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Dissociative electron attachment to H_2O_2: a very effective source for OH and OH^- generation

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Abstract

Dissociative electron attachment (DEA) to hydrogen peroxide (H_2O_2) is studied by two independent electron beam experiments using mass spectrometric detection of the product ions. The fragments OH^- and O^- are observed from a prominent low energy resonance peaking near 0.4 eV. The partial absolute DEA cross-sections are 6.8×10^{-17} and 1.7×10^{-17} cm^2 for the OH^- and the O^- channels, respectively. These numbers are several orders of magnitude higher than for the corresponding DEA processes in simple OH containing organic compounds. These numbers are also important from the point of view of radiation damage in biological tissues.
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1. Introduction

Hydrogen peroxide is one of the small molecules, which have attracted a lot of attention from the point of view of understanding molecular dynamics and a large number of experiments have been carried out on its photodissociation dynamics [1]. The dissociation dynamics of H_2O_2 is dominated by the channel, which leads to the formation of OH radicals. In this context it is of interest to see if the anion states of this molecule maintain this property. Dissociative electron attachment is an ideal tool to investigate this aspect.

In addition to the photodissociation dynamics of *neutral* H_2O_2, the anion state of H_2O_2 has been a subject of much discussion from the point of view of scattering experiments [2] involving O^- and H_2O, leading to the formation of OH and OH^-. The important question in this respect has been if the reaction follows a hydrogen-stripping mechanism or a compound mechanism involving a long-lived $H_2O_2^-$ intermediate. More recently the dissociative photodetachment of $H_2O_2^-$ leading to the formation of O^- has been reported [3]. Ab initio calculations [2,4] predict the negative ion states $H_2O_2^-$ to exist in a double-well potential as ion–dipole complex $(OH^-).OH$ or $O^-.H_2O$ separated by a shallow barrier and located by slightly more than 1 eV below the corresponding dissociation limits $OH^- + OH$ and $O^- + H_2O$, respectively. The situation differs in electron attachment

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as in this case a compound state $H_2O_2^{-*}$ is formed through a vertical transition from the neutral H_2O_2.

H_2O_2 has the structure HO–OH with an O–O distance of 147 pm which is larger than that in the oxygen molecule (121 pm). The two H–O–O planes are oriented at an angle of 115° with the O–O located at the axis connecting both planes. The H–O–O angle is 95°. As will be shown in this contribution H_2O_2 exhibits a high DEA cross-section for OH and OH^- formation, but also for O^- formation. It is several orders of magnitudes larger than the corresponding DEA cross-sections in small organic OH containing compounds like acids or alcohols (see discussion below).

From a practical side, hydrogen peroxide is important in the radiation damage of biological tissues as it is a product in the radiolysis of water [5]. It is generated by the recombination of hydroxy-radicals formed as one of the primary products of water decomposition by radiation and its behavior towards low energy electrons is directly related to radiation damage of biological material.

H_2O_2 is also an important minor constituent of the earth's atmosphere, which has a bearing on the formation of acid rain, as the oxidation of SO_2 by H_2O_2 in the gas phase or in water droplets may be the main source of H_2SO_4 in the atmosphere. In addition, hydrogen peroxide is an agent in the formation of HO_x in the troposphere and in the stratosphere [6]. It is an important molecule in the ozone cycle in the atmosphere as the product of the reaction of O_3 with H_2O. Though the OH emission from H_2O_2 photodissociation can be used to determine the concentration of H_2O_2, electron impact data are needed to use mass spectroscopic techniques. However, to our knowledge no electron impact data exist on this molecule, probably due to the difficulties in producing clean gaseous targets of this molecule. A similar situation exists for the OH radical, which is very important in planetary science and astrophysics. Since H_2O_2 is an ideal source for producing OH radical in well-defined states in the laboratory, any electron impact measurements on OH radical will have to be preceded by similar measurements on H_2O_2. Considering all these aspects, we report here the results of two independent measurements carried out on the dissociative electron attachment on H_2O_2.

2. Experimental

The measurements were carried out in T.I.F.R., Mumbai and Free University, Berlin, using different, but complementary techniques. The measurements in Mumbai were carried out using an apparatus which is optimized for the measurement of absolute cross-sections, whereas those in Berlin were optimized for higher electron energy resolution as well as mass resolution.

In the Mumbai experiment, an effusive molecular beam was allowed to intersect a magnetically collimated and pulsed electron beam. The ions formed were extracted by a high pulsed electric field, which followed immediately the electron pulse, into a segmented time of flight mass spectrometer and detected by a channel electron multiplier operated in pulse counting mode. The cross-sections were put on the absolute scale using the relative flow technique. The details of the apparatus has been described elsewhere [7,8]. The energy resolution of this experiment is about 0.5 eV. The important aspect of the experiment is the collection and detection of all the ions irrespective of their initial kinetic energy and angular distribution. One particular problem we had to overcome in these measurements was the difficulty in obtaining a relatively pure sample of H_2O_2 in the interaction region. To begin with a 50% solution of H_2O_2 in a glass bulb was continuously evacuated by a rotary pump till the volume decreased to about one-third. This bulb was connected to the stainless steel capillary tube through a 6-in. long all stainless steel gas line, while pumping the bulb simultaneously with a rotary vacuum pump. This resulted in a rather cleaner sample of H_2O_2 in the interaction region. The main impurities were found to be water vapour and oxygen as manifested by their respective dissociative attachment signals.

In order to obtain the absolute cross-sections, it was necessary to measure the relative concentration of H_2O_2, O_2 and H_2O in the interaction

region. This was achieved by determining the partial pressures of O_2 and H_2O using their respective dissociative attachment signal and normalising them by the relative flow technique with pure samples of H_2O and O_2 independently. The partial pressures of these two species were subtracted from the total pressure to get the partial pressure of H_2O_2.

The experimental setup at the Berlin laboratory has been described in detail elsewhere [9]. In brief, the electron attachment spectrometer is housed in a UHV chamber at a base pressure of 10^{-8} mbar and consists of a trochoidal electron monochromator (TEM) [10], a collision chamber and a quadrupole mass spectrometer (QMS). The TEM generates an electron beam of well-defined energy resolution (0.15 eV FWHM for the present experiments) interacting with the effusive molecular beam of H_2O_2. The procedure of introducing H_2O_2 into the vacuum system essentially corresponds to that described above. The molecular beam consists of some H_2O impurity. This does not affect the results obtained from H_2O_2 since DEA to H_2O is operative only at electron energies above about 4.5 eV. Negative ions are extracted from the interaction area by a small draw-out-field (<1 V cm^{-1}), analysed by the QMS and detected by single pulse counting techniques. The electron energy scale is calibrated by a small admixture of SF_6 yielding the well-known SF_6^- resonance near 0 eV.

3. Results and discussion

The measurements carried out at T.I.F.R. showed a single peak at mass 17 in the time-of-flight spectra corresponding to the formation of OH^- by electron attachment at about 0.5 eV. As the mass resolution of the segmented TOF spectrometer, which is optimized for complete collection of the ions, was poor, it was not clear if there was any contribution due to O^- or even H_2O^- to this peak. From the bond dissociation energies and electron affinities, it appeared that both O^- and OH^- could be formed at this energy (see below). The Berlin data (to be discussed later) clearly showed that at the low energy O^- and OH^- are

formed. The results of the measurements at Mumbai are shown in Figs. 1 and 2. In Fig. 1, the relative intensities of the negative ions from H_2O_2 are given as a function of electron energy. The small peaks above 4 eV are due to the resonant attachment to O_2 and H_2O present in the sample. The absolute cross-sections obtained after normalization using the relative flow technique are shown in Fig. 2.
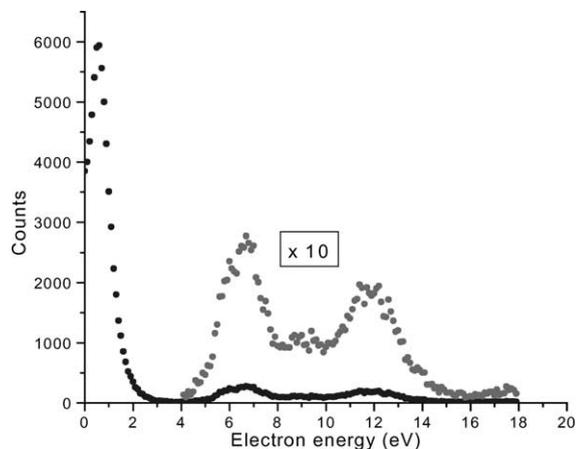

Fig. 1. Relative intensities of negative ions from H_2O_2 as a function of electron energy, obtained in segmented time-of-flight experiment (at Mumbai).
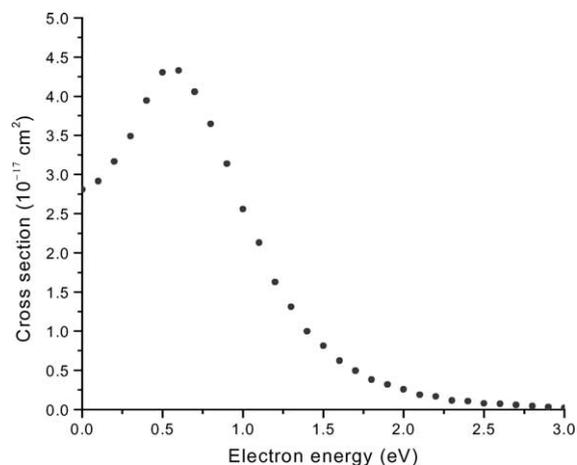

Fig. 2. Absolute cross-sections for the formation of negative ions from H_2O_2, obtained in the segmented time-of-flight experiment.

As mentioned above, formation of both O^- and OH^- could be clearly seen in the experiments conducted at Berlin where a quadrupole mass spectrometer was used for mass analysis. The yield curves for these two ions are shown in Fig. 3. The O^- curve is shifted slightly to lower energies as expected from thermochemical data with its peak at 0.25 eV as compared to 0.4 eV for the OH^- peak. The relative intensities of these ions at their peaks are in the ratio of 1:4. The small contributions due to dissociative attachment to O_2 and H_2O present in the sample could also be seen in the figure. A comparison of these results with that in Fig. 1 shows that the Berlin data have much superior energy resolution. Considering the difference in the energy resolution of the two experiments, it is expected that there will be a systematic error in the determination of the absolute cross-sections, as carried out in Mumbai. Excluding this systematic error, the uncertainty in the absolute measurements carried out in Mumbai is estimated to be about 30%, the major contributions coming from the errors in partial pressure measurements and the cross-sections used for normalization. In addition, the absolute cross-sections measured using the segmented time-of-

flight apparatus are the sum of the cross-sections for the formation of O^- and OH^-. Absolute partial cross-sections devoid of systematic error due to poor energy resolution were obtained by combining the two sets of results. The Berlin data were normalized to absolute values by equating the energy-integrated cross-sections at the T.I.F.R. experiment to the sum of the energy-integrated ion yield curves of O^- and OH^- obtained in the Berlin experiment. This procedure would be valid if the O^- and OH^- are produced with relatively little kinetic energies or there is no discrimination in the ion collection and mass analysis in the Berlin experiment. Since the O^- and OH^- ion peaks are fairly close to the respective threshold for their formation, we expect relatively little kinetic energy for the ions and hence the normalization procedure we employed to be devoid of significant error. The normalized cross-sections obtained thus are shown in Fig. 4. Due to the good statistics in the ion yield data, the uncertainty in the partial cross-section hardly changes from that in the total cross-section measurements and remains at 30%. However, this error is at the respective peaks and would be larger at other energies. As could be seen, the peak cross-section for OH^- alone is
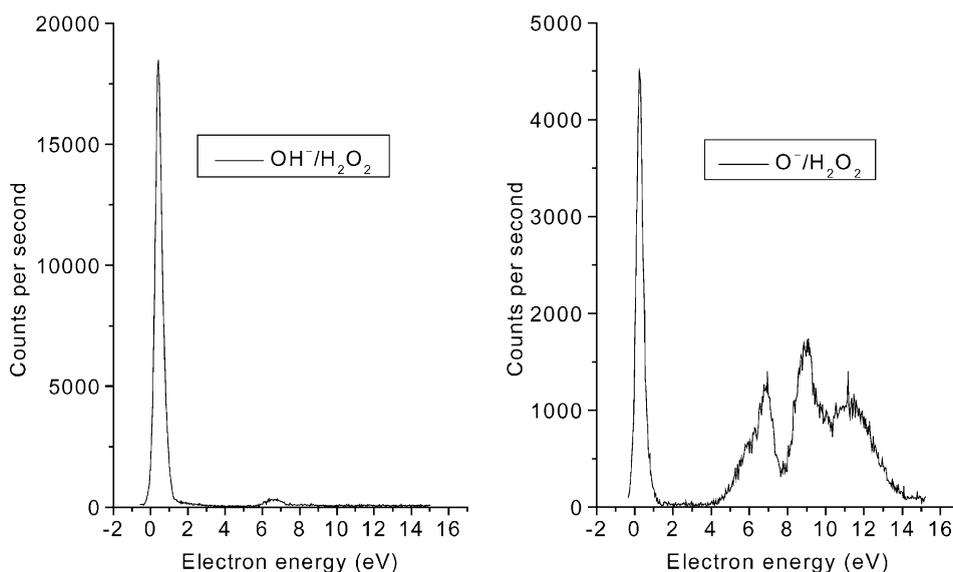

Fig. 3. Relative intensities of OH^- and O^- from H_2O_2 as a function of electron energy, obtained using the trochoidal electron gun and quadrupole mass spectrometer (Berlin experiment).
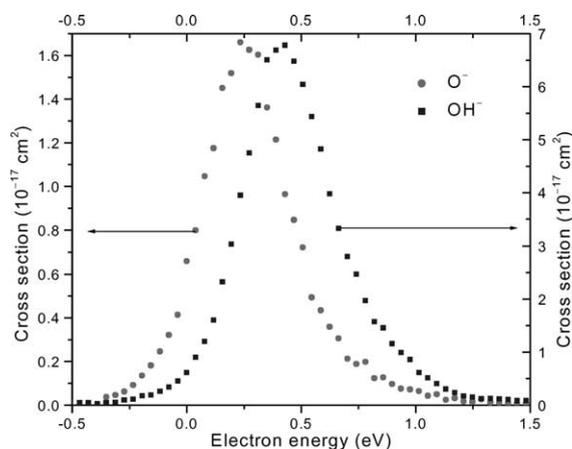
Fig. 4. Absolute partial cross-sections for the formation of O^- and OH^- by combining the Mumbai and Berlin data (see text).

considerably larger than the peak cross-section shown in Fig. 2. This highlights the importance of systematic error arising from the poor energy resolution in the measurement of resonance cross-sections. Due to the finite energy resolution, it is still possible to have a finite systematic error in the cross-sections we have obtained. As a result, the measured cross-sections may represent a lower limit at the resonant peaks.

The absolute cross-section of 6.8×10^{-17} cm^2 for OH^- and 1.7×10^{-17} cm^2 for O^- formation (peak maximum, Fig. 3) is considerably larger than from other OH containing compounds. In formic acid (HCOOH) [11] and acetic acid [12] the DEA cross-section for the channel OH^- was found to be about 1.5×10^{-19} and below 10^{-20} cm^2, respectively, with the O^- cross-section below that of OH^-. Although no quantitative data are available for methanol [13], the compound is a weak electron scavenger comparable to the acids. Common to these small organic molecules is the fact that OH^- is generated via core excited resonances located considerably (several eV) above the energetic threshold. In contrast to that, in DEA to H_2O_2 the products OH^- and O^- appear right at energetic threshold as can be seen from the thermodynamics for the associated DEA processes

$$e^- + H_2O_2 \rightarrow OH^- + OH \tag{1}$$

$$e^- + H_2O_2 \rightarrow O^- + H_2O \tag{2}$$

With the established gas phase thermochemical data (all taken from [14]): $\Delta H_f^0(H_2O_2) = -136$ kJ mol^{-1}, $\Delta H_f^0(H_2O) = -242$ kJ mol^{-1}, $\Delta H_f^0(OH) = -39$ kJ mol^{-1}, $\Delta H_f^0(O) = 249$ kJ mol^{-1}, and the electron affinities EA(OH) = 1.83 eV and EA(O) = 1.46 eV. From that we obtain the thermodynamic thresholds (reaction enthalpies) as $\Delta H_R^0(1) = 0.39$ eV and $\Delta H_R^0(2) = 0.02$ eV, i.e. O^- formation is about thermoneutral and OH^- formation endothermic. The fact that the relative partial cross-section curves extend to energies below the corresponding threshold is due to the limited energy resolution of the electron beam.

It is likely that both O^- and OH^- emerge from the same precursor state $H_2O_2^{-*}$ located near 0.4 eV in the Franck–Condon region (Fig. 5). We tentatively assign this state as a *single particle shape resonance* having an appreciable O–O antibonding character. This is manifested by the much larger cross-section into the energetically less favoured OH^- channel. Fig. 5 only illustrates the situation of DEA into OH^-. Included in the diagram is the thermodynamically stable structure of $H_2O_2^-$ associated to OH^-, namely $(OH)^-$.OH.

It should be mentioned that in the Berlin experiment small amounts of H_2O^- and HO_2^- (less
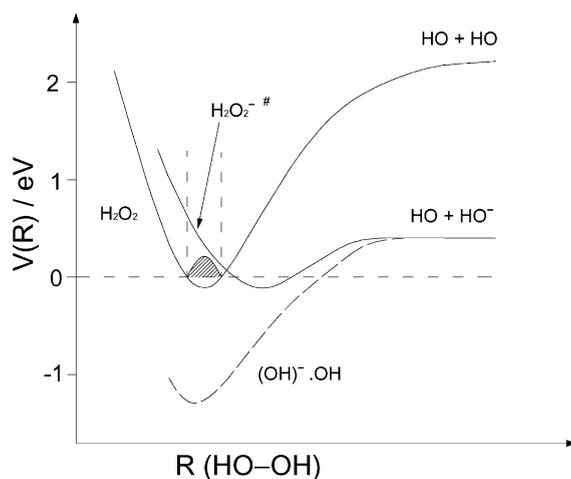

Fig. 5. Schematic potential energy diagram illustrating DEA into $OH^- + OH$. Note that the transient negative ion ($H_2O_2^{-*}$) accessible by the Franck–Condon transition possesses the structure of neutral H_2O_2 while the thermodynamic stable configuration of the negative ion is the ion–dipole complex $(OH)^-$.OH.

than 0.2% of the OH^- intensity) are detected, closely resembling the energy profile of OH^-. These ions are probably ion–molecule complexes formed via secondary reactions, i.e., collisions between OH^- (and O^-) with H_2O_2, as they are not expected to be formed at these energies.

Considering the large cross-sections from DEA, we note that hydrogen peroxide may be used as an effective source to generate OH^- for the study of bimolecular nucleophilic exchange (S_N2) reaction in the gas phase. The transformation of an alkyl-halogenide RX into an alcohol ROH via the S_N2 reaction

$$OH^- + RY \rightarrow HOR + Y^- \qquad (3)$$

plays an important role in organic synthesis [15].

As mentioned in Section 1, hydrogen peroxide is a product in the radiolysis of water [5]. It is generated by the recombination of hydroxy-radicals formed as one of the primary products of water decomposition by radiation and its behavior towards low energy electrons is directly related to radiation damage of biological material. It is well established that the interaction of high energy quanta with matter generates electrons as the most abundant secondary species. The interaction of these secondary electrons with the biological material is crucial to describe radiation damage on a molecular level. These secondary electrons are formed initially with an energy distribution up to some tens of eV [16]. They are rapidly slowed down through collisions on the femtosecond scale before they reach some stage of solvation. Damage of the genome in a living cell by ionising radiation is about one-third *direct* and two-third *indirect*. Direct damage concerns reactions directly in the DNA and its closely bound water molecules. Indirect damage results from energy deposition in water molecules and other biomolecules in the surrounding of the DNA. It is believed that almost all the indirect damage is due to the attack of the highly reactive hydroxyl radical OH. For the description of all these processes, the interaction of ballistic and solvated electrons are relevant. As we have demonstrated here, the hydroxy radical is effectively formed by ballistic (free) electrons at low energy from H_2O_2 which itself is generated from OH.

Acknowledgements

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