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Chemical signatures of Buckminsterfullerene, C_{60}, under chemical ionization conditions

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ABSTRACT

Chemical ionization (CI) spectra are reported for the Buckminsterfullerene molecule, C_{60}, with the CI reagents hydrogen, ammonia, water, hydrogen chloride, methane, ethylene and isobutane. The spectra are characterized by a strong peak for protonated C_{60}, $C_{60}H^+$, except with ammonia. The spectra with hydrogen and ammonia are striking in that they show extensive hydrogenation of $C_{60}^{\cdot+}$. $C_{60}H_x^+$ peaks up to $C_{60}H_{37}^+$ are observed in hydrogen, while the ammonia spectrum shows a preference for an odd number of hydrogen atoms below $x = 13$. The spectra with methane, ethylene and isobutane show complicated patterns of peaks corresponding to the derivatization of $C_{60}^{\cdot+}$ with $n\mathrm{CH}_x$ units, where n has values up to $n = 32$ in the case of methane. Ion/molecule reactions are discussed which may lead to the formation of $C_{60}H^+$, the further hydrogenation of this ion, and the derivatization of $C_{60}^{\cdot+}$ more generally. The results in general indicate a remarkable ability for C_{60} to become hydrogenated and derivatized under CI conditions.

Keywords: fullerenes; chemical ionization; ions; ion/molecule reactions.

INTRODUCTION

The chemical reactivity of Buckminsterfullerene, C_{60}, both in solution and in the gas phase, has become of great interest since the availability of this compound in bulk quantities [1]. Since the first detection of its cation in laser vaporization experiments with graphite, neutral C_{60} has been proposed as an important interstellar molecule [2]. The failure to detect C_{60} in interstellar environments [3] has shifted interest to the C_{60} cation [4] and its derivatives, particularly $C_{60}H^+$ [5]. The few experimental studies which have directly explored the chemical reactivity of C_{60} (for a review see ref. 6) show that this species is quite unreactive near thermal energies. For example, $C_{60}^{\cdot+}$ has been

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shown to be unreactive with H_2, O_2, NO, NH_3 and C_4H_2 at low pressures [7], while selected-ion flow tube (SIFT) studies at 0.40 Torr in helium have shown that $C_{60}^{\cdot+}$ and $C_{70}^{\cdot+}$ are unreactive, $k < 1 \times 10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$, with a wide variety of other molecules including CO, CH_4, H_2O, C_2H_6, C_2H_2, C_2H_4 and i-C_4H_8 [8]. However, addition reactions have been observed with ammonia and several aliphatic amines [9]. To date, the only bimolecular reactions of $C_{60}^{\cdot+}$ which have been reported are charge transfer reactions with neutral molecules, X, having $\mathrm{IE(X)} < \mathrm{IE}(C_{60}) = 7.61 \pm 0.11\,\mathrm{eV}$ [10]. Since $C_{60}^{\cdot+}$ displays so little reactivity with molecules, its reactivity with atoms and radicals becomes interesting, especially in view of the radical-sponge behaviour seen for neutral C_{60} with the species $H^{\cdot}$ [11], $F^{\cdot}$ [12], O [13,14], $OH^{\cdot}$ [14], CH_2 [14], $CH_3^{\cdot}$ [14–16], $CF_3^{\cdot}$ [16], $(CH_3)_3CO^{\cdot}$ [16], $C_6H_5^{\cdot}$ [15], $C_6H_5CH_2^{\cdot}$ [16], $C_6H_5S^{\cdot}$ [16] and $C(C_6H_5)_2$ [17]. Also, a very recent SIFT study has shown that $C_{60}^{\cdot+}$ will attach H atoms in sequential addition reactions [18].

Less is known of reactions of molecular ions with neutral C_{60}, although proton transfer and ion addition reactions have been reported in studies of the proton affinity of C_{60} [19]. Atomic ions have been shown either to add to C_{60} or transfer a charge, depending on the recombination energy of the atomic ion [20]. Here we report results of experiments in which the vapour of C_{60} is introduced into a conventional chemical ionization (CI) source along with a CI gas, viz. H_2, CH_4, NH_3, H_2O, HCl, C_2H_4 and i-C_4H_{10}. The resulting spectra show a remarkable ability for C_{60} cations to become derivatized and point a substantial chemistry for fullerene molecules under CI conditions.

EXPERIMENTAL

The experiments were performed with a modified VG-ZAB tandem mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector), which has been described in detail elsewhere [21]. CI of C_{60} was afforded by use of different reagent gases in a CI source (electron energy 100 eV; repeller voltage ≈ 0 V; source housing pressure $\approx 10^{-4}$ mbar). Source spectra were taken at a mass resolution $m/\Delta m$ of 2000 and the mass scale was calibrated with $(Cs_xI_{x-1})^+$ cluster ions. C_{60} was introduced into the source as a C_{60}:C_{70} mixture ($\approx 90:10$) via the solid probe inlet and heated to 480–550°C. The temperature of the ion source was increased to 300°C to reduce condensation of fullerenes in the source block[a]. The spectra were accumulated and processed on line with the VG 11/250 data system.

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[a] However, the large excess of reagent gas led to a serious coating of the source block with fullerenes so that frequent cleaning and maintenance of the ion source was necessary.

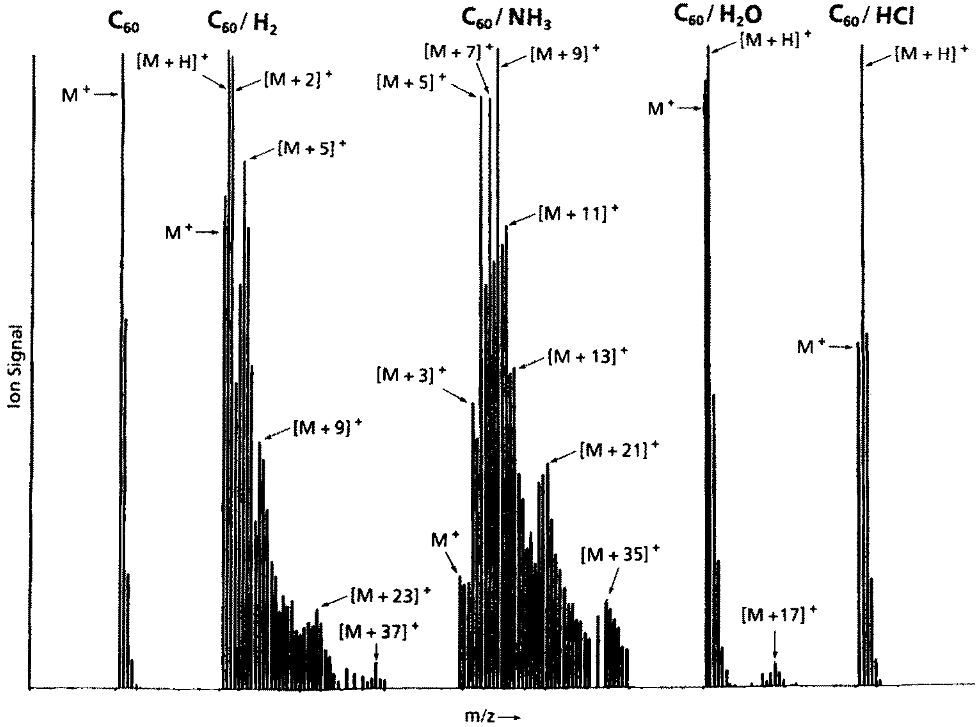

Fig. 1. CI spectra for C_{60}. From left to right: without CI gas; with H_2; with NH_3; with H_2O; and with HCl.

RESULTS AND DISCUSSION

Figures 1–4 summarize the spectra observed under CI conditions for mixtures of C_{60} with H_2, $N^{\cdot}_3$, H_2O and HCl (Fig. 1), CH_4 (Fig. 2), C_4H_4 (Fig. 3) and *i*-C_4H_{10} (Fig. 4). The spectra begin at around *m*/*z* 700. The spectra between *m*/*z* 20 and *m*/*z* 700 are not given since they showed only the peaks expected from the CI reagent gas. One feature of the spectra shown in Figs. 1–4 which is immediately striking is the relatively high abundance of protonated C_{60}, $C_{60}H^{\cdot +}$, in all spectra except that with ammonia. With HCl, $C_{60}H^+$ clearly dominates the spectrum. A second, perhaps more noteworthy feature of these spectra is the abundance of higher mass-satellite peaks, particularly with H_2, NH_3, CH_4, C_2H_4 and *i*-C_4H_{10}. The spectrum in methane is particularly remarkable in this regard.

A more detailed inspection of the spectra shown in Figs. 1–4 reveals still further interesting features:

(1) The "self-CI" spectrum of C_{60} shows no surprises. The $C_{60}^{\cdot +}$ peak predominates and, interestingly, there was no evidence for the formation of the dimer ion $(C_{60})_2^{\cdot +}$.

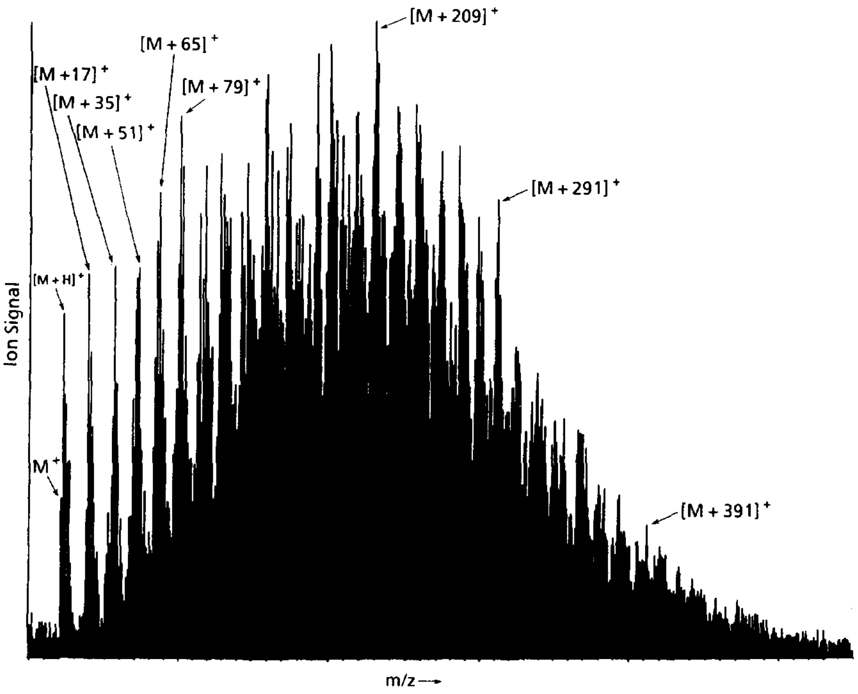

Fig. 2. CI spectrum of C_{60} with methane.

(2) Hydrogenation of $C_{60}^{\cdot+}$ with up to at least 37 hydrogen atoms is observed in hydrogen with apparent special stabilities for $C_{60}H_5^+$ and $C_{60}H_9^+$ and perhaps also for $C_{60}H_{23}^+$ and $C_{60}H_{37}^+$.

(3) The ammonia spectrum shows extensive hydrogenation. The strongest peaks correspond to $C_{60}^{\cdot+}$ hydrogenated with an odd number of hydrogen atoms, viz. $C_{60}H_x^+$ with $x = 3, 5, 7, 9, 11$ and 13. Values of $x = 5, 7$ and 9 particularly seem to be preferred. The peaks at $[C_{60} + 19, 20, 21]^+$ very likely reflect additional substitution by nitrogen.

(4) Aside from the presence of C_6H^+, there is little further evidence for the hydrogenation of $C_{60}^{\cdot+}$ in the water spectrum. The small peaks at $[C_{60} + 16]^+$ and $[C_{60} + 17]^+$ may correspond to $C_{60}O^{\cdot+}$ and $C_{60}OH^+$ respectively.

(5) Chlorine derivatives of $C_{60}^{\cdot+}$ are noticeably absent in the HCl spectrum which is dominated by $C_{60}H^+$.

(6) The CI spectrum in methane/C_{60} shows a complicated pattern of peaks corresponding to $C_{60}^{\cdot+}$ derivatized by nCH$_x$ units. The spectrum appears to peak at about $n = 14$ and extends to about $n = 32$. Interestingly, it is quite similar to the fast atom bombardment (FAB) mass spectrum reported by Krusic et al. [16b] for the products obtained by UV irradiation of a benzene

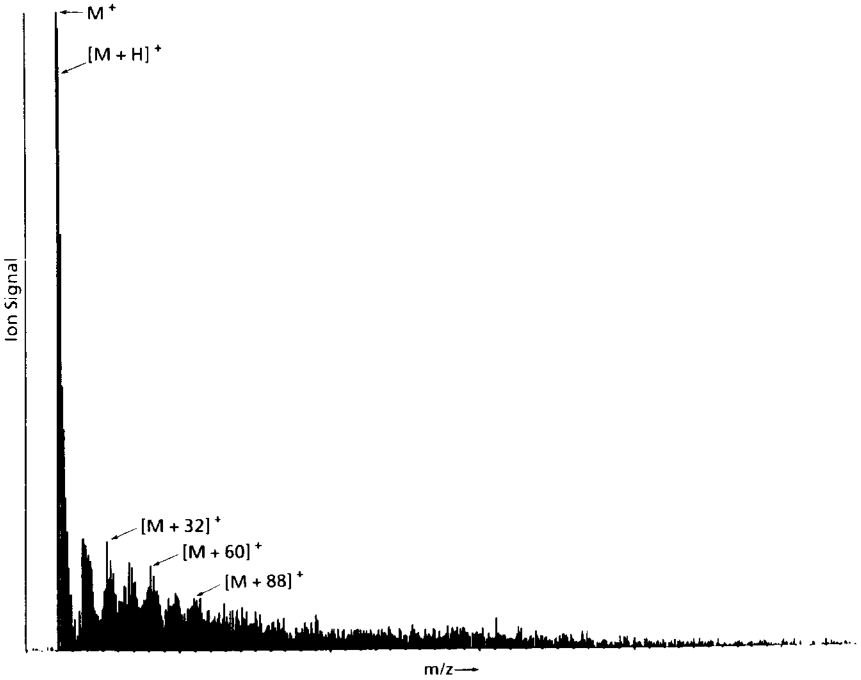

Fig. 3. CI spectrum of C_{60} with ethylene.

solution of C_{60} and di-*tert*-butylperoxide at 100°C that shows the formation of $C_{60}(CH_3)_n^+$ adducts with $n = 1$–34.

(7) The ethylene/C_{60} spectrum also shows derivative peaks corresponding to nCH$_x$ to $C_{60}^{\cdot+}$ but these peaks are much less intense relative to the $C_{60}^{\cdot+}$ and $C_{60}H^+$ peak heights and are readily discernible only up to approximately $n = 6$. The peaks at $[M + 32, 60 \text{ and } 88]^+$ appear to reflect a series of C_2H_4 additions.

(8) The spectrum with *iso*-butane also shows the pattern corresponding to the addition of CH_x units, in this case extending to at least $n = 11$.

Formation of $C_{60}H^+$

Nothing is known about the reactivity of the radical cations of the molecules used as CI reagents in this study toward C_{60}. Table 1 shows that their relatively high recombination energies and low deprotonation energies make both charge transfer and proton transfer thermodynamically possible as shown in reaction 1. The ionization energy of C_{60} is only 7.61 eV [10], but the

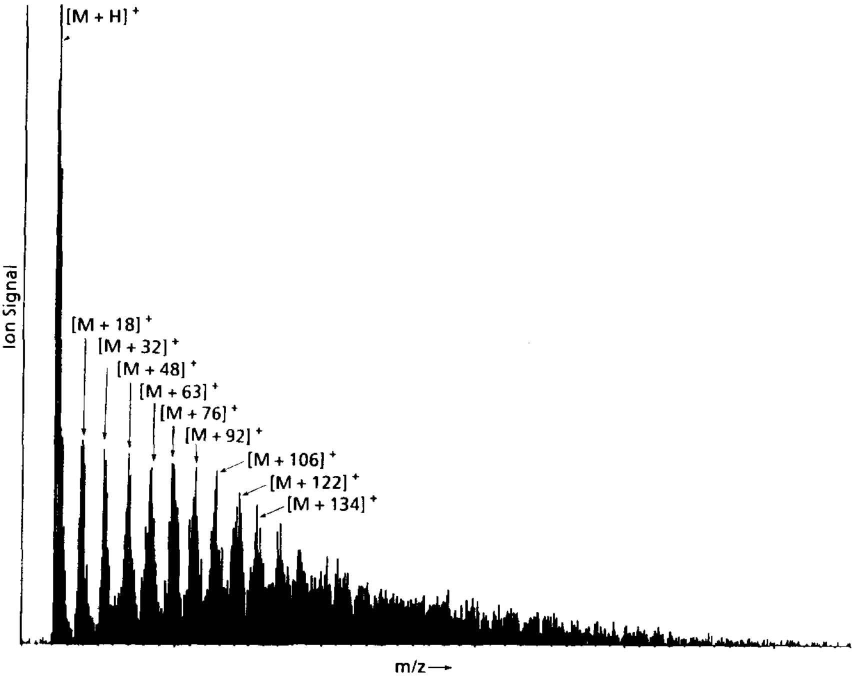

Fig. 4. CI spectrum of C_{60} with *iso*-butane.

TABLE 1

Thermochemical properties of gases used as CI reagents[a]

Molecule	IE (eV)	PA(XH)	PA(X)	HA(X)	HA(X^+)
H_2	15.43	101.3	62	104	62
CH_4	12.51	132.0	130	105	43
HCl	12.75	134.8	128	103	108
C_2H_4	10.51	162.6	174	103	63
i-C_4H_{10}	10.57	163.3	170	100	39
H_2O	12.61	166.5	142	119	128
NH_3	10.16	204.0	178	108	131

[a] IE = ionization energy; PA = proton affinity; HA = hydrogen atom affinity. Unless indicated otherwise, all values are in kcal mol^{-1}. Proton affinities for XH were taken from the compilation of S.G. Lias, J.F. Liebman and R.D. Levin, J. Phys. Chem. Ref. Data, 13 (1984) 695. Other values were taken or derived from the compilation of S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin and W.G. Mallard, J. Phys. Chem. Ref. Data, 17 (1988) 1.

proton affinity of C_{60} is very high, $PA(C_{60}) = 204\,kcal\,mol^{-1}$ [19].

$$XH^{\cdot +} + C_{60} \rightarrow C_{60}^{\cdot +} + XH \tag{1b}$$

$$\rightarrow C_{60}H^{+} + X^{\cdot} \tag{1b}$$

Of course the establishment of XH_2^+ by self-protonation makes reactions of type 2 very likely sources of $C_{60}H^+$. Proton transfer reactions of this type have been observed with CH_5^+, H_3O^+ and NH_4^+ [19]. The proton transfer reaction between NH_4^+ and C_{60} is slow because of the similarity in the proton affinities of C_{60} and NH_3 [19]; this may account for the relatively small $[C_{60} + 1]^+$ signal in the ammonia spectrum.

$$XH_2^+ + C_{60} \rightarrow C_{60}H^+ + XH \tag{2}$$

We can exclude hydrogen atom transfer reactions of type 3 with the CI reagent XH as a possible source of $C_{60}H^+$. The hydrogen atom affinity of $C_{60}^{\cdot +}$ is very low, $HA(C_{60}^{\cdot +}) = 63\,kcal\,mol^{-1}$ [22], compared with HA(X) which has values exceeding $100\,kcal\,mol^{-1}$ for the CI reagents studied here (see Table 1). Indeed, $C_{60}^{\cdot +}$ has now been shown to be unreactive at 294 ± 2 K toward H_2, H_2O, CH_4, C_2H_4 and i-C_4H_{10} and to react only slowly with NH_3 to produce the adduct ion $C_{60}NH_3^{\cdot +}$ [8,9].

$$C_{60}^{\cdot +} + XH \rightarrow C_{60}H^+ + X^{\cdot} \tag{3}$$

Further hydrogenation of $C_{60}^{\cdot +}$

The extensive hydrogenation, with a preference for the formation of $C_{60}^{\cdot +}$ with an odd number of hydrogen atoms, observed in the spectra with H_2 and NH_3 is most intriguing. Sequential hydrogenation reactions of type 4 are unlikely because of the relatively high hydrogen atom affinity of X.

$$C_{60}H_n^+ + XH \rightarrow C_{60}H_{n+1}^{\cdot +} + X \tag{4}$$

Derivatization of $C_{60}^{\cdot +}$

The derivatization of $C_{60}^{\cdot +}$ observed with ammonia, methane, ethylene and *iso*-butane is also difficult to rationalize, particularly in view of the observed non-reactivity of $C_{60}^{\cdot +}$ toward methane, ethylene and isobutane at 294 ± 2 K [8] which rules out reactions of type 5. Addition reactions between $C_{60}H_x^+$ ($x = 2$–4) and NH_3, in analogy with the observed addition reaction between $C_{60}^{\cdot +}$ and ammonia [9], may account for the formation of the peaks at $[C_{60} + 19, 20, 21]^+$.

$$C_{60}^{\cdot +} + XH \rightarrow C_{60}X^+ + H^{\cdot} \tag{5}$$

The analogous reaction 6 in which the reacting XH is ionized instead of C_{60}

is much more exothermic (by the difference in the ionization energies of X- and C_{60} which is at least 2.5 eV). Inspection of the hydrogen atom affinities of X^+ suggests that thermochemistry favours substitution with $C_4H_9^+$, CH_3^+, H^+ and $C_2H_3^+$ in reactions of type 6 and, more generally, type 7, both of which must compete with proton transfer

$$XH^{\cdot +} + C_{60} \rightarrow C_{60}X^+ + H^{\cdot} \qquad (6)$$

$$XH^{\cdot +} + C_{60}H_xX_y \rightarrow C_{60}H_xX_{y+1}^+ + H^{\cdot} \qquad (7)$$

$C_{60}H_xX_{y+1}^+$ ions are representative of the derivatized $C_{60}^{\cdot +}$ ions seen with CH_4, C_2H_4, i-C_4H_{10} and even H_2. Their formation depends on the availability of neutral molecules of type $C_{60}H_xX_y$ whose origin is questionable. In the CI source they may be derived by electron/ion recombination of $C_{60}X^+$, where $X = CH_3$, C_2H_3 or C_4H_9, or perhaps by reactions of $C_{60}X^+$ with radical species followed by electron/ion recombination. For example, $C_{60}H^+$ is known to react unusually rapidly with H atoms under SIFT conditions to form $C_{60}H_2^{\cdot +}$ [18].

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NOTE ADDED IN PROOF

At the 40th ASMS Conference on Mass Spectrometry, 31 May–5 June 1992, Washington, DC, C.N. McEwan reported results using C_{60} as a radical sponge. He suggested that radical adducts generated under chemical ionization conditions are largely due to surface processes rather than ion/radical gas-phase reactions. Results of his experiments are also described in the 20 May 1992 issue of the Journal of the American Chemical Society.

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