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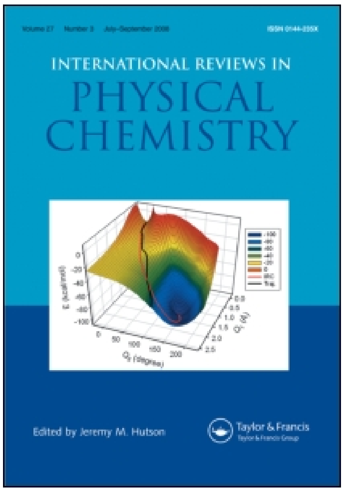

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Electron-transfer reactions with buckminsterfullerene, C_{60}, in the gas phase

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The fundamental process of electron transfer is viewed from the new perspective provided by recent gas-phase measurements of reactions that remove electrons from the C_{60} molecule or donate electrons to singly and multiply charged C_{60} cations. Experimental results are reviewed for the chemical ionization of C_{60} by Penning ionization with metastable rare-gas atoms, single-electron transfer to atomic or molecular ions, double ionization by electron transfer, electron detachment reactions with $He^{\bullet+}$ or $Ne^{\bullet+}$, and multiple ionization by multiple-electron transfer to multiply charged rare-gas cations. Also, experimental results are reviewed for single-electron transfer to $C_{60}^{\bullet+}$ and C_{60}^{2+}; a model previously proposed for the potential energy profile of single-electron transfer to C_{60}^{2+} is included which argues in favour of a reaction barrier arising from the Coulombic repulsion between the single charged product ions of such a process. Results of measurements previously reported for single and double-electron transfer reactions with $C_{60}^{\bullet 3+}$ are also summarized. The latter reactions are unprecedented in electron transfer research. Data for thermal electron transfer reactions with C_{60}^{n+} ($n \geqslant 4$) are not available, but results are indicated for electron transfer from Cs to C_{60}^{4+} at high collision energies. Intramolecular electron transfer is briefly discussed for exohedral and endohedral cation adducts of metal atoms and C_{60}, and of exohedral adducts of molecules and C_{60}^{2+}. Finally, the occurrence of electron transfer involving C_{60} anions is briefly considered.

1. Introduction

The transfer of an electron from one molecule to another is arguably the most fundamental process that occurs in chemistry. Our current understanding of the physico-chemical aspects of this process has come from studies of a large number and variety of inorganic and organic systems, both in the gas phase and in solution [1]. The recent birth of buckminsterfullerene, C_{60}, and related fullerene molecules [2] has added an important new dimension to electron-transfer research. This is a consequence of the remarkable stability of multiply-charged ions of C_{60} and related fullerenes: C_{60} has been shown to have at least 13 experimentally accessible charge states ranging from C_{60}^{6-} to C_{60}^{6+} [3]. Also, *ab initio* electronic-structure calculations have predicted that C_{60}^{10+}, C_{60}^{18+} and even C_{60}^{28+} are stable with respect to fragmentation! [4]. The availability of these singly and multiply-charged states for *one* molecular species, some in solution and some in the gas phase, is unprecedented in chemistry and extends considerably the scope of electron-transfer research. For example, reactions of type (1) can now be executed in the

$$C_{60}^{n+} + Y \rightarrow Y^{m+} + C_{60}^{(n-m)+} \qquad (1)$$

gas phase. Their experimental investigation should provide unique opportunities for the systematic exploration of physico-chemical aspects of single-electron and multiple-electron transfer as a function of the charge state of a *single* molecule, over

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a wide range in charge state. Furthermore, it should also soon become feasible to compare physico-chemical aspects of electron-transfer reactions of type (1) in the gas phase with those in solution!

Here I shall review *experimental* investigations of electron transfer involving C_{60} and its cations *in the gase phase* which have been reported since C_{60} first became available in macroscopic quantities in 1990 [2 (*b*)]. (Emphasis is given to processes occurring at thermal energies which is taken here to mean 298 K or room temperature.) Admittedly, this field is still young, but it will easily become apparent from this review that significant progress in revealing and understanding new physico-chemical aspects of electron transfer has already been made in the relatively short time since the discovery of C_{60}. Theory has lagged behind experiment in this field, but my hope is that this review will stimulate activity in theoretical aspects of electron-transfer reactions with fullerene molecules and cations.

The review begins with a brief survey of our current knowledge of the *adiabatic* ionization energies of C_{60}, since these provide a measure of the thermodynamics of electron-transfer reactions involving this molecule and its cations. Subsequently, experimental results are summarized which have revealed the occurrence of electron transfer from C_{60} to atomic and molecular cations. Included in this summary is a discussion of the ionization of C_{60} by metastable rare-gas atoms and the double ionization of C_{60} by unprecedented electron-transfer, electron-detachment reactions with rare-gas ions. The transfer of electrons from atoms and molecules to singly and multiply charged C_{60} cations is considered next. Reactions with $\mathrm{C}_{60}^{\bullet+}$, C_{60}^{2+}, $\mathrm{C}_{60}^{\bullet 3+}$ and C_{60}^{4+} will be discussed in turn. Special attention is given to the reactions with $\mathrm{C}_{60}^{\bullet 3+}$ which also give rise to double-electron transfer. The review concludes with a brief look at intramolecular electron transfer in derivatized C_{60} and multiply charged cations of C_{60}, and at electron-transfer reactions involving C_{60} anions.

2. Ionization energies of C_{60}

We need to be aware in a discussion of ionization energies of C_{60} that C_{60} has many isomers which may or may not have similar ionization energies (IE). The focus here is on the highly symmetrical and most stable I_h isomer of C_{60}. So far, the ionization energies of this spherical molecule and several of its cations, C_{60}^{n+}, have been explored experimentally for the charge states $n = 0$, 1 and 2.

Adiabatic ionization energies of large carbon clusters of the type C_n, including C_{60}, have been systematically investigated with Fourier-transform–ion-cyclotron resonance (FT-ICR) mass-spectrometric electron-transfer bracketing experiments [5]. The carbon-cluster ions were generated by the direct laser vaporization of graphite and allowed to thermalize before undergoing charge transfer. $IE_a(\mathrm{C}_{60})$ for C_{60} produced in this fashion was bracketed with two electron-transfer compounds to have a value of $7{\cdot}61 \pm 0{\cdot}11$ eV. The same value was obtained directly with free C_{60} as the parent molecule for $\mathrm{C}_{60}^{\bullet+}$ [6]. Accurate values for the vertical ionization energy of C_{60} have become available from gas-phase investigations with ultraviolet photoelectron spectroscopy ($IE(\mathrm{C}_{60}) = 7{\cdot}64 \pm 0{\cdot}02$ eV [7 (*a*)], slightly revised from a value of $7{\cdot}61 \pm 0{\cdot}02$ reported earlier [7 (*b*)]) and with vacuum ultraviolet (VUV) photoionization mass spectrometry of C_{60} ($7{\cdot}57 \pm 0{\cdot}01$ eV [8] and $7{\cdot}58(+0{\cdot}04, -0{\cdot}02)$ eV [9]). In one of these studies [9] the difference between the vertical and adiabatic ionization energies was estimated to be less than 0·2 eV, which is not surprising for a molecule of this size. A number of theoretical studies have predicted very similar ionization energies with values in the range from 7·5 to 7·9 eV [10].

The ionization energy $IE(C_{60}^{\cdot+}) = 11{\cdot}36 \pm 0{\cdot}05$ eV can be deduced from a measurement of the appearance energy of C_{60}^{2+}, $AE(C_{60}^{2+}) = 19{\cdot}00 \pm 0{\cdot}03$ eV, obtained with direct double ionization using synchrotron radiation [11], and from $I(C_{60}) = 7{\cdot}64 \pm 0{\cdot}02$ eV [7 (*a*)]. Other measurements involving charge-stripping of $C_{60}^{\cdot+}$ [12], VUV photoionization spectroscopy [7] and appearance-potential measurements [13] have led to similarly high values for $IE(C_{60}^{\cdot+})$. Electron-transfer bracketing measurements with C_{60}^{2+} cluster ions derived from graphite by laser evaporization have led to anomalously low values around 9·5 to 9·7 eV [6], but these have now been rationalized in terms of the presence of an activation energy arising from Coulomb repulsion between the two monocations produced in such reactions [14]. Previous theoretical studies have included a modified neglect of differential overlap (MNDO) calculation [15 (*a*)] yielding 13·1 eV, a local density approximation [10 (*e*)] giving 10·1 and 10·8 eV depending on the method used, and free-electron model calculations [15 (*b*)] resulting in a value of 11·2 eV. Recent *ab initio* SCF calculations for the process $C_{60}(I_h) \rightarrow C_{60}^{2+}(D_{5d})$ have yielded values of 18·9 and 19·6 eV for the adiabatic and vertical transitions respectively, which translate to adiabatic and vertical ionization energies for $C_{60}^{\cdot+}$ of 11·3 and 12·0 eV respectively [15 (*c*)].

Apparently, there have not yet been any measurements of the third ionization energy of C_{60}, $IE(C_{60}^{2+})$ by direct triple photoionization. Previously reported values of $IE(C_{60}^{2+})$ are $11{\cdot}2 \pm 0{\cdot}2$ eV obtained with FT-ICR electron-transfer bracketing measurements with ions derived from graphite [6] and $17{\cdot}0 \pm 0{\cdot}7$ eV obtained by stripping an electron from C_{60}^{2+} derived from C_{60} [12 (*a*)]. The discrepancy between these values is severe. However, the major portion of this discrepancy again can be resolved with a consideration of the Coulombic repulsion between the product ions of the electron-transfer reactions which are the basis of the bracketing method [17]. Selected-ion flow tube (SIFT) measurements of the kinetics of electron-transfer reactions to $C_{60}^{\cdot 3+}$ have provided a value of $15{\cdot}6 \pm 0{\cdot}5$ eV for $IE(C_{60}^{2+})$ when account is taken of the Coulombic repulsion [16]. A very recent electron-impact ionization study has provided a value for $IE(C_{60}^{2+})$ of $16{\cdot}6 \pm 1$ eV [16].

An extrapolated value has been reported for $IE(C_{60}^{\cdot 3+}) \sim 19{\cdot}5$ eV based on $IE(C_{60}) = 7{\cdot}61 \pm 0{\cdot}02$ eV, $IE(C_{60}^{\cdot+}) = 11{\cdot}39 \pm 0{\cdot}05$ eV and $IE(C_{60}^{2+}) = 15{\cdot}6 \pm 0{\cdot}5$ eV. This value is considerably below the value of 21·7 eV estimated by Walter *et al.* [18] using the same extrapolation technique but different values (those of Lifshitz *et al.* [12 (*a*)] for the second and third ionization energies.

3. Chemical ionization of C_{60}

So far, experimental studies of electron-transfer reactions with C_{60} have been focused primarily on reactions with atomic ions and metastable atoms. The energy-level diagram in figure 1 shows that single electron-transfer is energetically allowed with the rare-gas ions $He^{\cdot+}$, $Ne^{\cdot+}$ and $Ar^{\cdot+}$ as well as H^+ and $Si^{\cdot+}$. These five atomic ions, as well as many others having ionization energies above or slightly below that of C_{60}, have been reacted with C_{60}. Note that dissociative ionization leading to loss of C_2 is also exothermic for H^+ and the rare-gas ions, and that $He^{\cdot+}$ and $Ne^{\cdot+}$ have sufficiently high recombination energies to lead to the double ionization of C_{60}. The rare-gas metastable atoms included in figure 1 have a

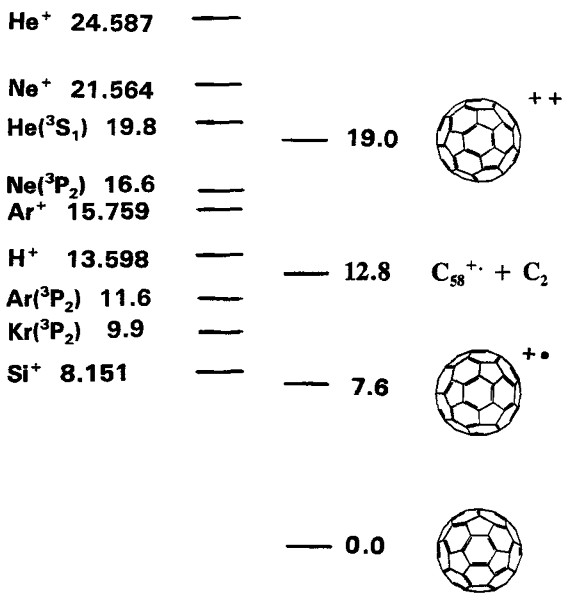


Figure 1. Energy-level diagram for various charge states of C_{60}, a selection of singly charged atomic ions, and several rare-gas metastable atoms.

sufficiently high energy to cause single ionization of C_{60} while metastable helium even may cause double ionization.

3.1. *Penning ionization*

Recent flow-tube studies have shown experimentally that C_{60} molecules may be ionized at thermal energies in chemical reactions with metastable rare-gas atoms in a

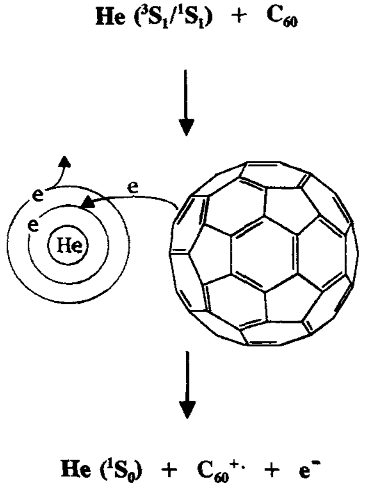


Figure 2. A possible mechanism for the Penning ionization of C_{60} by metastable helium atoms.

process commonly known as Penning ionization [19]. A possible mechanism for this process is shown schematically in figure 2 where it is seen to occur by the transfer of an electron from the C_{60} to the metastable noble-gas atom with the concomitant ejection of a second electron from the metastable atom. Penning ionization of C_{60} was observed with metastable rare-gas atoms of He, Ne, Ar and Kr, all of which have metastable levels which lie above the ionization energy of C_{60} (figure 1). The metastable atom energies are as follows: He* ($^1S_0$, $^3S_1$) = 20·6 and 19·8 eV, Ne* ($^3P_0$, $^3P_2$) = 16·7 and 16·6 eV, Ar* ($^3P_0$, $^3P_2$) = 11·7 and 11·6 eV, and Kr* ($^3P_0$, $^3P_2$) = 10·6 and 9·9 eV respectively [20]. Although rate coefficients were not measured, they can be expected to exceed $1 \times 10^{-10}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ in analogy with other Penning-ionization reactions [21]. However, the flow experiments showed no evidence for the occurrence of double ionization with He metastable atoms.

The Penning-ionization process $X^* + Y \rightarrow X + Y^+ + e^-$, where X^* is the metastable species, is generally understood in terms of the formation of an excited quasi-molecule $(XY)^*$ which undergoes autoionization to produce the final state $X + Y^+ + e^-$ [21]. The overall cross-section for Penning ionization is determined by the full interaction potential of the quasi-molecule and also the transition probability for autoionization. In principle, these can be calculated quantum mechanically, but this has not been done for the quasi-molecule $(XC_{60})^*$ where X is a noble-gas atom.

3.2. *Ionization by single-electron transfer*

Various experiments have shown that C_{60} may be chemically ionized at thermal and higher energies in single-electron transfer reactions with cations having an electron-recombination energy $(RE) \geqslant IE(C_{60})$. One of the earliest observations of electron transfer from C_{60} involved atomic metal ions reacting with C_{60} at near-thermal energies and low pressures [22]. The atomic metal ions $M^+(RE) = La^+$ (5·58 eV), Rh^+ (7·46 eV), Ni^+ (7·635 eV), Cu^+ (7·726 eV), Co^+ (7·86 eV) and Fe^+ (7·87 eV) were produced from pure metal targets by laser desorption in a Fourier-transform mass spectrometer and observed to react with C_{60} to form MC_{60}^+ by direct attachment and varying amounts of $C_{60}^{\cdot+}$ by electron transfer [22]. Rate coefficients and branching fractions for the electron-transfer channel were not reported, but Fe^+ was said to react with C_{60} predominantly by electron transfer.

Reactions of C_{60} with other atomic ions having higher RE values, D^+ (13·602 eV), $Si^{\cdot+}$ (8·151 eV) and the rare-gas ions $He^{\cdot+}$ (24·587 eV), $Ne^{\cdot+}$ (21·564 eV) and $Ar^{\cdot+}$ (15·760 eV) have been examined with selected-ion flow tube (SIFT) experiments in helium carrier gas at 0·35 Torr and 294 ± 2 K [23]. The C_{60} vapour was introduced directly into the flowing carrier gas by electrically heating the solid in a stainless steel tube to about 750 K. Once introduced, the C_{60} vapour experienced thermalizing collisions with the He buffer gas atoms. All five of these atomic ions were observed to extract an electron from C_{60} under these operating conditions, although rate coefficients were not measured. Adduct formation was preferred 2:1 over electron transfer in the reaction of C_{60} with $Si^{\cdot+}$ [23]. The $C_{60}^{\cdot+}$ dissociation energy for loss of C_2 has been estimated to be in the range from about 4·5 to 7·1 eV [24]. This makes dissociative electron transfer accompanied by the loss of C_2 exothermic for all three of the reactions with rare-gas cations, but this channel was not observed under SIFT conditions. The ability of the many degrees of freedom of $C_{60}^{\cdot+}$ to accommodate excess energy leads to a low dissociation rate (a long lifetime) for the intermediate excited $C_{60}^{\cdot+}$ and so to the predominance of collisional stabilization over dissociation under SIFT conditions.

Systematic octapole guided-ion beam mass-spectrometer experiments have been reported for the reactions of Ne^+, O^+, C^+, N^+, Li^+, Na^+, K^+, B^+, F^+ and Fe^+ in a range of collision energies from about 2 to 200 eV [25]. These experiments provide a measure of the onset energy for (endothermic) electron transfer, dissociative electron transfer, insertion and dissociative insertion as indicated by reactions (2)–(5) respectively.

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

$$X^+ + C_{60} \rightarrow C_{60-2n}^+ + C_{2n} + X, \tag{3}$$

$$X^+ + C_{60} \rightarrow X@C_{60}^+. \tag{4}$$

$$X^+ + C_{60} \rightarrow X@C_{60-2n}^+ + C_{2n}. \tag{5}$$

The collision-energy dependence measured for the reaction $Ne^+ + C_{60}$ is shown in figure 3. Note the onset of dissociative electron transfer, reaction (6*a*), at a collision energy of about 20 eV, and the onset of dissociative insertion of Ne into the initially empty C_{60} molecule, reaction (6*b*), at about 30 eV.

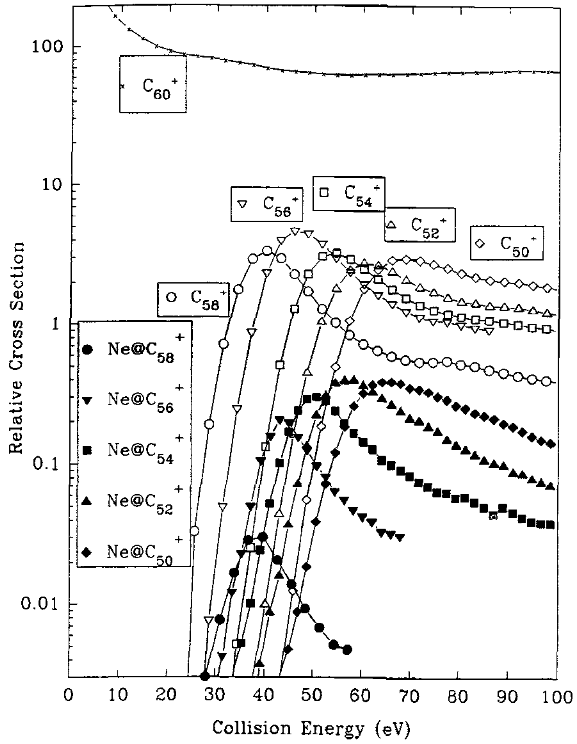


Figure 3. Collision-energy dependence for all significant product channels observed for the reaction of $Ne^{\cdot +}$ with C_{60} with an octapole guided-ion beam mass spectrometer [25 (*g*)].

$$\mathrm{Ne}^{\bullet +} + \mathrm{C}_{60} \rightarrow \mathrm{C}_{58}^{\bullet +} + \mathrm{C}_2 + \mathrm{Ne}, \tag{6a}$$

$$\mathrm{Ne}^{\bullet +} + \mathrm{C}_{60} \rightarrow \mathrm{Ne@C}_{58}^{\bullet +} + C_2. \tag{6b}$$

The apparent high-energy onset for dissociative electron transfer (which actually is exothermic by *ca.* 8·8 eV) at 20 eV is a consequence of the restricted (millisecond) time scale of the experiment and the long lifetime of the $C_{60}^{\bullet +}$ formed initially in the electron-transfer reaction. Production of C_{60}^{2+} and smaller dicationic fragments have also been noted for this reaction [25]. Numerical simulations of $He^{\bullet +}$ and Li^+ collisions with C_{60} at high energies have shown that the outcome of a particular collision at high collision energies depends strongly on the incident energy, the incident angle and the point of impact of the collision [26].

Studies of reactions of C_{60} with molecular ions have been less plentiful. A nearly resonant electron transfer has been reported between C_{60} and singly ionized corannulene, $C_{20}H_{10}^{\bullet +}$ [27]. Reaction (7)

$$\mathrm{C}_{20}\mathrm{H}_{10}^{\bullet +} + \mathrm{C}_{60} \rightarrow \mathrm{C}_{60}^{\bullet +} + \mathrm{C}_{20}\mathrm{H}_{10}, \tag{7}$$

has been observed in both directions in SIFT experiments at 294 ± 2 K and 0·35 ± 0·01 Torr (with adduct formation competing in both directions), but is preferred in the direction written. Clearly, this observation implies that the ionization energies of C_{60} and corannulene are nearly equal, with the latter being slightly higher: an ionization energy for corannulene of 7·7 ± 0·1 eV has been derived from these results [27].

Electron transfer between C_{60} and $C_2^{\bullet +}$ has been observed in the octapole guided-ion beam experiments at low collision energies. In this case adduct formation was again a predominant competing product channel and the exothermic elimination of C_4 from the intermediate adduct ion to produce $C_{58}^{\bullet +}$ was also reported [25 (*g*)].

3.3. *Double ionization of* C_{60} *by electron-transfer, electron-detachment reactions*

The reactions of $He^{\bullet +}$ and $Ne^{\bullet +}$ with C_{60} were observed in SIFT experiments to produce substantial amounts of C_{60}^{2+} in novel electron-transfer, electron-detachment reactions of type (8)

$$X^{\bullet +} + \mathrm{C}_{60} \rightarrow \mathrm{C}_{60}^{2+} + X + e^-, \tag{8}$$

proceeding at 294 ± 2 K in competition with single-electron transfer [23]. The product distributions recorded in these experiments for reactions of $He^{\bullet +}$, $Ne^{\bullet +}$ and $Ar^{\bullet +}$ with C_{60} are listed in table 1. The observations of dication formation in the reactions of $He^{\bullet +}$ and $Ne^{\bullet +}$, and its absence in the reaction of $Ar^{\bullet +}$, are in agreement with calculated exothermicities (ΔIEs) based on accepted values for the first and second ionization energies of C_{60} (table 1). The formation of C_{60}^{2+} in higher-energy collisions between $Ne^{\bullet +}$ and C_{60} has also been noted in an octapole guided-ion beam experiment [25 (*a*)].

The mechanism for the removal of two electrons from C_{60} in its reaction with $He^{\bullet +}$ or $Ne^{\bullet +}$ is not known, although several have been proposed [23]. In one proposed mechanism, the high exothermicity of the transfer of one electron from C_{60} to the rare-gas cation leaves the $C_{60}^{\bullet +}$ sufficiently electronically excited to autoionize. A more exotic mechanism which has been proposed involves an initial electron transfer to the approaching rare-gas cation to produce a metastable rare-gas

Table 1. Products and product distributions for the reactions of $He^{\bullet+}$, $Ne^{\bullet+}$ and $Ar^{\bullet+}$ with C_{60} at 294±2 K observed with the SIFT technique [23].

Reactant ion (*IE*/eV)	Products^a		$-\Delta IE^b$
$He^{\bullet+}$	$C_{60}^{\bullet+} + He$	[<0·90]	16·98
(24·587)	$C_{60}^{2+} + He + e$	[>0·10]	5·59
$Ne^{\bullet+}$	$C_{60}^{\bullet+} + Ne$	[<0·95]	13·95
(21·564)	$C_{60}^{2+} + Ne + e$	[>0·05]	2·56
$Ar^{\bullet+}$	$C_{60}^{\bullet+} + Ar$	[1·00]^c	8·15
(15·760)			

^{a}Product branching fractions are shown in parentheses. Only a lower limit could be assigned to the production of the dication because of the possibility of secondary single-electron transfer between C_{60}^{2+} and C_{60}.

^{b}Calculated using $IE(C_{60}) = 7{\cdot}64\,eV$ and $IE(C_{60}^{\bullet+}) = 11{\cdot}36\,eV$ [7 (*a*), 11].

^{c}Production of C_{60}^{2+} is calculated to be 3·24 eV endothermic for this reaction.

atom which then Penning ionizes the $C_{60}^{\bullet+}$ at smaller separations as illustrated in the reaction sequence (9),

$$He^{\bullet+} + C_{60} \rightarrow [He^{\bullet+} \cdots C_{60} \rightleftharpoons He^{*} \cdots C_{60}^{\bullet+} \rightleftharpoons He \cdots C_{60}^{2+} \cdots e] \rightarrow He + C_{60}^{2+} + e^{-}. \qquad (9)$$

The production of metastable (2^3S) He* and $C_{60}^{\bullet+}$ at infinite separation is endothermic by 2·8 eV and so this mechanism requires a very high $He^{*}/C_{60}^{\bullet+}$ interaction energy if it is to be energetically favourable. A similar situation holds for production of electronically excited Ne* and $C_{60}^{\bullet+}$ as a prerequisite to formation of C_{60}^{2+} in the reaction $Ne^{\bullet+} + C_{60}$ proceeding via this mechanism.

An interesting alternative mechanism for dication formation which has been proposed [28] views C_{60} with its 240 valence electrons (only 10 of which are in the highest occupied molecular orbital (HOMO)) to have metalloid character. An Auger emission mechanism has long been invoked to account for the ejection of electrons from metals by slow rare-gas ions [28]. With C_{60} this mechanism would involve the initial transfer of a deeply embedded electron followed by the Auger emission of an electron [29].

Production of a dication from a monocation by electron-transfer, electron detachment at thermal energies is unprecedented in the literature and may represent an important new class of electron-transfer reaction. It has been proposed that this process ought to occur whenever the recombination energy of the reactant ion exceeds the sum of the first two ionization energies of the neutral reactant, especially in the absence of competition with dissociative electron transfer [23]. It is likely that fullerenes represent a very favourable case for the occurrence of electron-transfer, electron-detachment reactions due to the low second-ionization energies and the exceptionally durable molecular structures of such species, although it should be noted that such a process has also recently been observed for the reactions of $He^{\bullet+}$ and $Ne^{\bullet+}$ with naphthalene [30].

3.4. *Multiple ionization of C_{60} by multiple electron transfer with multiply-charged cations*

C_{60} has recently been exposed to collisions with the multiply charged rare-gas cations Ar^{8+} and Xe^{14+} at energies of 10 keV q^{-1} [31]. For the collisions with Ar^{8+}

stable C_{60} cations were observed to be produced in charge states up to +6 corresponding to the transfer of six electrons to the projectile ion. The physical process involved in these collisions has been presumed to be similar to that described by the classical barrier model for the capture of electrons from atomic targets [32]. In such capture highly multiply-excited states are presumed to be populated which autoionize so that the projectile seldom retains more than two electrons, independent of how many it initially removes from the target.

4. Electron-transfer reactions with $C_{60}^{\bullet +}$

Several experiments have shown that $C_{60}^{\bullet +}$ removes an electron at thermal or near-thermal energies from those molecules which have an ionization energy below the recombination energy of $C_{60}^{\bullet +}$. For example, FT-ICR mass-spectrometer experiments, with the C_{60}^{+} cluster ions being produced either from the laser vaporization of graphite [5] or from electron ionization of bulk C_{60} vapour and allowed to undergo radiative and collisional relaxation prior to electron-transfer, have shown this to be the case with molecules with ionization energies in the range from 6·20 to 8·04 eV [6]. The molecule with the highest *IE* for which electron transfer was observed was *m*-toluidine (*IE* = 7·50 eV). Combined with the non-observation of electron transfer with aniline (*IE* = 7·72 eV), this result provided a bracketed ionization energy for C_{60} of 7·61 ± 0·11 eV, in agreement with the accepted value. Absolute rate coefficients were not determined, but the majority of the electron-transfer reactions which were observed were estimated to occur at near, or slightly slower than, the Langevin orbiting collision limit. The metallocenes nickelocene (*IE* = 6·20 eV), ferrocene (*IE* = 6·75 eV) and methylferrocene (IE = 6·45 eV) reacted somewhat slower and this has been tentatively attributed to poor electron orbital overlap in the corresponding ion/molecule pair [6].

The fullerene ion/fullerene molecule electron-transfer reaction (10) has been investigated in both

$$C_{60}^{\bullet +} + C_{70} \rightarrow C_{60} + C_{70}^{\bullet +}, \qquad (10)$$

directions and was observed to be faster in the direction as written. This latter result is consistent with the *IE*s of C_{60} and C_{70} being nearly the same, and *IE*(C_{60}) bieng slightly higher than *IE*(C_{70}) [6].

5. Electron-transfer reactions with C_{60}^{2+}

Rate coefficients measured with the SIFT technique have been reported [15, 33] for electron-transfer reactions at 294 ± 2 K between C_{60}^{2+} and a large number and variety of neutral molecules, viz. reactions of type (11). Figure 4 shows data for the reaction of C_{60}^{2+} with 2-pentanone in which adduct formation

$$C_{60}^{2+} + X \rightarrow C_{60}^{\bullet +} + X^{\bullet +}, \qquad (11)$$

effectively competes with electron transfer. SIFT results are summarized in table 2 for reactions of C_{60}^{2+} with neutral molecules having ionization energies in the range 9·0 to 13·0 eV. Recall that *IE*($C_{60}^{\bullet +}$) = 11·36 ± 0·05 eV so that single-electron transfer is energetically allowed for molecules having ionization energies less than this value.

The SIFT results in table 2 clearly show that electron transfer was not observed for molecules with *IE* ⩾ 9·58 eV. This is in keeping with FT-ICR results [5] which have indicated an ionization energy threshold of 9·48 eV. In the FT-ICR experiments electron transfer to C_{60}^{2+} was observed with *m*-nitrotoluene (*IE* = 9·48 eV) and seven

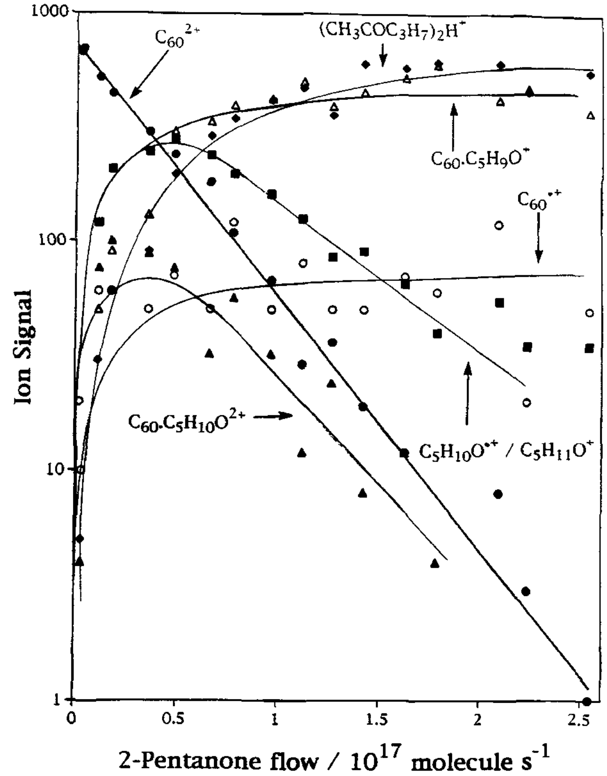


Figure 4. Experimental data for the reaction of C_{60}^{2+} with 2-pentanone, $CH_3COCH_2CH_2CH_3$, at 294±2 K and 0·348±0·001 Torr of helium. Addition (90%) is the dominant primary product channel and occurs in competition with electron transfer (10%). The dominant secondary reaction of the adduct $C_{60}.C_5H_{10}O^{2+}$ is proton transfer: the deprotonated adduct $C_{60}.C_5H_9O^+$ does not display further reaction. Protonated 2-pentanone also undergoes a subsequent reaction to form the proton-bound dimer of 2-pentanone. The data shown was obtained using the downstream quadrupole mass spectrometer (QMS) in the high-mass mode (0–1000 a.m.u.): in this mode, *m*/*z* 86 ($C_5H_{10}O^+$) and *m*/*z* 87 ($C_5H_{11}O^+$), both formed as reaction products, could not be resolved and are shown here as a composite signal (filled squares). With the QMS in the low-mass mode (0–200 a.m.u.), these signals could be satisfactorily resolved but the mass range of this mode was insufficient to allow detection of the fullerene reactant or product ions involved [33 (*b*)].

other molecules having lower ionization energies (*p*-nitrotoluene, benzene, fluorobenzene, *m*-dichlorobenzene, 1,2,4-trichlorobenzene, *p*-dichlorobenzene and toluene). Electron transfer was not observed with hexafluorobenzene ($IE = 9{\cdot}91$ eV) or xenon ($IE = 12{\cdot}13$ eV). The definition of the onset for electron transfer under SIFT conditions can be more complicated if adduct formation is sufficiently efficient to render electron transfer unobservable.

The absence of electron transfer to C_{60}^{2+} from molecules having ionization energies in the range from 9·58 to 11·36 eV, still below the ionization energy of $C_{60}^{\bullet+}$, has been accounted for with a model in which a reaction barrier arises from the Coulombic repulsion between the singly charged product ions of such an electron-transfer process [14]. Figure 5, in a schematic fashion, illustrates the expected

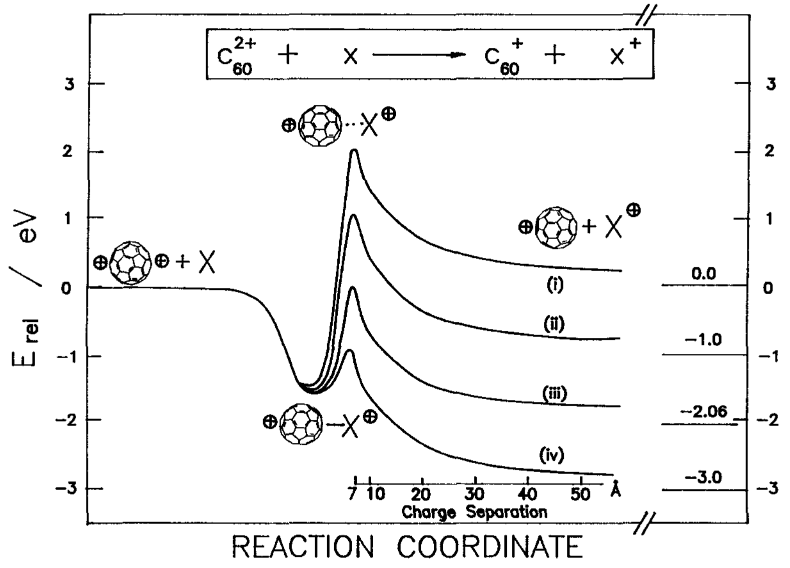


Figure 5. A schematic diagram of the potential energy surface for electron transfer from the dication C_{60}^{2+} to a neutral X. E_{rel} is the potential energy relative to the standard enthalpies of formation of the reactants at infinite separation. The diagram assumes that electron transfer occurs at the point of closest approach, and that the binding energy of the products is negligible in comparison to the electrostatic repulsion between them. The Coulomb repulsion term $q\phi_r$ is set at 2·07 eV, corresponding to an intercharge separation, at the point of electron transfer, of 7·0 Å. The curves shown are for the cases: (i), $IE(X)=IE(C_{60}^{\cdot+})$; (ii), $IE(X)=IE(C_{60}^{\cdot+})-1{\cdot}0\,\mathrm{eV}$; (iii), $IE(X)=IE(C_{60}^{\cdot+})-q\phi_r$; (iv), $IE(X)=IE(C_{60}^{\cdot+})-3{\cdot}0\,\mathrm{eV}$ [14].

potential energy curve for electron transfer from a neutral molecule X to C_{60}^{2+}. The Coulombic repulsion between the two monocations produced by such a reaction can constitute a barrier to the reaction unless the reaction is substantially exothermic, or unless the two monocations are produced at a sufficiently large separation that electrostatic repulsion is negligible. A substantially similar model has been used to account for the observed kinetics of charge-transfer and hydride-abstraction reactions involving alkaline-earth [34] and transition-metal containing [35] dications. The model for reactions of C_{60}^{2+} assumes that electron transfer is most likely to occur when the reactants are in close proximity and one of the charges has been localized by the electrostatic interaction between the reactants with the other charge diametrically opposed on the C_{60} surface. In general, the requirement for electron transfer from a dication to a neutral molecule, producing two monocations initially in close proximity, is that the reaction exothermicity must exceed $q\phi_r$, the electrostatic potential which denotes the Coulombic repulsion between the monocations at the moment of electron transfer. The Coulombic repulsion depends upon the distance separating the two charges. If it is assumed that the charge separation r at the moment of electron transfer is equal to or greater than the diameter of the fullerene cage ($d(C_{60}) \sim 7{\cdot}0$ Å) [22], then $q\phi_r < 2{\cdot}06\,\mathrm{eV}$. This assumption seems warranted—while the structure of C_{60}^{2+} has not been determined rigorously, the most likely model for such a structure involves two delocalized positive charges which are constrained by Coulombic repulsion to remain more-or-less opposite each other.

Table 2. Rate coefficients and product distributions for reactions of C_{60}^{2+} with molecules having ionization energies $9{\cdot}0\,\mathrm{eV} < IE(M) < 13{\cdot}0\,\mathrm{eV}$ measured with the SIFT technique [14, 33]

Reactants	Products[a]	k_{obs}[b]	k_c[c]	$IE(X)$[d]
$C_{60}^{2+} + N_2O$	none	<0·001	1·30	12·886
$C_{60}^{2+} + H_2O$	none	<0·01	3·36	12·612
$C_{60}^{2+} + CH_4$	none	<0·001	1·91	12·51
$C_{60}^{2+} + O_2$	none	<0·001	1·06	12·071
$C_{60}^{2+} + C_2H_6$	none	<0·001	1·84	11·52
$C_{60}^{2+} + C_2H_2$	$C_{60}{\cdot}C_2H_2^{2+}$	<0·001	1·78	11·400
$C_{60}^{2+} + HCOOH$	$C_{60}{\cdot}CH_2O_2^{2+}$	0·015	2·23	11·33
$C_{60}^{2+} + COS$	none	<0·001	1·74	11·1736
$C_{60}^{2+} + H_2CO$	none	<0·001	3·37	10·874
$C_{60}^{2+} + CH_3OH$	$C_{60}{\cdot}CH_3OH^{2+}$	0·007	2·92	10·85
$C_{60}^{2+} + HCOOCH_3$	$C_{60}{\cdot}C_2H_4O_2^{2+}$	0·011	2·43	10·815
$C_{60}^{2+} + CH_3COOH$	$C_{60}{\cdot}C_2H_4O_2^{2+}$	0·40	2·42	10·66
$C_{60}^{2+} + C_2H_4$	$C_{60}{\cdot}C_2H_4^{2+}$	<0·001	1·86	10·507
$C_{60}^{2+} + C_2H_5OH$	$C_{60}{\cdot}C_2H_5OH^{2+}$ [0·9] $C_{60}OH^+ + C_2H_5^+$ [0·1]	0·037	2·77	10·47
$C_{60}^{2+} + CH_3CCH$	$C_{60}{\cdot}C_3H_4^{2+}$	0·5	2·27	10·36
$C_{60}^{2+} + CH_3COOCH_3$	$C_{60}{\cdot}C_3H_6O_2^{2+}$	0·016	2·33	10·27
$C_{60}^{2+} + CH_3CHO$	none	<0·001	3·40	10·229
$C_{60}^{2+} + n\text{-}C_3H_7OH$	$C_{60}{\cdot}C_3H_7OH^{2+}$ [0·6] $C_{60}OH^+ + C_3H_7^+$ [0·4]	0·10	2·52	10·22
$C_{60}^{2+} + CH_3COCCH$	$C_{60}{\cdot}C_4H_4O^{2+}$	0·13	2·89	10·17
$C_{60}^{2+} + NH_3$	$C_{60}{\cdot}NH_3^{2+}$	1·2	3·37	10·16
$C_{60}^{2+} + i\text{-}C_3H_7OH$	$C_{60}OH^+ + C_3H_7^+$	0·23	2·56	10·12
$C_{60}^{2+} + CH_3OCH_3$	$C_{60}{\cdot}C_2H_6O^{2+}$	0·003	2·46	10·025
$C_{60}^{2+} + C_2H_5CHO$	$C_{60}{\cdot}C_2H_5CHO^{2+}$	0·06	3·15	9·953
$C_{60}^{2+} + NO_2^{\bullet}$	none	<0·01	1·35	9·75
$C_{60}^{2+} + CH_3CHCH_2$	$C_{60}{\cdot}C_3H_6^{2+}$	0·6	1·98	9·73
$C_{60}^{2+} + CH_3COCH_3$	$C_{60}{\cdot}C_3H_6O^{2+}$	0·27	3·42	9·705
$C_{60}^{2+} + CH_2CCH_2$	$C_{60}{\cdot}C_3H_4^{2+}$	0·08	1·85	9·69
$C_{60}^{2+} + 1\text{-}C_4H_8$	$C_{60}{\cdot}C_4H_8^{2+}$	2·2	1·94	9·58
$C_{60}^{2+} + CH_3COC_2H_5$	$C_{60}{\cdot}C_4H_8O^{2+}$	1·2	3·06	9·51
$C_{60}^{2+} + (CH_3CH_2)_2O$	$C_{60}{\cdot}C_4H_{10}O^{2+}$ [0·1] $C_{60}^{\bullet+} + (C_2H_5)_2O^{\bullet+}$ [0·9]	0·91	2·30	9·51
$C_{60}^{2+} + c\text{-}C_4H_8O$	$C_{60}{\cdot}C_4H_8O^{2+}$ [0·6] $C_{60}^{\bullet+} + c\text{-}C_4H_8O^{\bullet+}$ [0·4]	1·9	2·50	9·41
$C_{60}^{2+} + CH_3COC_3H_7$	$C_{60}{\cdot}C_5H_{10}O^{2+}$ [0·9] $C_{60}^{\bullet+} + CH_3COC_3H_7^{\bullet+}$ [0·1]	1·8	2·99	9·38
$C_{60}^{2+} + C_2H_5COC_2H_5$	$C_{60}{\cdot}C_5H_{10}O^{2+}$ [0·75] $C_{60}^{\bullet+} + C_2H_5COC_2H_5^{\bullet+}$ [0·25]	1·9	2·99	9·31
$C_{60}^{2+} + NO^{\bullet}$	$C_{60}^{\bullet+} + NO^+$	0·02	1·18	9·26436
$C_{60}^{2+} + c\text{-}C_5H_8O$	$C_{60}{\cdot}C_5H_8O^{2+}$ [0·3] $C_{60}^{\bullet+} + c\text{-}C_5H_8O^{\bullet+}$ [0·7]	2·8	3·31	9·25
$C_{60}^{2+} + C_6H_6$	$C_{60}^{\bullet+} + C_6H_6^{\bullet+}$	2·3	1·81	9·2459
$C_{60}^{2+} + (CH_3)_2CCH_2$	$C_{60}{\cdot}C_4H_8^{2+}$ [0·9] $C_{60}^{\bullet+} + C_4H_8^{\bullet+}$ [0·1]	2·4	2·03	9·239
$C_{60}^{2+} + (Z)\text{-}2\text{-}C_4H_8$	$C_{60}{\cdot}C_4H_8^{2+}$ [0·2] $C_{60}^{\bullet+} + C_4H_8^{\bullet+}$ [0·8]	3·4	1·96	9·108
$C_{60}^{2+} + CH_2CHCHCH_2$	$C_{60}{\cdot}C_4H_6^{2+}$ [0·8] $C_{60}^{\bullet+} + C_4H_6^{\bullet+}$ [0·2]	1·0	1·94	9·07[e]

It should be noted for the reactions in table 2 that the calculated average dipole orientation (ADO) collision rate coefficient (the calculation of which assumes a relatively close interaction) appears to serve as a good upper limit to the observed reaction rates for electron transfer. Note also from the results in table 2 that adduct formation is a reasonably efficient competing channel in the electron-transfer reactions observed under SIFT conditions. This observation is consistent with a model for electron transfer in which a potential well precedes the transition state for electron transfer. The existence of such a potential well would favour the occurrence of addition, especially in so far as it presents an opportunity for Coulombic relaxation by partial charge delocalization—that is, to reduce the repulsive force between the positive charges by increasing the charge separation in the adduct [36].

Results of SIFT experiments for reactions of C_{60}^{2+} with the aromatic molecules benzene, naphthalene, anthracene and corannulene, and the fullerene molecules C_{60} and C_{70} at 294 ± 2 K in helium gas at 0·35 to 0·40 Torr have shown that electron transfer is the only channel for these reactions [27, 37]. No evidence ($<1\%$) was obtained for the occurrence of adduct formation. This rules out the ability of doubly-charged fullerene molecules to act as nuclei for the condensation of aromatic molecules and the intriguing formation of doubly charged strings of beads of C_{60} by successive additions of C_{60} molecules under these operating conditions [37].

The product ions in reaction (12) are isobaric so that the two competing channels

$$C_{60}^{++} + C_{60} \rightarrow (C_{60})_2^{++}, \qquad (12a)$$

$$\rightarrow C_{60}^{\cdot +} + C_{60}^{\cdot +}, \qquad (12b)$$

could not be distinguished mass spectrometrically. This problem is absent in reactions (13) and (14).

$$C_{70}^{++} + C_{60} \rightarrow (C_{70}C_{60})^{++}, \qquad (13a)$$

$$\rightarrow C_{60}^{\cdot +} + C_{60}^{\cdot +}, \qquad (13b)$$

$$C_{60}^{++} + C_{70} \rightarrow (C_{60}C_{70})^{++}, \qquad (14a)$$

$$\rightarrow C_{60}^{\cdot +} + C_{70}^{\cdot +}. \qquad (14b)$$

---

[a] Where more than one product channel was detected, product branching fractions are reported in brackets.

[b] k_{obs} is the observed reaction rate coefficient, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}, at 294 ± 2 K and a helium pressure in the range from 0·35 to $0{\cdot}40 \pm 0{\cdot}01$ Torr. The uncertainty is estimated to be less than $\pm 40\%$.

[c] k_c is the calculated ADO collision rate coefficient, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}, calculated according to the method of Su, T., and Bowers, M. T., 1973, *Int. J. Mass Spectrom. Ion Phys.*, **12**, 247.

[d] $IE(X)$ is the ionization energy, in eV, of the neutral in question, as listed in the tabulation of Lias *et al.* [40(*a*)].

[e] $IE(CH_2CHCHCH_2)$ obtained from the C.R.C. *Handbook of Chemistry and Physics*, 1987, 67th edn, edited by R. C. Weast (Boca Raton: CRC), p. E-83.

The SIFT experiments showed no production ($\leqslant 10\%$) of an ion at *m/z* 780, C_{130}^{++}, when either C_{70}^{++} or C_{60}^{++} was selected in the SIFT source upstream of the reaction region[37]. This means that adducts formed in reactions (13) and (14) were not effectively stabilized in the helium carrier gas.

6. Electron-transfer reactions with $C_{60}^{\bullet 3+}$

6.1. *Single-electron transfer*

Single-electron transfer reactions with $C_{60}^{\bullet 3+}$ have been investigated qualitatively with FT-ICR mass spectrometry[6(*a*)] and quantitatively with the SIFT technique[16, 33]. The results of the FT-ICR study are summarized in table 3. It is interesting to note from these results that the threshold for electron transfer is at a rather low *IE* of 11·02 eV even though electron transfer is exothermic with molecules having an *IE* as high as 15·6±0·5 eV (=*IE*(C_{60}^{2+})).

Similar results have been obtained with the SIFT technique which are summarized in table 4. There is general agreement with the FT-ICR results for common molecules. Differences include the SIFT observation of a minor channel (10%) leading to electron transfer in the reaction with C_3H_8, and the failure to detect an O^- transfer reaction with CH_3NO_2. The latter difference has been ascribed to possible differences in the degree of collisional stabilization of $C_{60}^{\bullet 3+}$ prior to reaction in the two techniques[33]. It is evident from figure 6, which shows SIFT results for the reaction of $C_{60}^{\bullet 3+}$ with CH_3NO_2, and the SIFT results shown in table 4, that several product channels, such as hydride transfer, for example, and addition, can compete with electron transfer to $C_{60}^{\bullet 3+}$. With regard to the onset of electron transfer in the SIFT experiments, the results in table 4 indicate that rapid electron transfer occurs with molecules having $IE \leqslant 11{\cdot}2$ eV. Electron transfer with OCS ($IE = 11{\cdot}1736$ eV) is inefficient, and no electron transfer is seen with C_2H_2 ($IE = 11{\cdot}40$ eV) or with neutrals having a higher ionization energy. It is interesting to note that the reactions with HCOOH ($IE = 11{\cdot}33$ eV) and CH_3Cl ($IE = 11{\cdot}22$ eV) prefer hydride transfer.

Thus, both the FT-ICR and SIFT results indicate that the ionization-energy threshold for the occurrence of electron transfer to $C_{60}^{\bullet 3+}$ lies well below the thermodynamic threshold, by about $15{\cdot}6 - 11{\cdot}2 \approx 4{\cdot}4$ eV. Note that this is higher than the analogous difference observed for C_{60}^{2+} reactions. Again, the explanation

Table 3. Results of FT-ICR mass-spectrometer experiments for reactions of $C_{60}^{\bullet 3+}$ with various molecules[6(*a*)].

X	Observed reaction	*IE*(*X*)
Xe	none	12·13
C_2H_6	H^- abstraction	11·52
C_2H_2	adduct formation	11·40
CH_3NO_2	charge transfer O^- abstraction	11·02
C_3H_8	H^- abstraction	10·95
CH_3OH	charge transfer	10·85
C_2H_4	charge transfer	10·51
C_6F_6	charge transfer	9·91
C_6H_6	charge transfer	9·25

Table 4. Rate coefficients and product distributions for reactions of $C_{60}^{\cdot 3+}$ with various molecules having ionization energies 12·6 eV > $IE(M)$ > 9·26 eV measured with the SIFT technique [16, 33].

Reactants	Products[a]	k_{obs}[b]	k_c[c]	$IE(X)$[d]
$C_{60}^{\cdot 3+}+H_2O$	$C_{60}H^{\cdot 2+}+OH^+$	0·20	4·54	12·612
$C_{60}^{\cdot 3+}+O_2$	none	<0·001	1·59	12·071
$C_{60}^{\cdot 3+}+C_2H_6$	none	<0·005	2·76	11·52
$C_{60}^{\cdot 3+}+Cl_2$	$C_{60}Cl^{\cdot 2+}+Cl^+$	obs[e]	1·89	11·480
$C_{60}^{\cdot 3+}+C_2H_2$	$C_{60}.C_2H_2^{\cdot 3+}$	0·15	2·67	11·400
$C_{60}^{\cdot 3+}+HCOOH$	$C_{60}H^{\cdot 2+}+CO_2H^+$ [0·5]	2·5	3·34	11·33
$C_{60}^{\cdot 3+}+CH_3Cl$	$C_{60}H^{\cdot 2+}+CH_2Cl^+$	obs[e]	3·95	11·22
$C_{60}^{\cdot 3+}+COS$	$C_{60}^{2+}+COS^{\cdot +}$	0·048	2·61	11·1736
$C_{60}^{\cdot 3+}+CH_3NO_2$	$C_{60}.CH_3NO_2^{\cdot 3+}$ [0·9]	5·0	5·60	11·02
	$C_{60}^{2+}+CH_3NO_2^{\cdot +}$ [0·1]			
$C_{60}^{\cdot 3+}+C_3H_8$	$C_{60}H^{\cdot 2+}+C_3H_7^+$ [0·9]	4·2	2·84	10·95
	$C_{60}^{2+}+C_3H_8^{\cdot +}$ [0·1]			10·874
$C_{60}^{\cdot 3+}+H_2CO$	$C_{60}^{2+}+H_2CO^{\cdot +}$	1·8	5·06	10·85
$C_{60}^{\cdot 3+}+CH_3OH$	$C_{60}^{2+}+CH_3OH^{\cdot +}$ [0·8]	2·5	4·38	
	$C_{60}.CH_3OH^{\cdot 3+}$ [0·2]			10·815
$C_{60}^{\cdot 3+}+HCOOCH_3$	$C_{60}.C_2H_4O_2^{\cdot 3+}$	2·9	3·65	10·66
$C_{60}^{\cdot 3+}+CH_3COOH$	$C_{60}.C_2H_4O_2^{\cdot 3+}$	4·2	3·63	10·47
$C_{60}^{\cdot 3+}+CH_3CH_2OH$	$C_{60}OH^{\cdot 2+}+C_2H_5^+$ [0·7]	2·4	4·16	
	$C_{60}^{2+}+C_2H_5OH^{\cdot +}$ [0·2]			
	$C_{60}.C_2H_5OH^{\cdot 3+}$ [0·1]			
$C_{60}^{\cdot 3+}+H_2S$	$C_{60}H^{\cdot 2+}+HS^+$ [>0·5]	3·5	3·39	10·453
	$C_{60}^{2+}+H_2S^{\cdot +}$ [<0·5]			
$C_{60}^{\cdot 3+}+CH_3COOCH_3$	$C_{60}^{2+}+CH_3COOCH_3^{\cdot +}$ [0·1]	3·4	3·50	10·27
	$C_{60}.C_3H_6O_2^{\cdot 3\bullet}$ [0·9]			
$C_{60}^{\cdot 3+}+CH_3CHO$	$C_{60}^{2+}+CH_3CHO^{\cdot +}$	3·7	5·10	10·229
$C_{60}^{\cdot 3+}+CH_3CH_2CH_2CH_2OH$	$C_{60}^{2+}C_3H_7OH^{\cdot +}$ [0·5]	3·9	3·78	10·22
	$C_{60}.OH^{\cdot 2+}+C_3H_7^+$ [0·4]			
	$C_{60}.C_3H_7OH^{\cdot 3+}$ [0·1]			
$C_{60}^{\cdot 3+}+CH_3COCCH$	$C_{60}^{2+}+CH_3COCCH^{\cdot +}$ [0·8]	4·5	4·33	10·17
	$C_{60}.C_4H_4O^{\cdot 3+}$ [0·2]			
$C_{60}^{\cdot 3+}+(CH_3)_2CHOH$	$C_{60}OH^{\cdot 2+}+C_3H_7^+$ [0·7]	4·1	3·84	10·12
	$C_{60}^{2+}+C_3H_7OH^{\cdot +}$ [0·3]			
$C_{60}^{\cdot 3+}+CH_3OCH_3$	$C_{60}^{2+}+CH_3OCH_3^{\cdot +}$	3·0	3·69	10·025
$C_{60}^{\cdot 3+}+C_2H_5CHO$	$C_{60}^{2+}+C_2H_5CHO^{\cdot +}$ [0·75]	4·2	4·72	9·953
	$C_{60}.C_3H_6O^{\cdot 3+}$ [0·25]			
$C_{60}^{\cdot 3+}+CH_3COCH_3$	$C_{60}^{2+}+CH_3COCH_3^{\cdot +}$	5·8	5·13	9·705
$C_{60}^{\cdot 3+}+CH_3COC_2H_5$	$C_{60}^{2+}+CH_3COC_2H_5^{\cdot +}$	5·6	4·59	9·51
$C_{60}^{\cdot 3+}+(CH_3CH_2)_2O$	$C_{60}^{2+}+(CH_3CH_2)_2O^{\cdot +}$	3·3	3·45	9·51
$C_{60}^{\cdot 3+}+c\text{-}C_4H_8O$	$C_{60}^{2+}+c\text{-}C_4H_8O^{\cdot +}$	3·3	3·76	9·41
$C_{60}^{\cdot 3+}+CH_3COC_3H_7$	$C_{60}^{2+}+CH_3COC_3H_7^{\cdot +}$	4·8	4·48	9·38
$C_{60}^{\cdot 3+}+C_2G_5COC_2H_5$	$C_{60}^{2+}+C_2H_5COC_2H_5^{\cdot +}$	5·5	4·48	9·31
$C_{60}^{\cdot 3+}+NO^{\cdot}$	$C_{60}^{2+}+NO^+$	1·1	1·67	9·264
$C_{60}^{\cdot 3+}+c\text{-}C_5H_8O$	$C_{60}^{2+}+c\text{-}C_5H_8O^{\cdot +}$	4·3	4·96	9·25

[a] Where more than one product channel was detected, product branching fractions are reported in brackets.

[b] k_{obs} is the observed reaction rate coefficient, in units of $10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$, at 294 ± 2 K and a helium pressure in the range from 0·35 to 0·40 ± 0·01 Torr. The uncertainty is estimated to be less than ±40%.

[c] k_c is the calculated ADO collision rate coefficient, in units of $10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$, calculated according to the method of Su, T., and Bowers, M. T., 1973, *Int. J. Mass Spectrom. Ion Phys.*, **12**, 247.

[d] $IE(X)$ is the ionization energy, in eV, of the neutral in question, as listed in the tabulation of Lias *et al.* [40(*a*)].

[e] Reaction was observed as shown, but a rate coefficient was not determined. The reaction appeared to be efficient ($k > 10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$).

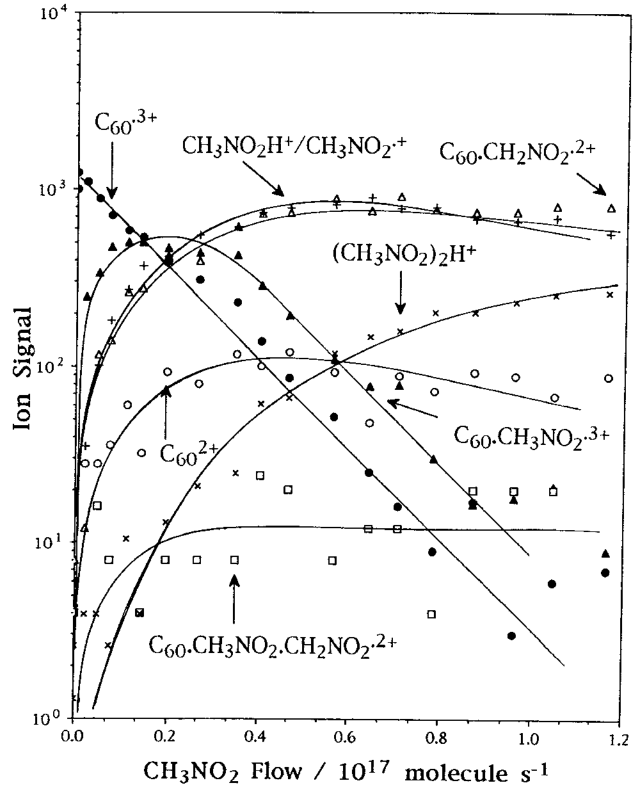


Figure 6. Experimentally observed data for the reaction of $C_{60}^{\cdot 3+}$ with CH_3NO_2 using the SIFT apparatus with helium buffer gas: $P = 0{\cdot}354$ Torr, He flow velocity $= 6{\cdot}2 \times 10^3$ cm s^{-1}, reaction length = 46 cm and $T = 294$ K. Primary product channels seen are electron transfer (10%) and adduct formation (90%), with several secondary processes also in evidence. The adduct $C_{60}.CH_3NO_2^{\cdot 3+}$ is seen to proton transfer rapidly to CH_3NO_2: some secondary adduct formation evidently occurs also (although this adduct $C_{60}.(CH_3NO_2)_2^{\cdot 3+}$ was not directly observable), since the deprotonated secondary adduct $C_{60}.CH_3NO_2.CH_2NO_2^{\cdot 2+}$ was detected. Protonated nitromethane, $CH_3NO_2H^+$, was observed to form the proton-bound dimer $(CH_3NO_2)_2H^+$. Data was collected in the high-mass mode of the downstream quadrupole mass spectrometer which did not permit resolution of the signals at *m*/*z* 61 ($CH_3NO_2^{\cdot +}$), from charge transfer) and *m*/*z* 62 ($CH_3NO_2H^+$) and so the signal ascribed to $CH_3NO_2H^+$ also contains some component from *m*/*z* 61; in further experiments performed in the low-mass mode, *m*/*z* 61 and 62 were well resolved [16].

lies in the effect of Coulombic repulsion since the products of single-electron transfer are both charged, in this case one singly and one doubly, and initially in close proximity to each other. The threshold for production of such an ion pair will be substantially above the threshold for production of the ions at infinite separation and so give rise to an activation energy. A barrier of $4{\cdot}5 \pm 0{\cdot}4$ eV has been estimated from a geometric model for the charge distribution in $C_{60}^{\cdot 3+}$ and the effects of Coulomb repulsion between the charged products [38].

6.2. *Double-electron transfer*

An unprecedented double-electron transfer reaction has been observed between triply charged buckminsterfullerene, $C_{60}^{\bullet 3+}$, and the polycyclic aromatic hydrocarbon (PAH) molecules anthracene, corannulene, benzo[rst]pentaphene and pyrene at room temperature. The measurements were made with a SIFT apparatus at 294±2 K in helium at 0·35±0·01 Torr [39]. The results of these measurements suggest that $C_{60}^{\bullet 3+}$ reacts at close to the collision rate with all four of the PAH molecules investigated. With anthracene, corannulene and pyrene, double-electron transfer was observed as a minor channel (<5%): single-electron transfer was the predominant channel. With benzo[rst]pentaphene, which requires the lowest energy for double ionization, single- and double-electron transfer were reported to proceed in almost equal amounts.

The overall change in standard enthalpy for double-electron transfer reactions with $C_{60}^{\bullet 3+}$, equation (15),

$$C_{60}^{\bullet 3+} + M \rightarrow M^{2+} + C_{60}^{\bullet +} \tag{15}$$

is determined by the difference in the sum of the second and third ionization energies of C_{60}, $IE_2(C_{60}) + IE_3(C_{60})$, and the sum of the first and second ionization energies of the molecule M, $IE_1(M) + IE_2(M)$, according to equation (16).

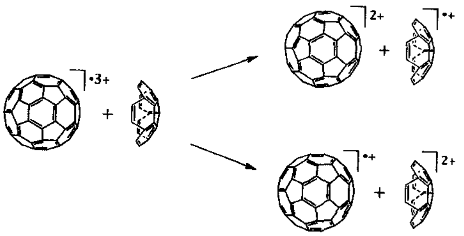
$$\Delta H^0 = IE_1(M) + IE_2(M) - [IE_2(C_{60}) + IE_3(C_{60})] = IE_1(M) + IE_2(M) - 27{\cdot}0 \pm 0{\cdot}6\,\text{eV}. \tag{16}$$

Here $IE_2(C_{60})$ is taken to be 11·39±0·05 eV and $IE_3(C_{60})$ is taken to be 15·6 ±0·5 eV [16]. Reaction (4) becomes exothermic when $IE_1(M) + IE_2(M) < 27{\cdot}0 \pm 0{\cdot}6$ eV. With an estimated barrier of 4·5±0·4 eV arising from Coulombic repulsion between the charged products [38], reaction (4) becomes kinetically favoured when $IE_1(M) + IE_2(M) < 22{\cdot}5 \pm 1{\cdot}0$ eV. The first and second ionization energies of corannulene are unknown. Anthracene (7·43+13·8 eV) and pyrene (7·41 = 14·4 eV) have first and second ionization energies (given in parentheses) [40] which add up to a value below 22·5 eV (21·2 and 21·8 eV respectively) and so should transfer two electrons to $C_{60}^{\bullet 3+}$ at thermal energies. Apparently, the second ionization energy of benzo[rst]pentaphene has not been measured or calculated, but can be estimated to be 12·5 eV from the correlation $IE_2(M) = 1{\cdot}8\, IE_1(M)$ which has been found to hold for many organic compounds [41]. Thus, the benzo[rst]pentaphene dication has a relatively low appearance energy of 19·5 eV and is favoured to be formed in the double-electron transfer reaction of benzo[rst]pentaphene with $C_{60}^{\bullet 3+}$ by as much as 3 eV.

Thermodynamic considerations indicate that single-electron transfer is energetically more favourable when $IE_2(M) > 11{\cdot}4$ eV and this is the case for the four PAH molecules investigated. The occurrence of electron-transfer, electron-detachment 'transfer ionization' according to reaction (17) can be ruled out on thermodynamic grounds since it is endothermic for these four PAH molecules.

$$C_{60}^{\bullet 3+} + M \rightarrow M^{2+} + C_{60}^{2+} + e^-. \tag{17}$$

The first observation of double-electron transfer to $C_{60}^{\bullet 3+}$ was recorded in an experiment with corannulene (cor) in which trace amounts of cor^{2+} and $C_{60}^{\bullet +}$ were observed to be produced in the presence of predominant formation of $\text{cor}^{\bullet +}$ and C_{60}^{2+} according to reaction (18).



(18 *a*)

(18 *b*)

A lower limit to the branching fraction of 0·01 was estimated for the double-electron transfer channel (18 *a*). Similar observations were made for the reactions of $C_{60}^{\cdot 3+}$ with anthracene and pyrene for which the branching fractions for double-electron transfer are estimated to be about 0·01 and 0·02 ± 0·01 respectively. The occurrence of double-electron transfer was most pronounced in the reaction with benzo[rst]pentaphene. For this reaction, the branching fractions for single-electron and double-electron transfer were estimated to be 0·6 ± 0·1 and 0·4 ± 0·1 respectively with account being taken of the occurrence of complicating secondary reactions. This result is perhaps not surprising since double-electron transfer with benzo[rst]pentaphene is energetically favoured by about 3 eV compared with only 1·3 eV and 0·7 eV for anthracene and pyrene, respectively.

Both sequential and concomitant electron transfer have been proposed as classical mechanisms of double-electron transfer to $C_{60}^{\cdot 3+}$ [39]. In the sequential mechanism the transfer of a single electron is proposed to occur first, followed by charge reorganization of the remaining two charges on C_{60} and then the transfer of the second electron. It is assumed in this mechanism that the three charge sites on $C_{60}^{\cdot 3+}$, if initially separated by Coulombic repulsion, are too far apart for two electrons to be transferred concomitantly to two different charge sites. The second classical mechanism proposed involves the concomitant transfer of two electrons to form an intermediate zwitterion, $C_{60}^{\cdot 2+,-}$.

It has also been noted that fragmentation of the doubly-charged PAH cation formed by double-electron transfer did not occur [39]. Fragmentation is energetically unfavourable, as is intramolecular C–C bond fission without fragmentation, particularly since the energy associated with Coulombic repulsion is expected to appear primarily as relative kinetic energy of the undissociated product ions. Photoionization studies [42] of naphthalene and azulene have suggested an internal-energy threshold for intramolecular fragmentation of about 7 eV which is much larger than the quantity which is expected to be partitioned into internal excitation of the PAH dications formed by the double-electron transfer reactions observed with $C_{60}^{\cdot 3+}$.

There appears to have been no previous report of the occurrence of double-electron transfer to a triply-charged cation. The reader is perhaps most familiar with double-electron transfer reactions involving singly-charged cations which are driven by accelerating the cations to several keV and are useful for the formation of fast negative ions as indicated in reaction (19) [43].

$$A^{+} + M \rightarrow A^{-} + M^{2+}. \tag{19}$$

Also, there have been several reports of the occurrence of double-electron transfer reactions of type (20)

$$A^{2+} + M \rightarrow A + M^{2+}, \tag{20}$$

in which a doubly charged cation is neutralized, both at thermal and elevated energies [44]. However, for the most part, the reactions of this type which have been studied have involved doubly-charged rare-gas cations reacting with rare-gas atoms or small molecules. With the latter, they have been observed to be largely dissociative.

7. Electron-transfer reactions with C_{60}^{n+}

Although C_{60}^{n+} cations with $n>3$ are expected to be stable against unimolecular decomposition, electron-transfer reactions with these multiply-charged ions at thermal energies have not yet been reported. C_{60}^{4+} has been produced in the gas-phase with a simple electron-impact ion source, and electron-transfer reactions of this ion (and $C_{60}^{\bullet 3+}$) have been observed with Cs vapour at about 2×10^{-4} Torr and laboratory energies of 1 to 2 keV [18]. The product mass spectra which were recorded provided evidence for sequential single-electron transfer reactions to produce $C_{60}^{\bullet 3+}$, C_{60}^{2+} and $C_{60}^{\bullet +}$. The occurrence of multiple-electron transfer was discounted because of the high second ionization energy of Cs [18].

The Coulombic-repulsion energy associated with single-electron transfer to C_{60}^{4+} has been estimated to be $7\cdot1\pm0\cdot6$ eV where it was assumed that the transfer occurs at $C_{60}\ldots X$ separations of $1\cdot0\pm0\cdot7$ Å [38]. This means that C_{60}^{4+} should undergo electron transfer at thermal energies with species X having $IE(X)\leqslant12\cdot4$ eV. However, the cumulative uncertainties involved in this estimate are high. Double-electron transfer to C_{60}^{4+} becomes exothermic with neutrals having $IE_1(M)+IE_2(M)$ less than about 35·1 eV. Since $IE_1(\mathrm{Cs})+IE_2(\mathrm{Cs})=29\cdot0$ eV, double-electron transfer to Cs would not be expected to occur unless the barrier due to Coulombic repulsion between the two doubly charged product ions is less than 6·1 eV. So it remains to be seen whether C_{60} cations with $n>3$ can accept more than one electron in a single collision with an energetically suitable electron donor.

8. Intramolecular electron transfer in derivatized C_{60} and C_{60} cations

8.1. *Adducts of C_{60} and atomic ions*

Recall the early observations of electron-transfer reactions between atomic metal ions and C_{60} at near-thermal energies which showed concomitant formation of adduct ions of the type MC_{60}^{+} [22]. The atomic metal ions typically have recombination energies slightly larger or slightly smaller than $IE(C_{60})$, $7\cdot64\pm0\cdot02$ [7(*a*)]: $M^{+}(RE)=\mathrm{La}^{+}$ (5·58 eV), Rh^{+} (7·46 eV), Ni^{+} (7·7635 eV), Cu^{+} (7·726 eV), Co^{+} (7·86 eV) and Fe^{+} (7·87 eV). Adjunct experiments involving the collision-induced dissociation (CID) of MC_{60}^{+} using Ar as a buffer gas at about 2×10^{-6} Torr, provided information about the degree of electron transfer within the MC_{60} adduct ion. CID on FeC_{60}^{+}, CoC_{60}^{+}, NiC_{60}^{+} and CuC_{60}^{+} gave C_{60}^{+}, while LaC_{60}^{+} produced La^{+}, and RhC_{60}^{+} produced a mixture of $C_{60}^{\bullet +}$ and Rh^{+}. These interesting results are in accordance with the differences in the ionization energies of C_{60} and the metal atoms and indicate the formation of two types of electron-transfer adducts: adducts in which there is a substantial shift in electron density so that an effectively neutral metal atom is appended to a C_{60} cation (as with Fe, Co, Ni and Cu), and adducts in which only a small shift in electron density has occurred so that effectively the metal ion is appended to a neutral C_{60} molecule (as with La^{+}). Reactivity measurements provide another test for intramolecular electron transfer in adducts of this type, but such studies have been few. The adduct of Y^{+} ($IE(\mathrm{Y})=6\cdot22$ eV) and C_{60} has been observed in an FT-ICR mass spectrometer [45]. Y^{+} has a recombination energy (6·22 eV) considerably smaller than that of $C_{60}^{\bullet +}$ so that no significant shift in electron density to Y^{+} is expected to occur in the adduct ion. Indeed, the reaction of YC_{60}^{+}

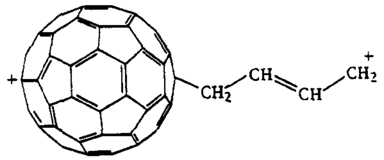


Figure 7. Structure postulated for the adduct of C_{60}^{2+} and 1,3-butadiene in which intramolecular electron transfer has occurred to maximize charge separation.

with N_2O has been reported to produce $YO^{\cdot+}+[C_{60}+N_2]$ instead of $C_{60}^{\cdot+}+[YO+N_2]$ [45].

8.2. *Adducts of neutral molecules and C_{60} cations*

As indicated earlier, addition of electron-donor molecules to multiply charged C_{60} cations also has often been observed to be a significant competing channel in electron-transfer reactions under SIFT conditions (at a He pressure of about 0·35 Torr). The formation of these adducts has been attributed to the occurrence of collisional stabilization of the intermediate adduct prior to complete charge transfer [46]. For example, it has been proposed that the observed addition of 1,3-butadiene to C_{60}^{2+} occurs by electrophilic addition with the formation of a C–C covalent bond and the concomitant transfer of an electron from the outermost C atom along the four-carbon chain. A possible structure is shown in figure 7. The observed additions of another five molecules has been viewed in a similar fashion with the chain ultimately extending to 24 carbon atoms. The electron transfer along the six chain members can be viewed classically to be driven by the accompanying Coulombic relaxation [46].

8.3. *Endohedral* M@*C_{60} cations*

The availability of the new family of endohedral $M@C_{60}$ molecules in which a metal atom is trapped within a C_{60} cage [47] raises the exciting prospect of intramolecular electron transfer between the encapsulated metal atom and the surrounding carbon cage, particularly if the cage or the metal is electron deficient (e.g. singly or multiply ionized) [48]. Such intramolecular electron transfer has not yet been demonstrated in the literature, but its observation may well be imminent.

9. Electron-transfer reactions with fullerene anions

This review has focused on the role of C_{60} cations as electron acceptors and C_{60} as an electron donor in electron-transfer reactions. Reactions of anions of C_{60} have not been discussed. However, it is known that neutral C_{60} has a high affinity for electrons. Both $C_{60}^{\cdot-}$ and C_{60}^{2-} have now been observed in the gas phase [49, 50]; the affinity of C_{60} for the first electron is quite large, $EA(C_{60})=2{\cdot}650\pm0{\cdot}50$ eV [49]. So far, kinetic studies of the reactivity of $C_{60}^{\cdot-}$ have not shown the occurrence of electron transfer [51]. But this is not surprising since the neutrals used as reagents in these studies did not have a sufficiently high electron affinity for electron transfer to be energetically allowed. Electron-transfer reactions of negative ions with C_{60} have not yet been attempted in the laboratory, but these should occur readily with negative ions having electron-detachment energies lower than 2·65 eV. Free electron attachment to C_{60} has been studied as a function of electron energy between about 0 and

14 eV and was seen to yield copious amounts of $C_{60}^{\bullet -}$ with an estimated cross-section approaching 10^{-12} cm^2 [52(*a*)]. The electron-attachment curve exhibits a strong zero-energy resonance and evidence for equally strong autoscavenging processes up to energies of 14 eV [52(*b*)]. Measurements of the rate coefficient for electron attachment as a function of electron temperature have indicated a range of values from about 10^{-9} cm^3 s^{-1} at 500 K to 3×10^{-7} cm^3 s^{-1} at 4500 K with an activation energy of 0·26 eV [52(*c*)].

Electrochemical experiments have demonstrated that C_{60} exhibits a rich reduction/oxidation (redox) chemistry in solution [48]. Six reversible reductions of C_{60} to C_{60}^{x-} ($x = 1$–6) have now been demonstrated by cyclic voltammetry at −10°C. The first four reductions have been verified as one-electron transfers by bulk electrolysis in benzonitrile [53]. The half-wave potentials, $E_{1/2}$, for the electrode reactions of C_{60} have been measured in selected solvent, electrolyte and temperature conditions and found to be sensitive to all three. They have been bound to correlate with donor/acceptor properties of the solvent and the nature and size of the supporting-electrolyte cation [54]. $E_{1/2}$ values have been measured as a function oftemperature in various media and values have been derived for the entropy change for each reduction step.

The redox properties of C_{60} have also been explored with solid-state electrochemical studies [55] and C_{60}^{3-} even has been implicated as a critical component in solid-state superconductivity [48], but these fascinating aspects lie outside of the scope of this review.

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