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Experimental results for ion-molecule reactions of fullerenes: implications for interstellar and circumstellar chemistry

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

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

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Abstract. Reactions of the ions D^+, $He^{+\bullet}$, and $Si^{+\bullet}$ with C_{60}, and of the ions $C_{60}^{+\bullet}$, C_{60}^{2+}, $C_{70}^{+\bullet}$ and C_{70}^{2+} with several neutrals of relevance to the chemistry of interstellar clouds and circumstellar envelopes recently have been studied with a selected-ion flow tube (SIFT) apparatus at 294 ± 3 K in helium at pressures of 0.35–0.40 Torr. The implications of the results of these studies are discussed for the chemical evolution of interstellar clouds and circumstellar shells surrounding carbon-rich stars. Notable features of the ion–molecule reactivity of fullerenes include: the production of fullerene dications in the reaction of $He^{+\bullet}$ with C_{60}; the high selectivity of $C_{60}^{+\bullet}$ and $C_{70}^{+\bullet}$ towards radicals and amines; the predominance of association as a reaction channel of $C_{60}^{+\bullet}$ with various neutral molecules; the tendency of fullerene dications to undergo association with unsaturated hydrocarbons; and the existence of activation energy barriers towards many charge-transfer and hydride abstraction reactions of fullerene dications, and proton transfer from functionalised fullerene dications. Other aspects of fullerene reactivity, not directly related to ion–molecule interactions, are also discussed. These include difficulties inherent in the dissociative recombination of fullerene ions and dications with electrons; the possible role of neutral and ionized fullerenes as a model for interstellar dust grain surface recombination of atomic hydrogen and other reactive species; production of fullerene dications by sequential cosmic-ray and UV photoionization and by cosmic-ray double ionization; and the possibility of fullerene cages acting as "traps" for cosmic rays within the interstellar medium. Possibilities for the interstellar detection of fulleranes, and fullerenes functionalised by amine and hydrocarbon moieties, are also discussed. It is argued that the fullerene cage structures, especially C_{60}, should be very durable within the interstellar environment because of the lack of destruction mechanisms available for these species. In contrast, substituents attached to fullerene cages as a consequence of ion–molecule chemistry occurring within the interstellar medium are likely to be readily removed by UV irradiation within diffuse regions. For this reason, functionalised fullerenes (except for the slightly hydrogenated fulleranes) are not expected to be abundant in diffuse regions although they may be present in reasonable quantities within dense clouds.

Key words: atomic and molecular processes – chemical reactions – interstellar medium: dust – interstellar medium: molecules – stars: carbon

1. Introduction

Polycyclic aromatic hydrocarbon (PAH) molecules have been postulated as abundant high-molecular-weight constituents of interstellar space (Omont 1986; Léger et al. 1987). Unidentified IR emission features between 3.3 and 11.3 μm have been attributed (Léger & Puget 1984; van der Zwet & Allamandola 1985) to PAHs of varying structure and varying degrees of functionalization. The proposal that fullerenes may also be present, and detectable, within interstellar environments is more recent and has to date received less attention, in keeping with the comparative novelty of fullerenes as a class of known substances (Kroto et al. 1985).

The relative importance of fullerenes and PAHs within the interstellar medium is not at all clear. Fullerene synthesis within circumstellar envelopes (or other sites within the interstellar medium) is problematic, since such environments generally contain a very high abundance of atomic and/or molecular hydrogen. Fullerene synthesis occurs efficiently in the absence of hydrogen, but is likely to be inhibited by hydrogen since the driving force for fullerene cage closure is the greater stability of a curved carbon-atom layer with fewer unsatisfied valences than a flat, graphitic layer of carbon atoms. The presence of hydrogen

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Send offprint requests to: Diethard K. Bohme as the predominant component of interstellar clouds and most circumstellar envelopes might be seen as a selection factor in favour of flat layers of carbon atoms, and for this reason PAHs (which would derive from such graphitic subunits) are held to be synthesised efficiently within interstellar environments. However, the production of fullerenes in sooting flames (Gerhardt et al. 1987) serves to indicate that such species can be produced under conditions involving many competing chemical processes, and Hare & Kroto (1992) have suggested that the presence of hydrogen and/or oxygen need not preclude substantial fullerene production.

In some interstellar environments, hydrogen is present at substantially less than the mean cosmic abundance. Stars such as R Corona Borealis represent an extreme case. The R CrB stars, of which XX Camelopardis and RY Sagittarius are other examples (Schönberger 1975), are characterised by anomalously low hydrogen abundances (Bidelman 1953; Searle 1961) ($H/He < 10^{-5}$), an approximately solar carbon-to-helium abundance ratio ($C/He \sim 0.004$), and an excess of carbon over oxygen (Cottrell & Lambert 1982) – all conditions which should favour fullerene synthesis in the ejecta of such stars (Hare & Kroto 1992). In particular, the paucity of hydrogen in such objects is likely to promote carbon shell closure: on these grounds, XX Cam – for which an upper limit of $H/He < 10^{-8.6}$ has been reported (Cottrell & Lambert 1982) – is an even better candidate for fullerene production than is R CrB itself. O'Keefe (1939) has proposed that irregular changes in the luminosity of R CrB can be explained by the ejection and condensation of carbon vapour from the star's surface. Jacoby & Ford (1983) have suggested a connection between R CrB stars and the helium- and carbon-rich ejecta of the Abell 30 and 78 planetary nebulae. Although R CrB stars appear to be relatively uncommon and short-lived objects (Cottrell & Lambert 1982), other types of carbon-rich, hydrogen-deficient stars are also worth considering as potential sources of interstellar fullerenes.

The circumstellar shells of carbon-rich stars such as IRC+10216 are known to contain the molecules C_3 and C_5 (Hinkle et al. 1988; Bernath et al. 1989) in addition to several other organic molecules and radicals. These species can arise as products of gas-phase processes or from photolysis of dust grains formed within the envelope (Hinkle et al. 1988). Jura & Kroto (1990) have also argued for the role of dust grain photolysis in the production of large quantities of HC_7N within the outer envelope of AFGL 2688. The apparent role of C_{60} in soot formation (Gerhardt et al. 1987; Kroto 1988, 1989) suggests that where grains are being formed, fullerenes will also result.

Fullerenes (Kroto et al. 1985), fullerene ions (Léger et al. 1988), fulleranes (McIntosh & Webster 1992, Webster 1992a) and endohedral fullerene complexes of Si and Mg with C_{60} (Ballester et al. 1990) have been proposed as the carriers of the diffuse interstellar bands classified by Herbig (1975, 1988). Braga et al. (1991) have considered C_{60} and $C_{60}^{+\cdot}$ as possible carriers of the strong absorption feature at 217 nm, while Kroto & Jura (1992) propose that this band may be due to a protonated fullerene species. Fullerenes and fulleranes have been implicated to explain observed features of interstellar extinction (Webster 1992b). The unidentified infrared bands attributed to planar PAHs may also be accounted for by hydrogenated, curved carbon networks with incomplete closure (Balm & Kroto 1990) or from partially or fully hydrogenated fulleranes (Webster 1991; Webster 1992c).

To date, spectroscopic attempts to detect fullerenes within the interstellar environment, in the spectra of several reddened stars (Snow & Seab 1989) and of the Egg Nebula CRL 2688 (Somerville & Bellis 1989), have been unsuccessful. The surveys which have been performed have concentrated on the diffuse 3860 Å feature reported (Heath et al. 1987a) in laboratory spectroscopic studies of C_{60}. Both surveys reported a broad but very faint absorption feature near the expected wavelength, which is claimed to be a blend of stellar lines unrelated to C_{60}. However, it should be noted that the chemistry of fullerenes is a very recent field of investigation, and that careful consideration needs to be applied to determine the most likely charge state, the nature and the degree of functionalisation of fullerenes within the interstellar environment. We have recently proposed (Petrie et al. 1992b) that prime candidates for spectroscopic detection are the slightly hydrogenated fulleranes $C_{60}H_n$, and we suggest additional candidates in this work.

Ion–molecule reactions have long been considered (Herbst & Klemperer 1973; Herbst 1990) as among the most important chemical processes occurring within circumstellar shells and interstellar clouds, particularly within dense clouds where the available internal energy of possible reactants is generally very low. Ion–molecule reactions are typically free of the activation energy barriers which inhibit many other classes of reaction, and thus can occur very efficiently at low temperatures. Since ions are among the most reactive species within dense interstellar clouds, and since fullerenes (by virtue of their low ionization energies) are likely to become easily ionized, the ion–molecule reactivity of fullerenes is central to their chemical processing within interstellar clouds and is also relevant to their reactivity within circumstellar shells (Bohme 1992).

We have recently embarked upon a study of the ion–molecule chemistry of the fullerenes C_{60} and C_{70} (Bohme et al. 1992; Javahery et al. 1992a, b; Petrie et al. 1992b–d), with particular regard to the reactivity of fullerene species with ions and neutrals detected within interstellar clouds and circumstellar shells. Aspects of the ion–molecule chemistry of fullerenes, uncovered by this work, have been and will be discussed in detail elsewhere. Here we concern ourselves with the implications of fullerene chemistry for their stability and reactivity within the interstellar environment.

2. Experimental

The results which are reported here were performed using a SIFT apparatus which has been described previously (Mackay et al. 1980; Raksit & Bohme 1983). Measurements were performed at room temperature (294 ± 3 K) and at a helium operating pressure of 0.35–0.40 Torr. Several of these results have been reported previously (Javahery et al. 1992a, b; Petrie et al. 1992 a, b–d).

3. Reactions of ions with neutral fullerenes

The three most likely consequences of collision of an ion with C_{60} are proton transfer

$$XH^+ + C_{60} \rightarrow C_{60}H^+ + X, \tag{1}$$

charge transfer

$$X^+ + C_{60} \rightarrow C_{60}^{+\bullet} + X \tag{2}$$

and the formation of an adduct (which under laboratory conditions most probably occurs as a termolecular association

$$X^+ + C_{60} + M \rightarrow C_{60}X^+ + M, \tag{3}$$

but which would be expected to occur by radiative stabilisation

$$X^+ + C_{60} \rightarrow C_{60}X^+ + h\nu \tag{4}$$

under interstellar conditions). Our experiments on C_{60} reactivity with atomic ions (see Table 1) have provided clear evidence for the occurrence of processes (2) and (3); other studies have determined the proton affinity ($PA(C_{60}) = 204\ \mathrm{kcal\,mol^{-1}}$) (McElvany & Callahan 1991) and ionization energy [$IE(C_{60}) = 7.61$ eV] (Zimmerman et al. 1991) so that the ionization and protonation of fullerenes under interstellar conditions can be assessed. C_{60} should be efficiently protonated in dense clouds by reaction with such abundant interstellar ions as H_3^+, $C_2H_3^+$, HCO^+, H_3O^+, $HCNH^+$ and perhaps NH_4^+: $PA(C_{60}) \sim PA(NH_3)$. As we have shown, C_{60} is readily ionized by the atomic ions $He^{+\bullet}$, D^+ (H^+), and $Si^{+\bullet}$. Reactions with other atomic ions (Fe^+, Co^+, Cu^+) (Roth et al. 1991; Huang & Freiser 1991) have also been shown to ionize C_{60}: these reactions may be significant within diffuse regions, while ionization by reaction with molecular ions such as $C_2H_2^{+\bullet}$, $C_3H_2^{+\bullet}$, and the cations of small aromatic hydrocarbons is likely to be important within dense interstellar clouds where such ions are held to be comparatively abundant.

Of the reactions included in this study, the major surprise is that the reaction of $He^{+\bullet}$ with C_{60} also produces the dication C_{60}^{2+}, by a process which we have termed charge-transfer electron detachment (Javahery et al. 1992a). This phenomenon has been observed also in the reactions of $Ne^{+\bullet} + C_{60}$ (Javahery et al. 1992a; Wan et al. 1992). The possible production of molecular dications within interstellar environments raises many questions concerning the role of such species in interstellar chemical evolution. We shall deal with some of these issues in Sects. 5, 7 and 8.

The likely efficiency of association reactions of type (4), within the interstellar environment, is difficult to assess. None of the measurements to date have yielded any information concerning the temperature or pressure dependence of these reactions. Nevertheless, the observation of efficient termolecular association under laboratory conditions suggests a long lifetime for the collision complex, which favours radiative association under interstellar conditions. Note also that while C_{60} has a very high degree of symmetry and few distinct modes of vibrational or electronic excitation, a much larger number of distinct modes are likely for a species $C_{60}{\cdot}X^+$ in view of its lower degree of symmetry. This should also favour the radiative stabilisation of its association products.

The association product $C_{60}{\cdot}Si^{+\bullet}$, formed here in competition with charge-transfer, can be compared to the adducts of $Si^{+\bullet}$ with benzene, naphthalene, and anthracene which have been observed (Bohme & Wlodek 1989, 1991; Bohme et al. 1992). The role of such "piggy-back" adducts (of which we presume $C_{60}{\cdot}Si^{+\bullet}$ to be another example) in interstellar chemistry has been discussed elsewhere (Bohme & Wlodek 1989, 1991). Naphthalene has been found to facilitate the formation of SiO_2:

$$C_{10}H_8{\cdot}Si^{+\bullet} + O_2 \rightarrow C_{10}H_8^{+\bullet} + SiO_2. \tag{5}$$

We note here that the reaction

$$C_{60}{\cdot}Si^{+\bullet} + O_2 \rightarrow \text{products}, \tag{6}$$

in which the fullerene cage might be considered as a surface for the reaction of Si and O_2, does not appear to be efficient: $k < 1.0\ 10^{-12}\ \mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

With the present experimental setup, we are unable to determine the rates for reactions of ions with C_{60}. Assignment of product distributions is also somewhat problematic. We anticipate that all of the reactions listed in Table 1 occur at close to the expected collision rate, since most of the observed product channels are highly exothermic. We are currently modifying the apparatus with the ultimate ambition of performing detailed kinetic measurements upon reactions of ions with C_{60}.

The rigidity of the fullerene structure is such that interactions with thermal-energy atomic and molecular ions are unlikely to cause fragmentation of a neutral such as C_{60}. Indeed, we did not observe any evidence for fragmentation of the fullerene product ion in the reaction of $He^{+\bullet} + C_{60}$, and $He^{+\bullet}$ has the highest recombination energy of any known (singly-charged) ion. This indicates that other ions will not cause fragmentation either, so that the primary methods of destruction of unfunctionalised fullerenes will be physical (UV photodestruction, cosmic-ray bombardment) rather than chemical. Within dense clouds, UV radiation is severely attenuated and the cosmic ray flux is also expected to be lower than the ambient flux

Table 1. Reactions of various ions with C_{60} at 294 ± 3 K in helium at 0.40 Torr

Ion	Products^a		k_c^b	ΔH^{oc}_{298}
D^+	$C_{60}^{+\cdot} + D^\cdot$		14.4	−138
$He^{+\cdot}$	$C_{60}^{+\cdot} + He$	[<0.9]	10.2	−391
	$C_{60}^{2+} + He + e$	[>0.1]		−129
$Si^{+\cdot}$	$C_{60}^{+\cdot} + Si$	[0.4]	3.9	−12
	$C_{60}.Si^{+\cdot}$	[0.6]		—

[a] Where more than one product ion was detected, branching ratios are given in square brakets.

[b] ADO collision rate coefficient, calculated according to the method of Su & Bowers (1973), and expressed in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. The calculation assumes $\alpha(C_{60}) = 7\,10^{-23}$ cm^3 (Ahlrichs 1992). Since $\mu_D(C_{60}) = 0$ Debye on the basis of molecular symmetry, the collision rate coefficient is independent of temperature.

[c] Calculated enthalpy of reaction in kcal mol^{-1}. Thermochemical values used are IE(C_{60}) = 7.61 eV (Yoo et al. 1992) and IE(C_{60}^+) = 11.39 eV (Steger et al. 1992); other values are taken from the compilation of Lias et al. (1988).

within diffuse regions. For this reason, fullerenes should be particularly resistant to destruction processes within dense clouds: indeed, given the observed photostability of gas-phase fullerenes (Heath et al. 1987b), destruction of unfunctionalised fullerenes within much more diffuse regions may also be very inefficient. This may not be the case for functionalised species such as fullerene adducts: UV bombardment, within diffuse regions, may effect "pruning" of the fullerene adducts to remove the extra atom or substituent. Our experiments showed that a voltage applied to the flow-tube nosecone (intended to facilitate sampling of the reactant and product ions) was sufficient under normal operating conditions to cause the "pruning" of adduct species produced in several ion–molecule reactions involving fullerenes. The process occurring here seems to be one of collisionally-induced dissociation of the product ions at their weakest point–apparently, the fullerene-substituent bond. Fragmentary ions resulting from $C_{60}.(AB)_x^{n+}$ species in this manner were invariably smaller adducts – $C_{60}(AB)_{x-m}^{n+}$ – or bare fullerenes C_{60}^{n+}. While we do not suggest that collision-induced dissociation necessarily provides a clear indication of the likely pathways for UV photofragmentation, we do contend that UV irradiation is more likely to cause fragmentation beyond the fullerene cage rather than of the fullerene cage itself.

4. Reactions of fullerene monocations with interstellar molecules

The reactions of $C_{60}^{+\cdot}$ with neutrals of relevance to interstellar chemistry are listed in Table 2. It is immediately apparent from an examination of this table that $C_{60}^{+\cdot}$ is exceptionally unreactive. The only product channel evident in any of these reactions is adduct formation, which under the experimental conditions is presumed to occur by termolecular stabilisation

$$C_{60}^{+\cdot} + X + M \rightarrow C_{60}.X^+ + M^*. \tag{7}$$

By analogy with the arguments mentioned in the preceding section, we anticipate that the radiative association reaction

$$C_{60}^{+\cdot} + H^\cdot \rightarrow C_{60}H^+ + h\nu \tag{8}$$

will be a significant loss process for $C_{60}^{+\cdot}$ within interstellar clouds since the corresponding termolecular process is seen to be efficient. Competing loss processes for this ion are dissociative recombination (which we will discuss in more detail in Sect. 7) and charge-transfer

$$C_{60}^{+\cdot} + X \rightarrow X^+ + C_{60} \tag{9}$$

which can only occur for neutrals having IE(X) < IE(C_{60}) [7.61 ± 0.02 eV (Lichtenberger et al. 1991)]. Under interstellar conditions, neutrals meeting this requirement are several metal atoms (e.g. Li, Na, Al, K, Ca) and some PAHs (e.g. anthracene, tetracene, coronene). The metal atoms are likely to be of low abundance – because of their low IEs, a substantial fraction of the free metal atoms will probably be ionized anyway, and many of these species are expected to be "locked up" within dust grains and hence underabundant in the gas phase. PAHs are expected to be of relatively high abundance (Omont 1986) but the total abundance of PAHs with which $C_{60}^{+\cdot}$ can undergo charge-transfer is probably some orders of magnitude below the expected hydrogen atom abundance. The total abundance of other species with which $C_{60}^{+\cdot}$ can undergo rapid radiative association is also likely to be much less than the hydrogen atom abundance within both dense and diffuse regions. For this reason, we expect reaction (8) to be the most significant ion-neutral process involving $C_{60}^{+\cdot}$.

The observation of efficient association in the reaction of $C_{60}^{+\cdot}$ with H· suggests that other association reactions of $C_{60}^{+\cdot}$ with radicals will also be significant. While an experimental study of such reactions would be very difficult to perform, the association of $C_{60}^{+\cdot}$ with $CH_3^\cdot$, $OH^\cdot$, $C_2H^\cdot$, $CN^\cdot$, and $C_2H_3^\cdot$ is likely to be efficient and would be well worth experimental investigation. In this context, we note that the exceptional ability of neutral fullerenes to add, repeatedly, radicals such as $CH_3^\cdot$ and $C_6H_5^\cdot$ has already been reported (Krusic et al. 1991). It seems very reasonable to expect, therefore, that repeated addition of radicals to ionized fullerenes is also efficient.

Reaction (8) can be considered as an ion-neutral association process, but also as a radical recombination reaction. We have also observed evidence for at least one subsequent addition reaction

$$C_{60}H^+ + H^\cdot \rightarrow C_{60}H_2^{+\cdot} \tag{10}$$

which, under our experimental conditions, presumably

Table 2. Reactions of $C_{60}^{+\bullet}$ and $C_{70}^{+\bullet}$ with various neutral molecules at 294 ± 3 K in helium at 0.40 Torr/.

Neutral	Products[a]	k_{60}^{b}	k_{70}^{c}	$k_{c,300}^{d}$	$k_{c,10}^{e}$
X[f]	none	<0.001	<0.001	—	—
$H^{\bullet}$	$C_{60}H^{+}$	>0.1	obs[g]	1.9	1.9
$D^{\bullet}$	$C_{60}D^{+}$	>0.3	obs[g]	1.35	1.35
NH_3	$C_{60}{\cdot}NH_3^{+\bullet}$	<0.001	<0.001	1.7	5.3
CH_3NH_2	$C_{60}{\cdot}CH_3NH_2^{+\bullet}$	0.015	<0.01	1.4	3.7
$(CH_3)_2NH$	$C_{60}{\cdot}(CH_3)_2NH^{+\bullet}$	0.85	obs[g]	1.2	2.4
$(CH_3)_3N$	$C_{60}{\cdot}(CH_3)_3N^{+\bullet}$	1.0	obs[g]	1.05	1.55
$CH_3CH_2NH_2$	$C_{60}{\cdot}CH_3CH_2NH_2^{+\bullet}$	0.05	obs[g]	1.3	2.9
c-C_5H_6	$C_{60}{\cdot}C_5H_6^{+\bullet}$	0.03	obs[g]	1.0	1.2

[a] Products shown are those for $C_{60}^{+\bullet}+X$. In all cases, the product channels observed for $C_{70}^{+\bullet}+X$ were entirely analogous.

[b] Observed effective bimolecular reaction rate coefficient for $C_{60}^{+\bullet}+X$, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}.

[c] Observed effective bimolecular reaction rate coefficient for $C_{70}^{+\bullet}+X$, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}.

[d] ADO collision rate coefficient (in units of 10^{-9} cm^3 molecule^{-1} s^{-1}), calculated according to the method of Su & Bowers (1973), for $C_{60}^{+\bullet}+X$ at 300 K. The difference in calculated collision rates for $C_{60}^{+\bullet}$ and $C_{70}^{+\bullet}$ is always less than 1%.

[e] ADO collision rate coefficient for reactants at 10 K.

[f] No reaction observed for $X = H_2$, D_2, N_2, O_2, CO, NO, CO_2, COS, H_2O, $(CH_3)_2O$, CH_4, C_2H_4, C_2H_4, C_2H_6, CH_3CCH, CH_2CCH_2, $CH_2CHCHCH_2$, C_6H_6, or $C_{10}H_8$. Because of the low vapour pressure of H_2O and $C_{10}H_8$, the upper limit for the reaction rate coefficient with H_2O and $C_{10}H_8$, from our experiments, is not as low as for other non-reactions: k_{60}, $k_{70} <$ 1.0 10^{-11} cm^3 molecule^{-1} s^{-1}.

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

occurs as a termolecular association. The possibility of the analogous radiative association reaction suggests that fullerene ions may act as a 'sink' for interstellar hydrogen atoms, and for this reason we have recommended (Petrie et al. 1992b) that the spectral characteristics of multiply-hydrogenated fullerene ions and neutrals, also known as fulleranes, should be compared with currently unidentified interstellar absorption and emission features.

The only other neutrals of significant interstellar abundance which were observed to add to $C_{60}^{+\bullet}$ are ammonia and the amines. The reaction with NH_3, again, presumably, involving termolecular association, was observed to be very inefficient, but more highly substituted amines such as $(CH_3)_2NH$ and $(CH_3)_3N$ were observed to add extremely rapidly (Petrie et al. 1992c). This tendency suggests that the amine and alkylammonium functionalities may be comparatively common substituents upon interstellar fullerenes, although saturated secondary and tertiary amines (the most effective reactants) are not likely to be major constituents of dense clouds.

We have also observed a slow association reaction of $C_{60}^{+\bullet}$ with cyclopentadiene (c-C_5H_6), indicating that addition with other large unsaturated hydrocarbons may occur also.

5. Reactions of fullerene dications with interstellar molecules

The observation of C_{60}^{2+} as a product of the reaction of $He^{+\bullet}$ with C_{60} is very significant, since it indicates that fullerene dications can feasibly be produced within the interstellar environment. Omont (1986) has noted that the production of doubly-charged PAHs in the analogous reaction

$$He^{+\bullet} + C_xH_y \rightarrow C_xH_y^{+} + He \qquad (11a)$$

$$\rightarrow C_xH_y^{2+} + He + e \qquad (11b)$$

$$\rightarrow C_{x-n}H_{y-m}^{+} + C_nH_m + He \qquad (11c)$$

is feasible, on energetic grounds, for large PAHs, and we have recently studied the reaction of $He^{+\bullet} + C_{10}H_8$ in which the naphthalene dication $C_{10}H_8^{2+}$ appears to be a major product (Petrie et al. 1992a). Leach (1988) has also proposed that PAH dications can be produced by sequential photoionization under interstellar conditions:

$$C_xH_y + h\nu \rightarrow C_xH_y^{+} + e \qquad (12a)$$

$$\rightarrow C_{x-n}H_{y-m}^{+} + C_nH_m + e, \qquad (12b)$$

$$C_xH_y^{+} + h\nu \rightarrow C_xH_y^{2+} + e \qquad (13a)$$

$$\rightarrow C_{x-n}H^{+}_{y-m} + C_nH_m + e \qquad (13b)$$

$$\rightarrow C_{x-n}H^{+}_{y-m} + C_nH_m\,. \qquad (13c)$$

Previous studies involving C_{60}^{2+} have indicated a discrepancy between the observed reactivity of this ion [from which the second ionization energy of C_{60} was determined as 9.7 ± 0.2 eV (McElvany & Bach 1991; McElvany et al. 1991)] and other determinations of the second ionization energy, mostly yielding values for this quantity of 11.4 eV or higher (for example, Steger et al. 1992; Yoo et al. 1992). We have recently studied the reactivity of C_{60}^{2+} and have concluded (Petrie et al. 1992d) that the apparent discrepancy can be explained in terms of a model which considers the Coulombic repulsion of reaction products (in the case of a reaction yielding two monocationic products). These studies demonstrate that C_{60}^{2+} is substantially less reactive than is to be expected upon thermochemical grounds: specifically, although the best current value for $IE(C_{60}^{+\cdot}) = 11.39 \pm 0.05$ eV (Steger et al. 1992), C_{60}^{2+} does not exhibit charge-transfer as a product channel in its reactions unless the neutral reactant involved has $IE < 9.7$ eV (Petrie et al. 1992d). Similar constraints apply to the occurrence of hydride transfer to fullerene dications, and proton transfer from functionalised fullerene dications. These observations argue for a greater stability of dicationic species within the interstellar environment than has heretofore been postulated, and a greater selectivity in the reactions of fullerene dications than might be anticipated.

Table 3. Reactions of C_{60}^{2+} and C_{70}^{2+} with various neutral molecules at 294 ± 3 K in helium at 0.40 Torr

Neutral	Products[a]		k_{60}^{b}	k_{70}^{c}	$k_{c,300}^{d}$	$k_{c,10}^{e}$
X[f]	None		<0.001	<0.001	—	—
$H^{\cdot}$	$C_{60}H^{2+\cdot}$		>0.3	obs[g]	3.8	3.8
$D^{\cdot}$	$C_{60}D^{2+\cdot}$		>0.3	obs[g]	2.7	2.7
NH_3	$C_{60}{\cdot}NH_3^{2+}$		1.2	0.7	3.4	10.5
CH_3NH_2	$C_{60}{\cdot}CH_3NH_2^{2+}$	[0.90]	2.6	obs[g]	2.9	7.4
	$C_{60}^{+\cdot} + CH_3NH_2^{+\cdot}$	[0.10]				
$(CH_3)_2NH$	$C_{60}{\cdot}(CH_3)_2NH^{+}$	[0.10]	2.9	obs[g]	2.4	4.9
	$C_{60}^{+\cdot} + (CH_3)_2NH^{+\cdot}$	[0.90]				
$(CH_3)_3N$	$C_{60}^{+\cdot} + (CH_3)_3N^{+\cdot}$		2.2	obs[g]	2.1	3.1
$CH_3CH_2NH_2$	$C_{60}{\cdot}CH_3CH_2NH_2^{2+}$	[0.70]	2.6	obs[g]	2.7	5.75
	$C_{60}^{+\cdot} + CH_3CH_2NH_2^{+\cdot}$	[0.30]				
C_2H_2	$C_{60}{\cdot}C_2H_2^{2+}$		<0.001	<0.001	1.8	1.8
C_2H_4	$C_{60}{\cdot}C_2H_4^{2+}$		<0.001	<0.001	1.9	1.9
CH_2CCH_2	$C_{60}{\cdot}C_3H_4^{2+}$		0.08	0.009	1.85	1.85
CH_3CCH	$C_{60}{\cdot}C_3H_4^{2+}$		0.5	0.03	2.3	4.0
CH_2CHCH_3	$C_{60}{\cdot}C_3H_6^{2+}$		1.3	>0.4	2.0	2.5
C_3H_8	$C_{60}H^{+} + C_3H_7^{+}$		0.002	<0.001	1.9	1.9
$CH_2CHCHCH_2$	$C_{60}{\cdot}C_4H_6^{2+}$	[0.80]	1.0	1.0	1.9	1.9
	$C_{60}^{+} + C_4H_6^{+\cdot}$	[0.20]				
$c\text{-}C_5H_6$	$C_{60}^{+\cdot} + C_5H_6^{+\cdot}$		fast[g]	fast[g]	1.9	2.4
C_6H_6	$C_{60}^{+\cdot} + C_6H_6^{+\cdot}$		2.3	0.14	1.8	1.8
$C_{10}H_8$	$C_{60}^{+\cdot} + C_{10}H_8^{+\cdot}$		9.0	10.0	1.9	1.9
$NO^{\cdot}$	$C_{60}^{+\cdot} + NO^{+}$		0.02	<0.001	1.2	1.4

[a] Products are those detected for C_{60}^{2+}. Unless otherwise indicated, the product channels detected for C_{70}^{2+} are entirely analogous. Where more than one product channel was detected, the branching ratio (for C_{60}^{2+}) is given in square brackets.

[b] Observed effective bimolecular reaction rate coefficient for $C_{60}^{2+} + X$, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}.

[c] Observed effective bimolecular reaction rate coefficient for $C_{70}^{2+} + X$, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}.

[d] ADO collision rate coefficient (in units of 10^{-9} cm^3 molecule^{-1} s^{-1}), calculated according to the method of Su & Bowers (1973), for $C_{60}^{2+} + X$ at 300 K. The difference in calculated collision rates for C_{60}^{2+} and C_{70}^{2+} is always less than 1%.

[e] ADO collision rate coefficient for reactants at 10 K.

[f] No reaction observed for $X = H_2$, D_2, N_2, O_2, CO, CO_2, COS, H_2O, CH_4, or C_2H_6. Because of the low vapour pressure of H_2O, the upper limit for the reaction rate coefficient with H_2O is $< 1.0\,10^{-11}$ cm^3 molecule^{-1} s^{-1}.

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

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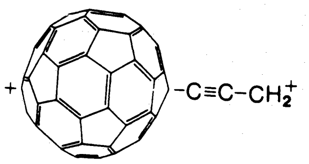
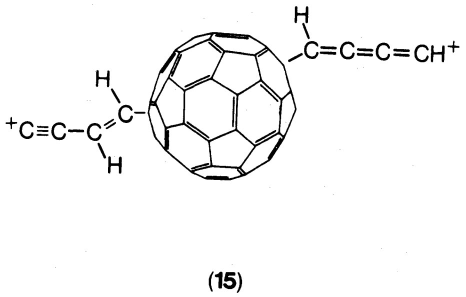
A particular product channel (which benefits from the barriers to charge-exchanging reactions) is adduct formation with unsaturated hydrocarbons, of which some examples are evident within Table 3. We have observed that some of these adduct ions also form secondary adducts: in the reaction of C_{60}^{2+} with butadiene ($CH_2CHCHCH_2$), we have detected the successive addition of at least six C_4H_6 units to the reactant dication. The driving force which we have proposed for these association reactions is the increasing stabilisation which results from increased charge separation (Petrie et al. 1992c). Simple calculations suggest that the radial addition of a C_4 hydrocarbon to C_{60}^{2+} can increase the maximum charge separation from 7 Å to approximately 11.5 Å, associated with a considerable reduction in the Coulombic repulsion between the two charges. Continued radial addition of unsaturated hydrocarbons to such an adduct can further reduce the electrostatic repulsion. Although butadiene is not identified as a significant interstellar molecule, repeated association has also been seen in the reaction of C_{60}^{2+} with CH_3CCH and is also likely to occur for diacetylene (HCCCCH). The most likely structures resulting from repeated association reactions of this type are the "ball-and-stick" and "spindle" structures typified by structures (14) and (15), both of which yield the maximum increase in charge separation possible for each addition step. Neutralisation of these dications, by a two-step sequence of charge transfer, proton transfer, and/or dissociative recombination, could yield a novel class of mono- and di-alkylated fullerenes. Production and detection of these species is discussed further in Sect. 8.



(14)



(15)

Association has also been observed in the reactions of C_{60}^{2+} and C_{70}^{2+} with ammonia and the amines. In these reactions, the secondary product channel is proton transfer:

$$C_{60}^{2+} + NH_3 \rightarrow C_{60}{\cdot}NH_3^{2+} \quad (16)$$

$$C_{60}{\cdot}NH_3^{2+} + NH_3 \rightarrow C_{60}{\cdot}NH_2^{+} + NH_4^{+}. \quad (17)$$

The reaction with ammonia is one of the first recorded instances of proton transfer from a dication to a neutral species (Javahery et al. 1992b). Although we have not yet studied the reactions of other dicationic adduct ions with NH_3, we anticipate that proton transfer will be the major channel for many such reactions, verifying that proton transfer processes constitute a likely "semi-neutralisation" step for most classes of hydrogenated fullerene dications – such as the adducts with hydrocarbons identified above.

It is worth noting also that the association reaction of C_{60}^{2+} with allene (CH_2CCH_2) shows a clear pressure dependence (Petrie et al. 1992c). This is the only C_{60}^{2+} association reaction we have yet investigated at different pressures: interestingly, extrapolation of our experimental results suggests that the association occurs by both bimolecular (radiative) and termolecular (collisional) association processes under our operating conditions. The extrapolation indicates an effective bimolecular rate coefficient, at zero pressure and 294±2 K, of $(2.6 \pm 1.3)\ 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. Under interstellar cloud conditions – for example, at a temperature of 20 K – the lifetime of the $C_{60}{\cdot}C_3H_4^{2+}$ collision complex should be longer and this radiative association reaction should thus be more efficient. While we have not yet studied the pressure dependence of other similar association reactions, we consider that radiative association is likely to be viable for those reactions which show efficient termolecular association under our experimental conditions.

At present, while the standard enthalpies of formation of C_{60}, $C_{60}^{+\cdot}$, and C_{60}^{2+} are fairly well established, there is virtually nothing known of the thermochemistry of (neutral or ionized) functionalised fullerenes. Thus, it is not possible to determine whether the reaction channels we have observed to date (adduct formation, charge transfer, and hydride abstraction) do represent the only accessible channels for reactions of C_{60}^{2+}. It seems notable, however, that in our studies to date no examples have been found of atom or group transfer between fullerene ions and reactant neutrals: that is, reaction channels of the following types

$$C_{60}^{2+} + AB \rightarrow C_{60}{\cdot}A^{2+} + B \quad (18a)$$

$$\rightarrow C_{60-n}^{2+} + ABC_n \quad (18b)$$

are not observed. The absence of channel (18b) in any of the reactions studied is easily comprehended in terms of the high structural rigidity and durability of the fullerene framework – in general, the energy available in an interaction between C_{60}^{2+} and a complex molecular species will not suffice to cause fragmentation or transfer of a portion of the fullerene cage. There are no obvious impediments to processes of type (18a), but we surmise that the bond energy for a bond of the type C–X [where C is a carbon atom within the fullerene skeleton and X is an atom within substituent A in reaction (18a)] is, generally, comparatively low – certainly less than the C–C bond strength for bonds within the fullerene itself, and very probably less than the strength of the A–B bond(s) which must be broken during the course of reaction (18a). Thus we suspect that processes of this type are generally endothermic, at least for the reactants which we have studied to date. We have already noted (in Sect. 3) some indirect experimental evidence for the fragility of the C–X bond.

6. Fullerenes as a model for interstellar dust grain surfaces

The laboratory detection (Kroto et al. 1985) and synthesis (Krätschmer et al. 1990) of C_{60} both resulted from studies aimed at understanding the properties of interstellar dust grains. For this reason, it is tempting to hypothesise that the fullerene surface may act in a similar capacity to the surfaces of interstellar dust grains which are thought to be the principal source of molecular hydrogen within interstellar clouds:

$$\text{grain} + H^{\cdot} \rightarrow \text{grain-H} \qquad (19)$$

$$\text{grain-H} + H^{\cdot} \rightarrow \text{grain} + H_2 . \qquad (20)$$

Fullerenes such as C_{60} may well be capable of such catalytic conversion of atomic to molecular hydrogen:

$$C_{60}H_n^{x+} + H^{\cdot} \rightarrow C_{60}H_{n+1}^{x+} + h\nu \qquad (21)$$

$$C_{60}H_{n+1}^{x+} + H^{\cdot} \rightarrow C_{60}H_n^{x+} + H_2 . \qquad (22)$$

We have observed experimentally that $C_{60}^{+\cdot}$ and C_{60}^{2+} both readily add $H^{\cdot}$ at the experimental conditions 300 K and 0.4 Torr, and we have hypothesised that the analogous radiative association reactions will also occur readily under the conditions prevailing within dense interstellar clouds. We have also observed that the primary and secondary adducts $C_{60}H_n^{+\cdot}$ and $C_{60}H_n^{2+}$ ($n=1, 2$) also add $H^{\cdot}$, presumably with similar efficiency although we have not yet been able to study the reaction rates for these latter processes. Furthermore, neutral C_{60} is seen to undergo addition of at least 34 methyl radicals and 15 benzyl radicals in solution chemistry studies (Krusic et al. 1991), from which we can anticipate that the association of neutral C_{60} with $H^{\cdot}$ should also be efficient. Thus, reactions of the type (21) have already been observed for fullerenes in the +1 and +2 charge states and are also possible for neutral fullerenes: it is interesting to consider also whether such reactions might occur involving fullerene anions [which are also likely species within dense interstellar clouds, by analogy with the postulated high abundance of negatively charged PAHs within dense clouds (Omont 1986)]. A possible competing channel in the case of anions, which would render them less efficient as a source of molecular hydrogen, is the associative detachment process

$$C_{60}H_n^{x-} + H^{\cdot} \rightarrow C_{60}H_{n+1}^{(x-1)-} + e \qquad (23)$$

which is usually efficient for negative ions (Howard et al. 1974).

We have not yet studied reactions of the type (22) which would be required to complete the catalytic cycle of molecular hydrogen production, although we have commented (Petrie et al. 1992b) that the observed high relative abundance of $C_{60}D_4^{2+}$, in experiments involving multiple D-atom addition to C_{60}^{2+}, is consistent with either a slow reaction rate for reaction (21) ($n=4$, $x=2$) or a rapid rate for reaction (22) ($n=5$, $x=2$). We note also that there appears to exist at least one analogous catalytic cycle for molecular hydrogen production:

$$C_2H_2^{+\cdot} + H^{\cdot} + M \rightarrow C_2H_3^{+} + M \qquad (24)$$

$$C_2H_3^{+} + H^{\cdot} \rightarrow C_2H_2^{+\cdot} + H_2 . \qquad (25)$$

Reactions (24) and (25) are both efficient under laboratory conditions (Hansel et al. 1989), and feature ions whose abundance within dense interstellar clouds is predicted to be comparatively high. Other such catalytic cycles almost certainly exist, and we anticipate that due to the reversibility of many chemical processes involving fullerenes – including hydrogenation (Hauffler et al. 1990), epoxidation (Creegan et al. 1992) and chlorination (Olah et al. 1991) – the formation of molecular hydrogen by reactions of type (22) will also be feasible.

7. Other aspects of fullerene reactivity

The reaction of $C_{60}^{+\cdot}$ with atomic hydrogen (see Sect. 4) is likely to influence the abundance of $C_{60}^{+\cdot}$. This reaction may also have a profound influence on the abundances of neutral fullerenes. Hare and Kroto (1992) have remarked that C_{60} should be readily ionized within the interstellar environment due to the low ionization energy of this species. Most molecular ions undergo extremely efficient neutralisation with electrons, by the process of dissociative recombination: for example,

$$N_2H^{+} + e \rightarrow N_2 + H^{\cdot} . \qquad (26)$$

A requirement for efficient dissociative recombination is that there exists a fragmentation channel which is exothermic. Most molecular ions have many such channels accessible – indeed, the dissociative recombination of $N_2H^{+} + e$ is somewhat unusual since only one exothermic fragmentation channel exists. We have suggested (Javahery et al. 1992a) that $C_{60}^{+\cdot}$ may not have any accessible fragmentation channels – the recombination energy of 7.61 eV (Lichtenberger et al. 1991) is very much lower than the apparent activation energy barrier of 18 eV (O'Brien et al. 1988) which exists for the fragmentation channel

$$C_{60}^{+\cdot} \rightarrow C_{58}^{+\cdot} + C_2. \tag{27}$$

While the appearance potential for analogous fragmentation of the neutral

$$C_{60} \rightarrow C_{58} + C_2 \tag{28}$$

[which is expected to be the most accessible fragmentation channel, given the repeated observation that C_{2n} fragments only are lost from ionized fullerenes under a wide variety of circumstances (O'Brien et al. 1988; McElvany & Callahan 1991; Weiske et al. 1991a)] has not been determined, we anticipate that it will require more energy than is available in the recombination of $C_{60}^{+\cdot} + e$. If this is indeed the case, then fullerene cations such as $C_{60}^{+\cdot}$ cannot be neutralised by dissociative recombination: the other avenues for neutralisation within the interstellar environment are (i) charge transfer

$$C_{60}^{+\cdot} + X \rightarrow C_{60} + X^{+}, \tag{29}$$

(ii) mutual neutralisation

$$C_{60}^{+\cdot} + M^{-} \rightarrow C_{60} + M, \tag{30}$$

(iii) radiative recombination

$$C_{60}^{+\cdot} + e \rightleftharpoons (C_{60})^{*} \rightarrow C_{60} + h\nu, \tag{31}$$

and (iv) dielectronic recombination

$$C_{60}^{+\cdot} + e \rightleftharpoons (C_{60})^{*} \rightleftharpoons (C_{60})^{\dagger} \rightarrow C_{60} + h\nu. \tag{32}$$

All of these processes may be of comparatively low efficiency. Within diffuse regions especially, the abundances of species with ionization energies less than that of C_{60} are likely to be low, and the abundances of anions in such regions are also expected to be small. Radiative recombination and dielectronic recombination are very inefficient processes for monatomic and diatomic ions – their efficiency in larger species has never been assessed because of the extremely rapid dissociative recombination processes which compete with them. Radiative recombination may be considerably more efficient for $C_{60}^{+\cdot}$ than for any monatomic ion, because of the longer lifetime expected from the many vibrational degrees of freedom of the complex $(C_{60})^{*}$. Also, the conversion of $C_{60}^{+\cdot}$ to $C_{60}H^{+}$ is promising for neutralisation since the dissociative recombination process

$$C_{60}H^{+} + e \rightarrow C_{60} + H^{\cdot} \tag{33}$$

should be more efficient than dissociative recombination of $C_{60}^{+\cdot}$ – although the efficiency of reaction (33) will depend upon the dynamics of energy distribution in the species $(C_{60}H^{\cdot})^{*}$. An experimental study of the relative recombination rates of $C_{60}^{+\cdot}$ and $C_{60}H^{+}$ would be very useful in this regard.

Similar constraints may also apply to the recombination of $C_{60}^{2+} + e$, although the recombination energy of this dication is higher [IE($C_{60}^{+\cdot}$) = 11.39 ± 0.05 eV (Steger et al. 1992)] and the barrier to C_2 fragment loss may be lower. Nevertheless, conversion of C_{60}^{2+} to $C_{60}H^{2+\cdot}$.

$$C_{60}^{2+} + H^{\cdot} \rightarrow C_{60}H^{2+\cdot} + h\nu \tag{34}$$

may promote the removal of such dicationic species

$$C_{60}H^{2+\cdot} + e \rightarrow C_{60}^{+\cdot} + H^{\cdot}. \tag{35}$$

Given the relatively low abundance of species to which C_{60}^{2+} can transfer a charge – for example,

$$C_{60}^{2+} + C_6H_6 \rightarrow C_{60}^{+\cdot} + C_6H_6^{+\cdot}, \tag{36}$$

the reaction sequence (34) and (35) is potentially a major loss process for fullerene dications.

Formation of dicationic fullerenes and PAHs by charge-transfer electron detachment reactions of $He^{+\cdot}$ has been described in the preceding sections. Another possible route to dicationic PAHs under interstellar conditions, by sequential UV photoionization, has been proposed by Leach (1986), and such a mechanism should also be viable for fullerene dication production. The observation of C_{60}^{2+} production in the experiments of Wan et al. (1992), in the reaction of $Ne^{+\cdot} + C_{60}$ which has been studied as a function of ion energy in the range 2–212 eV, indicates that cosmic-ray double ionization may also be a source of fullerene dications:

$$C_{60} + \text{c.r.} \rightarrow C_{60}^{2+} + e + e + \text{c.r.'}. \tag{37}$$

Sequential ionization by cosmic rays is also possible:

$$C_{60} + \text{c.r.} \rightarrow C_{60}^{+\cdot} + e + \text{c.r.'} \tag{38}$$

$$C_{60}^{+\cdot} + \text{c.r.} \rightarrow C_{60}^{2+} + e + \text{c.r.'} \tag{39}$$

provided that the cosmic ray has sufficient kinetic energy to overcome the Coulombic repulsion which would inhibit collision. Cosmic-ray interactions may also lead to the formation of endohedral complexes of atoms or atomic ions trapped within the fullerene cage. The formation of such endohedral complexes has been noted in high-energy collisions involving $C_{60}^{+\cdot}$ + He, C_{60}^{2+} + He, $C_{60}^{3+\cdot}$ + He, and $Ne^{+\cdot} + C_{60}$ among others (Weiske et al. 1991b; Ross & Callahan 1991; Wan et al. 1992). While a closer model to cosmic-ray trapping, a high-energy collision involving H^{+} and C_{60}, has not yet been studied experimentally, it is anticipated that any small ion should be capable of intercalation within the fullerene cage in this manner. Since most cosmic rays are protons, deuterons and alpha particles, the most likely candidates for formation of endohedral complexes in this manner are H, D and He.

There may also be a contribution to the abundance of circumstellar $C_{60}^{+\cdot}$ from the occurrence of the Penning ionization process

$$C_{60} + He^{*}(2\ {}^{3}S) \rightarrow C_{60}^{+\cdot} + He\ (1\ {}^{1}S) + e. \tag{40}$$

We have studied this reaction in our laboratory (Javahery et al. 1992c) and have verified that production of $C_{60}^{+\cdot}$ is the only product channel evident. Penning ionization of neutrals will not usually be important within dense interstellar clouds–the collision frequency is too low in comparison with the expected radiative half-life (2.2 h) of He (2 ^{3}S) (Drake 1971), the most common collision partner is $H^{\cdot}$ or H_2, and the low incidence of UV will ensure a low abundance of excited (including metastable) states. Several of these factors are more favourable for metastable generation within circumstellar envelopes – the incidence of exciting radiation is very much higher and the collision frequency is also substantially larger. Furthermore, within R Cor Bor envelopes, $H^{\cdot}$ and H_2 are deficient or absent as collision partners, and collisions of He (2 ^{3}S) with ground-state helium are inefficient at quenching the metastable state. Under these conditions (which we have noted earlier may especially favour fullerene production), reactions of metastable atoms with "trace" constituents such as fullerenes and other carbon-containing species may be significant as loss processes for metastable atoms and as ionization processes within the envelopes. Of course, other ionization processes – direct UV photoionization, for example, are also expected to occur under these conditions.

8. Likely candidates for interstellar detection of fullerenes

$C_{60}^{+\cdot}$ has been proposed (Léger et al. 1988; Hare & Kroto 1992) as a likely interstellar species. Our results confirm that $C_{60}^{+\cdot}$ is easily produced in the reactions of atomic ions with C_{60}, and that $C_{60}^{+\cdot}$ does not react with most of the interstellar molecules included in this survey. We have also suggested that the electron-recombination rate coefficient for $C_{60}^{+\cdot}$ might be substantially lower than would be expected for an ion of this size. Therefore, $C_{60}^{+\cdot}$ remains a promising candidate for interstellar detection in the UV, visible and IR wavelength ranges, once its spectrum is established. The lack of a permanent dipole moment disfavours its detection at long wavelength.

$C_{60}H^+$ has also been proposed as a likely interstellar species (Kroto & Jura 1992). Studies (McElvany & Callahan 1991) indicate that this ion will be formed by proton-transfer from several known interstellar ions: we have also detected this ion as the primary product of the reaction of $C_{60}^{+\cdot} + H^{\cdot}$, and of some slow reactions of alkanes with C_{60}^{2+}. Proton transfer is likely to be the dominant source of this ion within dense interstellar clouds (where molecular ion abundances are highest, and where the atomic hydrogen abundance is likely to be lower than in more diffuse regions). Conversely, the reaction of $C_{60}^{+\cdot}$ with $H^{\cdot}$ is likely to be the major source within more diffuse regions. The importance of reactions of fullerene dications with neutrals, and of dissociative recombination of functionalised fullerene dications such as $C_{60}H_2^{2+}$ with electrons, cannot be easily assessed; however, we anticipate that these processes will be of less significance in determining the abundance of $C_{60}H^+$. Again, the detection of this species is most likely to be achieved at short wavelength: the rotational spectrum of this ion is not known but, since the ion is unlikely to have a large dipole moment due to the nonpolar nature of the C–H bond and the anticipated high delocalisation of charge, radio-wave detection appears improbable.

More highly hydrogenated ions, and neutral fulleranes, are also likely candidates for detection as has been suggested elsewhere (Webster 1991). These can be formed by successive association reactions of fullerene cations with atomic hydrogen. A contribution from deprotonation and charge-transfer reactions of fullerene dications $C_{60}H_n^{2+}$ is also feasible. Again, we anticipate that such species will, due to low dipole moments, have weak or nonexistent absorption or emission features at long wavelength.

Fullerenes functionalised by ammonia or by amines are also candidates. The association reactions of fullerene monocations ($C_{60}^{+\cdot}$ and $C_{70}^{+\cdot}$) with ammonia and with methylamine are inefficient under the experimental conditions reported here, and are therefore expected also to be inefficient under interstellar conditions. However, in dense regions of interstellar clouds featuring a high $NH_3/H^{\cdot}$ abundance ratio, the reaction

$$C_{60}^{+\cdot} + NH_3 \rightarrow C_{60}NH_3^{+\cdot} + h\nu \qquad (41)$$

may be the most significant loss process for $C_{60}^{+\cdot}$. Neutralisation of this species by, for example, the reaction

$$C_{60}NH_3^{+\cdot} + c\text{-}C_3H_2 \rightarrow c\text{-}C_3H_3^{+} + C_{60}NH_2^{\cdot} \qquad (42)$$

produces a structure for which a very high dipole moment would be expected, due to the polar C–N bond and the large size of this structure [the fullerene cage of C_{60} has a diameter of 7.0 Å (Hawkins et al. 1991)]. For this reason, radio-wave features due to rotational transitions of this species might be detectable, although variously hydrogenated species $C_{60}H_nNH_2$ are also likely to be present from the probable association reactions of $C_{60}NH_3^{+\cdot}$ and $C_{60}NH_2^{\cdot}$ with $H^{\cdot}$. As mentioned above, the bonding between a fullerene and a substituent is more fragile than the bonding within the fullerene cage, and one consequence of such reactions may be the loss of the nitrogen functionality:

$$C_{60}H_nNH_3^{+} + H^{\cdot} \rightarrow C_{60}H_{n+1}NH_3^{+} + h\nu \qquad (43a)$$

$$\rightarrow C_{60}H_{n-1}NH_3^{+} + H_2 \qquad (43b)$$

$$\rightarrow C_{60}H_n + NH_4^{+}, \qquad (43c)$$

$$C_{60}H_nNH_2 + H^{\cdot} \rightarrow C_{60}H_{n+1}NH_2 + h\nu \qquad (44a)$$

$$\rightarrow C_{60}H_{n-1}NH_2 + H_2 \qquad (44b)$$

$$\rightarrow C_{60}H_n + NH_3. \qquad (44c)$$

Channels (43c) and (44c) represent destruction mechanisms for species involving a fullerene–nitrogen bond. The efficiency of these reactions has not yet been determined; we plan to investigate the reactions of $C_{60}H_nNH_3^{+} + H^{\cdot}$ experimentally. Nitrogen derivatization can also be accomplished in the reactions of the fullerene dications C_{60}^{2+} and C_{70}^{2+}, which are very efficient under laboratory conditions and are presumably also efficient under interstellar conditions. The reactions of dications with ammonia can be considered as production mechanisms for the neutral species $C_{60}NH$ and $C_{60}(NH_2)_2$:

$$C_{60}^{2+} + NH_3 \rightarrow C_{60}NH_3^{2+} + h\nu \tag{45}$$

$$C_{60}NH_3^{2+} + NH_3 \rightarrow C_{60}(NH_3)_2^{2+} + h\nu \tag{46a}$$

$$\rightarrow C_{60}NH_2^{+} + NH_4^{+}, \tag{46b}$$

$$C_{60}NH_2^{+} + X \rightarrow C_{60}NH + XH^{+} \tag{47}$$

$$C_{60}(NH_3)_2^{2+} + X \rightarrow C_{60}(NH_2)NH_3^{+} + XH^{+} \tag{48}$$

$$C_{60}(NH_2)NH_3^{+} + X \rightarrow C_{60}(NH_2)_2 + XH^{+}. \tag{49}$$

Note that, due to the scarcity of other accessible dissociation channels, the fullerene-nitrogen bond is likely to be broken if the method of neutralisation is dissociative electronic recombination rather than proton transfer. It might be expected that the difunctionalised species $C_{60}(NH_2)_2$ would be formed in very low abundance because of the probable high proton affinity of $C_{60}(NH_2)_2$: in our experiments, the signal due to $C_{60}(NH_2)NH_3^+$ was stable against high flows of NH_3, implying $PA(C_{60}(NH_2)_2) > PA(NH_3)$. If there are few interstellar neutrals X capable of accepting a proton from $C_{60}(NH_2)NH_3^+$, reaction (49) will be very inefficient and dissociative recombination (leading, very probably, to $C_{60}NH_2 + NH_3$) is likely to dominate as a loss process of this ion. In any event, the bifunctionalised species $C_{60}(NH_2)_2$ would be difficult to detect in the radio and microwave regions, even if its rotational/vibrational spectrum was determined: the dipole moment for this species is small because the two $-NH_2$ groups are expected to be opposite each other, or nearly so (Javahery et al. 1992b).

Alkylated fullerenes may arise from reactions of dications with unsaturated hydrocarbons. Within the interstellar environment, the most abundant hydrocarbons are the alkynes and polyynes: of these species, we have to date studied only the reactions of fullerene dications with C_2H_2 and CH_3C_2H. In general, association of fullerene dications with hydrocarbons leads to "ball-and-stick" structures such as (14), which can also yield ball-and-stick neutrals (by, for example, proton transfer):

$$C_{60}C_nH_m^{2+} + X \rightarrow C_{60}C_nH_{m-1}^{+} + XH^{+} \tag{50}$$

$$C_{60}C_nH_{m-1}^{+} + X \rightarrow C_{60}C_nH_{m-2} + XH^{+}. \tag{51}$$

Dissociative recombination may serve as a destruction mechanism for the fullerene–hydrocarbon bond. In dicationic species, one charge is expected to be localised on the terminal carbon of the hydrocarbon chain (in order to minimise Coulombic repulsive forces) and so dissociative recombination occurring at this site is likely to result in the loss of probably only one or two carbon atoms from this chain, in accordance with the expectation that bonds close to the centre of charge localisation are the most likely to be dissociated. Once a monocationic functionalised fullerene has been produced, however, Coulombic repulsion is no longer a factor and the charge on $C_{60}C_nH_m^+$ is likely to be delocalised over the fullerene surface. Recombination of such a cation is most likely to result in the dissociation of the fullerene–hydrocarbon bond, since this is the most accessible fragmentation process:

$$C_{60}C_nH_m^{+} + e \rightarrow C_{60} + C_nH_m. \tag{52}$$

Successive association reactions of fullerene dications with larger unsaturated hydrocarbons are also reasonably efficient in our laboratory studies. There are two likely general structures for such ions: longer ball-and-stick species such as (14), and spindle-shaped structures such as (15). Neutralisation processes for the spindle-shaped ions are likely to be analogous to those for the ball-and-stick species, except that the dissociative recombination of a spindle-shaped monocation is likely to leave at least one fullerene-hydrocarbon bond intact:

$$C_{60}(C_nH_m)C_xH_y^{+} + e \rightarrow C_{60}C_nH_m + C_xH_y \tag{53a}$$

$$\rightarrow C_{60}C_xH_y + C_nH_m. \tag{53b}$$

The assignment of observed spectral features to any particular hydrocarbon-functionalised fullerene is not likely to be a simple task: the multiplicity of possible structures (resulting from possible repeated association involving the various known interstellar hydrocarbons, followed by a multiplicity of possible neutralisation processes) is very large. Nevertheless, an investigation of general spectral features of this class of compounds is worthwhile and may result in correlations to observed interstellar features.

While the resilience of C_{60} to UV irradiation leads to the expectation that fullerenes will have a very long lifetime within diffuse regions of the interstellar medium, this does not hold true for the functionalised species discussed above. We believe that the bond between a fullerene and its functionality is in many cases intrinsically weak and is always a much more likely site for fragmentation than any of the bonds within the fullerene cage itself. Thus, while the species described above may well have long lifetimes within dense interstellar regions, they are expected to be rapidly destroyed (defunctionalised) within more diffuse regions. This does not apply so strictly to the hydrogenated species $C_{60}H_x$ and $C_{60}H_x^+$, which may be regenerated by association reactions involving atomic hydrogen within diffuse regions – although the efficiency of the radiative association process

$$C_{60}H_x^{+} + H^{\cdot} \rightarrow C_{60}H_{x+1}^{+} + h\nu \tag{54}$$

will be lower within more diffuse regions owing to the substantially shorter lifetime of the collision complex at the higher temperatures prevalent within more diffuse regions of the interstellar medium.

9. Conclusion

Results have been reported for several ion–molecule reactions involving neutral and ionized fullerenes. Implications of the reactions studied are:

— Thermal-energy ion–molecule reactions do not appear to serve as destruction processes for the fullerene cage. The fullerene cage structure is thus expected to be very stable within dense clouds where ion–molecule reactions constitute the dominant process for chemical evolution.

— Reactions of atomic ions with neutral fullerenes can produce fullerene monocations *and dications* under interstellar conditions.

— The fullerene cation $C_{60}^{+\bullet}$ is exceptionally unreactive. It appears that the dominant removal process for this species is its association reaction with atomic hydrogen. Reactions of this cation with other interstellar radicals may also be significant.

— The fullerene dication C_{60}^{2+} is stable against fragmentation but is considerably more reactive than $C_{60}^{+\bullet}$. Addition reactions of the dication with interstellar ammonia and with unsaturated hydrocarbons (for example, polyynes) are likely to yield functionalised fullerenes, of which further study seems warranted.

— The fullerene cage in its neutral or ionized form may constitute a surface upon which interstellar molecular synthesis may occur, in the manner which has been proposed for interstellar dust grain synthesis of hydrogen.

Study of further ion–molecule reactions involving fullerenes and important interstellar species such as HCN, CH_3CN, HC_3N, HCHO, C_4H_2, and molecular ions, appears warranted. Such studies may well reveal new features of fullerene reactivity of significance to interstellar chemistry.

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