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Reaction of Ar^{2+} with C_{60} to produce C_{60}^{3+}: first observation of double electron-transfer ionization?

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Abstract

The gas-phase reaction of translationally cold Ar^{2+} ($^1S_0$) ions with C_{60} has been studied using a selected-ion flow tube (SIFT) apparatus. Amongst several product channels detected, which arose from competing reactions of contaminants (N_2, O_2, H_2O) and from the He buffer gas itself as well as from the target process $Ar^{2+} + C_{60}$, we observed an apparently minor but unambiguous signal due to a C_{60}^{3+} product ion. We surmise that this product channel arises from Ar^{2+} ($^1S_0$) + C_{60} in a bimolecular fashion, most probably by an initial (and highly exothermic) direct double electron transfer leading to the generation of either highly excited $(C_{60}^{2+})^*$ or of electronically excited $(Ar)^*$. Trication formation from either of these possible high-energy intermediates would then follow according to either an autoionization or a Penning ionization mechanism.

Keywords: Double electron-transfer ionization; Ar^{2+}; C_{60}; SIFT; Molecular trications

1. Introduction

In the field of gas-phase ion/molecule chemistry, the reaction class of electron transfer

$$A^+ + B \rightarrow A + B^+ \quad (1)$$

is so well-established as to be commonplace. A rather more unusual occurrence is the exothermic release of a free electron accompanying formation of a cationic product. At least three fundamental types of process involving translationally cold species—namely, Penning ionization (2), associative ionization (3), and electron-transfer ionization by singly-charged ions (4):

$$A^* + B \rightarrow A + B^+ + e^- \quad (2)$$

$$A + B \rightarrow AB^+ + e^- \quad (3)$$

$$A^+ + B \rightarrow A + B^{2+} + e^- \quad (4)$$

have been demonstrated to effect such a result. While the mechanisms of these three reaction classes clearly differ in detail, they share the feature that electronic rearrangement in the transition from reactants to products is sufficiently exothermic to promote liberation of an electron.

In our studies on fullerene ion/molecule chemistry, we have demonstrated the occurrence of reactions (2) and (4) for the instance of A = He and B = C_{60} [1,2]. We have also found examples of two-electron transfer [3]:

$$C_{60}^{3+} + PAH \rightarrow C_{60}^{+} + PAH^{2+} \quad (5)$$

in the reactions of fullerene trications. This led us to question whether a new class of electron-producing reaction, *two-electron-transfer ionization by doubly-charged ions*, might be feasible:

$$A^{2+} + B \rightarrow A + B^{3+} + e^- \quad (6)$$

Reaction (6) is exothermic if the appearance energy $AE(B^{3+}/B)$ is smaller than $AE(A^{2+}/A)$. While it is not very difficult to find reactant combinations fulfilling this criterion, the requirements that competing product channels should be kept to a minimum, and that both A^{2+} and B should be tractable gas-phase species, have proved rather

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more difficult to meet. We have focussed on reactions of atomic (rare-gas) dications with fullerene molecules as being most likely to exhibit this reaction class: the appearance energies of rare-gas dications are typically large, the sequential ionization energies of fullerenes are characteristically quite small, and both reactants have very attractive structural features. Rare-gas dications are uncommon among electron-impact-generated atomic dications (particularly those which possess our desired property of a high recombination energy) in exhibiting only a generally minor degree of contamination from electronically excited states, and fullerenes are unusual among polyatomic structures by virtue of their extreme resistance to fragmentation when multiply charged. In the present work, we report results which demonstrate that the reaction of translationally cold Ar^{2+} with C_{60} does indeed lead to formation of $C_{60}{}^{3+}$.

2. Experimental methods

The reactions discussed here were investigated using a selected-ion flow tube that has been described previously [4,5]. Dicationic argon was produced in an ion source by electron impact on pure argon gas (HP grade, 99.998%, Air Products) and injected into a flowing helium carrier gas (chromatographic grade, 99.9999%, Air Products) at 0.35 ± 0.01 Torr. Neutral C_{60} was introduced into the reaction region via a side inlet, in which a fullerene sample ($\geq$99.5% C_{60}, SES Research Inc.) was heated to sublimation.

Despite the efforts detailed above, impurities in the reaction region arose via several mechanisms. First, it was not possible to avoid some contamination by H_2O and by air; N_2 [6–13] and O_2 [6,7,10–12,14] are both known to react rapidly with Ar^{2+}, while H_2O almost certainly also reacts rapidly with Ar^{2+} and is known to undergo charge-separation reactions at an appreciable rate with $C_{60}{}^{3+}$ [15]. Second, PAH impurities including corranulene $C_{20}H_{10}$ (*m*/*z* 250) were evolved on heating of the fullerene sample: all of these PAHs are expected to react rapidly, and in some cases dissociatively, with the reactant ion Ar^{2+}, the product ion of interest $C_{60}{}^{3+}$, and with other product or contaminant ions such as Ar^+, He^+, $C_{60}{}^{2+}$, N^+, and O^+. Third, the He buffer gas itself is sufficiently reactive with ground-state (^{3}P) argon dications [16] that, at the conventional operating pressure and temperature of the SIFT, it is highly likely that the Ar^{2+} (^{3}P) population, resulting from electron-impact ionization and introduced into the flow tube, is effectively completely removed prior to reaching the first reactant neutral port. A logical approach to permit study of the reaction initiated by ground-state Ar^{2+} would be the use instead of an argon buffer gas, since Ar has been found unreactive with Ar^{2+} (^{3}P) [16]; unfortunately, all attempts employing an Ar buffer in our instrument resulted in the presence of an unacceptably large and persistent H_3O^+ background signal arising from contaminant water vapour.

3. Results and discussion

The gas-phase ion chemistry and ion physics of fullerenes has been intensively studied over the past dozen years. Despite the scrutiny that C_{60} in its various charge states has received, the appearance energies of the dicationic and more highly ionized forms of buckminsterfullerene remain the subject of some contention. In the present context, an exact appraisal of the thermochemistry of several reaction channels is hampered by persistent uncertainty regarding the appearance energies $AE(C_{60}{}^{2+} + 2e^-)$ and $AE(C_{60}{}^{3+} + 3e^-)$. Nevertheless, it would appear that the recombination energy available from Ar^{2+} is sufficiently large that the imprecision in the C_{60} polycation thermochemistry is not of grave concern. Here, we have adopted the literature values $IE(C_{60}) = 7.64 \pm 0.02$ eV [17] and $AE(C_{60}{}^{2+} + 2e^-) = 19.00 \pm 0.03$ eV [18]. These values are photoionization measurements, and strictly reflect the vertical ionization energy rather than the adiabatic value relevant to gas-phase ion/neutral interactions, but excellent agreement of the photoionization measurement for $IE(C_{60})$ [17] with the value of $IE(C_{60}) = 7.61 \pm 0.11$ eV resulting from an electron-transfer bracketing study [19] demonstrates that there is negligible discrepancy between vertical and adiabatic energies for generation of the monocation. It is likely, but not certain, that the synchrotron-radiation determination of $AE(C_{60}{}^{2+} + 2e^-)$ [18] is a similarly good approximation to the true adiabatic ionization energy: unfortunately, attempts to determine $IE(C_{60}{}^+)$, or similar quantities relating to the fullerene dication, using kinetic methods are necessarily impeded by substantial uncertainty because of the Coulombic factors impinging on charge-separation reactions of fullerene polycations [20,21]. Electron-impact triple ionization of C_{60} has variously yielded $AE(C_{60}{}^{3+} + 3e^-)$ values of 33.2 ± 1.0 eV [22] and 35.6 ± 1.0 eV [23], indicating corresponding $IE(C_{60}{}^{2+})$ values of 14.2 ± 1.0 eV and 16.6 ± 1.0 eV, respectively. These values compare well with a kinetic bracketing measurement of 15.6 ± 0.5 eV [24], while a charge stripping experiment has delivered a value of $IE(C_{60}{}^{2+}) = 17.0 \pm 1.0$ eV [25]. Clearly, not all measurements are in agreement. In the present work, we make use of our own 'kinetic bracketing' value of 15.6 ± 0.5 eV [24], which has the virtue that its perceived uncertainty overlaps with the error bars quoted for the other 'adiabatic' determinations of this quantity. These thermochemical values, in conjunction with the rather more precisely characterized quantities relevant to argon ionization and excitation, are used to determine the overall reaction exothermicities compiled in Table 1.

We assume, based upon the studies of Smith et al. [16] and other independent investigations [12], that the principal products of electron-impact double ionization of argon are Ar^{2+} (^{3}P) and Ar^{2+} ($^1S_0$), with only the metastable excited state Ar^{2+} ($^1S_0$) expected to persist within the (helium-buffered) ion flow to arrive at the reaction region. As can be appreciated from the 'background' mass spectrum

Table 1
Relative energies (in eV) of product channels from the reaction of Ar^{2+} with C_{60}[a]

Product channel	E_{rel} (^3P)	E_{rel} ($^1S_0$)
(^3P) Ar^{2+} + C_{60}	0	−4.12
($^1S_0$) Ar^{2+} + C_{60}	+4.12	0
C_{60}^+ + ($^2P_{3/2}$) Ar^+	−19.97	−24.09
C_{60}^+ + ($^2S_{1/2}$) Ar^{+*}	−6.49	−10.61
C_{60}^{2+} + Ar	−24.39	−28.51
C_{60}^{2+} + ($^3P_2$) Ar^*	−12.84	−16.96
C_{60}^{2+} + ($^2P_{3/2}$) Ar^+ + e^-	−9.63	−13.75
C_{60}^{2+} + ($^2S_{1/2}$) Ar^{+*} + e^-	+3.85	−0.27
C_{60}^{3+} + Ar + e^-	−8.79	−12.91
C_{60}^{3+} + ($^3P_2$) Ar^* + e^-	+2.76	−1.36

[a] Relative energy, relative to ground-state Ar^{2+} and C_{60} reactants, for the indicated product channel arising from the specified Ar^{2+} electronic state. Appearance energies, and ionization energies, pertinent to fullerene ion products are discussed in the text. Energetic parameters for Ar in electronically excited and/or ionized forms are from the NIST website [27].

shown in Fig. 1, the problems due to contamination of the reactant Ar^{2+} ion signal are so severe that Ar^{2+} itself can almost be considered as a contaminant. Other ion signals apparent in Fig. 1 are largely consistent with the known reactivity of Ar^{2+} and of the Ar^+ and He^+ products from the reaction of Ar^{2+} (^3P) with He [7]. It should be stressed, however, that neither of the monocationic contaminants in Fig. 1, nor the He^+ whose *m/z* ratio was below the operating range of our instrument, is a viable precursor to C_{60}^{3+}.

C_{60}^{3+} is indeed an apparent product of the reaction of Ar^{2+} (($^1S_0$) + C_{60}), based upon the detection of a minor

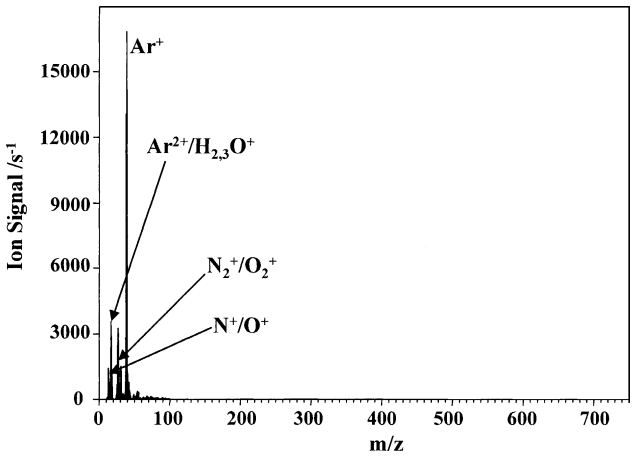

Fig. 1. Background ion signal detected via the downstream quadrupole mass filter, resulting from injection of Ar^{2+} produced by electron impact on Ar within the ion source. Contaminant signals due to N^+, O^+, H_2O^+, H_3O^+, N_2^+, O_2^+ and Ar^+ are notable, and in most cases are consistent with the reaction chemistry which has already been established for Ar^{2+} with He, N_2, and O_2: the reaction chemistry of Ar^{2+} with H_2O has not been explored previously, but a rapid reaction is expected for that process. He^+ (*m/z* 4) was not detected within the observable mass range of our instrument, but is expected as a significant component of the reactant ion mix owing to the reaction of ground-state Ar^{2+} with the He buffer.

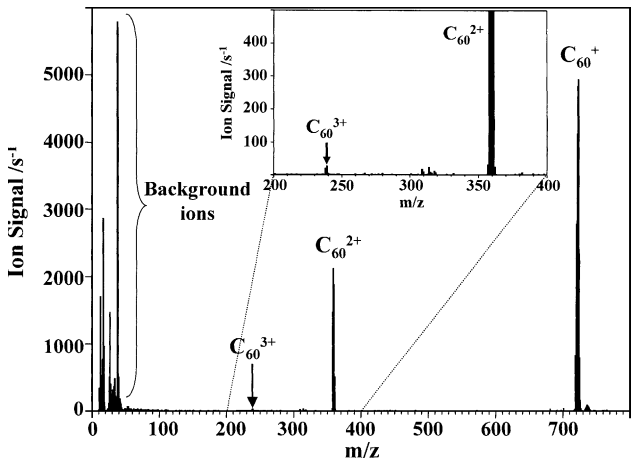

Fig. 2. Mass spectrum observed on introduction of C_{60} vapour into the reaction region. Major high-mass peaks at *m/z* 360 and *m/z* 720 can feasibly arise from various of the monocationic contaminants within the reactant ion mix, but the small signal seen at *m/z* 240, attributed to C_{60}^{3+}, cannot be explained in this manner. Also shown is a magnification of the *m/z* 200–400 range which clearly shows a peak at $m/z = 240$.

product ion signal at *m/z* 240 (see Figs. 2 and 3). Identification of this signal as C_{60}^{3+} rests upon detection of the dominant high-mass product ions at *m/z* 360 and *m/z* 720 (Fig. 3), which are respectively the di- and the monocation of C_{60}, and on the absence of any other product ions in the range *m/z* 100–720 with an overall intensity greater than that seen for *m/z* 240 (Figs. 2 and 3). Assignment of the C_{60}^{3+} signal to a single collision between Ar^{2+} and C_{60} is based upon the absence of any other viable mechanisms for C_{60}^{3+} production. For example, the impediment of an activation barrier of at least 4 eV to collision of C_{60}^{2+} with another reactant ion [21], in the context of efficient reactant ion thermalization by the helium buffer gas, coupled with the very much (several orders of magnitude) lower number density of reactant or product ions than of reactant neutrals

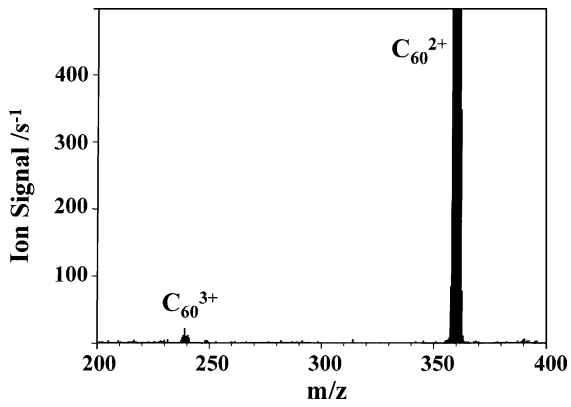

Fig. 3. High resolution mass spectrum, between *m/z* 200 and *m/z* 400, obtained by scanning in half-mass unit rather than one-mass unit steps as in Fig. 2. The lower sensitivity of this scan eliminates peaks due to the high-mass contaminants seen in Fig. 2 but the intensity ratio *m/z* 240:*m/z* 360 is similar.

within the flow tube, effectively precludes the possibility that C_{60}^{3+} could arise in detectable quantities by processes such as $C_{60}^{2+} + Ar^{+}$ or $C_{60}^{+} + Ar^{2+}$ collisions.

It is apparent, nevertheless, that some other product ions of comparatively high *m*/*z* were detected, for example in the range *m*/*z* 308–320, at *m*/*z* 682 and 700, and rather prominently at *m*/*z* ∼737 in Fig. 2. The origin of these contaminating products (which cannot be explained as possible products of simple fragmentation of the fullerene skeleton) remains unclear; they may well represent trace species present within the C_{60} sample used in these experiments. A very minor signal due to *m*/*z* 249 or 250, visible in Fig. 3, is consistent with the mass-to-charge ratio expected for corranulene $C_{20}H_{10}$, a plausible fullerene contaminant.

The C_{60}^{+} signal noted in Fig. 2 is probably formed principally from the reactions of $Ar^{+} + C_{60}$ and of $He^{+} + C_{60}$, particularly when consideration is given to the predominance of Ar^{+} (and, presumably, of He^{+}) within the reactant ion mix. Both of these rare-gas monocations are known to produce C_{60}^{+} [1], while He^{+} is also known to generate C_{60}^{2+} in an exothermic bimolecular fashion [1] and may well represent the major route to the *m*/*z* 360 product signal seen under our operating conditions. Of course, as can be appreciated from Table 1, the reaction of Ar^{2+} with C_{60} is also an entirely plausible source of C_{60}^{2+}, and it is hazardous to attempt to assign the relative contributions of He^{+} and Ar^{2+} to the *m*/*z* 360 product ion signal which we have detected.

Given that Ar^{2+}, presumably in the ($^1S_0$) electronic state, does evidently react with C_{60} to produce C_{60}^{3+}, the precise mechanism for this transformation remains uncertain. It is reasonable to expect that direct two-electron-transfer (TET):

$$Ar^{2+}(^1S_0) + C_{60} \rightarrow Ar + C_{60}^{2+} + 28.5\,eV \quad (7)$$

is efficient: the collision-rate reactions of Ar^{2+}, in both the ground (^3P) and metastable ($^1S_0$) states, with O_2, N_2, and CO_2 are all held to occur by direct TET followed by dissociation of the product molecular dication [7]. In the present case, the extreme resilience of the fullerene cage ensures against its fragmentation, while the very large exothermicity of TET is likely manifested in a tendency for substantial electronic excitation of C_{60}^{2+}, of Ar, or of both. Production of a highly excited electronic state of C_{60}^{2+} could very well precede autoionization:

$$(C_{60}^{2+})^* \rightarrow C_{60}^{3+} + e^{-} \quad (8)$$

while initial generation of excited Ar would enable a Penning ionization mechanism for trication production:

$$C_{60}^{2+} + (Ar)^* \rightarrow C_{60}^{3+} + Ar + e^{-} \quad (9)$$

Alternatively, as noted above, it would also seem feasible for the initial excitation energy to be distributed more equitably between C_{60}^{2+} and Ar. The thermochemical data in Table 1 suggests that C_{60}^{3+} production is energetically permitted even if the Ar product is not in its ground state, although the margin for error in $AE(C_{60}^{3+} + 3e^{-})$ renders this assertion uncertain. Analysis of the $Ar^{2+} + C_{60}$ reaction under different conditions—for example, in a single-collision experiment—may well provide a much more detailed insight into the reaction mechanism.

The reaction of $Ar^{2+}(^1S_0) + C_{60}$ is not the first example of a gas-phase process involving dicationic reactants leading to liberation of an electron among the products. For example, the reaction of He^{2+} with Hg yields a product channel [26]:

$$He^{2+} + Hg \rightarrow He^{+} + Hg^{2+} + e^{-} + 25.2\,eV \quad (10)$$

but this process has not been investigated at thermal energy: the lowest collision energy attained in the investigation of reaction (10) was 2 eV. In contrast, collision energies for translationally cold Ar^{2+} and C_{60} at 300 K are expected to be only a few meV. It would naturally be of considerable interest to learn whether the reaction of $Ar^{2+} + C_{60}$, which as far as we can establish is the first example of trication production from a dicationic precursor in a room temperature collision energy regime, is also a source of C_{60}^{3+} when ground-state Ar^{2+} (^3P) is used as a reactant. Further studies are envisaged to investigate this point.

4. Conclusions

Gas-phase reactions of dicationic reactant ions appear, in some instances, to be capable of tricationic product formation. Such a process has been exemplified here by the reaction between Ar^{2+} ($^1S_0$) and C_{60}, which yields a minor but apparently unambiguous product signal at *m*/*z* 240 which is assigned to the (highly exothermic) production of C_{60}^{3+}. While the reactant ion studied here is not formally in its ground state, the extent of its electronic excitation is modest (4.12 eV) when assessed against the exothermicity of C_{60}^{3+} production (∼12.9 eV), suggesting that the reaction of ground-state Ar^{2+} (^3P) + C_{60} is also a potential source of C_{60}^{3+}. The mechanism for tricationic product formation most probably involves an initial direct two-electron-transfer process followed by electron ejection accompanying electronic state relaxation: at present, it is not possible to determine whether, within such a mechanism, either autoionization of $(C_{60}^{2+})^*$ or Penning ionization by $(Ar)^*$ is involved.

Acknowledgements

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