Low energy electron attachment to platinum(II) bromide (PtBr₂)[§]

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[§]Dedicated to the 70th birthday of our colleague and friend Professor Tilmann D. Märk, a leading scientist in the field of electron-molecule interactions. We wish him all the best for his future.

Abstract

Dissociative electron attachment to PtBr₂ in the gas phase was studied in the low electron energy range from zero up to 10 eV with an energy resolution of 150 meV. The experiments were carried out using a hemispherical electron monochromator coupled with a quadrupole mass spectrometer and pulse counting acquisition system. The only anion observed was Br⁻. This ion is formed at three resonance electron energies: 0.4 eV, 1.2 eV and 7 eV. By the measurements of the Br⁻ formation at different sample temperatures (in the 360 – 460 K range) the 0.4 eV resonance was associated with the electron capture by HBr generated in the apparatus at elevated temperatures. In addition, the thermodynamic thresholds for dissociative electron attachment reactions for platinum(II) bromide were calculated and compared with the experimental results.

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Introduction

Platinum is a noble metal that alone shows a low toxicity to living organisms, whereas in a form of various salts and more complex derivatives has been proven to be a very powerful tool in cancer therapy [1,2]. Nowadays platinum-based chemotherapy drugs are among the most powerful and widely used against cancer [3-5]. One of the most known compound in tumour treatment is cis-diamminedichloroplatinum (II), also called cisplatin ($\text{Pt}(\text{NH}_3)_2\text{Cl}_2$). Since the discovery of its toxic properties in the mid 1960s [5], it has become not only one of the major drugs in cancer therapy but also precursor of many other chemotherapeutic compounds [6]. After entering the cancer cell, two chlorine atoms are lost from cisplatin predominantly due to hydrolysis and then bifunctional intrastrand DNA cross-linking through covalent bonds with guanine or purine nucleobases is formed. Such cross-links inhibit transcriptions of the cancer cell, block its reproducibility and result in the cell death. The same acting principles have other platinum based anticancer drugs as for example: carboplatin, oxaliplatin or nedaplatin [4]. However, currently used platinum related medicines have many dose limiting side effects which arise from the indiscriminate uptake of the drug into all rapidly dividing cells (not only tumors) and the organism attempts the drug excretion. The appearance of several severe side effects during such cancer treatment requires drug dose reduction, which may be sub-lethal to tumours. This means that cancer cells possibly surviving the therapy may then be able to develop resistance against the drug [7]. Therefore, new Pt compounds with different functional groups are sought and tested [3,4]. Extensive studies of platinum containing drugs led to a series of principles concerning their chemotherapeutical potential. The compound should be neutral to facilitate passive diffusion into biological cells. Additionally such a substance should contain non-leaving (with poor trans-labilizing ability) and leaving group(s) which enable its attachment to the DNA of the cancer cell.

In many cases both chemo- and radiation- therapy (ions, X-rays, etc.) are used simultaneously for cancer therapy [8]. It was shown earlier that such radiation may lead to the release of a large number of free low-energy (<100 eV) electrons in cells [9]. These electrons may then interact with other molecules – also with the drugs ones, if present in a cell and induce further damage. Thus it is very important to know the fragmentation pattern of the drug and the electron energies at which the Pt based molecule may dissociate. For example, using the ultrafast transient absorption spectroscopy it was suggested previously that depletion of cisplatin in the experiments is due to dissociative electron attachment (DEA)[10].

Knowledge of the mode of action of such compounds during low energy electron irradiation may be then useful in the cancer therapy for the energy and dose of radiation matching.

Apart from platinum-containing drugs, brominated compounds were also found to be efficient radio- and photosensitizers in clinical radiotherapy [11]. Therefore, an even more efficient drug may be developed if it contains both platinum and bromine. Thus, we conducted studies of the low energy electron interaction with platinum(II) bromide (PtBr_2).

The PtBr_2 molecule serves as a model molecule for more complex species containing platinum and it is also one of the representatives of the big group of metal halides (compounds comprising of metal atom(s) and halogen atom(s) (F, Cl, Br, I)). Metal halides have also many industrial applications, e.g. as catalysts for many chemical processes or in the production of electric discharge lamps. This was an additional motivation to study the behaviour of the PtBr_2 molecule under electron irradiation which may then have some relation in the explanation of processes in which the metal halides are used.

Although the electron interactions with many different types of metal halides were extensively studied previously [12-18], to our best knowledge there is no information available regarding electron attachment measurements for PtBr_2 .

Moreover, the majority of investigations concerned the positive ionization of metal halides, whereas only a few studied the dissociative electron attachment (DEA) process [12,13]. In the electron ionization (EI) studies of the MBr_2 molecules (where M – denote of the metal atom of Mn, Fe, Co, Sn, Pb, Hg, respectively) [13,15,17,18] which have similar atomic structure and by this also similar properties as the compound of interest, several fragmentation channels leading to the positive ion generation were confirmed. The formation of the parent molecule MBr_2^+ and the fragment ions MBr^+ , M^+ and Br^+ were observed. The appearance potentials of the listed ions increased with the reduction in the size of ionized species [13]. There exist also some discrepancies between the results concerning the generation of Br^+ ions by EI of SnBr_2 [17,18]. As was explained by Hirayama and Straw [17] this ion generation is probably directly connected with the ion pair Br^+ and Br^- formation process.

In the case of the DEA to PbBr_2 [13] two negative ions, Br^- and PbBr^- , were detected. The intensity of PbBr^- was only a fraction of 0.01 of that for the corresponding positive ion. However, the intensity of Br^- was comparable with that of Br^+ . This effect confirms that the ion pair process is very important in the Br^- anion formation for this molecule. The dependency of the Br^- current on the initial electron energy indicates resonant electron capture

at 2.0 ± 0.1 eV and additionally ion pair formation at higher energies. It has been reported previously [13] that Br^- generation at 2 eV must be attributed to the following reaction:

as the thermodynamical threshold of this reaction was calculated to be 2.1 eV. It was also mentioned that the generation of Br^- at higher electron energies was accompanied by secondary electron capture processes which also led to nonzero PbBr^- ion currents [13]. The PbBr^- ion signal had a similar shape as Br^- peaking at a slightly lower energy of 1.7 ± 0.1 eV.

Pabst et al. [12] provided very interesting results in studies of DEA to SnBr_4 . In their experiments, the vapour of SnBr_4 was introduced to the ion source through a gas inlet system. As SnBr_4 is a larger molecule than PbBr_2 , more fragmentation channels leading to the negative ions formation were detected. In these investigations the following anions were detected: SnBr_3^- , SnBr_2^- , Br_2^- and Br^- . For all of these anions only a single resonance was observed. As SnBr_4 is extremely hygroscopic, authors checked also the production of Br^- anions at energies characteristic for Br^- formation from HBr and concluded that such process did not occur for their sample.

Experimental

The electron attachment spectrometer used in the present studies comprises of a molecular beam system, a high resolution hemispherical electron monochromator (HEM) and a quadrupole mass filter with a pulse counting system for analysing and detecting the ionic products. The apparatus has been described previously in detail [19]. Briefly, as the platinum(II) bromide is in solid state at room temperature and does not vaporize sufficiently for generation of a molecular beam, the PtBr_2 sample was heated in a resistively heated oven. The evaporated PtBr_2 molecules were then introduced through a copper capillary with 1 mm diameter to the interaction chamber of the HEM where they interacted with the well-defined electron beam. The anions generated by the electron attachment process were extracted by a weak electrostatic field into the quadrupole mass filter where they were analysed and detected by the channeltron. After crossing the collision region, the remaining electrons were collected by a Faraday plate; the electron current was monitored during the experiments using a pico-amperemeter.

With the HEM one is able to achieve energy distributions of about 35 meV at full width half maximum (FWHM). To determine the energy spread and to calibrate the energy scale the well known cross sections for the formation of Cl^- or SF_6^- by electron attachment to CCl_4 or SF_6 [20], respectively, was used. In the present studies CCl_4 was used for calibration of the

energy scale. The formation of Cl^-/CCl_4 is characterized by two main resonances: at 0 eV and 0.8 eV [21,22]. The first one can be used for calibration of the electron energy scale and to determine the electron energy spread (the apparent FWHM represents the energy resolution of the electron beam). In the present experiments the FWHM and the electron current were 150 meV and 20 nA, respectively. This relatively low resolution used represents a reasonable compromise between the product ion intensity and the energy spread to resolve resonances in the ion yields. The HEM was constantly heated to the temperature of 360 K in order to prevent surface charging. During our experiments the oven temperature was varied in the 360 – 460 K range. The pressure in the main vacuum chamber of the mass spectrometer was about 10^{-6} mbar to ensure collision-free conditions. Prior to the investigations, the sample of the platinum(II) bromide was heated over several hours at the temperature of 360 K. Before the electron capture measurements, the composition of the molecular beam of PtBr_2 was checked for possible traces of its thermal decomposition. For that purpose the positive ion mass spectrum measured by electron ionization at the electron energy of 80 eV was collected at different temperatures of the sample.

The sample of the platinum(II) bromide with a purity > 99% was purchased from Sigma Aldrich, Vienna, Austria.

Results and discussion

The only product of DEA to PtBr_2 in the low electron energy range (from about 0 to 10 eV) detected in our crossed beam experiments was Br^- . We were not able to detect any other anionic species like PtBr^- or Br_2^- . The absence of the former is in contrast to previous studies of PbBr_2 , where PbBr^- was observed [13]. However, it should be noted that the authors of [13] did not mention the evaporation temperature of the sample. Therefore thermal decomposition prior to the electron attachment cannot be excluded in their studies. The dihalogen anions Cl_2^- and Br_2^- were observed previously only for bigger molecules like cisplatin [23] and SnBr_4 [12] respectively. Obviously the formation of Br_2^- anions seems to be not possible for small systems like the triatomic molecule PtBr_2 .

The corresponding Br^- ion yield curves measured at the temperatures of 370 K and 460 K are shown in Fig. 1. Two resonance features, one at low energies (0 – 4 eV) and a second one at higher energies (> 5 eV) were observed. Thereby the efficiency of the Br^- ion formation exhibits a pronounced dependence on the sample temperature. We observed a strong increase of the intensity of the low energy peak when increasing the sample temperature within the temperature range investigated. In contrast to that, the DEA channel

leading to the Br^- formation at higher energies (> 5 eV) exhibits only small changes on the temperature.

At first look, the results (Fig. 1) indicate that at the higher temperature (460 K) the peak with the maximum at 0.4 eV is by far the dominant one, whereas the second peak at 7 eV has an intensity about 10 times lower. The DEA resonance peak at 0.4 eV is asymmetric and broad in shape. The experimental appearance energy of this peak was derived as 0 eV and this resonance has a long energetic tail to 3.6 ± 0.2 eV. At lower temperature (370 K) the feature at 0.4 eV is almost invisible and a broad DEA channel with maximum at 1.2 eV appears which could be also responsible for broadening the 0.4 eV peak at 460K (see insert in Figure 1), whereas the peak at 7 eV is still comparable (twice lower) to that one detected at 460 K.

The present results indicate (i) an overall increase of ion yield with temperature and (ii) a much stronger temperature influence on the 0.4 eV resonance, compared to the higher energy feature. The first observation can be explained by the increase of the gas density in the molecular beam introduced to the interaction chamber of the HEM with higher temperature.

In our experiments temperature was varied from 370 to 460 K. During the temperature increase in the investigated range, the pressure in the vacuum chamber (measured by the ion gauge mounted onto the main chamber of the apparatus) rose from 4×10^{-6} mbar to 1×10^{-5} mbar. Taking into account that the pressure was measured far from the interaction chamber, the pressure in the interaction region could have been higher by factor of 10's than that indicated by the gauge. Nevertheless the pressure changes in the interaction chamber should correspond to these monitored by the gauge. Therefore the large changes of the Br^- ion current intensity at low electron energies cannot be attributed to the increase of the pressure in the interaction chamber with the temperature rise.

In order to elucidate the observed difference in the intensities of the 0.4 eV peak and to recognize which effect is responsible for it, additional measurements were performed by recording the ion yield at several different temperatures in the range between 380 K and 450 K. The resulting intensities of the peak maxima at 0.4 eV and 7 eV are shown in Fig. 2 for the various temperatures. The Br^- signal at 7 eV linearly increases with the sample temperature which confirms the dependence of this ion current intensity on the gas density. In the same temperature range the Br^- peak height for the 0.4 eV resonance follows an exponential growth. In Figure 2 the ratio of the Br^- signals for both resonances (at 0.4 and 7 eV, respectively) is also marked for better insight on the phenomena involved in DEA to PtBr_2 . It can be seen that in the whole temperature range studied the ratio of corresponding Br^- signals

shows an increase, which suggests that different and independent processes are involved in the Br^- formation at both resonances.

Concerning the much stronger increase of intensity of the 0.4 eV peak, the following possibilities may be considered (i) DEA reactions to vibrationally excited states (hotbands) of the molecule and (ii) the electron attachment to an impurity with different temperature dependent density. It was shown before [24-28] that for such a situation the DEA to the vibrationally excited molecule could be responsible. However, after checking the possible DEA channels of other bromine containing molecules which may also show the formation of Br^- at 0.4 eV, we came to the conclusion that this resonance most probably can be ascribed to an impurity. The Br^- formation at 0.4 eV is characteristic for dissociative electron attachment to the HBr molecule [28-30]. We suppose that in performed experiments HBr molecules can be formed by the interaction of PtBr_2 (or its fragments) with residual H_2O molecules in the mass spectrometer. Then generated HBr molecules could undergo dissociative electron attachment leading to the Br^- formation at 0.4 eV. It should be noted that the DEA process to hydrogenated halogens (HCl and HBr) is temperature dependent and was also measured previously by Fedor et al. [28] (between 310 to 870 K). At elevated temperatures additional peaks (at near 0 eV and 0.3 eV) appeared in the cross section of the Br^-/HBr channel [28] which were not observed presently due to the limited temperature range. In contrast to our studies, in their results of DEA to HBr at different temperatures [28], large increase of the yield of Br^- formation with the sample temperature was not observed. Taking this into account we assume that the yield of the HBr formation process is temperature dependent. This assumption can be confirmed by the previous results of negative surface ionisation studies of electron attachment to CH_3Cl and SF_6 [31, 32]. In those investigations the untypical (in comparison to other molecular anions observed) behaviour of the Cl^- and F^- ions signal was observed. The molecular ion currents disappeared 5 s after the gas addition was stopped, whereas the ion currents of Cl^- and F^- remained at the level of about 15% of its primary value for up to one minute after the respective CH_3Cl and SF_6 gas addition was stopped. This different behavior of the Cl^- and F^- anion formation was attributed not only as DEA to the neutral, parent molecules of interest, but also to HCl and HF respectively, which were produced from the studied sample and water in the ion source. The intensities of both Cl^- and F^- anions were temperature dependent. For the explanation of the possible HBr formation during our studies it should be also mentioned that the bond strength of halogen-containing compounds decreases with the atomic number of the halide (i. e., $\text{F} > \text{Cl} > \text{Br}$) [33]. This

holds also for hydrogen as connecting atom in the series from HF to HBr and therefore the Br⁻ formation from HBr in our experiments is an efficient process.

The closer inspection of positive ion mass scans collected during the first phase of our investigations has proved the presence and therefore the generation of the HBr from PtBr₂ in the apparatus. In Figure 3 two mass spectra in the m/z (mass/charge) region covering the Br⁺ and HBr⁺ ions are presented. These mass spectra were recorded at temperatures of 420 K and 460 K respectively. In both spectra four (major) peaks are observed at $m/z = 79, 80, 81$ and 82 . The ions with m/z equal 79 and 81 correspond to the two bromine isotopes with natural abundances of 50.7 % and 49.3 % respectively, whereas the next pair of ions ($m/z = 80$ and 82) reflects the HBr⁺ formation. The ion current in this figure was normalized to the signal of HBr⁺, Br⁺ ion intensity is almost the same at 420 K and 460 K. Hence the generation of HBr⁺ at the temperature range applied in our experiments is dominant and yields in this ion signal with the increase of temperature. However the mass spectrum recorded differs from that obtained for electron ionization and photoionization of the HBr molecule [34] which confirms that the Br⁺ is formed in IE to both HBr and PtBr₂. This also holds for the negative ion of bromine, it is formed both from the PtBr₂ and HBr respectively.

Quantum chemical calculations

To complement the experimental studies, quantum chemical calculations of the thermochemical thresholds for possible channels of DEA to the PtBr₂ were performed using the Gaussian 09 software [35]. For this purpose we first evaluated different model chemistries by comparison to experimental data for atomic and molecular electron affinities, where available, as well as the binding energy of Br₂, (see Table 1). In particular, we compared the performance of the M06-L functional [36] with different *ab initio* approaches, i.e. MP2, CCSD and CCSD(T). The M06-L functional has been found earlier to be especially suited for the treatment of molecular complexes including transition metals such as Pt [37]. The choice of the basis set, i.e. the aug-cc-pVTZ-PP basis set [38,39], has been based on test calculations employing also the SDD basis set [40] as implemented in Gaussian 09 [35] and the aug-cc-pVDZ-PP basis set [38,39]. It was found that neglecting polarization functions as well as diffuse functions and using a large-core basis result in quite large deviations, up to 0.7 eV from the experimental values given in Table 1. This is in line with the finding that the use of pseudo-potentials is better suited to describe heavy elements if small-core basis sets are used [41]. The use of the small-core basis sets aug-cc-pVDZ-PP and aug-cc-pVTZ-PP significantly improved the situation, except for the electron affinity of Pt which was still largely

underestimated by the *ab initio* methods. Increasing the number of basis functions by going from the double-zeta basis aug-cc-pVDZ-PP to the triple-zeta basis aug-cc-pVTZ led only to a slight change in the resulting values. Therefore, the aug-cc-pVTZ-PP basis set was chosen for the calculation of the reaction thresholds. In terms of methods, the M06-L functional predicts the considered experimental electron affinities and the binding energy of Br₂ within 0.3 eV, whereas the *ab initio* methods strongly underestimate the electron affinity of Pt as mentioned already above while being of the same accuracy as M06-L considering the other numbers. Thus, the thermodynamical reaction thresholds have been calculated at the M06-L/aug-cc-pVTZ-PP level of theory and are summarized in Table 2. They have been determined by calculating the difference between the electronic energies of the reaction products and the reactant, i.e. PtBr₂, including zero-point energies as well as thermal corrections for a temperature of 298.15 K.

The calculations show that the electron affinity of PtBr₂ using this model chemistry is 3.59 eV. Thus the present non-observation of the parent anion indicates rapid electron autodetachment from the parent molecular ion. The calculations show that from the energetic point of view all channels listed in the Table 2 are possible in the studied range of the electron energy. Though these channels are in competition therefore, the only fragment observed in our experiments was Br⁻. After identification of the 0.4 eV resonance as impurity we assign the 1.2 eV resonance to the dissociation reaction Br⁻ + PtBr (thermodynamical threshold of -0.54 eV), whereas for the resonance at 7 eV the dissociation channel Br⁻ + Pt + Br is energetically open (threshold of 3.03 eV).

Conclusions

Using electron attachment spectroscopy DEA to platinum(II) bromide was studied in the gas phase. The only detected anion was Br⁻. This anion formation was observed at three different resonance energies (0.4 eV, 1.2 eV and 7 eV). The resonance at 0.4 eV has shown pronounced dependence on the sample temperature. The energetic position of this resonance agrees with that for Br⁻ formation from HBr. Therefore the Br⁻ anion production at this electron energy was connected to the DEA to HBr, generated in the oven. The positive mass scans also confirmed this assumption. *Ab initio* calculations of the thermodynamical thresholds for the possible channels leading to the negative ion formation from PtBr₂ were also performed. Based on the calculations, the resonance at 1.2 eV is ascribed to the DEA reaction, in which Br⁻ and neutral PtBr are formed, whereas the resonance at 7 eV is attributed to DEA leading to the formation of Pt, Br⁻ and Br fragments, respectively.

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Table and Figure captions

TABLE 1: Electron affinities (EA) of Pt, Br and Br₂ and binding energy (BE) of Br₂ as obtained by M06-L, MP2, CCSD and CCSD(T), always in conjunction with the aug-cc-pVTZ-PP basis set, and obtained by experiment (references are given in brackets). All values are given in eV.

Quantity	M06-L	MP2	CCSD	CCSD(T)	Exp.
EA of Pt	1.86	1.36	0.86	1.16	2.13 [42]
EA of Br	3.13	3.44	3.27	3.35	3.36 [43]
EA of Br ₂	2.57	2.46	2.47	2.47	2.53 [44]
BE of Br ₂	2.12	2.34	2.00	2.17	1.97 [45]

TABLE 2: Thermochemical reaction thresholds calculated at the M06-L/aug-cc-pVTZ-PP level of theory including ZPE and thermal corrections at T = 298.15 K for dissociative electron attachment to PtBr₂.

Reaction: $e^- + \text{PtBr}_2 \rightarrow$	Thermochemical reaction threshold [eV]
Br ⁻ + PtBr	-0.54
Br ⁻ + Pt + Br	3.03
Br ₂ ⁻ + Pt	0.97
Pt ⁻ + Br ₂	1.68
Pt ⁻ + Br + Br	3.80
PtBr ⁻ + Br	0.31

Figure Captions

Fig. 1.

Formation of Br^- by dissociative electron attachment to PtBr_2 at two (370 K and 460 K) temperatures of the sample. The insert shows in detail the $\text{Br}^-/\text{PtBr}_2$ generation at 370 K in the electron energy range from about 0 up to 3.2 eV.

Fig. 2.

The ion Br^- current intensities at peak positions of 0.4 eV and 7 eV versus the sample temperature. The ratio of the Br^- signals for both resonances (0.4 and 7 eV, respectively) at peak energetic position is also included.

Fig. 3.

Positive ions mass spectra in the m/z ratio of 77 to 84 obtained at the oven temperature of 420 K and 460 K, respectively.

Fig. 1.

Fig. 2.

Fig.3