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Electron-transfer and chemical reactivity following collisions of Ar^{2+} with C_2H_2

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Dedicated to Zdenek Herman on the occasion of his 75th birthday.

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ABSTRACT

The reaction between Ar^{2+} and C_2H_2 has been studied, at centre-of-mass collision energies ranging from 3 to 7 eV, using a position-sensitive coincidence technique to detect the monocation pairs, which are formed. Sixteen different reaction channels generating pairs of monocations have been observed, these channels arise from double-electron-transfer, single-electron-transfer and chemical reactions forming ArC^+. Examination of the scattering diagrams and energetic information extracted from the coincidence data indicate that double-electron-transfer is a direct process, which does not involve a collision complex, and the derived energetics point towards a concerted, not stepwise, mechanism for the two-electron-transfer. As is commonly observed, single-electron-transfer from C_2H_2 to Ar^{2+} takes place *via* a direct mechanism, again not involving complexation. Most of the $C_2H_2^+$ products that are formed in the single-electron-transfer reactions possess significant (12–15 eV) internal energy and fragment rapidly within the electric field of the partner Ar^+ ion. The chemical reactions appear to proceed *via* a direct mechanism involving the initial formation of $ArCH^+$, which subsequently fragments to form ArC^+.

1. Introduction

As discussed in recent reviews [1,2], ethyne (C_2H_2) is the smallest stable hydrocarbon, which contains a carbon–carbon bond and has been studied in depth by many advanced theoretical and experimental techniques. Ethyne also has many technological uses, for example in arc-welding and as a fuel for flames [3]. In addition, plasmas composed of Ar and C_2H_2 are used for the surface deposition of diamond films [4–6]. Ethyne is also an important component of many planetary atmospheres [7], especially that of Titan [8], and is also found in the Earth's atmosphere [1]. All the above are environments where the formation of ions may be important, and it is therefore of fundamental interest to understand the ionisation of C_2H_2 and its consequences.

There are a considerable number of studies of the single and double ionisation of ethyne reported in the literature. Single ionisation of ethyne has been extensively investigated using photon ionisation [9–12], photoelectron spectroscopy ([13–15] and references therein) as well as coincidence techniques [16–20], and the electron ionisation of ethyne has recently been reviewed [21]. Double ionisation of ethyne has been studied *via* photon ionisation [22–24], electron ionisation [21], charge stripping [25–27] and Auger spectroscopy [28–30]. Far less attention has been paid to the reactions of ethyne with dications, or the reactions of doubly ionised ethyne itself. Roithová and Schröder have studied the reactions of various aromatic organic dications with neutral ethyne [31]. These experiments observed charge-conserving bond-forming processes, in addition to the expected electron-transfer, proton transfer, and collision-induced dissociation reactions; for example $C_7H_6^{2+}$ and C_2H_2 react to give $C_9H_7^{2+}$. Böhme and co-workers have studied the reactions of C_{60}^{x+} and C_{70}^{x+} (where $x = 1–3$) with C_2H_2 in a selected ion flow tube and found there was no simple bimolecular reaction, only three-body adduct formation [32]. Reactions of Ar^{2+} with C_2H_2 have been studied using an ion drift tube [33,34] and $C_2H_2^+$ and C_2H^+ were detected as products. These drift tube experiments indicated the reaction rate coefficient was large and remained constant over a range of collision energies below 1 eV.

This study will consider three of the general classes of reactivity [35–43] which can occur following collisions between a dication M^{2+} and a neutral species AB: double-electron-transfer (DET), single-electron-transfer (SET) and chemical reactions. In DET two electrons are transferred to M^{2+}, from the neutral, to generate AB^{2+}; hence, any monocationic products detected will be due to the dissociation of AB^{2+}. In SET one electron is transferred to M^{2+} from AB yielding M^+ and AB^+ as the primary products. Both the DET and SET mechanisms can be further categorized as *dissociative* or *non-dissociative*. If the reaction is non-dissociative then the ionic products from the primary electron-transfer are formed in stable electronic states. Conversely, if the reaction is dissociative one or both of the primary ionic products subsequently fragment

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further. As the position-sensitive coincidence (PSCO) method we employ detects only pairs of monocations, only dissociative DET will be detected by our experiments, even if there are non-dissociative channels operating. However, both dissociative and non-dissociative SET events can be probed by the PSCO methodology. In a “chemical” process new bonds are generated between atoms from the reactant dication and atoms from the neutral reactant. Again, chemical processes forming pairs of ions can be probed by the PSCO technique, but reactions, which generate dicationic products, will not be detected.

At low collision energies, below 100 eV, SET reactions of dications can be well explained using ‘reaction window’ models based on the Landau–Zener theory [40,44,45]. Briefly, for a dication reaction, this model pictures the electron-transfer occurring at a curve crossing (Fig. 1(b)) between a reactant potential energy curve ($M^{2+} + AB$), which is attractive at significant interspecies separations, and a product potential ($M^{+} + AB^{+}$), which is dominated by Coulomb repulsion. The one-dimensional Landau–Zener model indicates that, for efficient SET, this crossing of potential energy curves (PECs) should occur at interspecies separations between 3 and 6 Å. If the curve crossing is at larger interspecies separations than the favoured window, the coupling between the reactant and product potentials is not strong enough for efficient electron-transfer. Conversely, if the curve crossing is at too small an interspecies separation the coupling between the reactant and product potentials is strong. However, this strong interaction results in inefficient net electron-transfer, as the collision system has to pass through the curve crossing twice, on approach and separation.

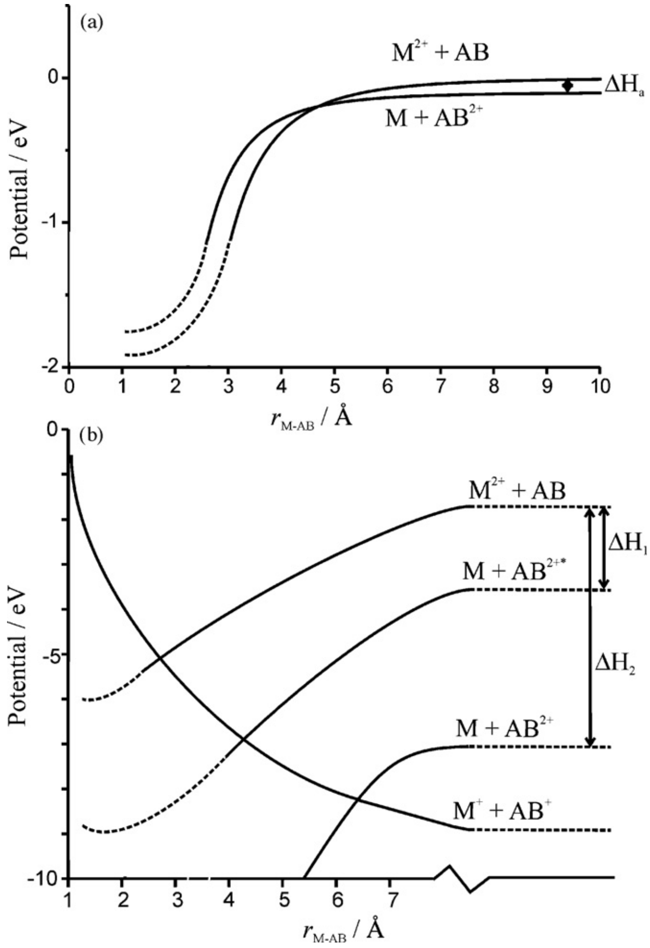

Fig. 1. Schematic potential energy curves for (a) concerted and (b) sequential double-electron-transfer following the reaction of M^{2+} with AB. (a) ΔH_a indicates the small reaction enthalpy which is required for the curve crossing to lie in the reaction window for the concerted mechanism. (b) The competition between single- and double-electron-transfer, which is implicit if the sequential mechanism for double-electron-transfer is operating. The sequential mechanism involves an initial single-electron-transfer to the repulsive potential corresponding to a pair of monocations. The system may then remain on this potential, resulting in single-electron-transfer, or cross again to reach an $M + AB^{2+}$ asymptote. ΔH_1 and ΔH_2 schematically indicate the limiting reaction exothermicities for which this pair of curve crossings will lie in the reaction window, a markedly larger range of exothermicities than for the concerted mechanism illustrated in (a).

For the DET reactions of dications with neutrals, the simple one-dimensional reactant and product potentials will have similar forms at larger interspecies separations, as both are dominated by dication-neutral polarisation attraction. At low collision energies, symmetric DET processes have been investigated for atomic species (e.g., $Ne^{2+} + Ne$) and the measured cross-sections agree reasonably well with simple models [46–50]. DET in non-symmetric collision systems involving dications, at low collision energies, has been observed before [44,51,52] but not, to our knowledge, investigated in any great detail. Within the constraints of the one-dimensional Landau–Zener model, non-resonant DET in low-energy collisions between the generic chemical species M^{2+} and AB can, in principle, occur by two routes. The first pathway is that the two electrons are both transferred at the crossing of the $M^{2+} + AB$ and the $M + AB^{2+}$ PECs, Fig. 1(a), a concerted process. Under a one-dimensional simple electrostatic model, the only differences in the forms of the reactant and product PECs, beyond the repulsive short-range interactions, are due to the differing polarisabilities of the respective neutral species. Thus, the concerted DET pathway requires the reactant and product asymptotes to lie close in energy, within 1 eV, to place the curve crossing in the reaction window (Fig. 1(a)). An alternative DET pathway, which has been proposed before [44], involves sequential electron-transfer *via* a repulsive $M^{+} + AB^{+}$ potential which links the attractive reactant and product potentials, as illustrated in Fig. 1(b). The reactive system first crosses from the $M^{2+} + AB$ potential to the $M^{+} + AB^{+}$ potential, followed by a second crossing to the $M + AB^{2+}$ surface. Interestingly, this sequential mechanism implies an intrinsic competition between DET and SET. Qualitatively, the relevant curve crossings in this sequential model of DET will lie in the reaction window for a much wider range of reaction exothermicities than for the concerted mechanism. Thus, if the sequential DET mechanism was favoured we would expect that DET should be a common outcome of dication-neutral collisions. The relative scarcity of dication DET reactions following dication-neutral collisions, at low collision energies, perhaps hints that the concerted, “near-resonant”, mechanism is the effective pathway for these processes [52].

This paper reports an investigation of the reactivity of Ar^{2+} with neutral C_2H_2, at collision energies from 3 to 7 eV in the centre-of-mass (CM) frame using a time-of-flight mass spectrometer, equipped with a position-sensitive detector (PSD). This apparatus allows the coincident detection of the monocation pairs formed following the reactive encounters. As well as identification of the monocation pairs, this PSCO technique allows the determination of the velocity vectors of the reaction products giving a unique insight into the dynamics of the dication reactions.

2. Experimental

The PSCO apparatus has been described in detail before in the literature [35,53–55]. Briefly, dications, and other ions, are generated from a suitable precursor gas by electron ionisation in a custom-built ion source. The cations are then extracted from the ion source and transmitted into a hemispherical energy-analyser where they are energy-selected to give an ion beam with an energy