quad (8)$$

If we now assume that the cross section for O_2^{-*} , N_2 collisions is given by the Langevin expression for spiralling collisions^{4,8} we obtain for the average time

between O_2^{-*} , N_2 collisions at 7000 torr ($T = 298^\circ K$) the value of $\sim 4 \times 10^{-12}$ sec.

Hence, we have for the autoionization lifetime, $\tau_a(O_2^{-*})$, of O_2^{-*} .

$$\tau_a(O_2^{-*}) = k_2^{-1} < [(k_3 + k_4)n_{N_2}]^{-1} \approx 4 \times 10^{-12} \text{ sec} \quad (9)$$

This value lies within the limits established by McCorkle, Christophorou and Anderson⁵ who obtained an estimate of the upper limit of the lifetime of O_2^{-*} as follows: From the Breit-Wigner formula the cross section for the formation of all compound states with vibrational number n arising from the initial vibrational ground state o is

$$\int \sigma_c^n(o; \epsilon) d\epsilon = 2\pi^2 \lambda^2 \left(\frac{C^n}{g} \right) \Gamma_o^n \quad (10)$$

In Eq. (10) $\lambda^2 = \frac{\hbar^2}{2m\epsilon}$, $2\pi\hbar$ is Planck's constant, m is the electron mass and ϵ is the incident electron energy. For O_2 , $\frac{C^n}{g} = \frac{2}{3}$ (see Refs. 5 and 8) and since we are concerned with very low energies ($\epsilon < 0.1$ eV), $n = 1$ and $\Gamma_o^{n=1}$ is the total width. From Eq. (10) McCorkle, Christophorou and Anderson⁵ obtained $\Gamma_o^{n=1} = 4.9 \times 10^{-6}$ eV which yielded an upper limit for the autoionization lifetime of O_2^{-*} as

$$\tau_a(O_2^{-*}) < \frac{\hbar}{\Gamma_o^{n=1}} \approx 1.3 \times 10^{-10} \text{ sec} \quad (11)$$

using for the left-hand-side of Eq. (10) the energy integrated cross section

$\int_0^\infty \sigma_a(\epsilon) d\epsilon$ for $P_{N_2} = 7000$ torr. For this pressure $\int_0^\infty \sigma_a(\epsilon) d\epsilon = 6.3 \times 10^{-19}$ eV cm²

and $\epsilon_{\max} \approx 0.04$ eV (see Table 1 and Fig. 4). It is to be noted, however, that the

use of this value for the left-hand-side of Eq. (10) overestimates⁹ the upper limit of $\tau_a(O_2^{-*})$, since it basically assumes that each O_2^{-*} , N_2 collision results in the formation of O_2^- , i.e., $k_4 = 0$. This is unlikely since at low P_{N_2} the three-body attachment coefficient for reaction (4) is⁵ ~ 0.03 times that for

for which it can be argued¹⁰ that the probability of O_2^- formation is unity. If we assume that the upper limit for $\tau_a(O_2^{-*})$ obtained through Eq. (10) should be multiplied by a factor of 0.03, the upper limit for $\tau_a(O_2^{-*})$ in Eq. (11) becomes $\sim 4 \times 10^{-12}$ sec which is in agreement with that in Eq. (9).

Similarly, from the second inequality (8) an upper limit to the autoionization lifetime of $[O_2^{-*} - N_2]$ can be estimated which is of the same order of magnitude as that for $\tau_a(O_2^{-*})$.

From a least squares fitting to the data in Fig. 5 we have

$$\frac{(\alpha\omega)_0}{P_{N_2}} = 88.3 + 0.025 P_{N_2} \quad (13)$$

Hence,

$$\frac{k_1 k_3}{k_2} \approx 88.3 \text{ sec}^{-1} \text{ torr}^{-2} \text{ and } \frac{k_5 k_7}{k_6} \approx 0.025 \text{ sec}^{-1} \text{ torr}^{-3}.$$

Finally, if it is assumed that Eqs. (6) and (7) hold over all N_2 densities up to that (0.81 g cm^{-3}) of liquid N_2 , from Eq. (13) we find that

$$(\alpha\omega)_0 (\epsilon \approx 0.04 \text{ eV}) \approx 0.74 \times 10^{10} \text{ sec}^{-1} \text{ torr}^{-1}$$

for O_2 in liquid N_2 . This value compares well with the value $(1.11 \times 10^{10} \text{ sec}^{-1} \text{ torr}^{-1})$ one obtains from $\pi\lambda^2$ where $\lambda = \frac{h}{2\pi m v}$ is the deBroglie wavelength for a 0.04 eV

electron. This is an interesting observation and may indicate that mechanisms (i) and (ii) describe reasonably well the process of electron capture by O_2 in the presence of N_2 throughout the whole range of N_2 densities up to that of the liquid. Efforts are in progress to investigate this by finding out the range of P_{N_2} over which a plot such as in Fig. 5 holds.

In conclusion, it has to be stressed once again that although high pressure electron attachment (electron-molecule interaction processes in general) studies are experimentally very difficult, the detailed analyses are obscured by the complexities of high densities and the lack of direct information as to the products formed, and any generalizations have to consider carefully the effects of many specific environments on a given process, such studies are profoundly important in efforts to relate and unite our knowledge on radiation interaction with low pressure gases and with condensed media.

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9. This was also pointed out in Ref 5.
10. This is a reasonable assumption as can be seen from the discussions in Ref. 4 (Chapter 6) and 8.

Table 1: Electron attachment data for O₂ in O₂, N₂ mixtures

Total Pressure	$\alpha w(\langle \epsilon \rangle_{\max})^*$ (sec ⁻¹ torr ⁻¹)	$\int_0^{\infty} \sigma_a(\epsilon) d\epsilon$ (eV cm ²)	$\epsilon_{\max}$ (eV)	$\Delta\epsilon^\S$ (eV)
300	2.2×10^4	0.63×10^{-20}	0.05; 0.24	0.19
500	5.2×10^4	1.69×10^{-20}	0.05; 0.25	0.20
1,000	1.3×10^5	5.58×10^{-20}	<0.01; 0.09	----
1,500	1.75×10^5	6.49×10^{-20}	<0.01; ~0.07 [#]	----
3,000	4.8×10^5	17.0×10^{-20}	<0.01; ~0.04 [#]	----
5,000	9.7×10^5	32.0×10^{-20}	<0.01; ~0.04 [#]	----
7,000	2×10^6	63.0×10^{-20}	<0.01; ~0.03 [#]	----
10,000	$3 \times 10^6(?)$	-----	-----	----

* $\langle \epsilon \rangle_{\max} \approx 0.5$ eV (see Fig. 2). See additional data in Fig. 5.

[§]Energy difference between the two maxima in the cross section function (see Fig. 4).

[#]Shoulder.

FIGURE CAPTIONS

- Fig. 1. $R_{e_{aq}}$ vs $(EA)_G$ (> 0 eV). For detailed values of $(EA)_G$ (which spread considerably) see Ref. 4. The broken line represents the average value of $R_{e_{aq}}$ for the molecules shown in the figure.
- Fig. 2. Attachment rates $(\alpha w)_0$, extrapolated to zero O_2 pressure, as a function of mean electron energy for various N_2 pressures.
- Fig. 3. Attachment cross sections for O_2 in O_2, N_2 mixtures, as a function of electron energy for N_2 pressures 300, 500, 1,000, and 1,500 torr. The solid circles were obtained using the data points in Fig. 2 and the open circles using the smoothed-out data shown as broken curves in Fig. 2.
- Fig. 4. Attachment cross sections for O_2 in O_2, N_2 mixtures as a function of electron energy for N_2 pressures 3,000, 5,000, and 7,000 torr. The solid circles were obtained using the data points in Fig. 2 and the open circles using the smoothed-out data shown as broken curves in Fig. 2.
- Fig. 5. $(\alpha w)_0 / P_{N_2}$ vs P_{N_2} . The values of $(\alpha w)_0$ plotted are those for $\langle \epsilon \rangle \approx 0.05$ eV, which basically correspond to the maximum value of $(\alpha w)_0$ at each P_{N_2} (see Table 1). The solid points are the data of McCorkle, Christophorou, and Anderson⁵ (Table 1) and the open circles are the data of Goans and Christophorou.⁷ The latter data have been taken with a much improved electronics system and are as follows: 3.6×10^4 , 1.17×10^5 , 2.8×10^5 , 7.5×10^5 , 1.43×10^6 , 2.2×10^6 , and 3.3×10^6 sec⁻¹ torr⁻¹ for P_{N_2} 400, 1,000, 2,000, 4,000, 6,000, 8,000, and 10,000 torr, respectively.

Fig 1

Fig. 2

Fig 3

Fig. 4