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LABORATORY STUDIES OF ION/MOLECULE REACTIONS OF FULLERENES: CHEMICAL DERIVATIZATION OF FULLERENES WITHIN DENSE INTERSTELLAR CLOUDS AND CIRCUMSTELLAR SHELLS

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ABSTRACT

We discuss recent experimental results for ion/molecule reactions of ionized and multiply-ionized fullerenes, and of derivatized fullerene ions, with molecules relevant to the chemistry of interstellar clouds and circumstellar envelopes These reactions were studied using a selected-ion flow tube (SIFT) at 294 ± 2 K in helium at a pressure of 0.35 ± 0.01 torr. The present study supplements an earlier discussion on aspects of interstellar fullerene ion chemistry explored by the same technique. Several implications are apparent for the chemical processing of fullerenes in various astrophysical environments. Triply charged fullerene ions, such as C_{60}^{3+}, may be formed under conditions prevailing within dense IS clouds, but their abundance will be very low owing to the large number of loss processes identified for such species. Derivatization of fullerene ions under interstellar or circumstellar conditions is less probable for larger fullerenes than for fullerenes smaller than C_{60}. Hydrogenation may severely impede the efficiency of fullerene ion association with polar molecules and small unsaturated molecules, but should not substantially affect the efficiency of addition of radicals or PAHs under these conditions.

We discuss prospects for neutralization of ionized fullerene adducts. Four classes of adduct ions are described, differing in their structure and expected neutralization tendencies. Adducts of fullerene ions with interstellar isonitriles, with radicals, and with linear polycyclic aromatic hydrocarbons (PAHs; class 1) are most likely to form derivatized fullerenes on neutralization, while fullerene ion adducts of nitriles, most hydrocarbons (class 3), and nonlinear PAHs (class 4) are most likely to yield the bare fullerene cage upon neutralization. Adducts of ammonia (class 2) appear to have an intermediate probability of surviving neutralization with the functionalizing group(s) intact.

Subject headings: ISM: clouds — ISM: molecules — methods: laboratory — molecular processes

1. INTRODUCTION

The possible presence of the novel spherical carbon molecule Buckminsterfullerene, C_{60} (see Fig. 1), and its analogs and derivatives within the interstellar (IS) medium and within the circumstellar (CS) envelopes of mass-losing carbon-rich stars has been the subject of considerable discussion (see, for example, Hare & Kroto 1992). The laboratory discovery (Kroto et al. 1985) and first reported synthesis (Krätschmer et al. 1990) of C_{60} both arose from studies aimed at understanding the diffuse IS bands (DIBs; Herbig 1975, 1988, 1995) attributed to large molecules or small dust grains. Several possible connections between fullerenes and the DIBs have since been advanced. Webster has argued that certain aspects of the DIBs (Webster 1991, 1992a 1992b, 1993b, 1993c, 1993f, 1995, 1996; McIntosh & Webster 1992), or the interstellar extinction (Webster 1993d, 1997), and of extinction and emission spectra seen for some nebulae (Webster 1993a, 1993e) are well explained by a model involving differential hydrogenation of fullerenes in regions of varying particle density. Ehrenfreund, Foing, and coworkers (Ehrenfreund & Foing 1996; 1997; Ehrenfreund et al. 1997; Foing & Ehrenfreund 1997; Sonnentrucker et al. 1997) have also suggested that various features of the DIBs are consistent with the presence of fullerenes, including the ions C_{60}^{+}, within the diffuse ISM. However, their attribution of two DIB features at 9577 and 9632 Å to the species C_{60}^{+}, and an inferred interstellar abundance of this ion corresponding to ∼0.9% of cosmic carbon (Foing & Ehrenfreund 1997), has been contested: Jenniskens et al. (1997) have noted that two other features expected for C_{60}^{+}, on the basis of laboratory data, are not seen among the DIBs, while Moutou et al. (1999) have recently set upper limits of 0.26% and 0.27% to C_{60} and C_{60}^{+}, respectively, due to the apparent absence of expected vibrational bands for these species within the spectrum of the bright reflection nebula NGC 7023. Edwards & Leach (1993) have compared the calculated rotational band contours of electronic transitions of C_{60} to the DIBs, and find reasonable agreement between calculated and observed peak width for rotational temperatures exceeding 100 K although none of the transitions observed correspond to any of the major DIBs. Jeffery (1995) and Leach (1995) have assessed a number of possible carriers of the UV extinction profile of carbon-rich H-deficient stars: while fullerenes can account for the extinction peak at 4.1 μm^{-1} (Jeffery 1995), they do not explain all of the observed features of the UV extinction. Justtanont et al. (1996) and Garcia-Lario et al. (1999) have attributed a 21 μm dust feature in the spectrum of cool post-AGB objects, such as the proto–planetary nebulae IRAS 16594 − 4656, to hydrogenated fullerenes.

Despite much speculation and substantial observational effort, detection of IS or CS fullerenes remains unconfirmed: the first searches were negative (Snow & Seab 1989; Somerville & Bellis 1989), and subsequent searches have proven, at best, ambivalent. Somerville & Crawford (1993) have reported the detection of a broad spectral feature 385 nm in the spectrum of the reflection nebula CRL 2688; this feature correlates closely with an absorption band originally attributed to C_{60} (Heath et al. 1987), but is more likely to be a

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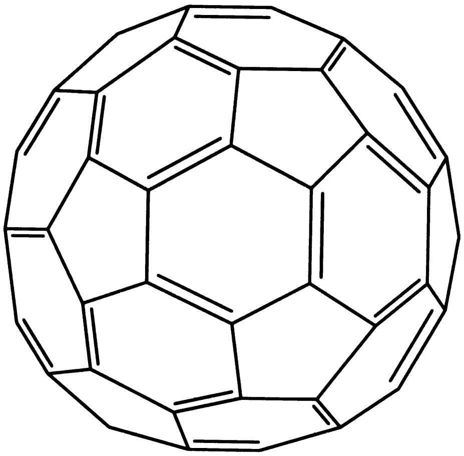

FIG. 1.—Structure 1

species somehow chemically related to C_{60}, since laboratory spectroscopy of chemically pure C_{60} does not display this feature (Leach et al. 1992). Adamson et al. (1994) have conducted a search within the Taurus dark cloud complex for the 1317.5 nm DIB, which has been attributed to C_{60}^{+} (Léger et al. 1988): this search could not detect this DIB within the object searched.

If fullerenes do exist within the ISM, they are generally considered most likely to have arisen within the envelopes surrounding mass-losing, H-deficient, C-rich stars such as R Coronæ Borealis. Goeres & Sedlmayer (1992) have suggested that the production of higher fullerenes, such as C_{70}, is favored over the formation of C_{60} under the conditions pertaining within R CrB gas/dust envelopes. Rao & Lambert (1993) have reported the observation of several diffuse optical features in emission in the R CrB star V854 Cen at minimum brightness: most of these features correspond to certain DIBs and have also been seen, in emission in the Red Rectangle (Scarrott et al. 1992). Some differences between the diffuse emission features in V854 Cen, and those in the Red Rectangle, have been noted (Rao & Lambert 1993) and are ascribed to differences in the hydrogenation of the carrier of these bands, for which C_{60} and its derivatives have been considered as candidates. Clayton et al. (1995) have searched for narrow emission features centered at 8.6 mm, possible associated with C_{60}, in three R CrB stars and in the AGB carbon-rich star IRC + 10216: no narrow features in this range were seen for the R CrB stars, although a weak emission feature was seen for IRC + 10216. Alternatively, Bettens & Herbst (1995, 1996, 1997) have explored the prospects for formation of very large carbon-containing molecules, including fullerenes, by a sequence of reactions (involving carbon chain growth and cyclization) within diffuse or dense interstellar clouds. Scott, Duley, & Pinho (1997) have postulated a further possible IS route to C_{60}: they suggest that PAHs and fullerenes may arise in the interstellar medium as products of UV-induced decomposition of solid hydrogenated amorphous carbon (HAC) within interstellar shocks. There exists, still, considerable uncertainty regarding the growth mechanism, of fullerenes under laboratory, IS, or CS conditions, and there are also many possible other candidates which have been considered as carriers of the various diffuse spectral features assigned to fullerenes (Leach et al. 1993).

While the astrophysical results have thus far been largely negative, some interesting findings associated with meteoritic impacts have emerged. Fullerenes were reported as constituents of chondritic material within the Allende meteorite (Becker et al. 1994a; Becker & Bunch 1997), although this identification has subsequently been queried in other studies (Heymann 1997; Kim & Yang 1998). Traces of C_{60} have also been reported from the Long Duration Exposure Facility (Radicati di Brozlo et al. 1994), from the Allende meteorite (Becker et al. 1994a), and in the geological strata of the Cretaceous-Tertiary boundary layer, associated with the alleged meteoritic impact on the Yucatan peninsular (Heymann et al. 1994; Chijiwa et al. 1999). While some of these findings, most notably the latter, are attributed to terrestrial phenomena such as wild fires, it is interesting to consider that some such findings may represent extraterrestrial material. Fullerenes have also been proposed (Heymann 1986) as the noble-gas–carrying species in carbonaceous chondrites. Most intriguing in this light is the report that, in the fullerene-bearing material associated with the Sudbury impact of ∼ 185 Bya, carbon isotopic abundances suggest an extraterrestrial origin (Becker et al. 1994b) for the fullerenes, while the encapsulated helium (Becker, Bada, & Poreda 1996a; Becker, Poreda, & Bada 1996) is thought to be interstellar. These findings are strongly suggestive of an IS, or CS, gas-phase origin for the Sudbury fullerenes and constitute the strongest support to date for the existence of fullerenes within the interstellar environment.

Our own studies in interstellar fullerene chemistry have focused on ion/molecule reactions, since this class of reactions is considered to play a major role in the chemical processing of dense IS clouds (Watson 1974; Herbst 1990). A previous review of astrochemical implications of our studies (Petrie, Javahery, & Bohme 1993a) has suggested that mechanisms exist for the production of singly *and doubly* charged fullerenes from neutral IS or CS fullerenes, that H-atom addition to fullerene ions is likely to be efficient under IS conditions, and that addition of various IS or CS molecules to ionized fullerenes is also likely (but is substantially more probable with doubly charged than singly charged fullerenes). We have argued elsewhere that charge-separating reactions of fullerene dications are a source of translational excitation to "drive" certain reactions under cold IS cloud conditions (Petrie & Bohme 1994b), and have also suggested (Petrie & Bohme 1994c) that hydrogenation of fullerenes within the CS envelopes of carbon-rich stars may favor the formation of fullerenes smaller than C_{60}. In the present work we explore several astrochemical aspects of fullerenes ion/molecule chemistry which were not discussed in our earlier studies.

2. MEASUREMENTS

The reactions whose results are discussed here have been reported elsewhere (Becker et al. 1993, 1994c; Bohme 1999; Javahery et al. 1992, 1993b, 1993c, 1993d, 1993e, Petrie & Bohme 1993; Petrie et al. 1993c, 1993e, 1994; Wang et al. 1993) and were studied using a selected-ion flow tube (SIFT) apparatus which has been described previously (Mackay et al. 1980; Raksit & Bohme 1983). All measurements were conducted at room temperature (294 ± 2 K) and at a helium bath gas pressure of 0.35 ± 0.01 torr, unless otherwise noted. Fullerene ions were generated from C_{60}/C_{70} mixtures (80% C_{60}) which were variously obtained from

Strem Chemicals Co., from Texas Fullerenes, Inc., and from Termusa, Inc.

3. IONIZATION MECHANISMS WITHIN IS CLOUDS AND CS SHELLS

Schemes for the production of ionized fullerenes C_{60}^{n+} within IS and CS environments are summarized in Figure 2. Most of the reactions involved in this figure have been discussed in some detail previously (Petrie et al. 1993a; Petrie & Bohme, 1994b).

3.1. *Negative Ions*

The role of C_{60}^- in dense IS clouds is uncertain. Millar (1992) has noted that the abundance of this ion should substantially exceed the cumulative abundance of the positive ions C_{60}^{n+}, but this hypothesis assumes the efficient attachment of a free electron

$$C_{60} + e \rightarrow C_{60}^- + h\nu \qquad (1)$$

at IS cloud temperatures. Recent studies of the temperature dependence of reaction (1) (Smith, Spanel, & Märk 1993; Jaffke et al. 1994) indicate an apparent activation energy barrier of 0.26 eV, which would very effectively inhibit the formation of C_{60}^- within dense IS clouds. Alternative routes to C_{60}^- involve electron transfer from molecular negative ions, e.g.,

$$\mathrm{PAH}^- + C_{60} \rightarrow C_{60}^- + \mathrm{PAH}\ , \qquad (2)$$

but the abundance of PAH^- is very probably much less than that of free electrons since electron attachment to PAHs is also inhibited by barriers in several instances (Canosa et al. 1994). The collision rate coefficient for ion/molecule processes such as reaction (2) is approximately 1 or 2 orders of magnitude less than the collision rate coefficient for electron/molecule interactions such as reaction (1). Consequently, Millar's prediction of a high abundance for C_{60}^- seems unduly optimistic; note, however, that electron attachment to other fullerenes in IS clouds may still be feasible. For example, Spanel & Smith (1994) have observed that *s*-wave electron capture by C_{70} lacks any observable barrier: thus C_{70}^- may be more abundance than C_{60}^-, even though C_{60} is most probably the more abundant neutral based on laboratory synthesis of fullerenes.

C_{60}^- may be a particularly long-lived negative ion under IS cloud conditions. Previous laboratory studies (Sunderlin

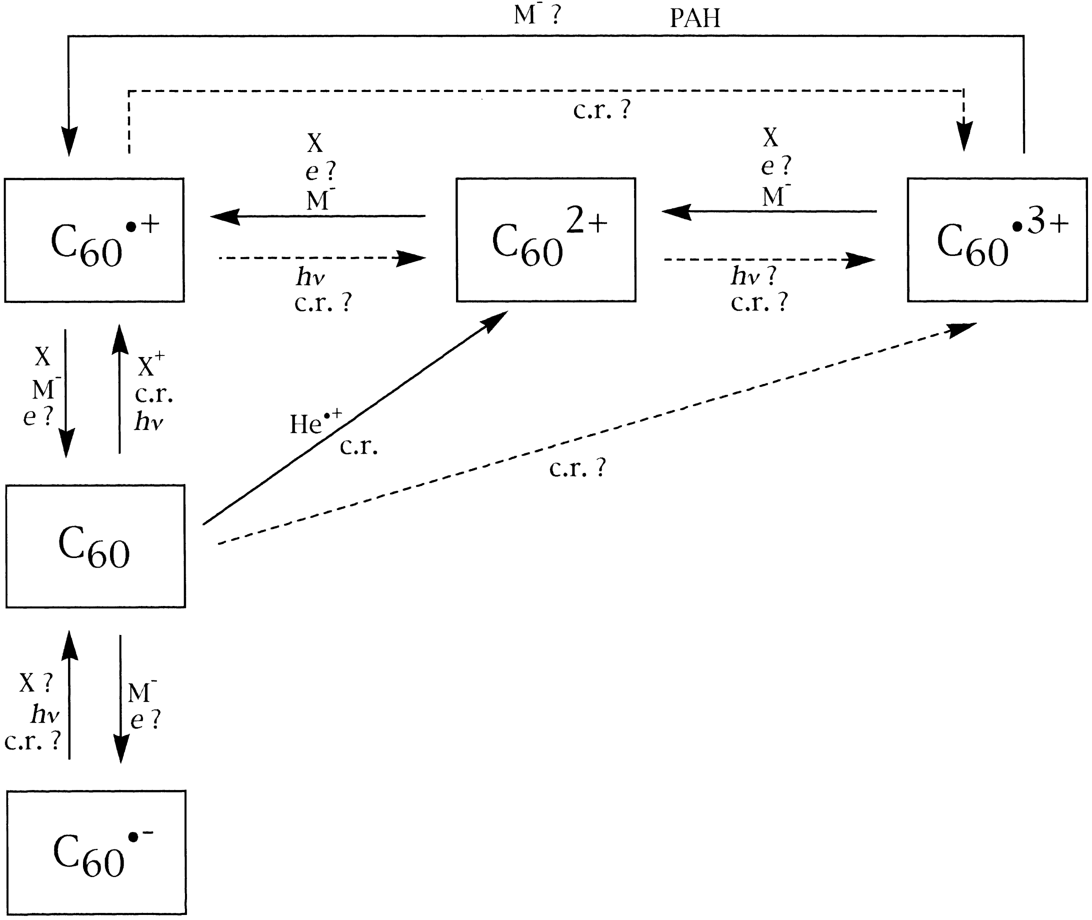

FIG. 2.—A schematic diagram summarizing routes to ionization and deionization of the Buckminsterfullerene molecule C_{60} within IS clouds. Processes shown are general rather than solely applicable to C_{60} and should be similarly viable for fullerenes other than C_{60} within the same environment. The scheme does not include pathways to derivatization of ionized or neutral fullerenes, which occur as processes in competition with ionization/deionization; however, in general these derivatization pathways may be considered to hasten the conversion of positively charged fullerenes C_{60}^{n+} to a lower charge state $C_{60}^{(n-1)+}$. Symbols used are: c.r., cosmic ray; *e*, free electron; *hν*, UV photon; M^-, polyatomic negative ion; PAH, polycyclic aromatic hydrocarbon molecule; X, neutral IS atom, radical or molecule; X^+, atomic ore molecular positive ion. Steps marked with a question mark are of questionable viability: these include all production mechanisms for C_{60}^{3+}, as detailed in the text, as well as all reactions of underivatized fullerenes with free electrons (dissociative recombination of C_{60}^{n+} may not be accessible due to high activation energy barriers (Petrie et al. 1993a, 1993b); attachment of electrons to neutral C_{60} may also be inefficient under IS conditions).

et al. 1991) have shown C_{60}^- to have very low reactivity; C_{60} has a very high electron affinity, possibly higher than any PAH, and therefore electron transfer from C_{60}^- to any other molecular IS species may not be viable. The dominant loss mechanisms for C_{60}^- are expected to be mutual neutralization,

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

and associative detachment involving abundance IS radicals, for example,

$$C_{60}^- + H^{\bullet} \rightarrow C_{60}H^{\bullet} + e\ . \tag{4}$$

3.2. *Positive Ions*

Previous studies (Millar 1992; Petrie et al. 1993a; Petrie & Bohme 1994b) have explored pathways to various charge states of C_{60}. While most ionization pathways lead to C_{60}^+, the possible production of doubly and triply charged fullerene ions under IS conditions is of much interest given the comparatively high reactivity of these species. C_{60}^{2+} may form (1) by sequential photoionization of C_{60}, (2) by charge transfer electron detachment from He^+,

$$He^+ + C_{60} \rightarrow C_{60}^{2+} + He + e\ , \tag{5}$$

and (3) by direct double ionization by cosmic-ray impact upon C_{60},

$$\text{cosmic-ray} + C_{60} \rightarrow C_{60}^{2+} + \text{cosmic-ray} + 2e\ . \tag{6a}$$

Pathway (1) is not viable within dense IS clouds given the minimal UV flux within such objects, but (2) and (3) may be sufficient to produce a significant abundance of C_{60}^{2+}. In an earlier study (Petrie & Bohme 1994b), we suggested that absolute rates for the latter two pathways will be of about equal magnitude as sources of C_{60}^{2+} within dense IS clouds, although this depends on the branching ratios for reactions (5) and (6) since C_{60}^{2+} production in either of these reactions occurs in competition with other processes. Given the variety of outcomes possible for cosmic-ray bombardment of C_{60} (ionization, multiple ionization, dissociative ionization), it is probable that reaction channel (6a) accounts for only a minority of cosmic-ray collisions with C_{60}: if reaction (5) is a major product channel of the $He^+ + C_{60}$ reaction, then this process will be the dominant pathway to C_{60}^{2+}.

In the following discussion, we assume a dense-cloud abundance, for C_{60} in all of its charge states (i.e., C_{60}^-, C_{60}, C_{60}^+, C_{60}^{2+}, and C_{60}^{3+}), of $n(C_{60}) \sim 10^{-7}\ n(H_2)$, accounting for approximately 4% of the gas-phase carbon. While this is a high fraction for such a large C-containing molecule, it may not be grossly unrealistic: Moutou et al. (1996) have suggested, based on the assignment of two DIBs at 9577 and 9632 Å to C_{60}^+ (Foing & Ehrenfreund 1994, 1997), that C_{60}^+ may account for 0.6 to 1.2% of cosmic carbon in the diffuse ISM. Our assumed dense-cloud abundance for C_{60} remains somewhat lower than that $[n(C_{60}) \sim 4 \times 10^{-7}\ n(H_2)]$ employed in Millar's (1992) study.

Previous studies (Petrie et al. 1993c) have indicated that C_{60}^{2+} is unreactive with the most abundant dense IS cloud molecules. Loss processes for C_{60}^{2+} include the partial-neutralization reaction $C_{60}^{2+} + e$, for which there are two possibilities (identified as model I and model II in Millar's 1992 study). In model I, recombination is insufficiently exothermic to cause any fragmentation of the fullerene cage, and hence occurs in a radiative fashion:

$$C_{60}^{2+} + e \rightarrow C_{60}^+ + h\nu\ . \tag{7a}$$

In model II, the recombination of C_{60}^{2+} is dissociative,

$$C_{60}^{2+} + e \rightarrow C_{60-2n}^+ + C_{2n}\ , \tag{7b}$$

and acts to destroy the C_{60} fullerene cage (which is then assumed to be incapable of "repair" within the IS environment). A possible shortcoming in Millar's models is that the rate coefficient assigned to the radiative process (7a) in model I equals that for the dissociative process (7b) in model II: it is by no means certain that this assumption is valid. Much lower rate coefficients are observed for radiative recombination of atomic ions than for dissociative recombination of molecular ions: thus we anticipate that reaction (7a) should be comparatively inefficient, with (say) $\alpha_{7a} \sim 10^{-9}$ cm^3 molecule^{-1} s^{-1} (which is approximately 2 orders of magnitude above that expected for radiative recombination of an atomic ion, and more than 4 orders of magnitude below that assumed in Millar's study).

Some problems can be identified also with Millar's treatment of model II, involving dissociative recombination of C_{60}^{2+}. Millar has recommended a value for the recombination coefficient of $\alpha_7 = 3.6 \times 10^{-5}$ cm^3 molecule^{-1} s^{-1}, in accordance with Bates's (1991) hypothesis that the recombination coefficient for a polyatomic cation is proportional to the number of chemical bonds possessed by the cation. This hypothesis is not supported by recent experimental studies on ions ranging in complexity from CH_5^+ (five bonds) to $C_8H_{17}^+$ (24 bonds): Rowe, Mitchell, coworkers (Abouelaziz et al. 1993; Lehfaoui et al. 1997) have obtained values for the recombination coefficients α for these ions (at 300 K) encompassing only the values $3.0 \pm 0.9 \times 10^{-7}$ to $(9.0 \pm 2.7) \times 10^{-7}$ cm^3 mol^{-1} s^{-1}. Furthermore, the smallest value of α was obtained for one of the most complex species, $C_{10}H_8^+$ (18 bonds) while a comparatively high value of $\alpha = 7.0 \times 10^{-7}$ cm^3 mol^{-1} s^{-1} was found for CH_5^+, the simplest hydrocarbon ion included in the study. Given the apparent lack of any trend toward increasing recombination coefficients with increasing molecular complexity, we suggest that the value of $\alpha_7 = 3.6 \times 10^{-5}$ cm^3 mol^{-1} s^{-1} recommended by Millar is unrealistic. If we instead adopt a value of $\alpha_7 = 1 \times 10^{-6}$ cm^3 mol^{-1} s^{-1}, the lifetime of the fullerene skeleton against fragmentation is considerably increased.

Another consequence of lower recombination rates for C_{60}^{2+} is that competing loss processes become more important. For example, a "catalytic cycle" involving efficient addition of $H^{\bullet}$,

$$C_{60}^{2+} + H^{\bullet} \rightarrow C_{60}H^{2+} + h\nu\ , \tag{8}$$

$$C_{60}H^{2+} + e \rightarrow C_{60}^+ + H^{\bullet}\ , \tag{9}$$

constitutes the dominant loss mechanism for C_{60}^{2+} in a revised model I, wherein the reaction sequence (8) and (9) competes with a slow radiative recombination reaction (7a): hydrogenation affords a facile dissociative pathway for neutralization of the doubly charged ion. There is currently no direct information regarding the efficiency of any radiative association reactions involving fullerene ions, but the termolecular process corresponding to reaction (8) is observed to occur with at least 15% efficiency under our experimental conditions of 300 K and 0.35 torr of helium (Petrie et al. 1995): here we make the very broad assumption that, under

IS conditions, reaction (8) occurs at an efficiency comparable to the termolecular process under our SIFT conditions, yielding $k_8 \sim 3 \times 10^{-10}$ cm^3 mol^{-1} s^{-1}. With the selection of plausible values for other parameters [$\alpha_9 \sim 1 \times 10^{-6}$ cm^3 mol^{-1} s^{-1} and $n(\mathrm{H}^\cdot) \sim 10^3\, n(e)$], we calculate that this revision of model I leads to a steady state abundance of $n(\mathrm{C}_{60}^{2+}) \sim 2.2 \times 10^{-11}\, n(\mathrm{H}_2)$, a factor of 20 greater than that suggested by Millar (1992). In model II also, the sequence (8)–(9) might serve to slow the destruction of the fullerene cage somewhat, although the rate coefficients which we have suggested above indicate that channel (7b) would still remain the dominant loss process for C_{60}^{2+} within dense clouds. To date, no experimental measurements have been reported for the recombination coefficients for any fullerene ion.

Confirmed detection of C_{60}^{+} within the diffuse ISM (Foing & Ehrenfreund 1994, 1997) would demonstrate the resistance of the fullerene cage to UV photodissociation, and might also indicate that the fullerene cage can withstand electron recombination without dissociating (since the most energetic UV photons within the ISM have $h\nu \sim 13.6$ eV, as governed by H atom absorption). Absorption of a 13.6 eV photon by C_{60}^{+} would result in a greater level of internal excitation than would the recombination of $\mathrm{C}_{60}^{2+} + e$ [$\mathrm{IE}(\mathrm{C}_{60}^{+}) = 11.39 \pm 0.05$ eV; Steger et al. 1992]: if UV irradiation does not destroy the fullerene cage (as Foing & Ehrenfreund's detection suggests), then it is very likely that electron recombination of C_{60}^{+} or C_{60}^{2+} does not destroy it either. This hypothesis, as well as our arguments above concerning a low rate for radiative recombination (7a), suggests that C_{60}^{2+} may be an important and comparatively abundant ion within dense clouds. A high C_{60}^{2+} abundance might also be anticipated within the diffuse ISM since the UV cutoff exceeds $\mathrm{IE}(\mathrm{C}_{60}^{+})$: determination of the spectral features expected for C_{60}^{2+} would aid in investigating this possibility.

Formation of the fullerene trication C_{60}^{3+} is also of interest. We anticipate that the sole significant source of this ion is the direct triple ionization of C_{60} by cosmic-ray bombardment:

$$\text{cosmic-ray} + \mathrm{C}_{60} \rightarrow \mathrm{C}_{60}^{3+} + \text{cosmic-ray} + 3e\,. \quad (6b)$$

We expect, also, that the principal loss routes for C_{60}^{3+} will be analogous to those for C_{60}^{2+}, namely electron recombination

$$\mathrm{C}_{60}^{3+} + e \rightarrow \text{products} \quad (10)$$

and addition followed by dissociative recombination

$$\mathrm{C}_{60}^{3+} + \mathrm{X} \rightarrow \mathrm{C}_{60}\mathrm{X}^{3+} + h\nu\,, \quad (11)$$

$$\mathrm{C}_{60}\mathrm{X}^{3+} + e \rightarrow \mathrm{C}_{60}^{2+} + \mathrm{X}\,. \quad (12)$$

We expect C_{60}^{3+} to be much more reactive than C_{60}^{2+} under dense-cloud conditions: however, it is probable that the most important reaction of type (11) will be that with $\mathrm{X} = \mathrm{H}^\cdot$ since we have observed efficient repeated addition of atomic hydrogen in the laboratory (Petrie et al. 1995).

The mode of electron recombination expected for reaction (10) is uncertain: the recombination energy for $\mathrm{C}_{60}^{3+} + e$ is about 4 eV greater than that for $\mathrm{C}_{60}^{2+} + e$ (Javahery et al. 1993a), so dissociative recombination appears a more probable consequence than in the case of reaction (7). Even if the recombination of $\mathrm{C}_{60}^{3+} + e$ is radiative, and slow, the expected dense-cloud abundance of C_{60}^{3+} is rather low: for a branching ratio of 10% for formation of C_{60}^{3+} via reaction (6b), and for a rate coefficient of $k_{11} = 1 \times 10^{-9}$ cm^{-3} mol^{-1} s^{-1}, a steady state abundance of $n(\mathrm{C}_{60}^{3+}) \sim 4 \times 10^{-14}\, n(\mathrm{H}_2)$ is obtained, corresponding to 4×10^{-7} of the total C_{60} abundance. Such a low abundance does not, in itself, preclude a significant role for C_{60}^{3+} in the chemical evolution of fullerenes within dense clouds: as we shall discuss, C_{60}^{3+} is highly reactive with several relatively abundant complex IS molecules such as NH_3, $\mathrm{C}_2\mathrm{H}_2$, $\mathrm{H}_2\mathrm{O}$, and HCN. Nevertheless, the necessity for any adduct ions $\mathrm{C}_{60}\mathrm{X}^{3+}$ to pass through three successive charge-reduction steps (before yielding a neutral species) makes it seem very improbable that the X—C_{60} bond would remain intact. For this reason, we do not expect that C_{60}^{3+} or any of its derivatized reaction products will be observable within dense IS clouds. A more important role for C_{60}^{3+}, in the circumstance that this ion undergoes dissociative recombination while the recombination of C_{60}^{+} or C_{60}^{2+} is purely radiative, is that reaction (10) may be the dominant route for destruction of the fullerene cage within dense clouds or within the diffuse ISM.

4. IS AND CS DERIVATIZATION OF IONIZED C_{60}

4.1. C_{60}^{+}

In a previous study (Petrie et al. 1993a) we noted the reactivity of C_{60}^{+} toward amines and H atoms, and a general lack of reactivity with other classes of compounds under our experimental conditions. We have now monitored the reactions of C_{60}^{+} with several polycyclic aromatic hydrocarbons (PAHs), as listed in Table 1; some such reactions involve competition between charge transfer and addition. Two types of addition product are envisaged. In the reactions of C_{60}^{+} with "linear" PAHs such as tetracene, Figure 3, the fullerene and the PAH are covalently bonded together in the resulting adduct; with "condensed" PAHs, for example corannulene (Fig. 4), the adduct is a charge-transfer complex involving ion/induced dipole interactions

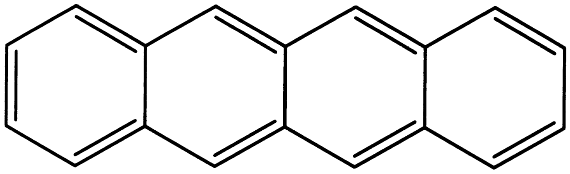

FIG. 3.—Structure 2

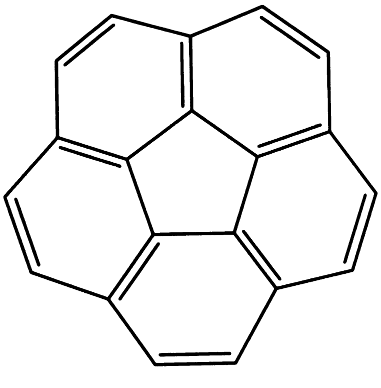

FIG. 4.—Structure 3

TABLE 1

REACTIONS OF FULLERENE IONS C_{60}^{+}, C_{60}^{2+}, AND C_{60}^{3+} WITH VARIOUS MOLECULES AT 294 ± 2 K IN HELIUM AT 0.35 ± 0.01 TORR[a]

Reactants	Products[b]		k_{obs}[c]	$k_{c,294}$[d]	$k_{c,10}$[e]
C_{60}^{+} + X[f]	None		<0.001	…	…
+ X[g]	None		<0.01	…	…
+ $C_{20}H_{10}$	$C_{60}.C_{20}H_{10}^{+}$	[0.9]	0.90	1.0	1.4
	$C_{20}H_{10}^{+} + C_{60}$	[0.1]			
C_{60}^{2+} + X[h]	None		<0.001	…	…
+ $C_{14}H_{10}$[i]	$C_{60}^{+} + C_{14}H_{10}^{+}$		–[j]	2.1	2.1
+ $C_{20}H_{10}$[k]	$C_{60}^{+} + C_{20}H_{10}^{+}$		–[j]	1.8	1.8
+ CH_3CN	$C_{60}.CH_3CN^{2+}$		0.080	5.9	27.7
+ HC_3N	$C_{60}.HC_3N^{2+}$		0.73	5.5	25.9
+ CH_2CHCN	$C_{60}.C_2H_3CN^{2+}$		0.070	5.5	24.6
+ CH_3CH_2CN	$C_{60}.C_2H_5CN^{2+}$		2.5	5.4	24.9
+ CH_3NC	$C_{60}.CH_3NC^{2+}$		–[j]	5.6	24.9
+ CH_3OH	$C_{60}.CH_3OH^{2+}$		0.007	3.4	14.0
+ CH_3CH_2OH	$C_{60}.C_2H_5OH^{2+}$	[0.9]	0.037	3.1	11.9
	$C_{60}OH^{+} + C_2H_5^{+}$	[0.1]			
+ CH_3OCH_3	$C_{60}.(CH_3)_2O^{2+}$		0.003	2.5	9.4
+ CH_3COCH_3	$C_{60}.(CH_3)_2CO^{2+}$		0.27	4.1	17.7
+ CH_3COCCH	$C_{60}.CH_3COCCH^{2+}$		0.13	3.4	13.9
+ $HCOOH$	$C_{60}.HCOOH^{2+}$		0.015	2.5	9.9
+ CH_3COOH	$C_{60}.CH_3COOH^{2+}$		0.40	2.7	10.8
+ $HCOOCH_3$	$C_{60}.HCOOCH_3^{2+}$		0.011	2.8	11.0
C_{60}^{3+} + CH_4	None		<0.001	2.9	2.9
+ C_2H_2	$C_{60}.C_2H_2^{3+}$		0.07	2.7	2.7
+ C_2H_4	$C_{60}.C_2H_4^{3+}$	[0.4]	1.7	2.8	2.8
	$C_{60}^{2+}C_2H_4^{+}$	[0.6]			
+ C_2H_6	$C_{60}H^{2+} + C_2H_5^{+}$		<0.005	2.8	2.8
+ CH_2CCH_2	$C_{60}^{2+} + C_3H_4^{+}$		4.0	2.8	2.8
+ CH_3CHCH_2	$C_{60}^{2+} + C_3H_6^{+}$		1.8	3.0	5.4
+ C_3H_8	$C_{60}H^{2+} + C_3H_7^{+}$	[0.9]	4.2	2.7	2.7
	$C_{60}^{2+} + C_3H_8^{+}$	[0.1]			
+ C_6H_6	$C_{60}^{2+} + C_6H_6^{+}$		–[j]	2.7	2.7
+ $C_{10}H_8$	$C_{60}^{2+} + C_{10}H_8^{+}$		–[j]	2.7	2.7
+ $C_{14}H_{10}$[i]	$C_{60}^{2+} + C_{14}H_{10}^{+}$	[>0.95]	–[j]	3.0	3.0
	$C_{60}^{+} + C_{14}H_{10}^{2+}$	[>0.05]			
+ $C_{16}H_{10}$[l]	$C_{60}^{2+} + C_{16}H_{10}^{+}$	[>0.95]	–[j]	2.8	2.8
	$C_{60}^{+} + C_{20}H_{10}^{2+}$	[<0.05]			
+ $C_{24}H_{14}$[m]	$C_{60}^{2+} + C_{24}H_{14}^{+}$	[0.6]	–[j]	3.0	3.5
	$C_{60}^{+} + C_{24}H_{14}^{2+}$	[0.4]			
+ NH_3	$C_{60}.NH_3^{3+}$		3.9	5.8	24.6
+ CH_3NH_2	$C_{60}^{2+} + CH_3NH_2^{+}$		3.8	4.5	17.0
+ $CH_3CH_2NH_2$	$C_{60}^{2+} + CH_3^{\cdot} + CH_2NH_2^{+}$[n]		3.4	4.0	13.7
+ HCN	$C_{60}.HCN^{3+}$		2.5	8.2	38.6
+ CH_3CN	$C_{60}.CH_3CN^{3+}$		5.9	8.9	41.6
+ HC_3N	Products		8.2	8.3	39.0
+ CH_2CHCN	$C_{60}.C_2H_3CN^{3+}$	[0.9]	4.0	8.2	36.9
	$C_{60}^{2+} + C_2H_3CN^{+}$	[0.1]			
+ CH_3CH_2CN	$C_{60}.C_2H_5CN^{3+}$		4.0	8.1	37.4
+ $NCCN$	$C_{60}.NCCN^{3+}$		0.01	2.9	2.9
+ CH_3NC	$C_{60}.CH_3NC^{3+}$		–[j]	8.5	37.4
+ H_2O	$C_{60}H^{2+} + OH^{+}$		0.20	6.4	29.3
+ CH_3OH	$C_{60}^{2+} + CH_3OH^{+}$	[0.8]	2.5	5.0	21.0
	$C_{60}.CH_3OH^{3+}$	[0.2]			
+ CH_3CH_2OH	$C_{60}OH^{2+} + C_2H_5^{+}$	[0.7]	2.4	4.6	17.9
	$C_{60}^{2+} + C_2H_5OH^{+}$	[0.2]			
	$C_{60}.C_2H_5OH^{3+}$	[0.1]			
+ CH_3OCH_3	$C_{60}^{2+} + CH_3OCH_3^{+}$		3.0	3.8	14.1
+ H_2CO	$C_{60}^{2+} + H_2CO^{+}$		1.8	6.4	29.0
+ CH_3CHO	$C_{60}^{2+} + CH_3CHO^{+}$		3.7	6.4	28.1
+ CH_3COCH_3	$C_{60}^{2+} + (CH_3)_2CO^{+}$		5.8	6.1	26.6
+ CH_3COCCH	$C_{60}^{2+} + C_4H_4O^{+}$	[0.8]	4.5	5.1	20.9
	$C_{60}.CH_3COCCH^{3+}$	[0.2]			
+ $HCOOH$	$C_{60}H^{2+} + CO_2H^{+}$	[0.5]	2.5	3.7	14.9
	$C_{60}.HCOOH^{3+}$	[0.5]			

TABLE 1—*Continued*

Reactants	Products[b]	k_{obs}[c]	$k_{\mathrm{c,294}}$[d]	$k_{\mathrm{c,10}}$[e]
+ CH_3COOH	$C_{60}.CH_3COOH^{3+}$	4.2	4.1	16.2
+ $HCOOCH_3$	$C_{60}.HCOOCH_3^{3+}$	2.9	4.2	16.6

[a] These results have been reported previously (Baranov et al. 1997; Javahery et al. 1993b, 1993c, 1993d; Milburn et al. 1999; Petrie et al. 1993c, 1994; Wang et al. 1996).

[b] Where more than one product channel was detected, the branching ratio is given in square brackets.

[c] Observed effective bimolecular reaction rate coefficient in units of 10^{-9} cm^3 mol^{-1} s^{-1}.

[d] Capture collision rate coefficient at 294 K, in units of 10^{-9} cm^3 mol^{-1} s^{-1}, calculated according to the method of Su & Chesnavich (1982).

[e] Capture collision rate coefficient at 10 K, in units of 10^{-9} cm^3 mol^{-1} s^{-1}.

[f] No reaction observed for X = HCN, CH_3CN, CH_2CHCN, CH_3CH_2CN, NCCN, CH_3NC, CH_3OH, CH_3CH_2OH, CH_3OCH_3, H_2CO, CH_3CHO, CH_3COCH_3, CH_3COCCH, $HCOOCH_3$, or HCOOH.

[g] No reaction observed for X = CH_3COOH or $C_{10}H_8$. The higher upper limit reflects the lower volatility of these compounds: it was not experimentally possible to add as large a flow of either CH_3COOH or $C_{10}H_8$ to the reaction vessel as was the case with the neutrals detailed in footnote (f).

[h] No reaction observed for X = HCN, NCCN, H_2CO, or CH_3CHO.

[i] $C_{14}H_{10}$ = anthracene.

[j] Reaction rate coefficient not determined; reaction observed, presumably occurring at the collision rate coefficient.

[k] $C_{20}H_{10}$ = corannulene. Collision rate calculated using the estimated values $\mu = 0.5$ and $\alpha = 30$ Å^3.

[l] $C_{16}H_{10}$ = pyrene.

[m] $C_{24}H_{14}$ = benzo[rst]pentaphene. Collision rate calculated using the estimated values $\mu = 0.3$ debye and $\alpha = 39$ Å^3.

[n] A minor [< 0.1] product channel leading to charge transfer (C_{60}^{2+} + $CH_3CH_2NH_2^+$) could not be discounted experimentally.

between the two species within the complex. As detailed in subsequent sections, the prospects for successful neutralization [that is, without fragmentation of the fullerene-PAH bond(s)] are much greater for those adducts involving covalent fullerene-PAH bonding than for the charge-transfer complexes.

4.2. C_{60}^{2+}

This ion is more reactive, both by addition and by electron abstraction, than is C_{60}^{+}. Nevertheless, C_{60}^{2+} does not appear reactive with the majority of closed-shell (i.e., experimentally accessible) interstellar molecules. Addition reactions involving the astrophysically significant species H, NH_3, and CH_3CCH have been discussed previously (Petrie et al. 1993a). Of the reactions that we have examined subsequently (see Table 1), only those with HCCCN, with CH_3NC, and with PAHs appear of any real significance in the dense-cloud chemistry of fullerenes. The association of C_{60}^{2+} with HCCCN is of interest given the high abundance of this neutral within TMC-1 and other sources. Rapid association of C_{60}^{2+} with HC_3N would outweigh slow radiative recombination of C_{60}^{2+} as a loss process for this ion, although association with other neutrals (especially H) may still predominate. We ascribe structure 4 (Fig. 5) to the adduct ion formed in the reaction with HC_3N. Nevertheless, proton transfer from $C_{60}.NC_3H^{2+}$ to HC_3N does not occur under SIFT conditions, suggesting that the dominant route to removal of $C_{60}.NC_3H^{2+}$ is dissociative recombination, almost certainly occurring as

$$C_{60}.NC_3H^{2+} + e \rightarrow C_{60}^{+} + HC_3N \,, \qquad (13)$$

and therefore not leading to any chemical derivatization of the fullerene skeleton itself.

The reaction of C_{60}^{2+} with CH_3NC is another addition process which is highly efficient under our experimental conditions: we ascribe the rapid and repeated addition, of methyl isocyanide molecules to C_{60}^{2+}, to carbene insertion. In connection with this mechanism, three points are worth noting. First, carbene insertion forms two bonds between the fullerene cage and the functionalizing unit, as in figure 6: therefore, the C_{60}—X connection (channel 14a) may not be the most easily broken bond in the molecular dication, perhaps allowing other channels (14b, 14c) to become significant in dissociative recombination:

$$\begin{aligned} C_{60}.CNCH_3^{2+} + e &\rightarrow C_{60}^{+} + CH_3NC \,, && (14a)\\ &\rightarrow C_{60}.CN^{+} + CH_3^{\cdot} \,, && (14b)\\ &\rightarrow C_{60}.CNCH_2^{+} + H^{\cdot} \,. && (14c) \end{aligned}$$

Second, the carbene insertion mechanism does not formally involve either of the positive charges on C_{60}^{2+}, and therefore the positive charges may remain delocalized upon the fullerene cage in the product ion $C_{60}.CNCH_3^{2+}$. This is significant because it may favor radiative rather than dissociative recombination in the reaction of $C_{60}.CNCH_3^{2+}$, with an electron, thereby further heightening the prospects for

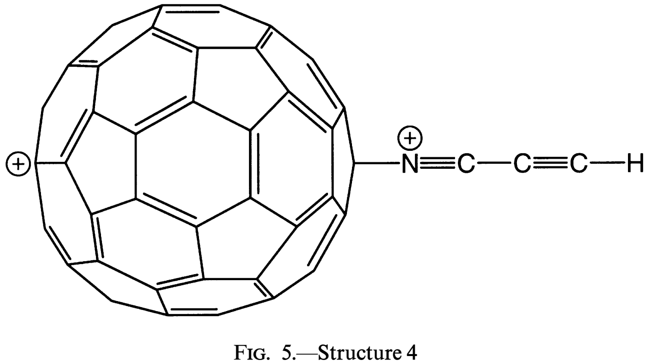

FIG. 5.—Structure 4

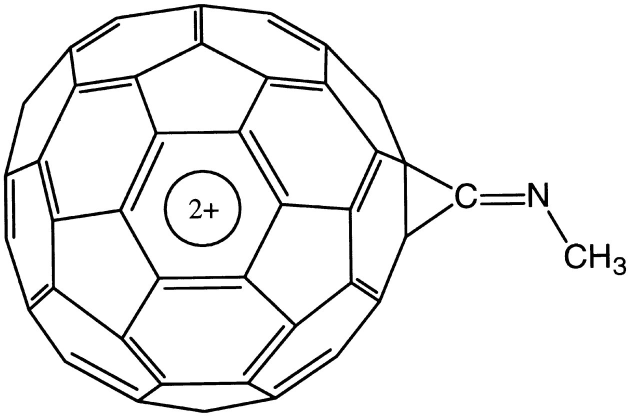

FIG. 6.—Structure 5

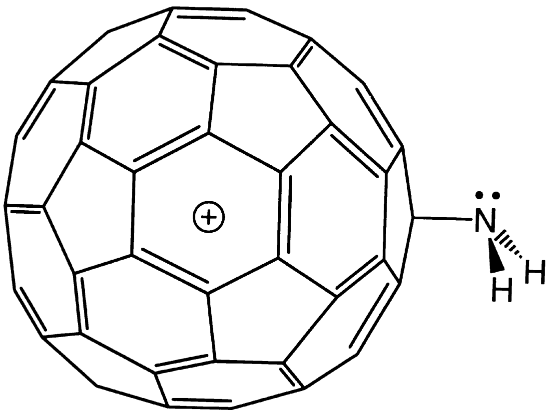

FIG. 8.—Structure 7

modification of the fullerene skeleton through chemical reaction under IS cloud conditions. Third, although methyl isocyanide itself is not of high abundance in most IS or CS environments, other carbenes, notably HNC, are important constituents of dense clouds such as TMC-1. If the reactivity of HNC parallels that of CH_3NC, the secondary product ion $C_{60}.CN^+$ may be an important species in fullerene dense clouds chemistry. See Figure 6.

Reactions of C_{60}^{2+} with PAHs occur exclusively by charge transfer for all examples studied: these reactions may be important loss processes for C_{60}^{2+} in regions of high PAH abundance.

The reaction of C_{60}^{2+} with NH_3, discussed in our earlier survey of fullerene astrochemistry (Petrie et al. 1993a), deserves further comment. The addition product, $C_{60}.NH_3^{2+}$, is seen to exhibit efficient proton transfer to NH_3 (Javahery et al. 1993c):

$$C_{60}.NH_3^{2+} + NH_3 \rightarrow C_{60}.NH_2^+ + NH_4^+ \ . \qquad (15)$$

If proton transfer from $C_{60}.NH_3^{2+}$ to abundant neutrals such as CO is viable under IS conditions (a hypothesis which we have not yet been able to test), then proton transfer from $C_{60}.NH_3^{2+}$ may compete effectively with, or even dominate over, the destruction of $C_{60}.NH_3^{2+}$ by dissociative recombination. There are two feasible structures, those indicated in Figures 7 and 8, for the product of such proton transfer: structure 6 has the positive charge formally localized upon the nitrogen atom, but in this structure the C_{60}—N bond may have a good chance of surviving dissociative recombination, since cleavage of an N—H bond is probably more facile than scission of the two C—N bonds linking the nitrogen atom to the fullerene skeleton. The structure in Figure 8 possesses only a sole C—N bond, but this one may survive recombination since the positive charge is formally delocalized over the fullerene skeleton and hence the reaction with an electron is unlikely to involve direct attack of the N atom itself. These structures may be compared with structure 8 in Figure 9, resulting from addition of ammonia to C_{60}^+: here the adduct ion possesses only a single C—N bond and features charge localization on the nitrogen atom, suggesting that dissociative recombination of Figure 9 is highly likely to occur by C—N bond scission. Thus, the reaction with NH_3 might be one instance where, counterintuitively, the addition product of C_{60}^{2+} has a higher probability of leading to a chemically modified (neutral) fullerene skeleton than does the addition product of C_{60}^+.

4.3. C_{60}^{3+}

Triply-charge fullerene ions react, by charge transfer, adduct formation, or hydride or hydroxide abstraction, with several known IS molecules; these reactions are listed in Table 1. However, while (termolecular) addition reactions

$$C_{60}^{3+} + X + M \rightarrow C_{60}X^{3+} + M^* \qquad (16)$$

with species such as NH_3, CH_3OH, HCCCN, and C_2H_4 are efficient under our experimental conditions and do lead to derivatization of the fullerene cage, it is most unlikely

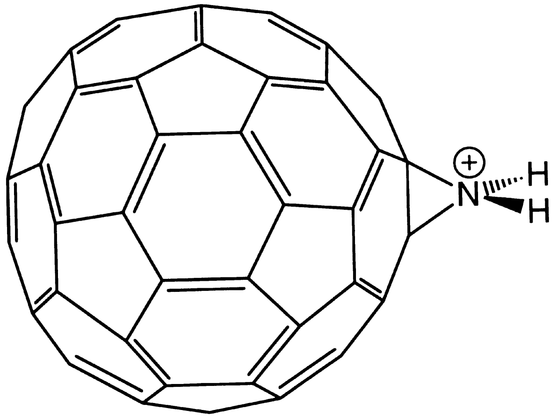

FIG. 7.—Structure 6

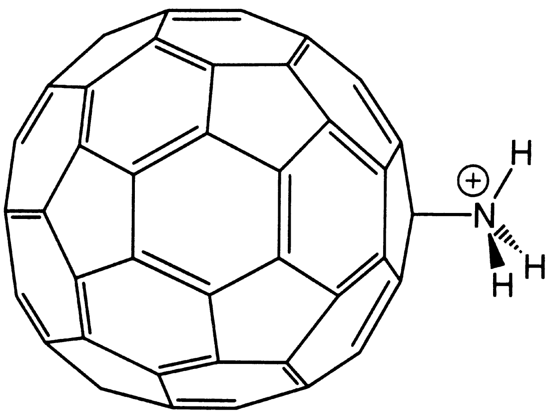

FIG. 9.—Structure 8

that the C_{60}—X bond can survive three successive neutralization steps (at least one of which is expected to involve dissociative recombination with an electron). Furthermore, the rate coefficients for the analogous bimolecular addition reactions (11), under IS cloud conditions, are problematic: we can only observe addition occurring under conditions which are expected to favor termolecular stabilization. We expect, accordingly, that ion/molecule reactions of C_{60}^{3+} will not lead to any significant external functionalization of the fullerene cage, although (as noted in § 3.2) such reactions may serve to prolong the life of the fullerene skeleton by providing alternative pathways to the dissociative recombination of C_{60}^{3+}. Given the low steady state abundance estimated for C_{60}^{3+} in even the most optimistic scenarios, we restrict our discussion of IS fullerene trication chemistry to the reactions with atomic hydrogen and with PAHs.

Reaction of C_{60}^{3+} with H is exclusively by addition (Petrie et al. 1995) and, in keeping with the analogous reactions of C_{60}^{+} and C_{60}^{2+}, is efficient under our experimental conditions. Within the limits of comparatively low H atom concentrations accessible in the SIFT apparatus, repeated addition of at least nine H atoms is evident (Petrie et al. 1995). Furthermore, the efficiency of the initial reaction

$$C_{60}^{n+} + H \rightarrow C_{60}H^{n+} \qquad (17)$$

appears to depend only slightly upon the charge state of the fullerene ion: lower limits to the effective bimolecular rate coefficient for reaction (17) are, respectively, 0.1, 0.3, and 1.0 (units = 10^{-9} cm^3 mol^{-1} s^{-1}) for $n = 1$, 2, and 3 (Petrie et al. 1995). This trend suggests that addition of H to neutral fullerene molecules may also occur with reasonable efficiency.

The reactions of C_{60}^{3+} with large PAHs are expected to be dominated by charge transfer as indicated in Table 1, but a minor channel of double-charge transfer

$$C_{60}^{3+} + PAH \rightarrow C_{60}^{+} + PAH^{2+} \qquad (18)$$

is evident in some cases (Javahery et al. 1993a). This is a novel IS pathway to the formation of large PAH dications, although several other (and probably more significant) production mechanisms for PAH^{2+} have been described previously (Omont 1986; Leach 1986; Petrie & Bohme 1994b; Petrie et al. 1993a, 1993d).

5. IS AND CS DERIVATIZATION OF THE IONS OF FULLERENES OTHER THAN C_{60}

5.1. *Adjacent-Pentagon Fullerenes*

We have investigated some aspects of the ion/molecule chemistry of the "small" fullerene ions C_{56}^{n+} and C_{58}^{n+} (Petrie & Bohme 1993). A few reactions of these ions are given in Table 2. It can be seen from this table that, under the operating conditions of our experiments, C_{56}^{n+} and C_{58}^{n+} are substantially more reactive than C_{60}^{n+} with all of the neutrals surveyed. This heightened reactivity indicates that the IS chemical processing of C_{56}^{n+} and C_{58}^{n+}, and other ions sharing their structural features, will differ substantially from that of C_{60}^{n+}. We have attributed (Petrie & Bohme 1993) the observed heightened reactivity of C_{56}^{n+} and C_{58}^{n+} to adjacent-pentagon "defects" on the carbon surfaces of these fullerene ions, as is required for the closure of structures of this size (Kroto 1987). Carbon atoms associated with the junction of two pentagons, as shown (*filled circles*) for the $\dot{C}_{58}CH_3CN^{2+}$ adduct structure (Fig. 10), are sites of comparatively high reactivity in these fullerenes.

Of course, the circumstellar synthesis of fullerenes remains hypothetical. We know nothing of the relative ease

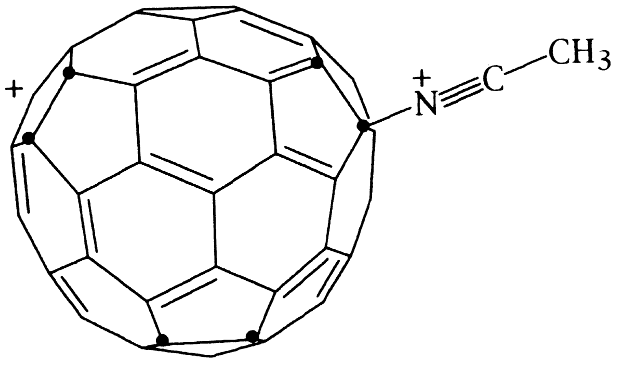

Fig. 10.—Structure 9

TABLE 2

Reactions of Fullerene Ions C_{56}^{n+} ($n = 1, 2$), C_{58}^{n+} ($n = 1, 2$), and C_{70}^{2+} with Various Neutral Molecules at 294 ± 2 K in Helium at 0.35 ± 0.01 torr

Reactants	Products[b]	k_{obs}[c]	k/k_{60}[c]	$k_{c,294}$[b]	$k_{c,10}$[b]
$C_{56}^{+} + NH_3$	$C_{56}NH_3^{+}$	0.0096	>9.6	1.9	8.2
$C_{56}^{2+} + C_2H_4$	$C_{56}C_2H_4^{2+}$	0.021	>21.0	1.9	1.9
$C_{56}^{2+} + n\text{-}C_4H_{10}$	$C_{56}H^{+} + C_4H_9^{+}$	0.027	>27.0	1.9	1.9
$C_{56}^{2+} + CH_3CN$	$C_{56}CH_3CH^{2+}$	4.3	53.8	5.9	27.7
$C_{58}^{+} + NH_3$	$C_{58}NH_3^{+}$	0.034	>34.0	1.9	8.2
$C_{58}^{2+} + C_2H_4$	$C_{58}C_2H_4^{2+}$	0.019	>19.0	1.9	1.9
$C_{58}^{2+} + n\text{-}C_4H_{10}$	$C_{58}H^{+} + C_4H_9^{+}$	0.034	>34.0	1.9	1.9
$C_{58}^{2+} + CH_3CN$	$C_{58}CH_3CN^{2+}$	4.2	52.5	5.9	27.7
$C_{70}^{2+} + HCN$	None	<0.0001	...	5.5	25.7
$C_{70}^{2+} + CH_3CN$	$C_{70}CH_3CN^{2+}$	0.029	0.36	5.9	27.6
$C_{70}^{2+} + CH_2CHCN$	$C_{70}CH_2CHCN^{2+}$	0.040	0.57	5.5	24.5
$C_{70}^{2+} + CH_3CH_2CN$	$C_{70}C_2H_5CN^{2+}$	1.6	0.64	5.4	24.8
$C_{70}^{2+} + C_2N_2$	None	<0.001	...	1.9	1.9

[a] These results have been previously reported (Petrie & Bohme 1993; Javahery et al. 1993b).

[b] See footnotes (b)–(e) for Table 1.

[c] Ratio of the observed rate of reaction to the observed rate for the analogous reaction of C_{60}^{n+}.

or efficiency of formation of, say, C_{60} and C_{58} under CS conditions: laboratory studies of fullerene synthesis (Rohlfing, Cox, & Kaldor 1984; Kroto et al. 1985) suggest that a wide range of conditions can yield a broad spectrum of fullerenes in the gas phase, including fullerenes smaller than C_{60}, while the conditions leading to the predominant production of C_{60} and C_{70} are more tightly constrained. We suspect, therefore, that CS production of C_{60} will be accompanied by formation (albeit possibly at trace abundances) of a wide range of other fullerenes including C_{58}, C_{56}, and other adjacent-pentagon fullerenes (APFs), and we have proposed elsewhere (Petrie et al. 1993d) that hydrogenation, in the diffuse ISM and in the CS envelopes where fullerenes production appears most probable, may act to stabilize such APFs relative to C_{60}. If, as we infer from our laboratory studies, the ions C_{56}^{n+} and C_{58}^{n+}, and other APF ions C_{2m}^{n+} (e.g., $20 \leq 2m \leq 68$; $2m \neq 60$) are also more reactive than the IPF (isolated-pentagon fullerene) ions C_{2m}^{n+} (e.g., $2m = 60, 70, 76, 78, 84$; Diederich & Whetten 1992) under IS cloud conditions, then such APF ions will be more readily derivatized than the analogous IPF ions prior to the occurrence of neutralization. This becomes especially significant if, as discussed below, reactions of fullerene ions with $H^{\cdot}$ inhibit subsequent association reactions of fullerene ions with IS molecules. We note also that, even if the IS and CS abundances of C_{56}, C_{58} and other APFs are much less than those of C_{60} and other IPFs, reactions of APF ions may be more important than reactions of IPF ions in the chemical processing of some IS molecules due to the greater reactivity of APF ions.

APFs may also be formed in the dissociative recombination of larger fullerene ions, for example,

$$C_{60}^{n+} + e \rightarrow C_{58}^{(n-1)+} + C_2 \,, \tag{19a}$$

$$\rightarrow C_{56}^{(n-1)+} + C_4 \,, \tag{19b}$$

although we have argued, in § 3.2 and elsewhere (Petrie et al. 1993a), that the recombination of C_{60}^{+}, and also of C_{60}^{2+}, most probably occurs by a radiative rather than dissociative process. "Ablation" during the cosmic-ray ionization of fullerenes, for example,

$$C_{60} + \text{cosmic-ray}$$

$$\rightarrow C_{60}^{n+} + ne + \text{cosmic-ray}' \,, \tag{20a}$$

$$\rightarrow C_{58}^{n+} + C_2 + \text{n}e + \text{cosmic-ray}' \,, \tag{20b}$$

$$\rightarrow C_{56}^{n+} + C_4 + \text{n}e + \text{cosmic-ray}' \,, \tag{20c}$$

is another possible IS source for APFs, and appears feasible for collisions involving high-energy cosmic rays given the observed efficiency of similar processes in the electron-impact ionization of fullerenes (Sai Baba et al. 1993) and in high-energy collisions of fullerenes with various atoms and atomic ions (Weiske et al. 1991; Ross & Callahan 1991; Christian, Wan, & Anderson 1992; Takayama 1992).

We note also that APFs may be more readily ionized than IPFs under IS conditions: APFs generally have lower first and second ionization energies than IPFs of comparable size. For example, McElvany and coworkers (McElvany, Ross, & Callahan 1991; Zimmerman et al. 1991) have determined $\text{IE}(C_{60})\text{-IE}(C_{56}) \sim 0.5$ eV and $\text{IE}(C_{60}^{+})\text{-IE}(C_{56}^{+}) \sim 0.7$ eV by an ICR (ion cyclotron resonance) bracketing technique. This means that C_{56}^{+} (and other APF ions) can be produced under IS conditions by charge transfer from a wider variety of ions

$$M^{+} + C_{56} \rightarrow C_{56}^{+} + M \tag{21}$$

than can C_{60}^{+}, and that fewer loss mechanisms exist for neutralization of C_{56}^{+} (and other APF ions) by charge transfer than for C_{60}^{+}—indeed, charge transfer to C_{56} (and other APFs) constitutes one of the loss processes for C_{60}^{+},

$$C_{60}^{+} + C_{56} \rightarrow C_{56}^{+} + C_{60} \tag{22}$$

although probably not an important one under most IS conditions. For this reason, also, we anticipate that association reactions of APF ions may be an important route to derivatized (neutral) fullerenes within IS or CS regions. Conversely, the bare APF fullerene cage is expected to be weaker than C_{60} and may be less resistant to dissociative recombination as a neutralization process. A more detailed appraisal of this issue necessitates further experimental study of the differences in ion/molecule chemistry of APF and IPF ions.

5.2. *Larger Fullerenes, Including* C_{70}

Table 2 also indicates some observations of the reactivity of C_{70}^{2+} with various molecules. It is apparent from the data in Table 2, and from previous studies (Petrie et al. 1992a, 1992b), that C_{70}^{2+} is generally less reactive than C_{60}^{2+}. This finding, especially in relation to the occurrence of association, is somewhat contrary to theoretical expectations that association efficiency will (in the absence of complicating factors) increase with the increasing size of the association product (Bates & Herbst 1988; Herbst & Dunbar 1991). We have interpreted the reduced efficiency of C_{70}^{2+} association as indicating that the depth of the potential well corresponding to the formation of a collision complex $[C_{2m}X^{n+}]^{*}$ is smaller for $C_{2m} = C_{70}$ than for $C_{2m} = C_{60}$, and that this effect dominates over the increase in degrees of freedom in going from a 60 atom to a 70 atom fullerene reactant ion in controlling the collision complex lifetime (Petrie & Bohme 1994a). A decrease in collision complex well depth with increasing fullerene reactant ion size can occur as a result of greater charge delocalization in the larger fullerene ion, if adduct formation requires a localization of charge. We anticipate that association efficiency for IPFs will continue to decrease with increasing fullerene ion size: thus, while fullerenes containing several hundred atoms have been characterized in laboratory studies, the derivatization of such giant fullerenes by ion/molecule association reactions will be of substantially lower efficiency (and, therefore, of less IS or CS significance) than the analogous derivatization of C_{60}^{n+}.

6. CHEMICAL PROCESSING OF PROTONATED/HYDROGENATED FULLERENES

IS clouds typically feature a high abundance of atomic hydrogen; as noted in an earlier study (Petrie et al. 1993c), the observed tendency for repeated H atom addition to fullerene ions C_{60}^{n+} ($n = 1, 2, 3$) under our experimental conditions (Petrie et al. 1995) implies that hydrogenated or protonated fullerenes will be significant in the IS chemical processing of fullerenes. Two contrasting effects deserve special comment in this respect.

First, we surmise that hydrogenated fullerene ions $H_mC_{60}^{n+}$ will be less prone to undergo addition reactions with closed-shell IS molecules than will their bare counterparts C_{60}^{n+}, because of the possibility of competing proton transfer channels for the hydrogenated ions:

$$H_mC_{60}^{n+} + X \rightarrow H_mC_{60}X^{n+} + h\nu \qquad (23a)$$

$$\rightarrow H_{m-1}C_{60}^{(n-1)+} + XH^+ \; . \qquad (23b)$$

If we consider the monohydrogenated fullerene ions $C_{60}H^+$ and $C_{60}H^{2+}$ as examples, it is significant that proton transfer from either of these species is expected to be rapid to virtually all of the closed-shell neutrals to which the corresponding "bare" ion C_{60}^{n+} adds under experimental conditions. This is highlighted in Figure 11, which shows the relationship between the gas-phase basicity (GB) of the neutral X and the efficiency of C_{60}^{2+} addition to X under our experimental conditions. It is rather striking that only those neutrals having a GB value higher than the observed threshold for proton transfer from $C_{60}H^{2+}$ are seen to add

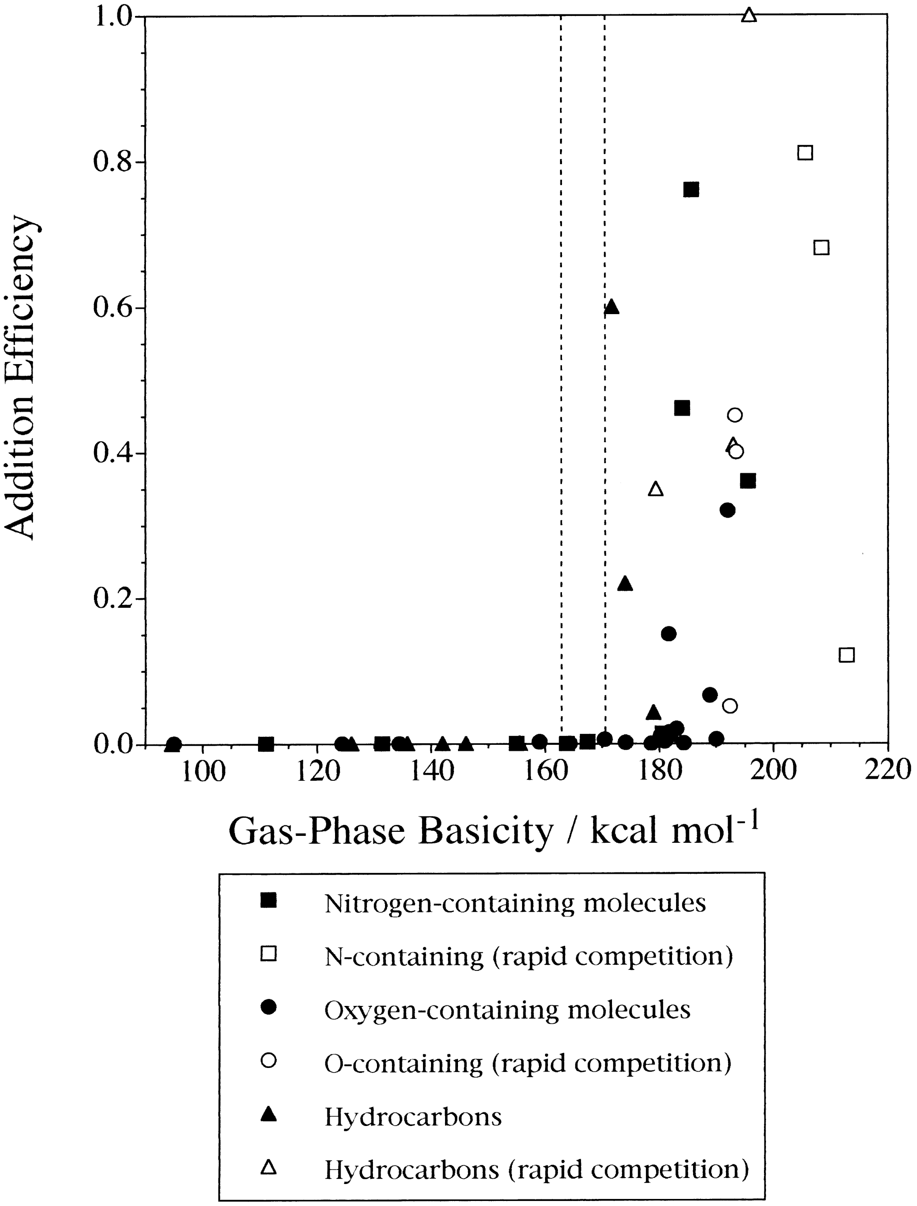

FIG. 11.—A representation of the observed efficiency of the association reaction $C_{60}^{2+} + X \rightarrow C_{60}.X^{2+}$, as a function of the gas-phase basicity GB(X) of the reactant molecule. All measurements, which have been reported in Tables 1, 2, 3, and elsewhere, were performed at an operating pressure of 0.35 to 0.40 torr of helium buffer gas, and a temperature of 294 ± 2 K. For the present purposes, we define the association efficiency as the ratio of the observed (effective bimolecular) rate coefficient for association to the calculated capture collision rate coefficient. There is no uniform dependence of addition efficiency upon gas-phase basicity, but within a broad class of compounds (for example, those containing nitrogen, or those containing oxygen, as the reactive center) there is a tendency for association efficiency to increase somewhat systematically with increasing compound size; the gas-phase basicity of the compounds also tends to increase with increasing molecular size. (Open symbols represent reactions in which addition competes with an efficient exothermic bimolecular process, most usually charge transfer. In these cases, the association efficiency is likely to be lower than in the absence of such a competing channel). The pair of vertical dashed lines denotes the lower and upper limits to the bracketed "apparent gas-phase basicity" of the hydrogenated species $C_{60}H^{2+}$ (Petrie et al. 1993e); all compounds whose GB places them to the right-hand side of the threshold value bracketed by this pair of lines are expected to react rapidly with $C_{60}H^{2+}$ by proton transfer, while compounds whose GB places them to the left-hand side of this threshold value will not undergo proton transfer with $C_{60}H^{2+}$ under cold IS conditions. A striking feature of the observed distribution is that, under our experimental conditions, *only* those species which will react with $C_{60}H^{2+}$ by efficient proton transfer are observed to add detectably to C_{60}^{2+}. If the intrinsic efficiency of addition of a compound to $C_{60}H^{2+}$ is, in the absence of competing reactions, equivalent to that for C_{60}^{2+}, then *none* of the molecules included in the present study will add effectively to $C_{60}H^{2+}$. It can be seen from this supposition that the hydrogenation of ionized fullerenes can, therefore, profoundly affect their derivation by other IS species.

TABLE 3

COMPARISON OF VIABLE CHARGE-SEPARATING REACTION CHANNELS (CHARGE TRANSFER AND PROTON TRANSFER) FOR REACTIONS OF C_{60}^{2+} AND $C_{60}H^{2+}$ WITH VARIOUS SMALL INTERSTELLAR MOLECULES AND RADICALS

$CT(C_{60}^{2+})$[a]	$CT(C_{60}H^{2+})$[a]	$PT(C_{60}H^{2+})$[a]	Requirements[b]	Reactants meeting requirements
No	No	No	IE(X) > 9.70 eV; GB(X) < 163 kcal mol^{-1}	H, H_2, C, CH_3, CH_4, N, NH, O, OH, H_2O, N_2, O_2, CO, CO_2, C_2H_2, C_2H_4, C_2H_6, CN
No	No	?	IE(X) > 9.70 eV; GB(X) = 167 ± 4 kcal mol^{-1}	CH, HCN, H_2CO, HCOOH
No	No	Yes	IE(X) > 9.70 eV; GB(X) > 171 kcal mol^{-1}	CH_2, C_2N, CH_3CCH, CH_2CCH_2, NH_2, NH_3, HNC, CH_3CN, HC_3N, C_2H_3CN, C_2H_5CN, CH_3OH, C_2H_5OH, $(CH_3)_2O$, CH_3CHO, CH_3COOH, $HCOOCH_3$
?	No	Yes	IE(X) = 9.59 ± 0.11 eV; GB(X) > 171 kcal mol^{-1}	H_2CCO
Yes	?	Yes	IE(X) = 8.9 ± 0.55 eV; GB(X) > 171 kcal mol^{-1}	C_2H_3, CH_3NH_2
Yes	Yes	No	IE(X) < 8.4 eV; GB(X) < 163 kcal mol^{-1}	C_2H_5, HCO, H_2COH

[a] Prospects for the occurrent of the indicated reaction channel [CT = charge transfer; PT = proton transfer] for the indicated reactant ion and the identified neutrals. An assignment of " ? " in this column indicates that the reaction channel is thermoneutral within the experimental uncertainty.

[b] Experimental thresholds, for the occurrence of charge transfer from C_{60}^{2+} and proton transfer from $C_{60}H^{2+}$, respectively, are IE(X) = 9.59 ± 0.11 eV (Petrie et al. 1992c) and GB(X) = 167 ± 4 kcal mol^{-1} (Petrie et al. 1993e). Prospects for CT from $C_{60}H^{2+}$ are based on a threshold of $IE(C_{60}^{+}) - IE(C_{60}H^{+}) = 0.7 \pm 0.45$ eV (Petrie et al. 1993e).

measurably to C_{60}^{2+}. In a reaction where a bimolecular product channel (e.g., proton transfer) competes with a unimolecular channel (i.e., the collision complex leading to a stable adduct ion) we would generally expect the bimolecular channel to dominate. Therefore, if we make the assumption that the factors relevant to adduct formation—binding energy, appropriate vibrational frequencies, and IR intensities, and structural characteristics—are essentially the same for the "bare" and "hydrogenated" adducts $C_{60}X^{2+}$ and $HC_{60}X^{2+}$, we can conclude that $C_{60}H^{2+}$ will exhibit efficient proton transfer rather than addition with those neutrals to which C_{60}^{2+} adds. The situation for $C_{60}H^{+}$ and C_{60}^{+} is broadly similar. We can generalize this observation to state that hydrogenation of bare fullerenes ions

TABLE 4

COMPARISON OF THERMODYNAMIC PARAMETERS FOR CHARGE TRANSFER FROM C_{60}^{+} AND PROTON TRANSFER FROM $C_{60}H^{+}$ TO VARIOUS SMALL MOLECULES AND PAHs

X	Formula	IE(X)[a]	GB(X)[b]	$CT(C_{60}^{+})$[c]	$PT(C_{60}H^{+})$[d]
Small molecules:					
Ammonia	NH_3	10.16	195.6		?
Methylamine............	CH_3NH_2	8.97	205.7		Y
Ethylamine..............	$C_2H_5NH_2$	8.86	208.5		Y
Dimethylamine	$(CH_3)_2NH$	8.23	212.8		Y
Trimethylamine	$(CH_3)_3N$	7.82	217.3		Y
PAHs:					
Benzene	C_6H_6	9.246	174.6		
Naphthalene	$C_{10}H_8$	8.14	187.8		
Anthracene..............	$C_{14}H_{10}$	7.45	199.9	Y	Y
Phenanthrene...........	$C_{14}H_{10}$	7.86	191.6		
Pyrene....................	$C_{16}H_{10}$	7.41	199.8	Y	Y
Fluoranthrene	$C_{16}H_{10}$	7.95	191.5		
Tetracene................	$C_{18}H_{12}$	6.97	210.4	Y	Y
Chrysene	$C_{18}H_{12}$	7.59	193.8	?	
Triphenylene............	$C_{18}H_{12}$	7.84	191.4		
Perylene	$C_{20}H_{12}$	6.90	204.3	Y	Y
1,12-Benzoperylene......	$C_{22}H_{12}$	7.15	201.1	Y	Y
Picene	$C_{22}H_{14}$	7.48	196.3	Y	?
Coronene................	$C_{24}H_{12}$	7.29	199.9	Y	Y

[a] Ionization energy, in eV, from the compilation of Lias et al. (1988) unless otherwise indicated.

[b] Gas-phase basicity, in kcal mol^{-1}, from the compilation of Lias et al. (1984) unless otherwise indicated.

[c] Prospects for the charge transfer reaction of C_{60}^{+} + X, under IS conditions. "Y" denotes that charge transfer is expected to be efficient ($k \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}) in the absence of competing product channels; " ? " indicates that charge transfer may or may not occur—current thermochemical values do not allow a sufficiently reliable assessment; a blank space indicates that charge transfer is not expected to be viable under IS conditions. The occurrence of charge transfer is assessed from the experimental determination of $IE(C_{60}) = 7.61 \pm 0.02$ eV (Lichtenberger et al. 1991).

[d] Prospects for the proton transfer reaction of $C_{60}H^{+}$ + X, under IS conditions. Symbols used are analogous to those for $CT(C_{60}^{+})$. The occurrence of proton transfer is assessed from the observation (McElvany & Callahan 1991) of near-thermoneutral proton transfer, at 300 K, in the reaction of $C_{60}H^{+} + NH_3$ (GB = 195.6 kcal mol^{-1}).

acts to effectively "poison" these ions against addition reactions with closed-shell neutrals—those further addition reactions of hydrogenated ions with radicals appear viable, as typified by our study of multiple H atom addition (Petrie et al. 1995).

Secondly, we consider the effect of hydrogenation *following* functionalization of the fullerene ion C_{60}^{n+} by an IS molecule X:

$$C_{60}X^{n+} + mH^{\cdot} \rightarrow H_mC_{60}X^{n+} + mh\nu\ . \tag{24}$$

In this instance, hydrogenation should result in an increased likelihood of the $C_{60}X$ linkage surviving the subsequent neutralization process, both by (perhaps) opening an avenue for proton transfer

$$H_mC_{60}X^{n+} + Y \rightarrow H_{m-1}C_{60}X^{(n-1)+} + YH^+ \tag{25}$$

to an appropriate neutral Y, and by providing a wider variety of dissociative recombination pathways, for example,

$$H_mC_{60}X^{n+} + e \rightarrow H_mC_{60}^{(n-1)+} + X\ , \tag{26a}$$

$$\rightarrow H_{m-1}C_{60}X^{(n-1)+} + H^{\cdot}\ , \tag{26b}$$

$$\rightarrow H_{m-2}C_{60}X^{(n-1)+} + H_2\ , \tag{26c}$$

than is accessible to the nonhydrogenated ion $C_{60}X^{n+}$. These effects are especially significant for adducts which do not have accessible pathways to partial neutralization by proton transfer (e.g., adducts of C_{60}^{2+} and with nitriles) or which retain a largely delocalized charge distribution (such as the adducts of C_{60}^{2+}, C_{70}^{2+} and C_{60}^{3+} with CH_3NC). To illustrate the prospects for neutralization by reaction (24), we have summarized the proton transfer reactivity of $C_{60}H^{2+}$, and the charge transfer reactivity of C_{60}^{2+}, with likely IS neutrals in Table 3. A large number of known or probable IS neutrals are expected to undergo proton transfer with $C_{60}H^{2+}$ but not charge transfer with C_{60}^{2+}. If we assume that the tendency of a hydrogenated adduct dication $HC_{60}X^{2+}$ to undergo proton transfer to a given neutral is generally similar to the tendency of $C_{60}H^{2+}$ to undergo proton transfer, then the hydrogenation of an adduct $C_{60}X^{2+}$ enhances the probability of the product ion to be neutralized, or partially neutralized, "gently" by an ion/molecule rather than "violently" by electron/ion recombination. Thus reaction (24) favors the formation, and possible detection, of neutral derivatized fullerenes. Similar considerations are pertinent for the association of C_{60}^{+} with H, and some relevant parameters for the singly charged fullerenes are summarized in Table 4.

The interplay between these competing effects is complex and is further hampered by a lack of knowledge concerning the rates of radiative addition of any neutral to C_{60}^{n+} under IS conditions. We can surmise that rapid H-atom addition will tend to favor chemical processing of neutral and ionized fullerenes by other IS radicals, via the "poisoning" effect described above; if H atom addition is not efficient under IS conditions, then the scope for fullerene derivatization by ion/molecule pathways is not significantly enhanced by inclusion of processes such as (24). Further studies are required to clarify this matter.

7. FUNCTIONALIZED FULLERENES: SOME CANDIDATES FOR INTERSTELLAR DETECTION

Our considerations of fullerene ion/molecule reactivity and of the various neutralization sequences indicate that the fullerene product ions can be divided into four general classes:

1. Ions in which all positive charge remains delocalized upon the fullerene surface, such as the adduct formed in the reaction of C_{60}^{2+} with CH_3NC (and, we presume, with other IS isonitriles such as HNC and HCCNC) and in the reactions of C_{60}^{n+} with radicals. These have the highest probability of undergoing neutralization without destruction of the bond between the fullerene and the substituent. Ions such as the adducts of C_{60}^{+} with "linear" PAHs (anthracene, tetracene, etc.) probably also fall into this class (Becker et al. 1994a).

2a. Ions in which one positive charge is formally localized upon the substituent atom which is directly attached to the fullerene surface, and which display ready deprotonation reactions with other molecules. Product ions in this class are those from reactions of C_{60}^{2+} with ammonia, with CH_3OH, and with HCOOH. The first neutralization step here will involve deprotonation by proton transfer, in competition with the destructive process of dissociative recombination. If the fullerene-substituent bond survives the first neutralization reaction, subsequent neutralization reactions may also leave this bond intact especially if little or no charge remains localized upon the substituent.

2b. Ions in which one positive charge is formally located on the substituent, but not on the atom directly attached to the fullerene surface: dissociative neutralization of such a species may well result in fragmentation of the substituent, with a portion remaining attached to the fullerene skeleton. Product ions in this class include those from the reactions of C_{60}^{2+} with unsaturated hydrocarbons such as CH_3CCH.

3. Ions in which one positive charge is formally localized upon the substituent atom which is directly attached to the fullerene surface, and which do not display ready deprotonation reactions. Product ions in this class are those from reactions of C_{60}^{+} with NH_3, and from C_{60}^{2+} with nitriles and with $HCOOCH_3$. The first neutralization step here will almost inevitably be that of dissociative recombination, which is expected to destroy the fullerene-substituent bond with near-unit efficiency.

4. Ions in which the charge is, formally, the binding force which connects the fullerene and substituent. Product ions in this class are those from reactions of C_{60}^{+} with "condensed" PAHs (coronene, pyrene, etc.): neutralization of these ions is expected to destroy the interaction between the fullerene and the substituent.

A comparison of ion/molecule pathways for C_{60}^{+} and C_{60}^{2+} is given in Figures 12 and 13, which depict possible neutralization channels for the various product ions. Some discussion of the importance (or lack of importance) of various reactions has been offered in the preceding sections; a more detailed assessment is hazardous given the many uncertain factors involved in extrapolation from laboratory observations to IS cloud conditions, especially since none of the neutralization steps are currently accessible to experimental study. However, if only class (1) and class (2) adducts are expected to lead to neutral derivatized fullerenes, and if class (1) adducts have a significantly greater probability of surviving neutralization than do class (2) adducts, an approximate ordering of reactants can be hazarded:

Dominant: radicals ($H^{\cdot}$, $CH_3^{\cdot}$, etc.)
Important: linear PAHs (anthracene, tetracene, etc.), HNC, NH_3

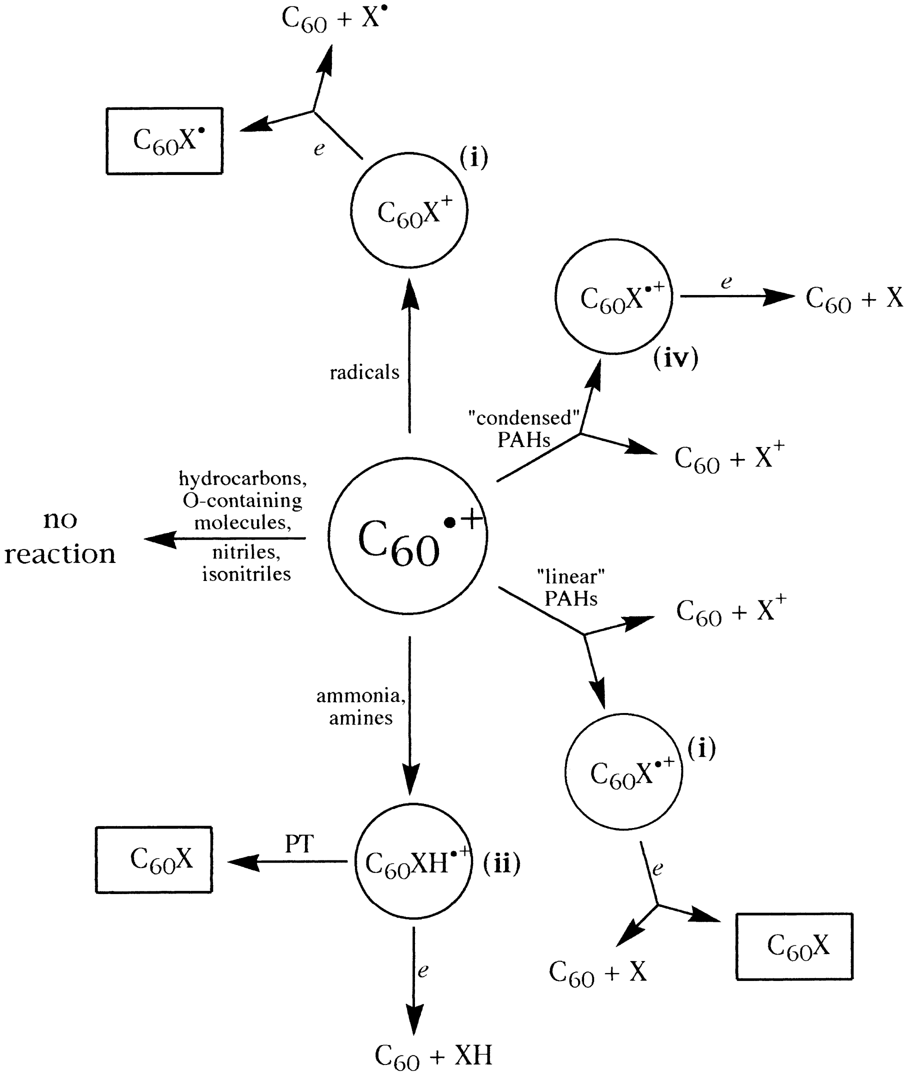

FIG. 12.—A schematic diagram depicting the proposed IS pathways to derivatization of C_{60}^{+} by ion/molecule reactions, and prospects for generation of neutral derivatized fullerenes by such reactions. Roman numerals beside the derivatized ions (encircled) identify the class of the derivatized ion—that is, its likely structure and reactivity with regard to neutralization—as we have discussed in § 7 of the text. Pathways leading to neutral derivatized fullerenes are highlighted.

Marginal: unsaturated hydrocarbons, oxygen-containing organic molecules

Irrelevant: nitriles, condensed PAHs (coronene, pyrene, etc.)

Reactions of radicals are expected to dominate because such reactions are found to be rapid for both C_{60}^{+} and C_{60}^{2+} (in the case of H-atom reactions; other examples have yet to be studied) and yield class (1) adducts. Reactions of linear PAHs and isonitriles also yield class (1) adducts, but addition of C_{60}^{+} + PAH often involves competition with rapid charge transfer, while addition with the isonitrile CH_3NC is observed with C_{60}^{2+} but not with the substantially more abundant ion C_{60}^{+}. Reactions of NH_3 are also classed as important even though these yield class (2) or (3) adducts, because the abundant ion C_{60}^{+} does add measurably to NH_3 under our experimental conditions. Various oxygen-containing molecules [class (2)] are regarded as of "marginal" significance because these do not add to C_{60}^{+} and, in general, add to C_{60}^{2+} with only low efficiency under laboratory conditions. Reactions leading to class (3) and class (4) adducts are considered to be "irrelevant" in the IS production of neutral derivatized fullerenes.

As discussed in § 6, hydrogenation affects fullerene ion reactivity: we anticipate that significantly hydrogenated fullerene ions will yield derivatized neutral fullerenes $H_mC_{60}X$ only by reactions of $H_{m+n}C_{60}^{n+}$ with radicals, and $H_{m+1}C_{60}^{+}$ with linear PAHs.

8. AREAS FOR FURTHER STUDY

The reactivity of neutral and ionized fullerenes with IS radicals is crucial in determining the likely distribution of derivatized fullerenes: as yet, very little investigation in this field has occurred. Perhaps the most important such reaction is that of C_{60} (probably the predominant charge state of the most abundant IS fullerene) with atomic hydrogen (the most abundant radical under most IS conditions):

$$C_{60} + H^{\cdot} \rightarrow C_{60}H^{\cdot} + h\nu \,. \qquad (27)$$

This reaction has yet to be studied in the gas phase although a low-temperature, matrix isolation study has

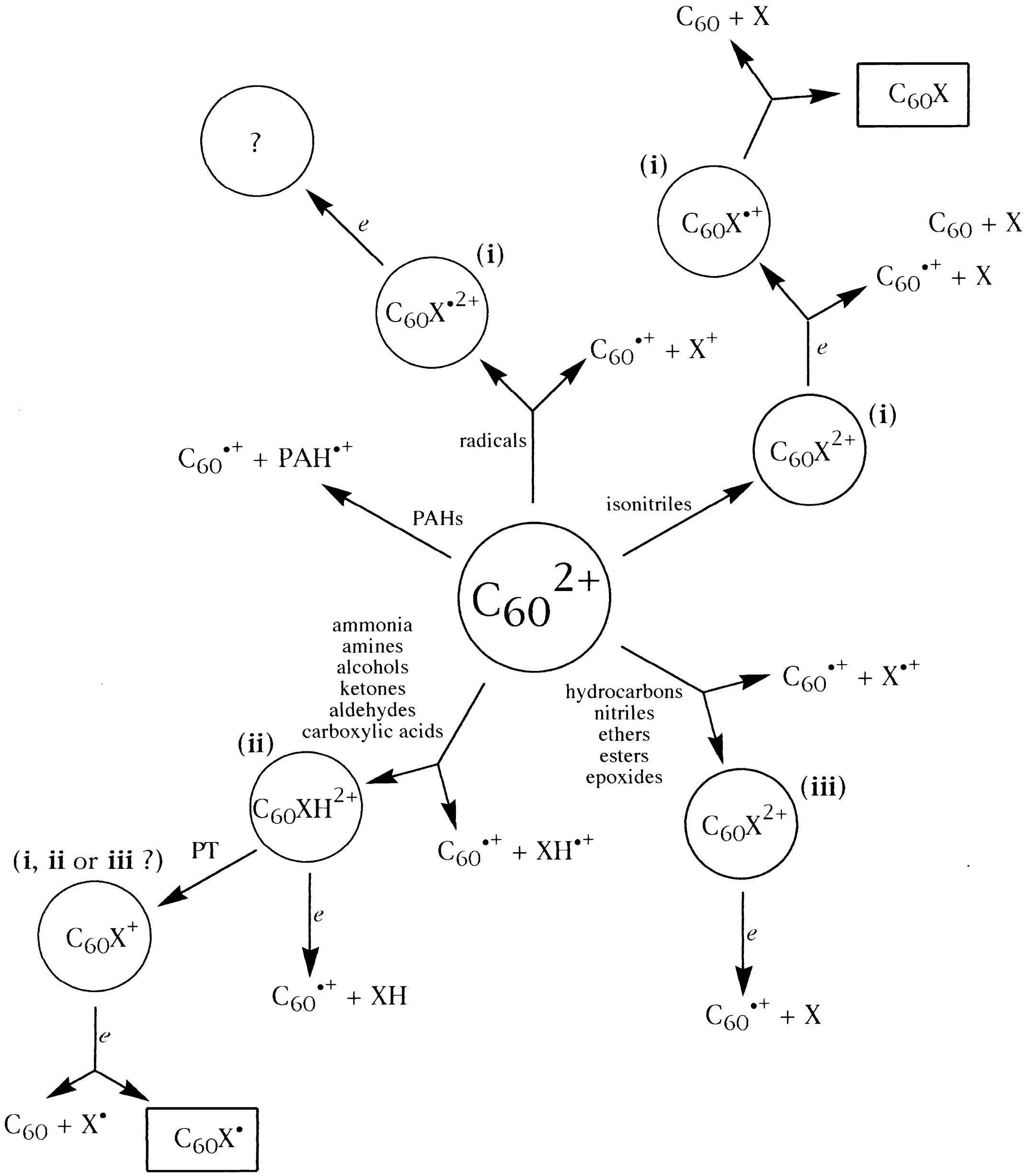

FIG. 13.—As Fig. 12, but for C_{60}^{2+}

been performed (Howard 1993). Howard's study reported a high degree of reactivity for C_{60} + H$^{\cdot}$, yielding products containing up to 36 hydrogen atoms. If neutral C_{60} is similarly reactive with H$^{\cdot}$ under IS conditions, then conversion of C_{60} to at least a partially hydrogenated state should be rapid and essentially quantitative except in regions of very low atomic hydrogen abundance. If this is so, then reactions of "bare" fullerene ions with other IS molecules will be of minor significance. However, little is known of the efficiency of neutral/neutral reactions at dense IS cloud temperatures: some recent temperature-dependence studies suggest that the activation energy for radical-unsaturated molecule reactions is typically very small (Lichtin & Lin 1986; Smith 1988; Rowe, Canosa, & Sims 1993), although it is not clear that any barriers are so small as to be surmountable under IS cloud conditions. If neutral C_{60} does not react measurable with H$^{\cdot}$ at cold cloud temperatures, perhaps because of an activation energy barrier or a short collision complex lifetime, then the reactions of the "bare" fullerene ions C_{60}^{+}, C_{60}^{2+}, and (to a lesser extent) C_{60}^{3+} with IS molecules will be important in determining the distribution of carbonaceous material in IS clouds. In any event, competition is likely to exist between the reactions of fullerene ions with molecules, such as those in the present study, and reactions of these ions with radicals.

A wider study of the reactivity of fullerene ions as a function of the size and stability of the fullerene structure is also desirable, since C_{60} is very probably not the sole IS fullerene. We have reported some preliminary measurements on C_{56}^{n+}, C_{58}^{n+}, and C_{70}^{n+}, but much remains to be done in this field. There also exists considerable scope for investigation of the reactivity of derivatized fullerene ions $C_{60}X^{n+}$ with various neutrals; at present, we have generally examined only the reactivity with the parent neutral X, although we have made somewhat sweeping generalizations concerning the expected reactivity with different neutrals.

Finally, but of considerable importance, is a study on the neutralization of derivatized fullerene ions, most particularly by electronic recombination reactions. Determination of the product channels of such reactions is likely to be difficult but would yield very valuable data concerning the likely neutral derivatives of fullerenes under IS cloud conditions.

9. SUMMARY

Chemical factors influencing the possible derivatization of fullerene ions with IS environments have been presented and assessed. The most likely sources of fullerene cation functionalization are those IS neutrals which undergo addition reactions with singly charged fullerene ions such as C_{60}^{+}: to date, the only neutrals which have been identified as satisfying this criteria are ammonia and methylamine, various PAHs, and atomic hydrogen, although addition of other radicals to C_{60}^{+} should also be highly efficient. Production of derivatized neutral fullerenes from these ions requires that neutralization must preserve the fullerene/neutral bond, a rule which is probably obeyed by proton-transfer reactions of the derivatized ions but disobeyed by ion/electron recombination reactions. For this reason and others, the reactions of neutral IS fullerenes with radicals may well predominate over ion/neutral reactions as a mechanism for the chemical evolution of fullerenes within interstellar environments.

Reactivity differences between adjacent-pentagon fullerenes (APFs) and isolated-pentagon fullerenes (IPFs) have been identified: it is likely that the chemical derivatization of the APFs will be substantially more efficient under IS conditions than will the processing of IPFs. Reaction schemes involving fullerene trications have also been discussed, although the IS abundance of fullerene trications is almost certainly too low for the reaction chemistry of these ions to leave a detectable imprint upon the chemical evolution of IS environments.

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