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Production of the molecular dication ArC^{2+} by ion–molecule reactions

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Abstract

ArC^{2+} doubly-charged ions have been produced in the reactions of Ar^{2+} with CO and CO_2. These reactions convert an atomic dication into a molecular dication, thus storing energy in a metastable state. For both reactions, we have measured integral cross-sections as a function of collision energy and evaluated reaction energetics. The observation that ArC^{2+} is produced also at collision energies largely exceeding the value needed for its dissociation suggests that reaction dynamics channels a substantial part of energy in product translation rather than in internal degrees of freedom of ArC^{2+}. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Molecular doubly-charged ions are a subject of continuing interest [1]. However, little is known about the chemical reactions of dications. For these processes, an important feature to be exploited concerns the characterisation of the role played by the huge energy content of the reactants [2].

The reactions considered in this Letter

$$Ar^{2+} + CO \rightarrow ArC^{2+} + O \qquad (1)$$

$$Ar^{2+} + CO_2 \rightarrow ArC^{2+} + 2O \qquad (2)$$
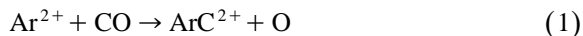
involve the Ar^{2+} ion, whose heat of formation is 43.38 eV. A substantial part of this energy is used for producing ArC^{2+}, whose heat of formation is estimated to be about 37 eV, as will be discussed in the following text. Thus the reactions studied in this work convert the energy-rich Ar^{2+} atom into the energy-rich molecule ArC^{2+}. However, the dissociation limit of ArC^{2+} ($Ar^+ + C^+$) lies below the local potential well minimum, due to an avoided crossing between the attractive curve correlating with $Ar + C^{2+}$ and the repulsive curve correlating with $Ar^+ + C^+$. As a consequence, the ground state of ArC^{2+} is metastable, and if the dissociation barrier is overcome part of the energy stored in ArC^{2+} can be released by Coulomb repulsion. Vincent and Hillier [3] calculated a dissociation barrier of 1.38 eV, while Wong and Radom [4] calculated a dissociation barrier of 1.1 eV and a kinetic energy release of 4.6 eV.

In spite of the expected stability of this dication, attempts [5] to observe ArC^{2+} by charge stripping the ArC^+ precursor have not been successful. To the best of our knowledge, the present Letter reports the first experimental observation of ArC^{2+}. In particu-

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lar, we have addressed the question of the production of ArC^{2+} in chemical reactions. Reactions (1) and (2) are examples of bond-forming processes, involving doubly-charged ions both as reactants and products. At the present, there exist only a few examples of such reactions [1,6] since collisions of dications with neutral particles usually produce singly-charged ions [7].

In this Letter, we report total cross-sections as a function of collision energy for reactions (1) and (2) and we discuss the thermochemistry of the ArC^{2+} dication.

2. Experimental

The experiment was performed in a modified version of the ion–molecule reaction mass spectrometer, which has been described before [8]. Briefly, Ar^{2+} ions produced by electron bombardment of Ar were extracted from the differentially pumped ion source, mass selected by a magnet mass spectrometer, and finally injected into a radio-frequency octopole ion guide which was surrounded by the reaction cell. Changing the octopole dc potential varies the collision energy. The axial energy distribution of the ion beam was measured by using the octopole field as a retarding field energy analyser. Typical ion energy distributions have a full width at half-maximum (FWHM) of about 1.8 eV in the laboratory reference frame. The neutral reactant gas is introduced in the reaction cell at pressures below 5×10^{-5} mbar to avoid multiple collisions. Reactant and product ions were collected, guided to a quadruple mass spectrometer and finally counted by an electron multiplier.

Absolute integral cross-sections σ were obtained by using the formula $\sigma = \alpha I_p / I_s$, where α is a constant, I_p and I_s are the intensities of product and primary ions, respectively. The constant α was determined by normalising our data on well-known cross-sections, such as those of reactions $Ar^+ + CO$ and $Ar^+ + CO_2$ [9,10]. The absolute cross-sections thus determined may be affected by large errors. We conservatively estimated that the errors are within $\pm 30\%$.

3. Results and discussion

Fig. 1 shows the cross-section for the reaction $Ar^{2+} + CO \rightarrow ArC^{2+} + O$ as a function of relative energy. The cross-section declines by increasing the collision energy, as it is typical for an exoergic reaction. In addition, a change in the slope is present between 2 and 4 eV. This feature might be due to the opening of an endothermic channel superimposed on an exothermic process.

Ab initio calculations yield values of the dissociation energy $D_0(ArC^{2+})$ of -3.37 [3] and -2.86 eV [11]. These numbers can be used to estimate the heat of formation $\Delta_f H^0(ArC^{2+}) = \Delta_f H^0(Ar^+) + \Delta_f H^0(C^+) - D_0(ArC^{2+})$. By using the auxiliary values $\Delta_f H^0(Ar^+) = 15.76$ eV and $\Delta_f H^0(C^+) = 18.63$ eV, we get $\Delta_f H^0(ArC^{2+}) = 37.76$ and 37.25 eV, respectively. Then the energetics of the reaction $Ar^{2+} + CO \rightarrow ArC^{2+} + O$ can be easily calculated. By using $\Delta_f H^0(Ar^{2+}) = 43.38$ eV, $\Delta_f H^0(CO) = -1.18$ eV and $\Delta_f H^0(O) = 2.556$ eV, eventually one finds that reaction (1) is exoergic, as suggested by experimental results. The value of the exothermicity is 1.89 or 2.40 eV, depending on the value assumed for the heat of formation of ArC^{2+}. It is interesting to note that the estimated values for the exothermicity are larger than the calculated dissociation barriers for ArC^{2+}. Thus the observation of this dication means that the reaction dynamics has placed a substantial part of the available energy in
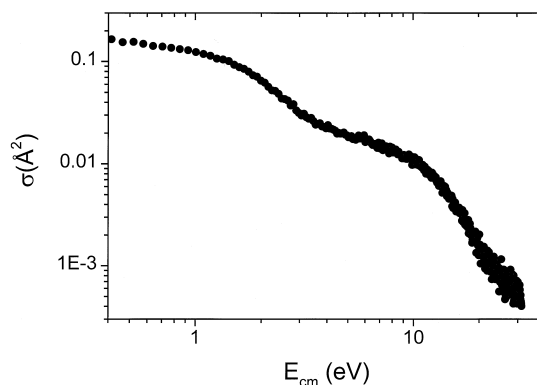

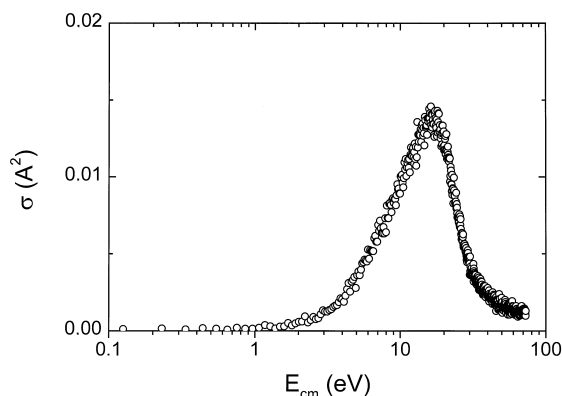Fig. 1. Energy dependence of integral cross-sections for the production of ArC^{2+} in the reaction of Ar^{2+} with CO.

Fig. 2. Energy dependence of integral cross-sections for the production of ArC^{2+} in the reaction of Ar^{2+} with CO_2.

product translation rather than in internal energy of ArC^{2+}.

In the collinear configuration, the reaction $Ar^{2+}(^3P) + CO(^1\Sigma^+)$ occurs on two potential energy surfaces, of Σ and Π symmetry, respectively. While the $^3\Sigma$ surface correlates with ground state products $ArC^{2+}(^1\Sigma^+) + O(^3P)$, the $^3\Pi$ surface correlates diabatically with the first excited state $ArC^{2+}(^3\Pi) + O(^3P)$ (another $^3\Pi$ surface correlates ground state products with $CO^{2+}(^3\Pi) + Ar$ reactants). $ArC^{2+}(^3\Pi)$ is calculated to lie 3.17 [3] or 2.84 eV [4,11] over the $^1\Sigma^+$ ground state. On the $^3\Pi$ surface, reaction (1) is therefore endothermic by 1.28 or 0.44 eV, depending on the different theoretical values used in the calculation. Whether the opening of this endoergic channel might be responsible for the feature observed around 3 eV is at present an open question.

The energetics of reaction (2), $Ar^{2+} + CO_2 \rightarrow ArC^{2+} + 2O$, can be easily derived given $\Delta_f H^0(CO_2) = -4.074$ eV. This process was found to be endothermic by 3.56 [3] or 3.05 eV [4], depending on the value assumed for the heat of formation of ArC^{2+}. Fig. 2 shows the cross-sections as a function of collision energy. The reaction starts at around 2 eV and the peak in the energy dependence of the cross-section is located at about 17 eV. This value exceeds the sum of the endothermicity and the dissociation barrier. Thus, similar to reaction (1), for reaction (2), also the energy is released mainly in translation rather than in internal excitation.

For both the reactions (1) and (2), cross-sections are quite small ($< 10^{-1}$ Å^2) compared to the values characteristic of ion–molecule reactions. This may be rationalised on the basis of a model developed by Herman and co-workers [2,12]. They suggested that the formation of products $AB^{2+} + C$, via the chemical rearrangement of reactants $A^{2+} + BC$, is in competition with charge-transfer processes leading, for example, to the formation of $A^+ + BC^+$ and $AB^+ + C^+$. As a consequence, the synthesis of AB^{2+} occurs only if the system survives the charge-transfer crossings during its evolution along the reaction path.

In conclusion, we have demonstrated the possibility of producing ArC^{2+} by the reaction of Ar^{2+} with CO and CO_2. These processes convert an atomic dication into a molecular one, storing energy in a metastable state. This energy (ca. 4.6 eV [4]) can be subsequently released by triggering the Coulomb explosion.

Acknowledgements

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