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High-energy collision induced dissociation of iridium hexa-halide dianions: Observation of triple electron detachment and other decay pathways

William E. Boxford [a], Mohamed O.A. El Ghazaly [a], Caroline E.H. Dessent [a,*], Steen Brøndsted Nielsen [b]

[a] *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*
[b] *Department of Physics and Astronomy, University of Aarhus, Ny Munkegade, DK-8000, Aarhus, Denmark*

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Abstract

Lifetimes of the $IrBr_6^{2-}$ and $IrCl_6^{2-}$ gas-phase ions were measured in an electrostatic ion storage ring as 3.3 ± 0.1 s and 3.1 ± 0.1 s, respectively. The lifetimes indicate that the dianions are not subject to spontaneous decay under ambient conditions, since they are associated with decay resulting solely from high-energy collisions with residual gas ($\sim 5 \times 10^{-11}$ Torr) that is present in the ring. To further investigate the high-energy collisional decay dynamics, $IrBr_6^{2-}$ and $IrCl_6^{2-}$ were subjected to high-energy collision induced dissociation measurements in an accelerator mass spectrometer (ion translational energy in laboratory frame = 100 keV). A number of daughter ions were formed following the high-energy collisions (e.g., $IrCl_6^{2-}$ produced $IrCl_6^-$, $IrCl_5^-$, $IrCl_4^-$, $IrCl_3^-$ and Cl^-). The presence of the intact monoanion (i.e., $IrCl_6^-$) indicates that electron detachment is a prominent decay process, in contrast to low-energy collisional excitation where $IrCl_5^-$ and Cl^- are produced via ionic fragmentation. The predominance of electron detachment occurring as a result of high-energy collisions was further illustrated by charge-reversal measurements where cationic daughter fragments were observed, consistent with triple electron detachment. This measurement indicates that high-energy collisional activation of dianions should represent a general approach for studying triple electron detachment of molecular anions.

Keywords: Multiply charged ions; Dianions; Ion storage ring; High-energy collision induced dissociation; Triple electron detachment

1. Introduction

The intrinsic properties of gaseous multiply charged anions (MCAs) have been the subject of considerable recent interest through the application of modern experimental and theoretical techniques [1–7]. MCAs represent highly energetic species in the gas-phase due to the uncompensated Coulombic repulsion that exists between the excess charges, and are therefore susceptible to decay through either electron detachment, fragmentation into two ionic moieties or by loss of a neutral fragment.

In this paper, we investigate the high-energy collisional decay dynamics of the iridium hexahalide dianions ($IrBr_6^{2-}$ and $IrCl_6^{2-}$). These dianions are classical Werner-type transition metal complexes [8], and have been studied extensively in the condensed phase as constituents of melts and solids, and as electron transfer agents in solution [9]. Over recent years, $IrBr_6^{2-}$ and $IrCl_6^{2-}$ have also been the subject of a broad range of gas-phase studies [10–13], and can therefore be considered to have become the prototypical, aprotic gas-phase MCAs. While a large number of MCAs, (including the iridium hexahalides) have been investigated using photodetachment photoelectron spectroscopy [10], $IrCl_6^{2-}$ and $IrBr_6^{2-}$ are currently the only MCAs to have been studied using laser photodissociation spectroscopy [11]. Furthermore,

* Corresponding author. Tel.: +44 1904 434092; fax: +44 1904 432516.
E-mail address: ced5@york.ac.uk (C.E.H. Dessent).

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resonance excitation measurements of $IrCl_6^{2-}$ and $IrBr_6^{2-}$ have revealed that the Repulsive Coulombic Barriers (RCBs) for ionic fragmentation lie below the RCBs for electron detachment [12].

While most of the previous studies of $IrCl_6^{2-}$ and $IrBr_6^{2-}$ have focused on the MCAs ground states, we aim to use high-energy collision-induced dissociation (CID) to provide preliminary information on the excited state potential energy surfaces and dynamics. Experiments are performed in a unique accelerator mass spectrometer (acceleration voltage: 50 kV) that is equipped with an electrospray ion source [14]. The dianions achieve 100 keV of translational energy, and move several orders of magnitude faster than in a typical low-energy CID experiment. The high collision energies achieved should therefore provide access to a range of excited state surfaces, and hence, complement the previous low-energy measurements [12]. We begin the study by measuring the lifetimes of $IrCl_6^{2-}$ and $IrBr_6^{2-}$ in the ELISA heavy-ion storage ring [15] to firmly establish whether the dianions are subject to spontaneous decay under ambient conditions, and hence ensure that the high-energy CID measurements are not contaminated by metastable decay products.

2. Experimental

2.1. Storage ring experiments

The instrumental details have been described in detail previously [15]. In the current experiments, the $IrCl_6^{2-}$ and $IrBr_6^{2-}$ dianions were prepared via electrospray from 1:1 water–methanol solutions of K_2IrCl_6 and K_2IrBr_6 (Sigma–Aldrich). The ions were equilibrated with a room temperature He buffer gas within the 22-pole trap for 15 s before being accelerated as an ion bunch to a kinetic energy of 44 keV, and mass selected by a magnet. Ion revolution times were 41.4 μs and 53.5 μs for $IrCl_6^{2-}$ and $IrBr_6^{2-}$, respectively. Ions with m/z greater than that of the dianion were detected with a channeltron, while neutral fragments were detected with a microchannel plate detector. In contrast to FT-ICR experiments where a high magnetic field is used, the ions move only under the influence of electric fields in the ring and electron autodetachment processes are therefore not perturbed by magnetic fields in our experiment.

2.2. High-energy CID experiments

The experimental set-up for the high-energy collision experiments has also been described previously [14]. A schematic diagram of the accelerator mass spectrometer is displayed in Fig. 1. Accelerated ions (again produced via electrospay) of 100 keV kinetic energy were mass selected with a magnet and subjected to single-collision activation in a Neon collision cell, so that the ion beam intensity is reduced to ∼2/3 of its original intensity. Mass-analysed ion kinetic energy (MIKE) scans of the anions exiting the collision cell

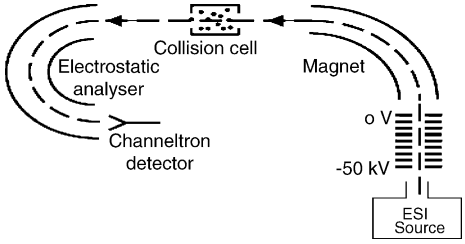

Fig. 1. Schematic of the accelerator mass spectrometer used for high energy CID experiments. Neon was employed as the collision gas in the current series of experiments.

were recorded using an 180° hemispherical electrostatic analyser coupled to a channeltron detector. Additionally, charge reversal spectra were acquired by switching the polarity of the analyser optics to monitor the production of any cationic products resulting from triple electron detachment.

3. Results and discussion

3.1. Lifetimes of $IrBr_6^{2-}$ and $IrCl_6^{2-}$ measured in an ion storage ring

Fig. 2a displays the number of neutral fragments produced from decay of $IrBr_6^{2-}$ as a function of storage time in the ELISA ion-storage ring, illustrating that the number of neutrals detected decreases at a constant rate. The time dependence of the parent ion decay can be fitted by a function of the form $\exp(-t/\tau)$, where τ is the lifetime. Fig. 2a illustrates the first order fit to the data which produces a lifetime of 3.3 ± 0.1s for $IrBr_6^{2-}$. The time dependence for production of daughter ions (Fig. 2b) displays almost identical behaviour, consistent with a lifetime for decay of $IrBr_6^{2-}$ into ionic fragments of 3.2 ± 0.1 s. The production of *both* ionic and neutral daughter fragments, along with the identical lifetimes for decay into the neutral and ionic product channels, indicate that decay of $IrBr_6^{2-}$ on this timescale is resulting purely from high-energy collisions with residual gas ($\sim 5 \times 10^{-11}$ Torr) that is present in the ring [15].

Similar measurements on $IrCl_6^{2-}$ revealed that this dianion also decayed with production of ionic and neutral daughter fragments, with a decay lifetime of 3.1 ± 0.1 s in both cases. Once again, this indicates that $IrCl_6^{2-}$ is intrinsically stable with respect to decay on the timescale of the measurement, with fragmentation only resulting from high-energy collisions with residual gas. Indeed, the $IrCl_6^{2-}$ results support our conclusions regarding the $IrBr_6^{2-}$ measurements, since it would be highly unlikely that metastable decay of both dianions would be characterised by the same lifetime.

The lifetime measurements therefore indicate that the isolated $IrCl_6^{2-}$ and $IrBr_6^{2-}$ dianions are intrinsically stable with respect to electron detachment and ionic fragmentation. These results are consistent with previous experiments that have been performed on $IrCl_6^{2-}$ and $IrBr_6^{2-}$ [10–12]. However, the fact that both neutral and charged fragments are pro-

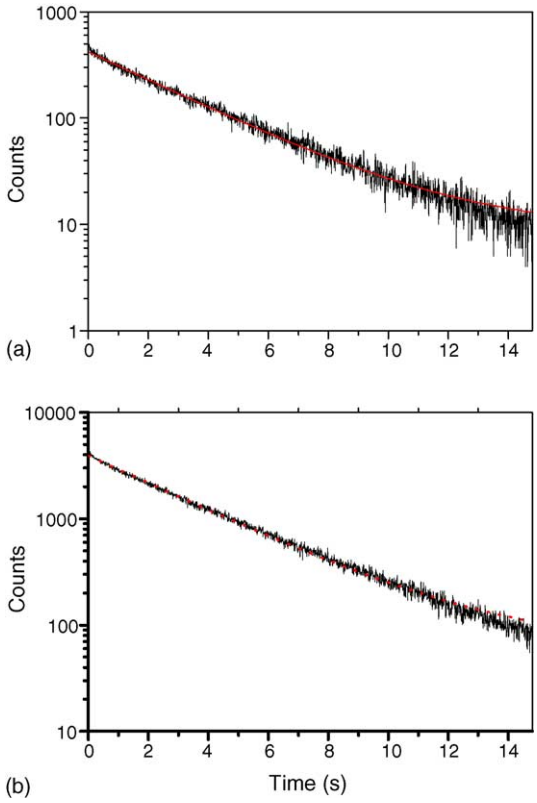

Fig. 2. (a) Count rate of neutral fragments produced by $IrBr_6^{2-}$ dianions as a function of time spent in the ELISA ion storage ring. A first order exponential decay fit to the data is displayed (solid line). (b) Count rate of charged particles produced by fragmentation of $IrBr_6^{2-}$. A first order exponential decay fit to the data is displayed (dashed line).

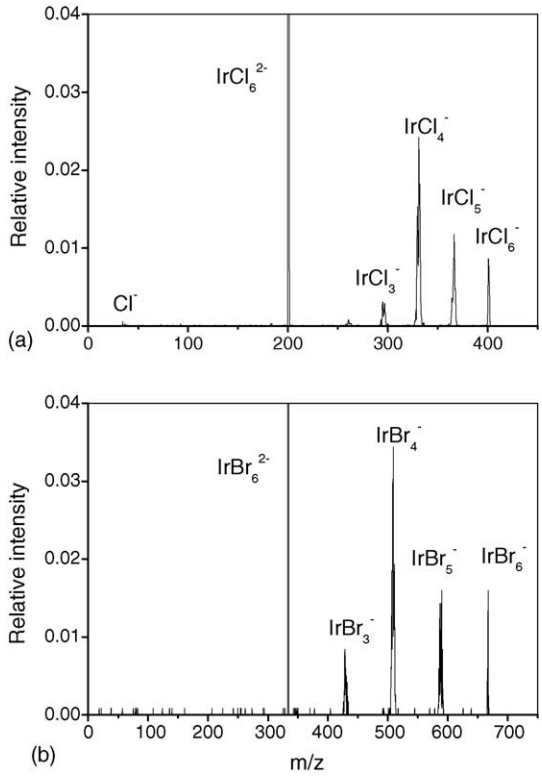

Fig. 3. (a) MIKE spectrum of $IrCl_6^{2-}$ following high energy (100 keV) collisions with Neon. The peak intensity is relative to the parent $IrCl_6^{2-}$ dianion (total counts at m/z 205 = 8667) having an intensity of 1. The most abundant isotopomer is selected prior to collision by the bending magnet. (b) MIKE spectrum of $IrBr_6^{2-}$ taken under the same conditions as used for $IrCl_6^{2-}$. The peak intensity is relative to the parent $IrBr_6^{2-}$ dianion (total counts at m/z 333 = 1190) having an intensity of 1.

duced indicates that decay is not simply occurring via ionic fragmentation as in low-energy collisional excitation, i.e.,

$$IrCl_6^{2-} \rightarrow IrCl_5^{-} + Cl^{-} \quad (1)$$

It appears that the dianions are excited to new excited state surfaces where decay occurs with the production of neutral atoms or molecules such as Cl and Cl_2. This issue will be investigated further in the next section [16].

3.2. High-energy collision induced dissociation of $IrBr_6^{2-}$ and $IrCl_6^{2-}$

Fig. 3a displays a 100-keV CID MIKE spectrum of $IrCl_6^{2-}$. In addition to the parent dianion which represents the most intense peak, the daughter ion peaks that appear, in descending order of intensity, are $IrCl_4^{-}$, $IrCl_5^{-}$, $IrCl_6^{-}$, $IrCl_3^{-}$ and Cl^{-}. This result can be contrasted with the low-energy CID behaviour of $IrCl_6^{2-}$, where the only decay pathway observed is that of ionic fragmentation to produce $IrCl_5^{-}$ via loss of Cl^{-} [12]. At the high energies used in this experiment, a variety of alternative decay pathways clearly become activated. We note that the high-energy collision conditions will lead to vertical transitions due to the short interaction time between the 100 keV ion and neon.

The presence of $IrCl_6^{-}$ indicates that the collisional electron detachment pathway is operative at this energy. The question is whether the other fragments result from ionic fragmentation, or decay from the $IrCl_6^{-}$ monoanion. Previous MIKE studies of transition metal complex ions have shown that dissociation is induced by a single-collision process [18], and therefore we can assume that all products result from single-collision excitations. While the presence of $IrCl_6^{-}$, and Cl^{-} and $IrCl_5^{-}$ can be attributed to (ground or excited-state) electron detachment and ionic fragmentation processes, respectively, the $IrCl_4^{-}$ and $IrCl_3^{-}$ fragments are of particular interest since they illustrate the existence of new excited state surfaces which decay with production of these ions.

Information can be gained from the width of the spectral peaks which reflect the magnitude of kinetic energy release upon dissociation [18,19]. The peak widths of all the fragment ions recorded in this work are similar to those previously recorded for CID MIKE of $Pt(CN)_4^{2-}$ and $Pt(CN)_6^{2-}$, where the kinetic energy release is on the order of 0.5 eV [18]. This kinetic energy release is consistent with production of the Cl^{-} and $IrCl_5^{-}$ daughter fragments from excited state surfaces or via spontaneous decay of the $IrCl_6^{-}$ monoanion, since the

KE release from excitation into the region of the ground state RCB is estimated to be ~2 eV [11].

The CID-MIKE spectrum of $Pt(CN)_6^{2-}$ reported previously [18] revealed the presence of the $Pt(CN)_5^{2-}$ dianion, due to initial knockout of a neutral CN molecule. The absence of $IrCl_5^{2-}$ in the spectrum presented in Fig. 3a illustrates that other decay dynamics are operative for the larger hexa-cyano transition metal complex dianions compared to the hexa-halide complexes. The smaller $IrCl_5^{2-}$ dianion will be unable to delocalize its excess charge as efficiently as $Pt(CN)_5^{2-}$ and may therefore have too short a lifetime to be observed at the detector (travel time of a few microseconds).

Fig. 3b shows a MIKE spectrum of the $IrBr_6^{2-}$ dianion. As in the ion storage ring experiments, the behaviour of the chloride and bromide complexes is again highly similar. By analogy with $IrCl_6^{2-}$, $IrBr_6^{2-}$ is observed to fragment with production of the $IrBr_4^-$, $IrBr_5^-$, $IrBr_6^-$, $IrBr_3^-$ and Br^- daughter ions which appear with a similar intensity pattern as in the corresponding $IrCl_6^{2-}$ experiment.

The results from the CID MIKE spectra support the results of the ion-storage ring lifetime experiments. High-energy collisional activation of the iridium hexahalide dianions in the accelerator mass spectrometer produced a range of ionic fragments. While the presence of the IrX_6^-, IrX_5^-, and X^- (X = Cl and Br) daughter ions can be explained as resulting from electron detachment or ionic fragmentation, the production of IrX_4^- and IrX_3^- must be accompanied by the production of neutral fragments. This observation explains why the rate of change of detected neutral and charged fragments is the same in the ion-storage ring following high-energy collisional excitation with background gas.

Fig. 4 shows the charge reversal CID-MIKE spectrum of $IrCl_6^{2-}$. A total of six cations were observed (Cl^+, Ir^+, $IrCl^+$, $IrCl_2^+$, $IrCl_3^+$ and $IrCl_4^+$), all at significantly lower intensity than in the anion CID-MIKE spectrum. The range of Iridium cations observed correspond to the transition metal in its +I, +II, +III, +IV, and +V, oxidation states. No stable complexes

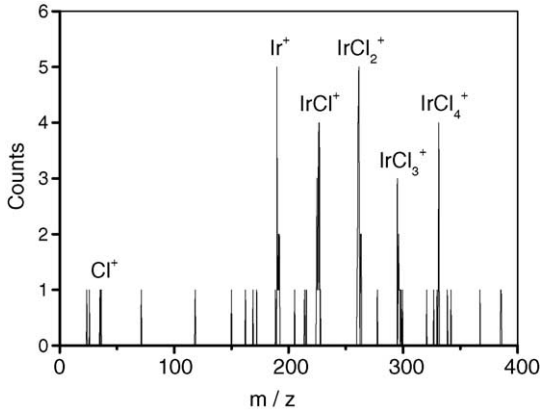

Fig. 4. Charge reversal MIKE spectrum following high-energy (100 keV) collisions of $IrCl_6^{2-}$ dianions with Neon. All of the peaks showing an intensity of 1 count (except for the peak assigned to Cl^+) are due to background noise.

with Iridium in the +VI and +VII oxidation states are known to exist [8], and it is therefore interesting to note that $IrCl_5^+$ and $IrCl_6^+$ do not appear as daughter fragments in the CID-MIKE spectrum.

The monocationic complexes observed in the charge-reversal measurements should all arise from triple electron detachment from the parent $IrCl_6^{2-}$ dianion, followed by subsequent dissociation to a more stable complex, e.g.,

$$IrCl_6^{2-} - 3e^- \rightarrow [IrCl_6^+]^* \rightarrow IrCl_4^+ + Cl_2 \quad (2)$$

We note that since the cross section for double electron detachment will be greater than that for triple electron detachment, it seems reasonable to expect that double electron detachment from $IrCl_6^{2-}$ also represents a prominent decay pathway under these conditions. The observation of the atomic ions Ir^+ and Cl^+ hints that even higher order electron detachment processes may be occurring, resulting in Coulombic explosion of any dications formed [20], e.g.,

$$IrCl_6^{2-} - 4e^- \rightarrow [IrCl_6^{2+}]^* \rightarrow IrCl_4^+ + Cl^+ + Cl \quad (3)$$

This would be worth investigating in further work, since improved spectra should reveal broadened peaks (associated with substantial kinetic energy release) if a Coulombic explosion has occurred [19].

To our knowledge, collision-induced triple electron detachment has only been observed in a small number of experiments previously, namely in collisions of two H^- ions at collision energies of up to 100 keV [21], and in extremely high-energy collisions (4–36 MeV) of C_{60}^- with N_2 [22]. In addition, the H_3O^+ ion was observed following high-energy CID (50 keV) of $Pt(CN)_6^{2-} \cdot (H_2O)_2$, and attributed to charge-transfer decay of a triple-electron detachment product [23]. The results presented in this study indicate that high-energy collisional activation of molecular dianions will provide a useful methodology for studying triple electron detachment of molecular ions. Collisional electron detachment of negative ions is of considerable interest from a fundamental point of view as it can serve as a probe of electron correlation [24]. Triple electron detachment is of particular theoretical interest since accurate modelling of the process requires a two-electron simultaneous tunnelling model for its accurate quantitative description [25]. The dianionic complexes studied in this work, provide an excellent model system for studying multi-electron detachment since they have a rich supply of valence electrons [8,10], thus facilitating electron detachment at lower collision energies. This situation contrasts with that for the atomic singly charged ions systems studied previously where multi-electron detachment generally occurs as a result of core-ionization [24].

4. Conclusions

CID-MIKE spectra of IrX_6^{2-} (X = Cl, Br) reveal that high-energy collisional excitation results in the production of

a number of anionic fragments, namely IrX_4^-, IrX_5^-, IrX_6^-, IrX_3^- and X^-. The IrX_6^-, and IrX_5^- and X^- daughter fragments can be attributed to (ground or excited-state) electron detachment and ionic fragmentation processes, but the $IrCl_4^-$ and $IrCl_3^-$ fragments are of particular interest since they illustrate the existence of new excited state surfaces which decay with production of these ions. The presence of IrX_6^- indicates that electron detachment is a prominent decay process, a result that contrasts sharply with the previous low-energy CID experiments [12] where thermal excitation leads to decay via the lowest energy decay pathway of ionic fragmentation to $IrCl_5^-$ and Cl^-. Furthermore, the predominance of high-energy collision induced electron detachment occurring is illustrated by the charge-reversal measurements where the daughter fragments indicate that triple (and possibly higher order) electron detachment from $IrCl_6^{2-}$ occurs.

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