Double-Ionization Energies to Ground and Excited States of the Tungsten Hexacarbonyl Dication

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Tungsten hexacarbonyl was investigated by double-charge-transfer (DCT) spectroscopy, and the double-ionization energies to ground and electronically excited states of $W(CO)_6^{2+}$ determined. The double-ionization energies corresponding to the first two distinct peaks in the spectra are 22.8 ± 0.3 eV and 28.5 ± 0.3 eV, but numerous overlapping peaks at higher energies are evident. It is shown that the DCT spectra can explain the main features of a previously determined (*J. Am. Soc. Mass Spectrom.* 1990, 1, 16–27) internal energy distribution curve for $W(CO)_6^{2+}$ ions formed by 70-eV electron ionization of $W(CO)_6$ molecules. (*J Am Soc Mass Spectrom* 1991, 2, 108–112)

In an article that appeared in the first issue of this journal, Cooks et al. [1] reported the results of a detailed investigation into the energy deposited in tungsten hexacarbonyl dications as a result of (1) charge stripping of $W(CO)_6^+$ ions, (2) collisional activation of $W(CO)_6^{2+}$ ions, and (3) the formation of the dications from $W(CO)_6$ in electron ionization. They found that the distribution $P(\epsilon)$ of internal energies ϵ in charge stripping falls exponentially with increasing ϵ , and that this distribution is similar to that obtained by collisional activation of $W(CO)_6^{2+}$. For 70-eV electron ionization of $W(CO)_6$, however, the distribution of internal energies of $W(CO)_6^{2+}$ showed considerable structure which the authors suggest is due to a Franck-Condon gap in excitation probability. A structured $P(\epsilon)$ distribution curve was also obtained for singly charged ions generated by 70-eV electron ionization of $W(CO)_6$ molecules. This is also probably due to a Franck-Condon gap in excitation probability which the authors note is evident in the photoelectron spectrum of $W(CO)_6$ [2]. Unfortunately, similar information about the electronic states of the dication does not exist. The purpose of the investigation reported here was to obtain this information by double-charge-transfer (DCT) spectroscopy, a technique which allows the double-ionization energies to ground and excited states of dications to be measured [3].

Experimental

DCT Spectroscopy

In DCT spectroscopy, fast-moving, singly charged positive ions (usually having several keV of translational energy) undergo double-electron-capture (DEC)

reactions in collisions with the molecules under investigation. These reactions are endothermic, and the energy to drive them comes from the translational energy of the projectile ions. Thus, the negative ions formed have a translational energy which is lower than that of the incident positive ions. This energy reduction is measured in the experiment. If the projectile ion is denoted by A^+ , and the target molecule by M (which can be regarded as at rest), the DEC reaction can be represented by

If the difference in the translational energies of A^+ and A^- is denoted by ΔE , then the energy-balance equation for reaction 1 is

$$\Delta E = IE_2(M) - E(A^+ \rightarrow A^-) \quad (2)$$

where $IE_2(M)$ is the double-ionization energy of M (assuming M to be initially in its ground state), and $E(A^+ \rightarrow A^-)$ is the energy made available when A^+ converts to A^- . The latter energy can, in many cases, be equated to $[IE_1(A) + E_a(A)]$, the sum of the single-ionization energy and electron affinity of A . It will be shown that $E(A^+ \rightarrow A^-)$ need not be known in order to determine $IE_2(M)$, but its value does have an influence on the cross section for reaction 1. Another term which could be included in eq. 2 is the recoil energy of M^{2+} , but under the conditions of the present investigation (light projectile ions and a heavy target molecule) it is negligibly small.

$IE_2(M)$ in eq. 2 represents the double-ionization energy to populate the ground electronic state of M^{2+} . The energies $IE_2(M)$, $IE_2^*(M)$, etc., required to populate higher-lying states of M^{2+} will necessitate larger translational-energy losses, $\Delta E'$, $\Delta E''$, etc., and these will give extra peaks in the measured energy-loss spectrum. Thus, by determining the energy losses

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associated with peaks in DCT spectra, the double-ionization energies to ground and excited states of M^{2+} can be evaluated.

Apparatus and Experimental Procedure

The apparatus used in this investigation is an MS9 spectrometer (manufactured by GEC-AEI (Electronics) Limited, now Kratos Analytical Limited, Manchester UK) that was modified [4] for DCT spectroscopy experiments. $W(CO)_6$ molecules were introduced into a collision-gas cell located close to the intermediate focal point between the magnet and the electric sector. The cell is connected via a heated line to a reservoir that can be heated to selectable temperatures up to a maximum of 150°C . A quantity of $W(CO)_6$ was introduced into the reservoir at room temperature, and then the reservoir was immersed in liquid nitrogen, sealed off from the atmosphere, and evacuated. The liquid-nitrogen bath was removed, and by heating the reservoir to 70°C a concentration of $W(CO)_6$ molecules in the cell was generated, adequate to carry out the DCT spectroscopy experiments. At this temperature, there is no likelihood of thermal dissociation of the $W(CO)_6$ molecule.

The scanning procedure adopted with the MS9 spectrometer to carry out DCT spectroscopy was described in detail previously [4], and only a brief outline is given here. The translational energy of the A^+ projectile ions entering the collision-gas cell was varied by using the peak-matching unit of the spectrometer. The transmission energy of the A^- ions passing through the magnet was kept constant by working with a fixed value of the magnetic field. If the negative-ion transmission energy is denoted by E^- , a peak in the A^- ion spectrum appeared when the energy of A^+ reached a critical value, $(E^+)_M$ with molecules M in the cell, when the energy-balance equation

$$(E^+)_M - E^- = IE_2(M) - E(A^+ \rightarrow A^-) \quad (3)$$

is satisfied. As in most translational-energy-loss experiments involving ions, the energy-loss scale has to be calibrated by carrying out the experiment with a calibrant molecule or atom for which the energetics of the reaction under investigation are known. In the present investigation, xenon atoms were used in the calibration procedure. With xenon gas in the cell, the energy of A^+ to ensure transmission of A^- becomes $(E^+)_{Xe}$, given by

$$(E^+)_{Xe} - E^- = IE_2(Xe) - E(A^+ \rightarrow A^-) \quad (4)$$

Thus,

$$(E^+)_M - (E^+)_{Xe} = IE_2(M) - IE_2(Xe) \quad (5)$$

from which $IE_2(M)$ is readily calculated, since $(E^+)_M$ and $(E^+)_{Xe}$ are measured in the experiment, and $IE_2(Xe)$ is known [5]. If an excited state of M^{2+} is populated, $IE_2(M)$ in eq. 3 is replaced by $IE_2^*(M)$ and a

higher positive-ion translational energy $(E^+)_M$ is required to transmit the negative ion. Thus, by scanning the translational energy of A^+ and recording the negative-ion current, a spectrum is obtained, the peaks in which correspond to the population of ground and excited states of M^{2+} .

The present investigation used three different projectile ions (S^+ , OH^+ , and F^+) generated by dissociative electron ionization of CS_2 , H_2O , and CF_4 , respectively. The translational energy of the projectile ions was about 8 keV, and the scan range was 39 eV when using S^+ and OH^+ , and 73 eV when using F^+ . It will be seen that each projectile ion enhances certain peaks in the spectra. This is a consequence of a "reaction-window" effect, which is discussed later in the context of the spectra obtained.

Tungsten hexacarbonyl of 99% purity (supplied by the Aldrich Chemical Co. Ltd., Milwaukee, WI) was used. The spectrometer was, in general, operated with the mass resolution set at approximately 7000 (10% valley definition). The projectile-ion beam width at this setting is approximately 0.7 eV at half-height.

Results

Spectra Obtained with OH^+ as the Projectile Ion

A typical spectrum obtained with $W(CO)_6$ molecules in the collision-gas cell, and using OH^+ as the projectile ion, is shown in Figure 1. Based on experience gained in numerous similar experiments carried out in this laboratory [6-13], checks were made to see if the peaks observed were due to the DEC reaction

or due to the sequential, single-electron-capture reac-

Figure 1. Double-charge-transfer spectrum of OH^- ions formed by DEC reactions of OH^+ projectile ions in collisions with $W(CO)_6$ molecules. For the significance of the arrows and numbers above them, see the Discussion section.

Figure 2. Double-charge-transfer spectrum of OH^- ions formed by DEC reactions of OH^+ projectile ions in collisions with Xe atoms.

tions

The yield of OH^- ions from reaction 6 depends on single collisions, and is thus linearly dependent on $\text{W}(\text{CO})_6$ pressure. However, the yield of OH^- from reactions 7 and 8 is quadratically dependent on the pressure because there are two $\text{W}(\text{CO})_6$ molecules involved. Spectra obtained at several pressures over a range, the limits of which differed by a factor of three, showed that the height of both the main peaks A and B in the spectra varied approximately linearly with pressure, and thus were due to OH^- ions formed by reaction 6. The actual pressures in the cell were not measured, but pressures proportional to them were measured by using an ionization gauge situated above the diffusion pump that evacuates the housing containing the cell.

A typical calibration spectrum obtained with xenon in the cell is shown in Figure 2. This was recorded at a very low cell pressure, which ensured that the peak was due to a DEC reaction in a single collision. It is known [4] that three triplet states of Xe^{2+} ($^3\text{P}_0$, $^3\text{P}_1$, and $^3\text{P}_2$) could be populated, the energies of which are separated at maximum by 1.2 eV. Thus, the mid-position of the peak close to the top was taken to correspond to $\text{IE}_2(\text{Xe})$ of 33.94 eV, the value midway between the highest and lowest energies of the triplet states.

Twelve spectra similar to that of Figure 1 were recorded, together with twelve corresponding calibration spectra taken immediately after each one, and the double-ionization energies were calculated from the positions of the peaks by using eq. 5. The mean value for the peak marked A is 22.8 eV, with a standard deviation of ± 0.3 eV, and that for peak B is 28.5 ± 0.3 eV.

Spectra Obtained with S^+ and F^+ as Projectile Ions

It is probable that the reaction which gives rise to peak A in Figure 1 results in the population of ground-state $\text{W}(\text{CO})_6^{2+}$ ions. Support for this comes from the value for the minimum energy, Q_{min} , to remove an electron from $\text{W}(\text{CO})_6^+$ measured previously [1]. This is 15.0 ± 0.3 eV which, when added to the vertical single-ionization energy of $\text{W}(\text{CO})_6$, measured in a photoelectron spectroscopy experiment [14] as 8.56 eV, predicts a double-ionization energy of 23.56 ± 0.3 eV. This value is close to the present result of 22.8 ± 0.3 eV when combined errors are taken into account. Further, it has been shown [15] that for many organic molecules the double-ionization energy is about 2.7 times the single-ionization energy. This factor has been confirmed in numerous measurements of double-ionization energy carried out by DCT spectroscopy in this laboratory (see, for example, ref. 16). Even though this "rule of thumb" may not apply to all molecules, it is of interest to see what it would predict for $\text{W}(\text{CO})_6$. Multiplying the single-ionization energy by 2.7 gives 23.1 eV, a value in agreement with the double-ionization energy of 22.8 eV from peak A.

The characteristics of the spectrum in Figure 1 are governed primarily by the cross sections for populating the individual states of $\text{W}(\text{CO})_6^{2+}$. Two theoretical studies [17, 18] showed that the cross section for DEC reactions is dependent on a quantity β which, although it is a complex function, is strongly dependent on the endothermicity of the reaction. A particularly important prediction of the theories is that the cross section should pass through a maximum at a particular value of β , i.e., that a "reaction window" exists in which β , and hence the endothermicity, must be for a DEC reaction to take place. The existence of a reaction window was confirmed in an experiment [19] that measured the relative cross sections for DEC reactions with different endothermicities. A subsequent DCT spectroscopy study [20] established that for the CH_3Br molecule a reaction window existed in the range of endothermicities from about 8 to 22 eV. In that study, the endothermicity [$\text{IE}_2(\text{M}) - \text{E}(\text{A}^+ \rightarrow \text{A}^-)$] was changed systematically by using different projectile ions. As mentioned earlier, the energy $\text{E}(\text{A}^+ \rightarrow \text{A}^-)$ can be approximated by the sum [$\text{IE}_1(\text{A}) + \text{E}_\text{a}(\text{A})$]. By using S^+ , OH^+ , and F^+ for A^+ , this sum becomes 12.44 eV, 14.84 eV, and 20.82 eV. With CH_3Br as the target molecule, the DCT spectrum profile was found to change as the projectile ion was changed [20]. With S^+ , only the ground state of the dication was populated, but with OH^+ , the ground-state peak was marginally smaller than the peak due to the dications being formed in the first excited state. The use of F^+ gave peaks due to higher excited states, but that due to the ground state was barely discernible.

A similar situation may exist for $\text{W}(\text{CO})_6$. The en-

Figure 3. Double-charge-transfer spectrum of S^- ions formed by DEC reactions of S^+ projectile ions in collisions with $W(CO)_6$ molecules.

dothemicity of the reaction giving rise to peak A of Figure 1 is about 8 eV (22.8 – 14.84). Although the reaction window for $W(CO)_6$ is not known, the figure of 8 eV is close to the lower value of the window for CH_3Br . On the other hand, if peak B is considered, the value $IE_2(W(CO)_6)$ enters into the equation for endothermicity, i.e., $28.5 - 14.84 \approx 14$ eV which, on the evidence for CH_3Br , is well within the window. With these facts in mind, the DCT spectroscopy study of $W(CO)_6$ was extended to include the projectile ions S^+ and F^+ .

A typical spectrum obtained with S^+ is shown in Figure 3. The one main peak has been marked A because from its position it corresponds to a double-ionization energy of about 22.8 eV. Thus, as expected, the ground-state peak has been enhanced and the peak B considerably suppressed by using S^+ as the projectile ion. (The position of peaks in Figures 1 and 3 should not be directly compared because the magnetic field settings were different. In practice, the field is arbitrarily set to position the spectrum conveniently within the scan range chosen. This setting is unaltered when calibrating with a calibrant gas.)

With F^+ incident on $W(CO)_6$, negative-ion currents were obtained over a large (73-eV) translational-energy range, as shown in the typical spectrum of Figure 4. The position of the first peak on the low-energy side corresponds to a double-ionization energy of about 28.5 eV, so it has been marked B to correlate with peak B of Figure 1. The spectrum of Figure 4 indicates that there are many higher-lying excited states of $W(CO)_6^{2+}$ which overlap and are not resolved in the present investigation. The translational energies indicated by C and D, for example, correspond to double-ionization energies of 34.9 eV and 43.1 eV, respectively.

Figure 4. Double-charge-transfer spectrum of F^- ions formed by DEC reactions of F^+ projectile ions in collisions with $W(CO)_6$ molecules. For the significance of the arrows and numbers above them, see the Discussion section.

Discussion

It is of interest to attempt to correlate the spectra obtained in the present investigation with the distributions in internal energy of $W(CO)_6^{2+}$ determined previously [1], in particular that resulting from 70-eV electron ionization. Cooks et al. [1] determined the critical energies for reactions involving the loss of nCO ($n = 1-6$) from $W(CO)_6^{2+}$ and used these values, together with the mass spectrum of doubly ionized ions, to construct the $P(\epsilon)$ versus ϵ curve. Relevant data from the article [1] are included in Table 1. It can be seen that the yield of the stable parent $W(CO)_6^{2+}$ is higher than that of the first fragment ion, $W(CO)_5^{2+}$, but that as n increases, the yield increases, becoming a maximum for $W(CO)_2^{2+}$.

Consider first the energy region in which the low critical energies fall. $W(CO)_6^{2+}$ ions with internal energies < 1.0 eV do not dissociate, but at 1.0 eV the dissociative reaction involving the loss of one carbonyl group can occur. This is the only reaction that takes place as the internal energy increases until the onset at $\epsilon = 3.8$ eV of the competing reaction with the loss of two carbonyl groups. Because the yield of $W(CO)_5^{2+}$ is low, Cooks et al. [1] deduced that the $P(\epsilon)$ curve has a pronounced minimum at about 2 eV. In order to compare the present spectra with the $P(\epsilon)$ curve, the critical energies E_0^{2+} from Table 1 were marked above the abscissa axes of Figures 1 and 4. It is assumed that the maximum of peak A corresponds to zero internal energy. If the structures of $W(CO)_6$ and $W(CO)_6^{2+}$ are essentially the same, this assumption is reasonable. If they are not (if some of the critical bond lengths are different, for example), the maximum in peak A would correspond to a vibrationally excited $W(CO)_6^{2+}$ ion, i.e., to an internal energy greater than 0 eV, perhaps even up to 0.5 eV, which is half the lowest energy of dissociation. As

Table 1. Data used by Cooks et al. [1] to construct a distribution curve of internal energies acquired by $W(CO)_6^{2+}$ ions formed by 70-eV electron ionization of $W(CO)_6$

Ion	Ion yield ^a in mass spectrum	Reaction $W(CO)_6^{2+} \rightarrow W(CO)_{6-n}^{2+} + nCO$	
		<i>n</i>	Critical energy E_0^{2+} (eV)
$W(CO)_6^{2+}$	15	—	—
$W(CO)_5^{2+}$	7	1	1.0
$W(CO)_4^{2+}$	26	2	3.8
$W(CO)_3^{2+}$	67	3	6.2
$W(CO)_2^{2+}$	100	4	8.5
$W(CO)^{2+}$	67	5	12.2
W^{2+}	8	6	15.1

^aRelative to the most abundant doubly charged ion.

will be seen, whether 0 eV or a value up to 0.5 eV is used, the conclusions resulting from the following discussion are virtually the same. For convenience, the maximum of peak A was taken to correspond to zero internal energy. The critical energies were marked relative to this zero position on Figures 1 and 4. It can be seen that the valley between peaks A and B is located between the 1.0-eV and 3.8-eV critical energies, suggesting that the formation of $W(CO)_6^{2+}$ ions with internal energies in this range is unlikely, and thus that the yield of $W(CO)_6^{2+}$ is small. Because this is in fact the case, it follows that this part of the DCT spectrum confirms that a minimum should exist in the $P(\epsilon)$ curve. The ϵ at the minimum of about 2 eV [1] is in reasonable agreement with the position of the minimum in the valley between peaks A and B (Figure 1).

The spectrum of Figure 4 was obtained with the F^+ projectile ion which, because of the reaction-window effect, enhances the population of excited states of $W(CO)_6^{2+}$. The maximum yield of F^- ions, and hence of excited $W(CO)_6^{2+}$ ions, corresponds approximately to the position marked C, which is located just below the critical energy of 12.2 eV. This corresponds to a high yield of $W(CO)_2^{2+}$ ions (critical energy for the relevant dissociation reaction is 8.5 eV [1]), which is what is observed in the mass spectrum (Table 1).

Conclusions

It has been shown above that the main characteristics (energies for minimum and maximum population of excited states) of the $P(\epsilon)$ versus ϵ curve for $W(CO)_6^{2+}$ ions generated by 70-eV electron ionization are identifiable in the distribution of electronic states determined in the present investigation by DCT spectroscopy.

In order to construct the internal energy distribution curve from doubly charged ion spectra, it was necessary to know the critical energies for dissociation of excited $W(CO)_6^{2+}$ ions [1]. A valuable feature of DCT spectroscopy is that it gives information on electronic states of doubly charged ions without the requirement that the fate of the ions formed in DEC reactions be known. Thus, in the present work, the OH^- ions and F^- ions carry in their translational energies information about states of $W(CO)_6^{2+}$ even

though the doubly charged ions formed with internal energies > 1 eV dissociate.

Acknowledgments

P. J. Jackson and J. A. Rontree are grateful to the Science and Engineering Research Council and ICI Pharmaceutical and Agrochemical Divisions, respectively, for financial support. We thank Professor D. E. Games for his unwavering support and encouragement throughout the investigation.

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