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Rapid Communication

Charge-transfer reactions of fullerene dications with aromatic hydrocarbon and fullerene molecules in the gas phase

Gholamreza Javahery, Simon Petrie, Jinru Wang and Diethard K. Bohme
Department of Chemistry and Centre for Research in Earth and Space Science, York University, North York, Ont. M3J 1P3 (Canada)

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ABSTRACT

Results of selected-ion flow tube experiments are reported for reactions of C_{60}^{2+} and C_{70}^{2+} with benzene, naphthalene, anthracene, C_{60} (buckminsterfullerene) and C_{70} at 294 ± 2 K in helium gas at 0.35–0.40 Torr. Charge transfer was the only observed product channel. No evidence was obtained for the occurrence of adduct formation. This rules out the ability of doubly-charged fullerene molecules to act as nuclei for the condensation of aromatic molecules and the formation of doubly-charged "strings of fullerene beads" by successive additions of fullerene molecules under these operating conditions.

Keywords: charge transfer; dications; fullerenes; aromatic hydrocarbons.

INTRODUCTION

The dications of fullerene molecules can be readily produced both by physical (e.g. electron or photon impact) and chemical ionization. The latter has been achieved only recently with unprecedented charge-transfer electron-detachment reactions at thermal energies between noble gas ions and fullerene molecules; we have drawn attention to the significance of such reactions with $He^{\cdot +}$ in the chemistry of interstellar environments [1]. Here we report experimental results for reactions of the fullerene dications C_{60}^{2+} and C_{70}^{2+} with the aromatic hydrocarbon molecules benzene, naphthalene and anthracene, and the fullerene molecules C_{60} and C_{70}. The intent of this study was to explore whether doubly-charged fullerene molecules can act as nuclei for the "condensation" of aromatic molecules, in a fashion envisaged for charged graphitic dust particles in space [2], and whether they can initiate the formation of doubly-charged fullerene clusters or "strings of fullerene beads" in circumstellar envelopes by successive additions of fullerene molecules. We have already

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Correspondence to: D.K. Bohme, Department of Chemistry and Centre for Research in Earth and Space Science, York University, North York, Ont. M3J 1P3, Canada.

emphasized elsewhere how C_{60}^{2+} and C_{70}^{2+} are ideally suited for the study of dication chemistry in general [3]. The observations reported here provide further insight into this chemistry.

EXPERIMENTAL

The experiments were performed with a selected-ion-flow tube (SIFT) apparatus which has been described previously [4]. The fullerene dications were produced in a conventional electron-impact source by electron bombardment (at 50 eV) of C_{60} and C_{70} vapour entrained in argon carrier gas. The fullerene sample was obtained from Strem Chemicals Co. and was a mixture of C_{60} and 2–12% C_{70}. A heated stainless-steel inlet tube was used to allow addition of vaporized C_{60} into the helium carrier gas. All the measurements were performed at 294 ± 2 K in helium carrier gas at a pressure of 0.35 to 0.40 Torr.

The rate coefficients for the reactions with naphthalene were determined using helium saturated with naphthalene vapour as the reagent gas. Saturation was achieved by passing helium through a column packed with powdered naphthalene, upstream of a needle valve which was used to adjust the flow. The bulk (reagent) gas flow was monitored in the usual manner and the effective flow of naphthalene was calculated using eqn. (1)

$$\text{Flow } (C_{10}H_8) = \text{Flow } (\text{He}/C_{10}H_8) \times P_{\text{vap}}(C_{10}H_8)/P_{\text{res}}(\text{He}) \qquad (1)$$

where $P_{\text{vap}}(C_{10}H_8)$ is the vapour pressure of $C_{10}H_8$ (0.18 Torr at 21°C) and P_{res} is the pressure of the bulk reservoir of helium. We have previously used this technique to study the reactions of $He^{\cdot +}$, $Ne^{\cdot +}$ and $Ar^{\cdot +}$ with $C_{10}H_8$ for which we have obtained rate coefficients in very good agreement with the Langevin collision rate coefficients for these three reactions [5]. The technique could not be used for anthracene or the fullerenes for which the vapour pressures are too low.

RESULTS AND DISCUSSION

Equation (2) illustrates with C_{60}^{2+} the two reaction channels of interest in the reactions of fullerene dications: adduct formation and charge transfer.

$$C_{60}^{2+} + M \rightarrow C_{60}M^{2+} \qquad (2a)$$

$$\rightarrow C_{60}^{\cdot +} + M^{\cdot +} \qquad (2b)$$

We have discussed elsewhere, for small molecules, M, how the formation of adduct ions in reactions of this type must compete with charge transfer and how the occurrence of the latter cannot simply be predicted strictly on thermodynamic grounds [3]. For $M = C_{60}$ or other fullerene molecules the occurrence of channel (2a) could initiate a sequence of analogous addition reactions and so perhaps develop a doubly-charged string of fullerene beads. The formation of strings rather than clusters of fullerenes provides a quicker way to separate the two positive charges and so to optimize Coulomb relaxation. For M = aromatics, sequential adduct formation might lead to the deposition of aromatic molecules onto the doubly-charged fullerene core.

The best current value for the ionization energy (IE) of $C_{60}^{\cdot+}$, IE($C_{60}^{\cdot+}$) = 11.39 ± 0.05 eV [5,6], makes the charge-transfer reactions with benzene, naphthalene and anthracene exothermic by 2.14 ± 0.05, 3.25 ± 0.06 and 3.94 ± 0.08 eV respectively. Here the IEs have been taken to be 9.2459 ± 0.0002, 8.14 ± 0.01 and 7.45 ± 0.03 eV, respectively [7]. The IEs of C_{60} and C_{70} are approximately equal with a value of 7.61 ± 0.11 eV [8] so that charge transfer to these molecules is also quite exothermic, by 3.78 ± 0.16 eV.

In reaction (3), and its C_{70} analogue, the products are isobaric so that the two competing channels

$$C_{60}^{2+} + C_{60} \rightarrow (C_{60})_2^{2+} \tag{3a}$$

$$\rightarrow C_{60}^{\cdot+} + C_{60}^{\cdot+} \tag{3b}$$

cannot be distinguished mass spectrometrically. This problem is absent in reactions (4) and (5).

$$C_{70}^{2+} + C_{60} \rightarrow (C_{70}C_{60})^{2+} \tag{4a}$$

$$\rightarrow C_{70}^{\cdot+} + C_{60}^{\cdot+} \tag{4b}$$

$$C_{60}^{2+} + C_{70} \rightarrow (C_{60}C_{70})^{2+} \tag{5a}$$

$$\rightarrow C_{60}^{\cdot+} + C_{70}^{\cdot+} \tag{5b}$$

The experiments showed no production ($\leqslant$10%) of an ion at *m/z* 780, C_{130}^{2+}, when either C_{70}^{2+} or C_{60}^{2+} was selected in the SIFT source upstream of the reaction region. This means that adducts formed in reactions (3) and (4) were not effectively stabilized in the helium carrier gas at 0.35 to 0.40 Torr.

Only ions at *m/z* 720 and *m/z* 840 were observed as product ions when either C_{60}^{2+} or C_{70}^{2+} was selected upstream and allowed to react with the fullerene sample downstream, although the degree of conversion ($\leqslant$ 1%) was small at the concentrations of the neutral fullerenes which could be established by evaporization in the flowing helium gas. These results establish that charge transfer is the predominant reaction channel ($\geqslant$90%) in reactions (3) and (4). These reactions are probably fast since the observed conversion is comparable to that recorded for the charge-transfer reactions of noble gas cations with C_{60} which are likely to proceed at the collision rate (see Table 1) [1]. The observations are less definitive about the occurrence of reaction (4b) and the analogous reaction of C_{70}^{2+} with C_{70}, because of the much lower levels of C_{70}

TABLE 1

Reactions of fullerene cations with aromatic hydrocarbon and fullerene molecules at 294 ± 2 K in helium at 0.35 to 0.40 Torr

Reaction	k_{obs} [a]	k_c [b]
$C_{60}^{2+} + C_6H_6 \rightarrow C_{60}^{\cdot+} + C_6H_6^{\cdot+}$	2.3 ± 0.9	1.81
$C_{70}^{2+} + C_6H_6 \rightarrow C_{70}^{\cdot+} + C_6H_6^{\cdot+}$	1.4 ± 0.6	1.80
$C_{60}^{2+} + C_{10}H_8 \rightarrow C_{60}^{\cdot+} + C_{10}H_8^{\cdot+}$	9.0 ± 4.5	1.90
$C_{70}^{2+} + C_{10}H_8 \rightarrow C_{70}^{\cdot+} + C_{10}H_8^{\cdot+}$	10.0 ± 5.0	1.87
$C_{60}^{2+} + C_{14}H_{10} \rightarrow C_{60}^{\cdot+} + C_{14}H_{10}^{\cdot+}$	obs[c]	2.05
$C_{70}^{2+} + C_{14}H_{10} \rightarrow C_{70}^{\cdot+} + C_{14}H_{10}^{\cdot+}$	obs[c]	2.02
$C_{60}^{2+} + C_{60} \rightarrow C_{60}^{\cdot+} + C_{60}^{\cdot+}$	obs[c]	2.14
$C_{70}^{2+} + C_{60} \rightarrow C_{70}^{\cdot+} + C_{60}^{\cdot+}$	obs[c]	2.07

[a] k_{obs} is the observed reaction rate coefficient (10^{-9} cm^3 molecule^{-1} s^{-1}). The uncertainties represent estimates of the absolute accuracy of the measurements. The relative uncertainty for reactions involving the same neutral is better than 15%.

[b] k_c is the Langevin collision rate coefficient (10^{-9} cm^3 molecule^{-1} s^{-1}), calculated according to the method of Gioumousis and Stevenson [9]. The polarizability of C_{60} has been estimated by Ahlrichs [10] to be 7×10^{-23} cm^3.

[c] Reaction observed, but rate coefficient not determined.

which were introduced into the flow tube, and because of the known charge-transfer reaction (6) [8] which we were also able to observe in separate experiments in which $C_{60}^{\cdot+}$ was selected and injected upstream of the reaction region.

$$C_{60}^{\cdot+} + C_{70} \rightarrow C_{70}^{\cdot+} + C_{60} \qquad (6)$$

The reactions of benzene, naphthalene and anthracene also were observed to proceed by charge transfer with both C_{60}^{2+} and C_{70}^{2+}, and again there was no evidence for the information of adduct ions ($\leqslant 1\%$). The results obtained are summarized in Table 1. The measured rate coefficients with naphthalene exceed the collision rate coefficients by a substantial amount. The origin of this discrepancy is not completely understood, but we have observed similar results for other charge-transfer reactions with doubly-charged C_{60} [3]. Also, it should be noted that the Langevin theory is of limited value for reactions of this type since the large reactant ions are hardly point charges and the quadrupole moments of the large neutral reactants could be significant. Both of these effects will increase the collision rate above that predicted by Langevin theory. The relatively lower efficiency for charge transfer with benzene may be due to the kinetic barrier which, in this case, is expected to lie closer to the initial energy value because of the lower exothermicity.

The observation of charge transfer rather than adduct formation for all of the reactions in Table 1 rules out the ability of these, and presumably related, doubly-charged fullerene cations to initiate the formation of doubly-charged fullerene clusters or strings of fullerene beads or to act as nuclei for the condensation of aromatic molecules in helium gas at 0.35 to 0.40 Torr and 294 ± 2 K. Since all of these reactions are bimolecular and fast, or likely to be fast, a similar situation may be assumed for most interstellar and circumstellar environments.

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