Dissociative Electron Attachment to Ozone: Rate Constant

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Abstract:

The rate constant for dissociative electron attachment to ozone has been derived over the energy range of 0-10 eV by using previously measured cross section data revisited here in regards to discrimination effect occurring during the extraction of ions. The obtained data for both possible channels exhibit the maximum at mean electron energies close to 1 eV.

Introduction

The attachment of electrons to molecules is an important process in discharge plasma, as it substantially affects the concentration of electrons and therefore the macroscopic properties of the plasma. Moreover, if the capture of an electron by an electronegative molecule proceeds via the dissociative channel this can actively affect the kinetics of plasmachemical and ion-molecule reactions in the gas discharge gap and therefore influence the equilibrium in the concentration of chemical compounds. Both the neutral molecular components of gaseous mixtures as well as the molecular products formed due to plasmachemical reactions can be dissociated. Hence the dissociative electron attachment is an additional process to direct electron impact dissociation of neutral gas components, which can play an important role in many industrial plasma technologies.

The dissociative electron attachment to ozone molecules in ozonisers is a typical example of such a process. Ozone, which is generated in the discharge gap can by destroyed by electron impact either directly [1]

$$e + O_3 \rightarrow O + O_2 + e \qquad (1)$$

or via two competitive dissociative electron attachment processes

$$e + O_3 \rightarrow O^- + O_2 \qquad (2)$$

$$e + O_3 \rightarrow O + O_2^- \qquad (3)$$

The cross section for (2) exhibits a maximum in the range of 1.2 – 1.5 eV according to several studies [2]-[8]. The maximum for process (3) was observed at electron energies slightly below that corresponding to process (2). In addition, the existence of a very narrow resonance for process (2) at nearly zero electron energy has been reported recently [7] and [8]. This resonance was observed only if an electron beam of very low FWHM values was used in crossed-beams experiment. Moreover two further resonances in cross section data at 3.5 eV and 7.4 eV have been reported recently [2] and [3].

Despite of the importance of the dissociative process (2) and (3) in ozonisers, there are only several experimental studies reporting rate constants for these processes. Those, conducted over the period 1967-75, were surveyed by Caledonia [9]. Low values of the thermal rate constant at near zero electron energy, smaller than 1×10^{-11} cm^3s^{-1}, are typical for all earlier swarm data [9]. According to Stelman et al.[10] the rate constant k increases with the electron energy $\varepsilon_k = k_B T_e$ (k_B is Boltzmann constant and T_e is the electron temperature) expressed in eV as follows

$$k = 1.9\times10^{-9}(\varepsilon_k)^{1.46} \qquad (4)$$

Formula (4) was used by Kastelewitz et al. [11] for low energy electrons $\varepsilon_k < 0.5$ eV. At higher energies the rate constant was derived from Currans relative cross section data [3], and then were normalised to Stelman's data. A Maxwell-Boltzman electron energy distribution function was used for these calculation yielding

$$k = 5.87 \times 10^{-9} (\varepsilon_k)^{-1.5} . \exp[-1.59/\varepsilon_k] \qquad (5)$$

which exhibits a flat maximum of 1.2 x 10^{-9} $cm^3.s^{-1}$ at a mean electron energy close to 1.5 eV. As to the author's knowledge there existed no new data for this rate constant.

In contrast to these values for the attachment rate constant determined by swarm experiments several papers report values of k higher that 1 x 10^{-9} cm^3s^{-1} using low temperature gas discharge plasmas [12, 13, 14]. Also from the attachment rate coefficient data obtained in oxygen-ozone [15] and air-ozone [16] mixtures in drift tubes higher values for the rate constant can be surmised. Finally, the modelling of ozone generation in a negative corona discharge has shown that the dissociative attachment processes (2) and (3) participate in the mechanism of ozone destruction [17]. There is however one contradictory data reported by Klopovskij et al. [18] who found a value of 5×10^{-10} cm^3s^{-1}, which does not depend on the electron energy.

In the current paper new attachment rate constant data are reported in the electron energy range (0 –10) eV.

Analysis of the extraction efficiency of a TEM and results.

The rate constant for the dissociative electron attachment has been calculated both for process (2) and (3) by using the earlier measured cross-section data [6] and [7]. Those were revisited in respect to the discrimination effect that occur during the extraction of ions from the collision region.

The operation of the TEM (Trochoidal Electron Monochromator [19]) at high energy resolution regime requires the extraction electric field in the collision chamber to be very small in order to minimise electric field effects on the electron energy distribution in the incidental electron beam. The beam is characterised by the full-width-half-maximum (FWHM). Under such conditions, the efficiency for the extraction of ions having higher kinetic energy is reduced. Therefore the experimentally measured yield of ions per time unit is not proportional to the rate of the ion formation in the collision region. Hence there is no direct proportionality between the measured yield and the cross section data, which is usually assumed to be valid converting the relative cross section data to absolute values [20]. Better to say, the shape of ion yield measured as a function of electron energy does not correspond to the real shape of the attachment cross section as a function of electron energy. The problem has been discussed in detail recently [21].

In order to avoid effects of the discrimination on the shape of the measured ion yield the extraction efficiency for ions has to be taken into account. Therefore this effect has been calculated by the program SIMION for the geometry of the TEM used in earlier experiments [6] and [7]. The calculated extraction efficiency for both O^- and O_2^- ions is shown in Fig. 1a, and 1b respectively.

The extraction efficiency is at its maximum (100%) when the high extraction electric field (extraction potential of 10 V) is applied only for ions having kinetic energies smaller than about 0.4 eV. At higher ion energies the efficiency is strongly reduced down to about 20%. In the case of low extraction electric field (extraction potential below 1 V) only a small fraction of ions having low energy is extracted completely. All other ions are strongly discriminated and the efficiency sharply decreases down to 20 % of maximum.

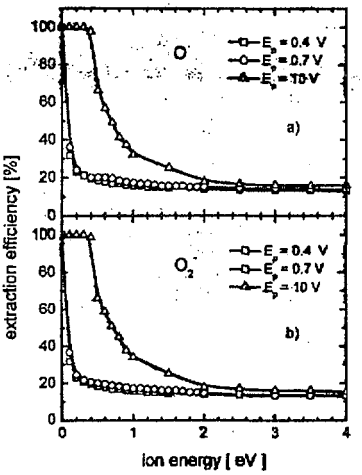

Figure 1

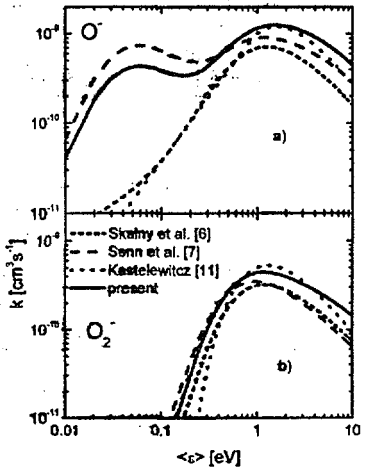

Figure 2

The earlier published absolute cross section data [6] and [7] were revisited by using this calculated extraction efficiency, assuming that the excess of the kinetic electron is transferred to the negative ion product. Absolute calibration of the corrected relative cross sections has been carried out by calibrating our O^- data at 1.3 eV (resonance maximum) to the O^- cross section values of Rangwalla et al. [2] at the same position. Knowing the absolute cross section values $\sigma(\varepsilon)$, a rate constant for the processes (2) and (3) was then calculated using the formula

$$k_{ab} = \sqrt{\frac{8}{\pi m_e}} \int_0^{\infty} \sigma(\varepsilon)\varepsilon_k^{3/2}\varepsilon \exp\left[-\varepsilon/\varepsilon_k\right] d\varepsilon \qquad (6)$$

where m_e is an electron mass, $\varepsilon_k = 2/3 <\varepsilon>$ and $<\varepsilon>$ is the mean electron energy.

The calculated values of k as a function of the mean electron energy both for process (2) and (3) are plotted in Fig. 2a) and 2b) respectively together with the data determined from the original cross section data published earlier [6, 7]. For the comparison also the data reported by Kastelewitz and Bachman [11] are displayed.

The current data are evidently shifted in comparison to the earlier data and are in good agreement with that obtained from parameters of various discharges [12, 13, 14]. Moreover the current data are fairly well consistent with those determined by Kastelewitz and Bachman at electron energies above 1 eV by using the formula (4), and (5) [11]. At lower energies the differences between current data and earlier calculated are evident. The results confirm the fact that dissociative electron attachment to ozone under certain conditions typical for low temperature gas discharges (mean energy close to 1 eV) is a process which considerably contributes to mechanism of the ozone decomposition by an electron impact and must be considered, besides the direct electron impact dissociation (1), in the kinetic models of ozone formation by electrical discharges.

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