Fullerene cation and dication production by novel thermal energy reactions of He^+, Ne^+, and Ar^+ with C_{60}

G. Javahery, S. Petrie, J. Wang and D.K. Bohme

Department of Chemistry and Centre for Research in Experimental Space Science, York University, North York, Ontario, Canada M3J 1P3

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The reactivity of buckminsterfullerene C_{60}, with the rare gas ions He^+, Ne^+ and Ar^+ has been examined in a selected-ion flow tube (SIFT) at 294±2 K. All three ions are observed to undergo charge transfer to C_{60}. The reactions of He^+ and Ne^+ also produce substantial amounts of C_{60}^{2+} in unprecedented charge transfer electron detachment reactions. Dissociative charge transfer processes, although expected to be exothermic in some cases, were not observed in any instance. Possible mechanisms are discussed for the production of doubly charged ions in these systems.

1. Introduction

The chemistry of buckminsterfullerene, C_{60}, has been under intensive investigation [#1] since its recent discovery [2] and synthesis [3]. Experiments have illustrated that C_{60} and the ionized species C_{60}^{3+}, C_{60}^{2+}, C_{60}^{+}, C_{60}^{-} and C_{60}^{2-} are all unusually stable, due principally to the high degree of rigidity and symmetry of the fullerene cage structure.

Some results have been reported previously for reactions for atomic metal ions with fullerenes which are characterized by the occurrence of charge transfer and adduct formation [4–6]. Ni^+ has also been observed to add sequentially two C_{60} units to form a "dumbbell" complex $Ni(C_{60})_2^+$ [6]. Other thermal energy studies of ions reacting with neutral fullerenes have centred on rapid proton transfer and charge transfer reactions, allowing the bracketing of the proton affinities and ionization energies of C_{60} and C_{70} [7,8]. The observation of slow proton transfer from NH_4^+ to C_{60} and the observation of proton transfer from $C_{60}H^+$ to C_{70}, establishes $PA(C_{70}) > PA(C_{60}) \approx PA(NH_3) = 204$ kcal mol^{-1} [9]. Hydrocarbon ions have been observed to form adducts with C_{60} in competition with proton transfer [7].

C_{60}^{+} has not yet been observed to react in any manner other than charge transfer. It is unreactive with H_2, O_2, NO, NH_3 and C_4H_2 [10,11]. The ionization energies of C_{60} and C_{70} are similar, $IE(C_{60}) \approx IE(C_{70}) = 7.61 \pm 0.11$ eV, as deduced from the observation of charge transfer to *m*-toluidine (IE=7.50 eV), and the absence of charge transfer to aniline (IE=7.71 eV) [8].

Previous studies of ion-neutral interactions involving C_{60} and rare gases, always at higher than thermal energies, include the mass spectrometer experiments of Schwarz and co-workers [12–15], Ross and Callahan [16], and Gross and co-workers [17,18] which demonstrated inclusion of helium and neon atoms within ionized fullerenes under high-energy impact conditions. Wan et al. [19] have performed a guided ion beam MS study of the reaction $Ne^+ + C_{60}$ over a range of collision energies from 2 to 212 eV, in which the onset of dissociative charge transfer was observed to occur at approximately 20 eV. Production of C_{60}^{2+} and smaller dicationic fragments has also been noted by these authors [20].

Our interest in the ion–molecule chemistry of fullerenes relates, in part, to the potential significance of such reactions in the field of interstellar chemistry. This topic has been explored in a recent review

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

[#1] For a recent review, see ref. [1].

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by Bohme [21]. Fullerenes have been postulated as a constituent of circumstellar envelopes and dense interstellar clouds, as well as of more diffusive regions, and much chemical processing within these environments arises via reactions of cations with the predominant neutral species present. In this context, the reactivity of C_{60} with He^+ is particularly important since He^+ is one of the principal ions encountered within the interstellar environment.

Table 1
Observed product ratios for the reactions of He^+, Ne^+ and Ar^+ with C_{60} at 294 ± 2 K

Reactant ion	Products [a]	ΔH^0 [b]
He^+	$C_{60}^{+} + He$ (<0.90)	-391 ± 3
	$C_{60}^{2+} + He + e$ (>0.10)	-168 ± 6
Ne^+	$C_{60}^{+} + Ne$ (<0.95)	-322 ± 3
	$C_{60}^{2+} + Ne + e$ (>0.05)	-98 ± 6
Ar^+	$C_{60}^{+} + Ar$ (1.00) [c]	-188 ± 3

[a] Product branching ratios are shown in parentheses. Only a lower limit could be assigned to the production of the dication because of the possibility of charge transfer between C_{60}^{2+} and C_{60}. Secondary reactions could not be identified because the flow of C_{60} could not be varied in a controlled fashion.

[b] Standard enthalpy of reaction in kcal mol^{-1}. Calculated using $IE(C_{60}) = 7.61 \pm 0.11$ eV [8] and $IE(C_{60}^{+}) = 9.7 \pm 0.2$ eV [24]. Other values are taken from the tabulation of Lias et al. [25].

[c] Production of C_{60}^{2+} is calculated to be 36 ± 6 kcal mol^{-1} endothermic for this reaction.

2. Experimental

The measurements reported here were obtained using a SIFT which has been described previously [22,23]. Measurements were obtained at 294 ± 2 K, using helium buffer gas at a pressure of 0.35 ± 0.01 Torr. All gases were of research grade. A C_{60} sample was provided by John C. Fetzer of the Chevron Research and Technology Company (Richmond, California). This sample was deduced, on the basis of He^+ chemical ionization, to contain less than 1% detectable impurity (mainly C_{70}). A heated stainless-steel inlet tube was used to allow addition of vaporized C_{60}, entrained in helium, to the reaction region of the flow tube. The typical operating temperature of the inlet was approximately 750 K. The use of an Extrel 162-8 quadrupole mass filter in the downstream detection region allowed detection of product ions at up to m/z 1200.

3. Results and discussion

The product distributions recorded for the reactions of He^+, Ne^+ and Ar^+ with C_{60} are listed in table 1. In addition to the products reported here for C_{60}, very small signals (<1%) were observed at m/z 840 and, for He^+ and Ne^+, at m/z 420, which we attribute to a small C_{70} impurity in the C_{60} sample. The ion at m/z 360 is attributed to C_{60}^{2+} because the other possible product channel, $C_{30}^{+} + C_{30}$, is extremely improbable – it requires the cleavage of at least ten aromatic C–C bonds. Other fragmentation channels (for example, $C_{58}^{+} + C_2$) are not observed (<0.5%) even though they are exothermic [26] and require much less bond breaking. We have made a similar case, in a SIFT study of the reaction $He^+ + C_{10}H_8$, for our observation of m/z 64 which we have attributed to the production of $C_{10}H_8^{2+}$ rather than $C_5H_4^{+}$ [27]. The formation of C_{60}^{2+} in collisions between Ne^+ and C_{60} has also been noted by Christian et al. [20], in an experiment involving collision energies between 2 and 212 eV.

Dication formation in the present study is less exothermic than many fragmentation processes, but can very probably occur without the energetic barriers which appear to inhibit fragmentation of fullerene ions. The higher velocity of the ejected electron over any molecular fragment may also favour dictation formation by this process of charge transfer electron detachment. The observations of dication formation in the reactions of He^+ and Ne^+, and its absence in the reaction of Ar^+, are in agreement with the currently accepted values for the first and second ionization energies of C_{60} (see table 1). A possible mechanism for the removal of two electrons from C_{60} in these reactions involves an initial charge transfer while the rare gas ion is still approaching, to produce a metastable rare gas atom which then further ionizes the fullerene cage upon collision: for example,

$$He^+ + C_{60} \rightarrow [He^+ ... C_{60} \rightleftharpoons He^* ... C_{60}^{+} \rightleftharpoons He ... C_{60}^{2+} ... e]$$

$$\rightarrow He + C_{60}^{2+} + e \,. \quad (1)$$

In this scenario, many of the reactant helium ions will be converted to metastable ($2\,^1S$) and ($2\,^3S$) He atoms. (The production of metastable ($2\,^3S$) He* and C_{60}^+ is, for products at infinite separation, endothermic by 2.8 eV and so this mechanism requires a large quantity of interaction energy if it is to be exothermic. A similar situation holds for production of electronically excited Ne* and C_{60}^+ as a prerequisite to formation of C_{60}^{2+} in the reaction $Ne^+ + C_{60}$. No information is at present available concerning interaction energies for these species.) The metastable atoms resulting from the initial charge transfer are, in most instances, still committed to a closer encounter with the fullerene cage. This close encounter results in a Penning ionization of C_{60}^+. Penning ionization of many molecular species is known to occur in a substantial fraction of collisions with metastable helium and neon atoms. Penning ionization of a cation has not, to our knowledge, been suggested before; but we see not reason why such a process should not be efficient. The observed C_{60}^+ signal arises from collisions in which ground state He is formed initially; from charge transfer at large impact parameter so that a close collision to quench metastable He does not occur; and from collisions at small impact parameter in which the metastable He is not quenched by further ionization. The product distributions observed for He^+ and Ne^+ suggest that, if the proposed reaction mechanism is correct, a significant fraction of the encounters in which C_{60}^+ and metastable rare gas atoms are produced also result in collisions which quench the metastable atom by further ionization of the collision partner.

An alternative approach to the mechanism for dication formation does not require the high interaction energy necessary to the mechanism suggested above. The dication production channel can be viewed instead as a type of dissociative charge transfer. Charge transfer results in the deposition of a large quantity of internal energy into the fullerene cage:

$$He^+ + C_{60} \rightarrow [He^+ ... C_{60} \rightleftharpoons He ... C_{60}^{+*} \rightleftharpoons He ... C_{60}^{2+} ... e]$$
$$\rightarrow He + C_{60}^{2+} + e\,. \qquad (2)$$

The release of this energy can occur only by the further loss of an electron, since C_2 loss (the most accessible molecular fragmentation channel) is inhibited by a barrier of approximately 20 eV [19] while charge transfer is exothermic by only 16.98 ± 0.11 eV. Presumably, the most favourable circumstance for dication production is if most of the excess energy resulting from the initial charge transfer is partitioned into electronic energy of C_{60}^+. Energy deposited into the fullerene ion's vibrational or rotational modes, or into product translational energy, appears much less likely to become localized in such a fashion as to favour electron loss to form C_{60}^{2+}.

With regards to the reactivity of C_{60} within the interstellar environment, our observations indicate that reactions of He^+ with fullerenes provide a source for doubly charged fullerene ions. Also, it appears that reactions with He^+ (and by implication other cations, since He^+ has the highest recombination energy of any ion known) will not serve as a direct method for the destruction or fragmentation of the fullerene cage. Fragmentation may still occur in an indirect manner in the dissociative recombination of fullerene cations with electrons, although in this case also it is quite possible that the exothermicity of recombination is not sufficient to overcome barriers to cage fragmentation. If this is so, then recombination of fullerene cations would occur only as a radiatively stabilized process which would be expected to have a much lower efficiency that dissociative recombination.

4. Conclusion

Reactions of rare gas cations with C_{60} are observed to occur without fragmentation of the fullerene cage. The production of singly and doubly charged cations of C_{60} appears facile whenever generation of such ions is exothermic. The absence of fragmentation or endohedral adduct formation channels is consistent with earlier experiments which indicate considerable energetic barriers to such processes.

Production of a dication from a monocation reactant, by charge transfer electron detachment in a thermal energy reaction, is unprecedented in the literature and may represent an important new class of reactions. We believe that such a process will be rather general in situations where the recombination energy of the reactant ion exceeds the sum of the first two ionization energies of the neutral reactant, especially for systems that are not likely to dissociate. It is likely that fullerenes represent the most favourable case for the occurrence of charge transfer electron detachment reactions, due to the low second ionization energies and the exceptionally durable molecular structures of such species.

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References

[1] R.E. Smalley, Sciences (NY Acad. Sci.) 31 (1991) 22.
[2] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl and R.E. Smalley, Nature 318 (1985) 162.
[3] W. Krätschmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffmann, Nature 347 (1990) 354.
[4] L.S. Roth, Y. Huang, J.T. Schwedler, C.J. Cassady, D. Ben-Amotz, B. Kahr and B.S. Freiser, J. Am. Chem. Soc. 113 (191) 6298.
[5] Y. Huang and B.S. Freiser, J. Am. Chem. Soc. 113 (1991) 8186.
[6] Y. Huang and B.S. Freiser, J. Am. Chem. Soc. 113 (1991) 9418.
[7] S.W. McElvany and J.H. Callahan, J. Phys. Chem. 95 (1991) 6187.
[8] J.A. Zimmerman, J.R. Eyler, S.B.H. and S.W. McElvany, J. Chem. Phys. 94 (1991) 3556.
[9] S.G. Lias, J.F. Liebman and R.D. Levin, J. Phys. Chem. Ref. Data 13 (1984) 695.
[10] S.W. McElvany, H.H. Nelson, A.P. Baronavski, C.H. Watson and J.R. Eyler, Chem. Phys. Letters 134 (1987) 214.
[11] D.E. Richardson, C.H. Christ, P. Sharpe and J.R. Eyler, J. Am. Chem. Soc. 109 (1987) 3894.
[12] T. Weiske, D.K. Bohme, J. Hrusak, W. Krätschmer and H. Schwarz, Angew. Chem. Intern. Ed. 30 (1991) 884.
[13] T. Weiske, J. Hrusak, D.K. Bohme and H. Schwarz, Chem. Phys. Letters 186 (1991) 459.
[14] T. Weiske, J. Hrusak, D.K. Bohme and H. Schwarz, Helv. Chim. Acta 75 (1992) 79.
[15] T. Weiske, T. Wong, W. Krätschmer, J.K. Terlouw and H. Schwarz, Angew. Chem. Intern. Ed. 31 (1992) 183.
[16] M.M. Ross, J.H. Callahan, J. Phys. Chem. 95 (1991) 5720.
[17] K.A. Caldwell, D.E. Giblin, C.S. Hsu, D. Cox and M.L. Gross, J. Am. Chem. Soc. 113 (1991) 8519.
[18] K.A. Caldwell, D.E. Giblin and M.L. Gross, J. Am. Chem. Soc., in press.
[19] Z. Wan, J.F. Christian and S.L. Anderson, submitted for publication.
[20] J.F. Christian, Z. Wan and S.L. Anderson, in preparation.
[21] D.K. Bohme, Chem. Rev., submitted for publication.
[22] G.I. Mackay, G.D. Vlachos, D.K. Bohme and H.I. Schiff, Intern. J. Mass Spectrom. Ion Phys. 36 (1980) 259.
[23] A.B. Raksit and D.K. Bohme, Intern. J. Mass Spectrom. Ion Phys. 55 (1983) 69.
[24] S.W. McElvany, M.M. Ross and J.H. Callahan, Mater. Res. Soc. Symp. Proc. 206 (1991) 697.
[25] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin and W.G. Mallard, J. Phys. Chem. Ref. Data 17 Suppl. 1 (1988).
[26] C. Lifshitz, M. Iraqi, T. Peres and J.E. Fisher, Intern. J. Mass Spectrom. Ion Proc. 107 (1991) 565. /
[27] S. Petrie, G. Javahery, A. Fox and D.K. Bohme, in preparation.