

# Formation and charge-separation reactions of large molecular di-cations within interstellar clouds: consequences for cold cloud chemical evolution

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## ABSTRACT

The presence is suggested of significant abundances of large molecular di-cations (of fullerenes and polycyclic aromatic hydrocarbons) within the interstellar medium. Possible roles are discussed for charge-separating reactions of interstellar di-cations in the chemical evolution of cold, dense interstellar clouds. Several features of such charge-separation reactions are seen to be ideally suited for the production of internally cold, highly kinetically excited ions, and in this capacity such reactions may serve as a driving force for the subsequent occurrence of hydrogen-atom abstraction reactions with the dominant dense-cloud species  $H_2$ . Factors influencing reaction sequences of this type are discussed, as are some examples relevant to the formation of molecules detected within interstellar clouds.

**Key words:** molecular processes – ISM: clouds – ISM: molecules.

## 1 INTRODUCTION

A large number of polyatomic molecules, radicals and ions have been identified as constituents of cold, dense interstellar (IS) clouds (Turner 1989). To date, no species containing more than 13 atoms ( $HC_{11}N$ ) has been positively identified within dense IS clouds, although considerably larger compounds have been considered as the possible carriers of the diffuse IS bands. Among the large molecules that have been considered in this regard are the polycyclic aromatic hydrocarbons (PAHs) (Léger & Puget 1984; Omont 1986), fullerenes (Hare & Kroto 1992; Kroto & Jura 1992), fulleranes (hydrogenated fullerenes) (Webster 1991), and even small ‘diamonds’ (Allamandola et al. 1992). The probable existence of significant abundances of positively and negatively charged PAHs (Omont 1986; Lepp & Dalgarno 1988; Salama & Allamandola 1992; Szczepanski & Vála 1993) and fullerenes (Bohme 1992; Kroto & Jura 1992) within the IS medium has also been discussed. Derivatized or functionalized fullerene or PAH mono-cations can also be formed under IS conditions by ionization or protonation of the derivatized neutrals or by radiative association reactions. Here we examine several mechanisms by which the doubly charged ions (di-cations) of such species may feasibly be generated within quiescent IS clouds.

Chemical evolution of dense clouds is dominated by the occurrence of exothermic reactions lacking activation

barriers, since the thermal energy of the reactants at typical cloud temperatures ( $T \sim 10\text{--}50$  K) is minimal. Only a few classes of chemical reactions meet the energetic constraints thus imposed, notably ion/molecule reactions (which are generally efficient whenever exothermic); other reaction types such as radical/radical and radical-unsaturated molecule also appear to lack activation energy barriers (Lichtin & Lin 1986; Smith 1988; Clary, Stoecklin & Wickham 1993; Rowe, Canosa & Sims 1993). One exception exists to the requirement that only exothermic and barrier-less reactions are possible: namely, in the reactions of kinetically excited radicals or ions with the dominant dense cloud species  $H_2$  (Adams, Smith & Millar 1984; Brown, Cragg & Bettens 1990; Petrie 1991). In the present work, we present a case for the possible IS significance of hydrogen-atom abstraction reactions driven by the kinetically excited products of ion/molecule reactions of doubly ionized species.

## 2 MECHANISMS FOR DI-CATION FORMATION IN DENSE INTERSTELLAR CLOUDS

While the existence of small, singly charged molecular ions within IS clouds is well established, the existence of di-cations within these environments is less certain. Nevertheless, at least three general mechanisms exist for the formation of di-cations in the interstellar medium.

Leach (1986) has proposed that di-cationic PAHs may form within the IS medium by sequential photoionization:



Omont (1986) has suggested that PAH di-cations may also result from the reactions of the abundant IS ion  $\text{He}^{*+}$ :

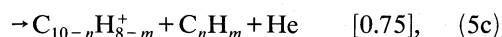
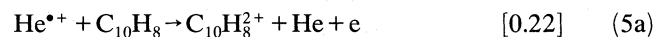


A third possibility is the formation of di-cations by the action of cosmic radiation (Petrie, Javahery & Bohme 1993c):

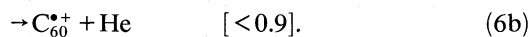


Conditions under which these processes are feasible vary. The process of sequential photoionization is more important within diffuse regions than regions of high particle density, since the penetration of UV radiation within dense IS clouds is poor. Furthermore, only species having a second-ionization energy  $IE(X^{*+}) < IE(\text{H}^*)$  are likely to produce di-cations in this manner. Few, if any, small molecular species meet this criterion; however, Leach (1986) has observed that this condition is met by PAHs of moderate size and larger, and recent studies of the ion thermochemistry of  $\text{C}_{60}$  indicate that its second-ionization energy  $IE(\text{C}_{60}^{*+}) = 11.39 \pm 0.05$  eV (Steger et al. 1992) is sufficiently low to permit the occurrence of sequential photoionization.

The double ionization of a neutral  $X$  in reactions with  $\text{He}^{*+}$  requires that  $IE(X) + IE(X^{*+}) \leq IE(\text{He})$  (24.587 eV). This is unlikely to be met by small molecular species such as have currently been identified within dense IS clouds, but is feasible for larger species such as PAHs and fullerenes which have substantially lower first- and second-ionization energies than do small molecules and radicals. Reaction (3) has now been experimentally observed in the reaction of the smallest PAH, naphthalene (Petrie et al. 1993d):

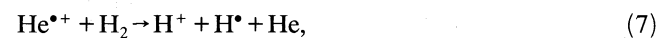


and in the analogous reaction of  $\text{C}_{60}$  (Javahery et al. 1992b):



The occurrence of the ‘charge-transfer electron detachment’ reactions (5a) and (6a) suggests that this reaction process will be viable for other large molecules – larger PAHs generally have lower ionization energies, and presumably also lower second-ionization energies, than naphthalene, and the first- and second-ionization energies of  $\text{C}_{60}$  are also higher than those of most fullerenes (Zimmerman et al. 1991).

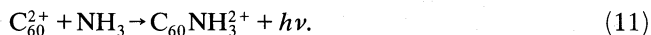
Di-cation formation by cosmic-ray bombardment (4) involves no known energetic restrictions, although the efficiency of such a process is not known at present. This process (if it occurs) is likely to be of some significance throughout dense IS clouds, since cosmic rays can penetrate deep within such clouds. The relative importance of the dense-cloud processes (3) and (4) cannot be reliably assessed at present, but will depend, in part, upon the efficiency of the competing loss processes for  $\text{He}^{*+}$ :



Assuming the relative abundances  $n(\text{C}_{60}) \sim 10^{-7} n(\text{H}_2)$ ,  $n(\text{CO}) \sim 10^{-4} n(\text{H}_2)$ , and  $n(e) \sim 10^{-7} n(\text{H}_2)$ , reaction (8) will be the dominant loss process for  $\text{He}^{*+}$ , unless the rate coefficient for the inefficient dissociative charge-transfer reaction (7) has a value  $k_7 > 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  under dense-cloud conditions. If reaction (8) does dominate, and if an efficiency of 0.1 is assigned to di-cation formation in reaction (6), it can be estimated that formation of the di-cation  $\text{C}_{60}^{2+}$  accounts for approximately  $1 \times 10^{-4}$  of all reactive collisions of  $\text{He}^{*+}$ . This value is consistent with the suggestion, by Millar (1992), that  $\text{C}_{60}^{2+}$  arising from reaction (6a) can reach a peak abundance of  $n(\text{C}_{60}^{2+}) \sim 10^{-12} n(\text{H}_2)$ . The efficiency of the cosmic-ray double-ionization process (4) in producing interstellar  $\text{C}_{60}^{2+}$  may well be comparable, if it is considered that a high proportion of cosmic-ray collisions with  $\text{C}_{60}$  may result in double ionization, and if a ‘hard-sphere’ collision cross-section  $\sigma(\text{C}_{60}) \sim 10^2 \sigma(\text{H}_2)$  is assumed to be based upon the respective geometry of  $\text{C}_{60}$  (Hawkins et al. 1991) and  $\text{H}_2$ . In this scenario, cosmic-ray ionization of  $\text{C}_{60}$  would account for  $\sim 10^{-5}$  of all IS cosmic-ray ionization events; the cosmic-ray ionization of He is generally considered to account for  $\sim 16$ – $20$  per cent of overall cosmic-ray ionization (Watson 1974). Similarly, cosmic-ray double ionization of other fullerenes or of PAHs may be as significant as production of these di-cations by the reaction of the neutral with  $\text{He}^{*+}$ . These estimations are necessarily approximate, but they suggest that it is unreasonable to assume that molecular di-cations can account for  $> 10^{-3}$  of the positive-charge-carrying species within dense IS clouds. Nevertheless, di-cations are highly reactive species, and thus their role in the chemical evolution of dense clouds is worthy of further consideration.

Another factor affecting di-cation production is the di-cation’s stability. Formation of a di-cation is impeded by competition with efficient, dissociative ionization processes, and we anticipate that formation of di-cations from acyclic neutrals is improbable; cleavage of any bond within such a species will lead to its fragmentation. Thus the known linear IS molecules (cyanopolynes, polyacetylenes, cumulene monoxides and monosulfides, etc.) are unlikely to form di-cations by the mechanisms discussed here. In contrast, cyclic (especially polycyclic) neutrals feature a high degree of connectivity, and hence have a comparative paucity of accessible fragmentation channels involving the destruction of only one bond. The fullerenes represent an apotheosis in this respect, since loss of *any* fragment necessitates cleavage of several bonds; the simplest observed fragmentation process for  $\text{C}_{60}$ , that of  $\text{C}_2$  loss, requires the destruction of four bonds. The lack of observed dissociative ionization product channels in reaction (6) (Javahery et al. 1992b) serves to underscore the relative ease of dissociation and of di-cation formation in this instance. Several dissociative ionization channels compete with di-cation formation in reaction (5) (Petrie et al. 1993d). All of these channels, with the exception of hydrogen atom loss, require the destruction of at least two bonds. This is also true of all larger PAHs, and we anticipate that larger PAHs will form di-cations with higher efficiency than does naphthalene (they also generally possess lower first- and second-ionization energies).

It is likely that all of the above avenues for di-cation formation are applicable also to formation of derivatized di-cations – fulleranes, derivatized fullerenes, and derivatized PAHs – although the greater variety of dissociative ionization channels accessible to such species may reduce the efficiency of di-cation formation. Derivatized di-cations can also be formed in the reactions of non-derivatized di-cations with the appropriate neutrals; for example, in the case of fullerenes,

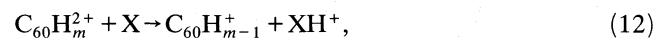


We have observed the efficient occurrence of reactions (10) and (11), and of many related processes initiated by  $\text{C}_{60}^{2+}$ , in selected-ion flow tube (SIFT) experiments (Javahery et al. 1992a, 1993a,b; Petrie et al. 1992a,b; Petrie, Javahery & Bohme 1993b), although under these experimental conditions the mode of adduct stabilization is generally expected to be collisional rather than radiative. These results suggest that a wide variety of functionalized fullerene di-cations should be produced under IS conditions, although the abundances of these species are, as yet, subjects only of conjecture.

### 3 THE REACTIVITY OF MOLECULAR DI-CATIONS: CHARGE-SEPARATION REACTIONS

Conventional wisdom suggests that a molecular di-cation should be highly chemically reactive, due to the substantial Coulombic repulsion that exists between two like charges in close proximity. In fact, Coulombic repulsion serves in some respects to impede the reactivity of molecular di-cations. These species are therefore quite strongly selective in their reactivity, and are unreactive with many neutrals. For example, charge transfer from  $\text{C}_{60}^{2+}$  to a neutral X is exothermic for neutrals having  $IE(X) < 11.39 \pm 0.05$  eV, but is only observed for neutrals with  $IE(X) < 9.59 \pm 0.11$  eV (Petrie et al. 1992c). Similarly, proton transfer from  $\text{C}_{60}\text{H}^{\bullet 2+}$  to a neutral X is an efficient process for neutrals having a proton affinity  $PA(X) > 170$  kcal mol<sup>-1</sup>, but does not occur measurably for neutrals having  $PA(X) < 163$  kcal mol<sup>-1</sup> (Petrie et al. 1993e). Thus  $\text{C}_{60}\text{H}^{\bullet 2+}$  is expected to be unreactive with the dominant IS neutrals H<sub>2</sub>, He, CO, N<sub>2</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and O<sub>2</sub>.

The most probable charge-separation reactions of fullerene di-cations are proton transfer (from functionalized or hydrogenated fullerene di-cations) and charge transfer, but other charge-separating reactions such as hydride abstraction (Petrie et al. 1992b) and hydroxide abstraction (Javahery et al. 1993b) are also feasible, and have been experimentally observed. There are several factors that suggest that proton transfer will be the most significant of these processes under IS conditions. First, proton transfer,



is unique among these charge-separation processes in generating a product (XH<sup>+</sup>) that is more complex than the neutral (X) from which it was formed; proton transfer therefore appears to offer the greatest scope for production of higher complexity species from the reactant X. Furthermore, our experiments suggest that, where competition apparently exists between proton transfer and other charge-separation

reactions, proton transfer is the dominant product channel; hydride-abstraction and hydroxide-abstraction reactions observed to date are intrinsically less efficient at room temperature and may not occur under IS conditions. We shall therefore consider specifically the energetic factors affecting proton transfer from a fullerene di-cation. Several of these factors apply also to other classes of charge-separation reactions.

The occurrence of proton transfer from  $\text{C}_{60}\text{H}^{\bullet 2+}$ , which we have studied experimentally (Petrie et al. 1993e), is impeded by Coulombic repulsion between the positive charges on the product ions:

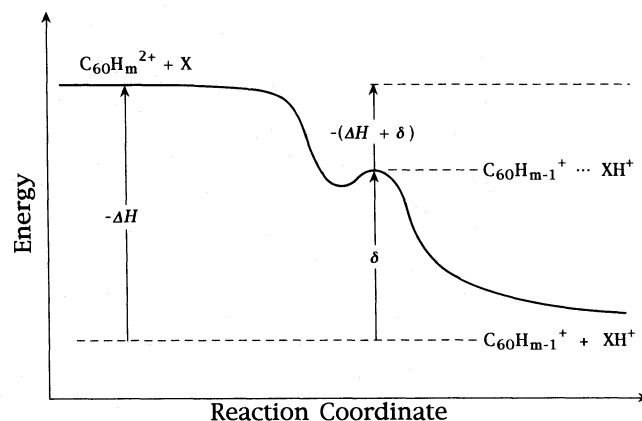


Since the two cationic products of reaction (13) are initially produced in close proximity to each other, the enthalpy of formation of the close ion pair [ $\text{C}_{60}^{\bullet +} \dots \text{XH}^+$ ] can be expressed as

$$\Delta H_f^\circ([\text{C}_{60}^{\bullet +} \dots \text{XH}^+]) = \Delta H_f^\circ(\text{C}_{60}^{\bullet +}) + \Delta H_f^\circ(\text{XH}^+) + \delta, \quad (14)$$

where  $\delta$  is the height of the reverse activation barrier to charge separation at the initial interchange distance between the two product ions. We have elsewhere (Petrie, Javahery & Bohme 1993a; Petrie et al. 1993e; Petrie, Wang & Bohme 1993f) adopted a value of  $\delta \sim 1.80 \pm 0.16$  eV for the barrier height in reaction (13), corresponding to an interchange separation of  $8.0 \pm 0.7$  Å. This value of  $\delta$ , which is presumed to be essentially independent of the degree of hydrogenation of the fullerene di-cation  $\text{C}_{60}\text{H}_m^{\bullet 2+}$ , is derived from the difference in the experimentally observed threshold for charge transfer from  $\text{C}_{60}^{2+}$  to a neutral molecule (Petrie et al. 1992c) and the second-ionization energy of  $\text{C}_{60}$  (Steger et al. 1992).

The significance of the reverse activation barrier to proton transfer, in the context of IS chemistry, is twofold. First, it ensures that any proton-transfer reactions of  $\text{C}_{60}\text{H}^{\bullet 2+}$  that occur will be highly exothermic (by at least  $\sim 1.8$  eV  $\equiv 41$  kcal mol<sup>-1</sup>). Secondly, while the immediately available excess energy  $-(\Delta H + \delta)$  (i.e. the height of the reactants above the barrier as shown in Fig. 1) will be partitioned among all of the available translational, rotational and vibrational modes (assuming no excited electronic states are also accessible), the Coulombic component  $\delta$  will become manifested at greater charge separations, and is likely to be channelled



**Figure 1.** Schematic diagram illustrating the energetic parameters relating to a charge-separation reaction (in this example, proton transfer) from a large molecular di-cation ( $\text{C}_{60}\text{H}_m^{\bullet 2+}$ ) to a neutral molecule X.



almost exclusively into relative translational motion of the product ions. For reaction (13) involving a small, neutral species X, most of this Coulombic repulsion will be partitioned into translational excitation of the protonated species  $XH^+$ , yielding a Coulombic component to the translational excitation of this ion:

$$E_{T,\delta}[(XH^+)^*] = \delta \frac{M_{C_{60}H_n}}{M_{C_{60}H_n} + M_{XH}} \quad (15)$$

Using a simplistic statistical approximation that the remaining 'excess' energy of reaction  $-(\Delta H + \delta)$  will be partitioned equally between product translation, rotation and vibration, the 'non-Coulombic' component,  $E_{T,xs}$ , to  $XH^+$  translational excitation is

$$E_{T,xs}[(XH^+)^*] = \frac{-(\Delta H + \delta)}{3} \frac{M_{C_{60}H_n}}{M_{C_{60}H_n} + M_{XH}} \quad (16)$$

and, if it is assumed that both components act along the same axis, the total translational excitation of this ion is

$$E_T[(XH^+)^*] = \frac{2\delta - \Delta H}{3} \frac{M_{C_{60}H_n}}{M_{C_{60}H_n} + M_{XH}} \quad (17)$$

Table 1 shows several IS neutrals X to which proton transfer from  $C_{60}H^{2+}$  is observed, or expected, to be efficient. This table also shows the estimated translational energy deposited into the product ion  $(XH^+)^*$  by the occurrence of reaction (13).

While proton transfer from other derivatized fullerene dications  $C_{60}H_m^{2+}$  ( $m > 1$ ) or  $C_{60}XH^{2+}$  (Petrie et al. 1993a), or from PAH di-cations, has not been studied in much detail, the features discussed above are applicable to all proton-transfer reactions of molecular di-cations (Roth & Freiser 1991), although the amount of energy partitioned into  $XH^+$  translational excitation will, of course, depend upon the reactants involved. In general, therefore, proton transfer

**Table 1.** Charge-separation reactions of potential interstellar significance.

Reactants <sup>a</sup>	CS <sup>b</sup>	X <sup>+</sup> <sup>c</sup>	$E_{T,\delta}$ <sup>d</sup>	$-(\Delta H + \delta)$ <sup>e</sup>	$E_T$ <sup>f</sup>
$C_{60}^{2+} + C_6H_6$ <sup>g</sup>	CT	$C_6H_6^{*+}$	37.5	7.8	39.8
$C_{60}^{2+} + C_{10}H_8$ <sup>h</sup>	CT	$C_{10}H_8^{*+}$	35.2	33.4	44.7
$C_{60}^{2+} + C_3H_8$ <sup>i</sup>	H A	$C_3H_7^+$	39.2	20.5	45.7
$C_{60}^{2+} + CH_3CH_2OH$ <sup>j</sup>	OHA	$C_2H_5^+$	39.9	> 0	> 39.9
$C_{60}H^{2+} + CH_2CHCN$ <sup>k</sup>	PT	$C_2H_3CNH^+$	38.6	14.9	43.2
$C_{60}H^{2+} + CH_3OH$ <sup>k</sup>	PT	$CH_3OH_2^+$	39.7	7.1	42.0
$C_{60}H^{2+} + HCOOH$ <sup>k</sup>	PT	$HC(OH)_2^+$	39.0	4.7	40.5
$C_{60}^{2+} + C_{14}H_{10}$ <sup>l,m</sup>	CT	$C_{14}H_{10}^{*+}$	33.3	49.3	13.2
$C_{60}H^{2+} + HC_3N$ <sup>m</sup>	PT	$HC_3NH^+$	38.7	13	42.7
$C_{60}H^{2+} + CH_3COCH_3$ <sup>m</sup>	PT	$(CH_3)_2COH^+$	38.4	21.9	45.2
$C_{60}H^{2+} + NH_3$ <sup>m</sup>	PT	$NH_4^+$	40.5	37	52.5
$C_{60}H^{2+} + CH_3NH_2$ <sup>m</sup>	PT	$CH_3NH_3^+$	39.7	47.1	54.7

Notes.

<sup>a</sup>All reactions listed are estimated to have an exothermicity in excess of the reverse activation energy barrier arising from product-ion Coulombic repulsion. Several of these reactions have been studied experimentally, using a selected-ion flow tube (SIFT) operating at  $298 \pm 2$  K and at a helium buffer gas pressure of 0.35–0.40 Torr.

<sup>b</sup>Charge-separation product channel observed. CT=charge transfer; H<sup>-</sup>A=hydride abstraction; OHA=hydroxide abstraction; PT=proton transfer.

<sup>c</sup>Product ion derived from the reactant neutral.

<sup>d</sup>Translational excitation of X<sup>+</sup> arising from Coulombic repulsion in kcal mol<sup>-1</sup>, calculated according to equation (15) as shown in the text, and assigning  $\delta = 1.80 \pm 0.16$  eV (41.5 kcal mol<sup>-1</sup>) as determined experimentally for charge transfer from  $C_{60}^{2+}$ .

<sup>e</sup>'Excess' reaction exothermicity in kcal mol<sup>-1</sup> (see Fig. 1). Fullerene ion thermochemical values used are as summarized by Petrie et al. (1993e). Other thermochemical values used are from the compilations of Lias et al. (1984, 1988).

<sup>f</sup>Total translational excitation of X<sup>+</sup> in kcal mol<sup>-1</sup>, calculated according to equation (22) as shown in the text.

<sup>g</sup> $C_6H_6$  = benzene. Result previously reported (Petrie et al. 1992c).

<sup>h</sup> $C_{10}H_8$  = naphthalene. Result previously reported (Javahery et al. 1992c).

<sup>i</sup>Result previously reported (Petrie et al. 1992b). This reaction is intrinsically inefficient at room temperature and may not occur under IS conditions.

<sup>j</sup>Result previously reported (Javahery et al. 1993b). This reaction is intrinsically inefficient at room temperature and may not occur under IS conditions. The exothermicity of this reaction is not known.

<sup>k</sup>Result previously reported (Petrie et al. 1993e).

<sup>l</sup> $C_{14}H_{10}$  = anthracene.

<sup>m</sup>This reaction has not been studied experimentally: an accessible charge-separation product channel exists and is expected to occur with high efficiency.

from a large molecular di-cation to a small neutral X serves to produce a highly translationally excited ion  $(XH^+)^*$ . The reactivity of this translationally excited ion may well differ significantly from that of a 'slow' thermalized ion  $XH^+$ , as discussed below.

#### 4 FACTORS AFFECTING KINETICALLY DRIVEN HYDROGEN-ATOM ABSTRACTION REACTIONS

Since  $H_2$  and He are the sole IS neutrals with which collision of a translationally excited ion  $(XH^+)^*$  is likely, the possible consequences of such a collision are hydrogen-atom abstraction (18a) or thermalization (18b and 19):



In fact, complete thermalization will require many collisions with  $H_2$  and He; however, if reaction (18a) is endothermic or inhibited by an activation energy barrier, a comparatively small number of collisions is likely to quench  $(XH^+)^*$  sufficiently so that the probability of a subsequent reactive collision (18a) with  $H_2$  is vanishingly small.

The effect of translational excitation upon the IS reactivity of ions and radicals has been explored previously, for the examples of  $N^+$  (Adams et al. 1984; Galloway & Herbst 1989; Brown et al. 1990), hydrocarbon ions such as  $C_6H^+$  (Brown et al. 1990), and the hydroxyl radical  $OH^*$  (Petrie 1991). In these instances, the source of the translational excitation is a highly exothermic dissociative charge transfer (e.g.  $He^{*+} + N_2$ ) or dissociative recombination ( $HOCO^+ + e$ ) reaction.

The occurrence of a translationally driven H-atom abstraction reaction (18a) with an energy requirement  $E_a$ , where  $E_a$  may represent either an activation energy barrier to reaction or the endothermicity of this reaction, necessitates that the translational excitation of the reactant ion  $(XH^+)^*$  must considerably exceed  $E_a$  (Brown et al. 1990; Petrie, 1991):

$$E_T[(XH^+)^*] \geq FE_a, \quad (20)$$

where the factor  $F$  has the value

$$F = 1 + M_{XH}/m. \quad (21)$$

The quantities  $M_{XH}$  and  $m$  are, respectively, the molecular masses of the reactants  $(XH^+)^*$  and  $H_2$ . Since for almost all possible reactants  $M_{XH} \gg m$ , it can be appreciated that a large amount of translational excitation is required to overcome an apparently small energetic barrier. It should also be noted that, in general, the reaction that has produced the translationally excited ion  $(XH^+)^*$  is likely to have many available modes for energy dispersal, so a highly exothermic reaction may nevertheless produce only mildly translationally excited products. It is important to stress, in this regard, that the charge-separation reactions of large molecular di-cations differ greatly from other classes of reactions in that they are expected to deposit an unusually high fraction of the total reaction exothermicity into the translational excitation of the smaller product ion.

For the discussion that follows, we shall limit our attention to H-atom abstraction reactions with  $0 < E_a \leq 3 \text{ kcal mol}^{-1}$ , since these are the only reactions likely to be promoted by translational excitation. This energetic restriction proves somewhat problematic, since the cumulative uncertainties in  $\Delta H_f^\circ(XH^+)$  and  $\Delta H_f^\circ(XH_2^+)$  often exceed this energy range. In addition, while many ion-molecule reactions of the form (18) have been studied experimentally (for thermalized reactants), the number of studies performed at varying temperatures is comparatively small, and few reactions have been found with well-characterized activation energy barriers. Ion/ $H_2$  reactions are also complicated because of the experimental difficulty in attaining thermal equilibrium between the ortho- and para-states of  $H_2$  at very low temperatures. Several H-atom abstraction reactions which are inefficient at room temperature or above display negative temperature dependence; for example, the reactions of  $C_4^{*+}$  and  $C_4H^+$  with  $H_2$  fall into this category (Giles, Adams & Smith 1989). The inefficiency of these reactions suggests that the reaction process involves rearrangement on a time-scale that is short compared to the collision complex lifetime at higher temperatures. We note that reaction (18) with  $C_4H^+$  has been considered in the model of Brown et al. (1990) as possessing an activation barrier, based on an earlier and apparently incorrect report of the non-occurrence of this reaction at 80 K (Herbst, Adams & Smith 1983).

Only two ion/ $H_2$  reactions listed in the compilations of Anicich et al. (Anicich & Huntress 1986; Anicich 1993) appear to fulfil the energetic constraints that we have imposed above. These reactions are



and



for which an activation energy barrier  $E_a \leq 1 \text{ kcal mol}^{-1}$  has been reported by Giles et al. (1989) based on kinetic measurements at 80 and 300 K. Neither of these reactions is ideal as a 'test case' for assistance by kinetic excitation resulting from a previous charge-separation reaction.  $C_6H^+$  could be produced by proton transfer from  $C_{60}H^{*2+}$  (or another hydrogen-bearing di-cation) to  $C_6$ , but the proton affinity of  $C_6$  is not known and so such proton-transfer reactions may not be viable.  $N^+$  cannot easily arise from a charge-separating reaction of a di-cation:  $IE(N^*) = 14.534 \text{ eV}$ , probably too high to permit charge transfer from any IS di-cation. The current absence of clear examples of possible kinetically assisted H-abstraction reactions does not, however, invalidate our central argument that charge-separation reactions of di-cations provide for the partitioning of unusually large quantities of energy in the smaller ionic products for these reactions, and that this energy offers pathways for the avoidance of energetic bottlenecks in the chemical evolution of dense IS clouds.

#### 5 CONCLUSION

Several mechanisms for the production of large molecular (fullerene, fullerane or PAH) di-cations within dense IS clouds have been discussed. We suggest that the most significant of these processes, in the context of dense-cloud chemistry, are charge-transfer electron detachment reactions

initiated by  $\text{He}^{*+}$ , and double ionization by energetic cosmic rays.

Efficient charge-separation (charge-transfer, proton-transfer, hydride-abstraction or hydroxide-abstraction) reactions of large molecular IS di-cations are highly exothermic, and are expected to partition a large fraction of this exothermicity into the translational excitation of the protonated product. This translational excitation may assist the occurrence of subsequent endothermic or barrier-inhibited hydrogen atom abstraction reactions involving  $\text{H}_2$ ; however, few if any of the H-atom abstraction reactions studied to date appear to meet the energetic constraints required to permit their occurrence in this fashion. We reiterate that several obstacles exist to the identification of slightly inhibited or endothermic H-atom abstraction reactions of ions. Therefore, while reactions (22) and (23) are the only currently known appropriate candidates for such kinetically driven H-atom abstraction reactions, we expect that other kinetically driven reactions of possible IS significance exist also and await identification. The general features of dication charge-separation reactions (highly exothermic whenever efficient; substantial translational excitation of product ions) may be of importance in avoiding (as yet unidentified) bottlenecks in the chemical evolution of dense IS clouds.

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