

# Proton Transfer Reactions of Derivatized Fullerene Trications

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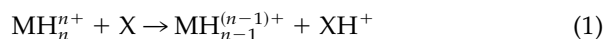
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The occurrence or absence of proton transfer from derivatized fullerene trications  $C_{60}H^{3+}$ , to the parent neutral  $XH$ , is employed to obtain upper or lower limits to the apparent gas-phase acidity  $GA_{app}$  as well as to the estimated absolute gas-phase acidity. A comparison with the reactivity of analogous dicationic adducts indicates that  $C_{60}XH^{3+}$  is generally more acidic than  $C_{60}XH^{2+}$ : for example, the difference in  $GA$  values for  $C_{60}NCCH_3^{n+}$  ( $n = 2, 3$ ; formed in the addition reaction of  $C_{60}^{n+}$  with  $CH_3CN$ ) is estimated to be at least  $42 \text{ kcal mol}^{-1}$ . In almost all instances, estimated  $GA$  values for the tricationic adducts are far below the gas-phase basicities of the parent neutral  $XH$ , mirroring a trend seen from the proton-transfer reactivity of multiply protonated protein molecules: a qualitative difference between the fullerene adducts and the multiply protonated biomolecules routinely produced by electrospray ionization is that the fullerene adduct ions (with the exception of  $C_{60}NH_3^{3+}$ ) appear to possess only one acidic proton. (J Am Soc Mass Spectrom 1998, 9, 114–120) © 1998 American Society for Mass Spectrometry

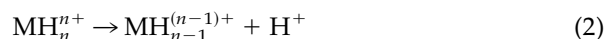
Recent advances in ionization techniques, most notably the implementation of electrospray ionization methods [1–3], have promoted the experimental study of multiply protonated biomolecules such as proteins. There exists a growing body of studies on the chemical and physical characteristics of multiply charged peptide and protein ions [4–17], in particular their reactivity with regard to proton transfer:



Perhaps somewhat counterintuitively, reactions of type 1 are not necessarily efficient when exothermic: the proximity of the positively charged products immediately following proton transfer (which necessarily occurs at a finite separation of the reactants) is associated with Coulombic repulsion between the product ions, and this Coulombic interaction is manifested as a “reverse activation barrier” which can very effectively impede the occurrence of substantially exothermic proton-transfer reactions [18–22].

The presence of a large reverse activation barrier in reaction 1 is an obstacle, also, to the derivation of thermochemical data on the deprotonation of multiply

charged biomolecules. Although the tendency of an ion  $MH_n^{n+}$  to react by proton transfer may be well characterized experimentally by bracketing studies, this does not directly allow determination of the gas-phase acidity ( $GA$ ) of  $MH_n^{n+}$ :



for which  $GA(MH_n^{n+}) = \Delta_f G^\circ(MH_{n-1}^{(n-1)+}) + \Delta_f G^\circ(H^+) - \Delta_f G^\circ(MH_n^{n+})$ . Rather, the parameter most conveniently obtained from bracketing studies of proton transfer from  $MH_n^{n+}$  is an “apparent gas-phase acidity”  $GA_{app}(MH_n^{n+})$ , which may be defined [21] as

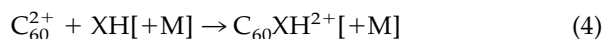
$$GA_{app}(MH_n^{n+}) = GA(MH_n^{n+}) + \delta \quad (3)$$

where  $\delta$  is a parameter corresponding to the difference in energy between the transition state (which may be considered as a “repulsive ion pair”  $[MH_{n-1}^{(n-1)+} \cdots XH^+]$ ) and the product ions  $MH_{n-1}^{(n-1)+}$  and  $XH^+$  in eq 1. At close separation of these product ions,  $\delta$  is dominated by the Coulombic repulsion between the products: it follows that the difference between  $GA$  and  $GA_{app}$  is dependent upon the reaction distance at which the proton is transferred, and upon the distribution of effective charges within the reactant ion  $MH_n^{n+}$  and within its deprotonated product

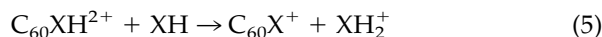
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$\text{MH}_{n-1}^{(n-1)+}$ . The charge distribution within multiply protonated molecules is generally very difficult to determine: most of the multiply protonated protein molecules amenable to experimental study feature more possible sites for protonation than are actually protonated, while the three-dimensional structure of a multiply protonated, long-chain molecule will also be very different from that of the parent molecule in the gas phase (and different again from this molecule's structure in aqueous solution, or in the crystalline state). A recent study by Jarrold and co-workers [12, 23] serves to illustrate how great an influence the degree of protonation exerts over a protein molecule's configuration in the gas phase. Although techniques such as ion chromatography [12, 17, 23], collision-induced or surface dissociation [6], and molecular modelling [9, 11, 15, 24] are of value in analyzing the overall structure of large, multiply protonated molecules  $\text{MH}_n^{n+}$ , and while experimental determination of the reverse activation barrier height may be possible by kinetic energy release measurement [14, 15], there appears also to be a need for reaction studies involving multiply charged, hydrogen-bearing ions which are structurally well-defined (hence easily interpreted) and comparatively small (hence more susceptible to computational methods).

We have studied many reactions of the fullerene ions  $\text{C}_{60}^+$ ,  $\text{C}_{60}^{2+}$ , and  $\text{C}_{60}^{3+}$ , using a selected-ion flow tube [25–27]. During these studies, one common feature [21, 28] of the reaction chemistry of  $\text{C}_{60}^{2+}$  with hydrogen-bearing molecules (XH) is the sequence involving adduct formation



followed by proton transfer



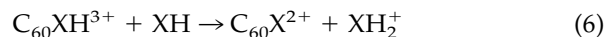
The reactivity evidenced by the adduct dication  $\text{C}_{60}\text{XH}^{2+}$  can be related to its  $\text{GA}_{\text{app}}$  if the proton-transfer reaction 5 occurs [implying  $\text{GA}_{\text{app}}(\text{C}_{60}\text{XH}^{2+}) \leq \text{GB}(\text{XH})$ ] or if this reaction is not detected in the absence of efficient competing product channels [which implies that  $\text{GA}_{\text{app}}(\text{C}_{60}\text{XH}^{2+}) > \text{GB}(\text{XH})$ ]. We have determined upper or lower limits to  $\text{GA}_{\text{app}}(\text{C}_{60}\text{XH}^{2+})$ —and, by estimating the electrostatic term  $\delta$ , to  $\text{GA}(\text{C}_{60}\text{XH}^{2+})$ —for several different examples of  $\text{C}_{60}\text{XH}^{2+}$  [21]. In one instance, we have also been able to bracket the apparent gas-phase acidity of a derivatized fullerene dication, yielding  $\text{GA}_{\text{app}}(\text{C}_{60}\text{H}^{2+}) = 166 \pm 4 \text{ kcal mol}^{-1}$  and  $\text{GA}(\text{C}_{60}\text{H}^{2+}) = 128 \pm 8 \text{ kcal mol}^{-1}$  [29]. We have also noted instances [30–35] in which proton transfer is observed from a derivatized fullerene trication  $\text{C}_{60}\text{XH}^{3+}$ . Here we examine the examples of proton transfer from  $\text{C}_{60}\text{XH}^{3+}$ , and discuss the trends evident as a function of charge state and of the nature of the derivatizing species XH.

## Experimental

The reactions discussed here were investigated using a selected-ion flow tube that has been described previously [36, 37].  $\text{C}_{60}$  trications were produced in an ion source by electron impact on the vapor of a commercial fullerene sample ( $\sim 90\%$   $\text{C}_{60}$ ,  $\sim 9\%$   $\text{C}_{70}$ ) obtained from Termusa Inc. The trications were then mass selected with a quadrupole mass spectrometer and injected into a flowing helium carrier gas at  $0.35 \pm 0.01$  torr and  $294 \pm 3$  K. Further downstream, after experiencing  $\sim 4 \times 10^5$  collisions with He atoms, the  $\text{C}_{60}$  trications were allowed to react with added XH molecules. Both the primary and higher-order reactions were monitored with a second quadrupole mass spectrometer still further downstream after a few milliseconds of reaction time. The experimental data for the secondary reaction of  $\text{C}_{60}\text{XH}^{3+}$  with XH were fitted with the solution of the differential equation for the formation and loss of  $\text{C}_{60}\text{XH}^{3+}$  to provide the rate coefficient for the secondary reaction. Reactions of  $\text{C}_{60}\text{XH}^{3+}$  with  $\text{H}_2$  were investigated by producing  $\text{C}_{60}\text{XH}^{3+}$  upstream and adding hydrogen downstream.

## Results and Discussion

To date, we have identified 12 instances in which the proton transfer reaction 6 occurs:



namely for  $\text{XH} = \text{NH}_3$ ,  $\text{C}_2\text{H}_4$ ,  $\text{HCN}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{NO}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{CHO}$ ,  $\text{HCOOH}$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{CH}_3\text{COOCH}_3$ . The reactivities of these tricationic adducts, and of others for which the absence of proton transfer is informative, are summarized in Table 1.

The observation of reaction 6 for 12 different tricationic adducts compares with 16 observed examples [21, 33] of the analogous dicationic proton transfer reaction 5, under the same experimental conditions and for the same overall range of reactant neutrals. We have not found any examples of monocationic adducts  $\text{C}_{60}\text{XH}^+$  which undergo proton transfer to XH under our experimental conditions, although the observation of secondary adducts in the reactions of  $\text{C}_{60}^+$  with  $\text{NH}_{(3-n)}(\text{CH}_3)_n$ , for  $n = 0-2$  but *not* for  $n = 3$ , is attributed to the formation of proton-bound adducts in which a proton is shared between the two N atoms of the secondary adduct [30].

The slightly larger number of dicationic adducts, versus tricationic adducts, which are observed to exhibit proton transfer to the reactant neutral XH does not, in any way, indicate that the tricationic proton transfer reaction 6 is thermodynamically disfavored, or is less exoergic than the analogous dicationic reaction 5. On the contrary, we expect that all of the dicationic adducts  $\text{C}_{60}\text{XH}^{2+}$  that are observed to exhibit proton transfer 5 to the corresponding neutral would remain

**Table 1.** Measured rate coefficients, for the reactions of  $C_{60}^{3+}$  and  $C_{60}XH^{3+}$  with XH, at  $295 \pm 2$  K and  $0.35 \pm 0.02$  torr of helium

XH <sup>a</sup>	$k_0^b$	$f_A^c$	$k_1^d$	$f_{PT}^e$	$k_c^f$
NH <sub>3</sub>	$3.9 \pm 1.6$	1.0	(F)	>0.5	5.0
C <sub>2</sub> H <sub>4</sub>	$1.7 \pm 0.5$	0.3	$0.55 \pm 0.20$	<0.5	2.8
HCN	$4.3 \pm 1.4$	1.0	$7.2 \pm 2.4$	1.0	6.4
CH <sub>3</sub> CN	$6.5 \pm 1.9$	1.0	$5.8 \pm 2.3$	0.34	8.8
CH <sub>3</sub> NO <sub>2</sub>	$3.8 \pm 1.1$	1.0	$4.0 \pm 1.2$	1.0	5.6
CH <sub>3</sub> OH	$2.5 \pm 1.0$	0.2	(F)	>0.5	4.4
CH <sub>3</sub> CH <sub>2</sub> OH	$2.4 \pm 1.0$	0.1	(F)	>0.5	4.2
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	$3.9 \pm 1.5$	0.1	(F)	>0.5	3.8
CH <sub>3</sub> CH <sub>2</sub> CHO	$4.2 \pm 1.6$	0.25	(F)	obs	4.7
HCOOH	$2.5 \pm 1.0$	0.5	(F)	obs	3.3
CH <sub>3</sub> COOH	$4.2 \pm 1.6$	1.0	(F)	>0.5	3.6
CH <sub>3</sub> COOCH <sub>3</sub>	$3.4 \pm 1.3$	0.9	(F)	>0.5	3.5
HCCCN	$8.2 \pm 2.5$	1.0	$8.2 \pm 2.5$	0	8.3
CH <sub>3</sub> CH <sub>2</sub> CN	$4.0 \pm 1.6$	1.0	(F)	0	6.6
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CN	$6.3 \pm 2.5$	1.0	(F)	0	6.2
(CH <sub>3</sub> ) <sub>2</sub> CHCN	$4.8 \pm 1.9$	1.0	(F)	0	5.9

<sup>a</sup>Reactant neutral employed in the SIFT experiment. The reactants listed here are restricted to those with which  $C_{60}XH^{3+}$  is observed to exhibit proton transfer, or with which  $C_{60}XH^{3+}$  does not exhibit collision-rate charge transfer. We have deliberately excluded those systems featuring efficient charge transfer as a secondary reaction because such systems do not appear to offer any insight into the thermochemistry of proton transfer; however, we expect that proton transfer from  $C_{60}XH^{3+}$  is able to compete efficiently with association and abstraction reactions with XH, provided that  $GA_{app}(C_{60}XH^{3+}) < GB(XH)$ .

<sup>b</sup>Observed effective bimolecular rate coefficient, in units of  $10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, for the reaction of  $C_{60}^{3+} + XH$ . In most instances, the primary rate coefficient shown has been reported elsewhere [30–34]. The most recent results with CH<sub>3</sub>NO<sub>2</sub> are found in [35].

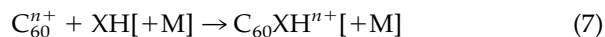
<sup>c</sup>Branching ratio for adduct formation in the reaction of  $C_{60}^{3+} + XH$ .

<sup>d</sup>Observed effective bimolecular rate coefficient, in units of  $10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, for the reaction of  $C_{60}XH^{3+} + XH$ . In some instances, measurement of the secondary rate coefficient was precluded by the experimental conditions; the symbol (F) indicates a fast secondary reaction, with an estimated value of  $k_1 \geq 1 \text{ m} \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

<sup>e</sup>Branching ratio for proton transfer in the reaction of  $C_{60}XH^{3+} + XH$ . In some instances, it was not possible to obtain, from the experimental results, a reliable branching ratio for an observed proton transfer channel: we have indicated such cases as obs.

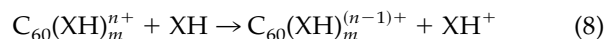
<sup>f</sup>ADO collision rate coefficient for the reactions of  $C_{60}^{3+}$  and  $C_{60}XH^{3+}$  with XH, calculated according to the method of Su and Bowers [38], in units of  $10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

energetically capable of proton donation to XH upon increasing the charge state on the adduct ion  $C_{60}XH^{n+}$  from  $n = +2$  to  $+3$ ; the failure to observe reaction 6 in many of these instances is a consequence of competition from other product channels which are highly efficient for  $C_{60}XH^{3+}$ . Trications are, not unexpectedly, more reactive in the gas phase than are dications:  $C_{60}^{3+}$  undergoes partial charge transfer with a substantially greater number of neutrals than does  $C_{60}^{2+}$ , while for those neutrals with which neither  $C_{60}^{2+}$  nor  $C_{60}^{3+}$  react by partial charge transfer, the association reaction 7 is always more efficient for  $C_{60}^{3+}$  than for  $C_{60}^{2+}$ . It appears, also, that this trend in



reactivity holds for the dicationic and tricationic adducts as well as for the bare fullerene cations, so that the

tricationic adducts are more prone to undergo partial charge transfer to XH by reaction 8, or further addition of XH, than are their dicationic counterparts:



As previously noted, the effect of Coulombic repulsion between the product ions of any charge-separating reaction—such as proton transfer from  $C_{60}XH^{3+}$ —is to introduce a reverse activation energy barrier into the reaction profile, with the magnitude of this barrier depending principally upon the distance separating the newly formed product ions. The determination of this reaction distance is therefore crucial to interpreting the reactivity of these fullerene tricationic adducts. In a review of transition-metal dication chemistry, Roth and Freiser [39] have noted that partial charge transfer from an atomic dication  $M^{2+}$  to a reactant neutral XH is likely to dominate over other product channels if the curve crossing for the  $[M^{2+} + XH]$  and  $[M^+ + XH^+]$  potential energy curves occurs at a reactant separation of  $\sim 6$  Å or less. Roth and Freiser [38] have also noted that the “window of opportunity” for transfer of a chemical subunit—typified, in their studies, by  $H^-$  abstraction from the reactant XH—is significantly narrower, peaking at  $\sim 5$  Å but losing in competition with partial charge transfer at most reactant separations either smaller or larger than this value. The potential energy curve for reaction 8 involving a fullerene trication is likely to be quite different from that for partial charge transfer from an atomic dication—for example, bracketing studies suggest that the separation between a multiply charged fullerene ion and a reactant neutral XH must be fairly small, e.g.,  $< 3$  Å, before partial-charge transfer can occur [40]—nevertheless, it is intuitively reasonable that abstraction of an electron from XH by  $C_{60}XH^{3+}$  can occur on a shorter time scale or at a greater separation than transfer of a proton from  $C_{60}XH^{3+}$  to XH. In the present work, we assume that the reactants must be essentially “in contact”—i.e., at a reaction distance of zero—in order to permit the occurrence of proton transfer. Note that, due to the comparatively large diameter of the fullerene cage, this rather simplistic assumption need not result in too severe an uncertainty in the Coulombic term  $\delta$ .

We present, in Table 2, a summary of the upper limits to  $GA_{app}$  and to  $GA$  for those adducts seen to exhibit proton transfer to the corresponding neutrals. The determination of  $GA_{app}$  is, as indicated above, a straightforward result of the observation of proton transfer: the estimation of  $\delta$  (which is then used to derive an upper limit to  $GA$ ) does, however, require some further comment. For each adduct, a structure I(a–h) was deduced as the most likely product to result, from the addition of the nucleophile XH to the electron-deficient fullerene cage  $C_{60}^{3+}$ , in reaction 7. The structures and protonation sites ascribed for these adducts are shown in Figure 1. The diameter of the  $C_{60}$  subunit

**Table 2.** Parameters used to determine upper bounds to the gas-phase acidities of the tricationic adducts  $C_{60} \cdot (XH)_n^{3+}$ 

Species	$GA_{app}^a$	$r_{ij}^b$	$V_3^c$	$\delta^d$	$GA^e$
$C_{60} \cdot NH_3^{3+}$	<195.6	7.38	3.91	97.5	<98
$C_{60} \cdot CH_2CH_2^{3+}$	<155.6	8.03	3.59	90.2	<66
$C_{60} \cdot NCH_3^{3+}$	<163.8	8.06	3.58	89.9	<74
$C_{60} \cdot NCCH_3^{3+}$	<180.6	8.90	3.24	82.1	<99
$C_{60} \cdot O_2NCH_3^{3+}$	<171.9	9.79	2.94	75.2	<97
$C_{60} \cdot O(H)CH_3^{3+}$	<174.1	7.34	3.93	98.0	<76
$C_{60} \cdot O(H)C_2H_5^{3+}$	<180.2	7.34	3.93	98.0	<82
$C_{60} \cdot O(H)C_3H_7^{3+}$	<183.0	7.34	3.93	98.0	<85
$C_{60} \cdot OC(H)CH_2CH_3^{3+}$	<181.8	9.39	3.07	78.2	<104
$C_{60} \cdot OC(H)OH^{3+}$	<171.0	9.31	3.10	78.9	<92
$C_{60} \cdot OC(CH_3)OH^{3+}$	<181.7	9.31	3.10	78.9	<103
$C_{60} \cdot OC(CH_3)OCH_3^{3+}$	<190.0	9.39	3.07	78.2	<112

<sup>a</sup>Upper limit to the apparent gas-phase acidity,  $GA_{app}$ , in kcal mol<sup>-1</sup>. The value shown is equal to the gas-phase basicity (GB) of XH as tabulated in ref 41.

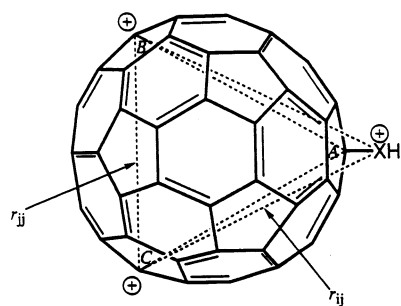
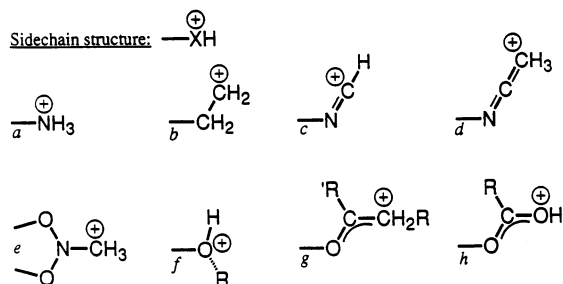
<sup>b</sup>Intercharge separation, in Ångstroms, between the site of protonation and the sites of charge localization upon the fullerene cage, estimated by the method described in the text and employed to approximate the intercharge separation within the transition state to proton transfer.

<sup>c</sup>Calculated Coulombic repulsion, in eV, between the site of protonation and the sites of charge localization on the fullerene cage.

<sup>d</sup>Calculated height of the reverse activation barrier  $\delta$ , in kcal mol<sup>-1</sup>, for proton transfer to XH.

<sup>e</sup>Estimated upper limit, in kcal mol<sup>-1</sup>, to the absolute gas-phase acidity of the fullerene tricationic adduct indicated.

was assumed to be 7.0 Å [42], with the site of functionalization (*A*) and the locations of the two positive charges formally remaining on the fullerene cage (*B*, *C*) forming the vertices of an equilateral triangle inscribed within the fullerene's "equator": the distance  $r_{ij}$  between these two positive charges is thus 6.06 Å. The distance,  $r_{ij}$ , of the protonated atom from each of the two other formal positive charges was then calculated

**1a-h**

**Figure 1.** Proposed structures for the tricationic adducts  $C_{60}XH^{3+}$  discussed in the present work. Sidechains, with assumed site of protonation, are shown for: *a*,  $NH_3$ ; *b*,  $C_2H_4$ ; *c*,  $HCN$ ; *d*,  $CH_3CN$ ; *e*,  $CH_3NO_2$ ; *f*,  $CH_3OH$ ,  $C_2H_5OH$ , and  $C_3H_7OH$ ; *g*,  $C_2H_5CHO$  and  $CH_3COOCH_3$ ; *h*,  $HCOOH$  and  $CH_3COOH$ .

using C–C, C–N, and C–O bond distances of between 1.30 and 1.54 Å, and bond angles of between 108° and 120°, depending upon the formal order of each bond.

Our description of the charge distribution upon  $C_{60}XH^{3+}$  is somewhat speculative, but is well-supported by a range of experimental studies that offer information on the charge distribution upon the "bare" fullerene polycations  $C_{60}^{n+}$  ( $n = 1-7$ ). For example, the observed threshold for charge transfer from  $C_{60}^{2+}$  to various reactants [40], as a function of  $IE(Y)$ , is best interpreted via a model in which the proximity of the reactant neutral *Y* "polarizes" the  $C_{60}^{2+}$  charges, localizing one positive charge at the point of the fullerene surface closest to *Y*, with the other charge diametrically opposed. This model of the  $C_{60}^{2+} \cdots Y$  interaction is validated by a very recent experimental study performed by Cameron and Parks [42], concerning relative rates of reaction for charge transfer from  $C_{60}^{n+}$  ( $n = 1-3$ ) to Li and to Cs. Cameron and Parks [42] note that the Langevin model, which treats the total positive charge as a point source, fails to account for the dependence of charge-transfer reaction rate upon charge state. Other models, involving a uniformly charged fullerene surface or fixed, symmetrically distributed point charges, were also unable to satisfactorily describe the observed kinetic behaviour, while good agreement was obtained with a model featuring a symmetric distribution of point charges, free to move on the fullerene surface in response to the relative motion of  $C_{60}^{n+}$  and *Y* [42]. A very similar model, of symmetrically distributed and localized point charges, has been applied to the fragmentation processes of highly charged fullerene ions  $C_{60}^{n+}$  ( $n = 3-7$ ) by Märk and co-workers [43]. Given the body of evidence which supports a "symmetric, localized, mobile, point-charge" model of the charge distribution for bare fullerene polycations, we feel justified in

extending such a model to describe the  $C_{60}XH^{3+}$  charge distribution.

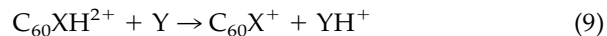
While the fullerene surface can reasonably be regarded as a rigid, well-characterized structure (we assume that the fullerene diameter of 7.0 Å, appropriate to  $C_{60}$  itself [44], is also valid for the trication), the geometries that we have assigned for each sidechain are more uncertain: it is not clear to what degree the sidechain's bond lengths and bond angles are affected by Coulombic repulsion. Furthermore, the structures ascribed to some of the adducts may not correctly describe the reacting species: for example, the adduct with HCN may instead be  $^{2+}C_{60} \cdot CNH^+$ , if rearrangement of the adduct occurs between the addition step and the subsequent deprotonation reaction. For these reasons, we assign a large uncertainty of  $+10/-30$  kcal mol $^{-1}$  to the parameter  $\delta$ .

The uncertainty in  $\delta$  is not symmetrical, because the interpretation that the reverse activation barrier height is equal to the Coulombic repulsion (between the protonated atom and the fullerene cage charges) is expected to represent an extreme case. The chief uncertainties in an estimate of the reverse activation barrier are, firstly, the charge separation at the transition state to proton transfer to XH and, secondly, the value of the dielectric polarizability of the transition state. The values which we have chosen for these parameters are likely lower limits in each case, and since the Coulombic repulsion is inversely proportional to both the intercharge separation and the dielectric polarizability, our estimated reverse activation barriers may be too high. A recent ab initio study by Gronert [22] has suggested that the "model system" of proton transfer from diprotonated diamines  $^+H_3N(CH_2)_nNH_3^+$  to  $NH_3$ , which has previously been studied both theoretically [20] and experimentally [24], is characterized by exceptionally long  $N \cdots H^+ \cdots N$  bond lengths in the transition state, and therefore the assumption that we have made here, of a close interaction between reactants, may not be valid. However, Roth and Freiser [39] have inferred, from experimental studies on metal-containing dications, that the charge separation in ion-transfer reactions such as proton transfer and hydride abstraction is generally appreciably less than the charge separation in electron transfer reactions involving dications, and our bracketing studies of charge transfer from  $C_{60}^{2+}$  to various neutrals [40] indicate that partial-charge transfer from  $C_{60}^{2+}$  is viable only at close interactions ( $\sim 1-2$  Å) of the reactants. We therefore expect that proton transfer from multiply charged fullerene adduct ions will also only be viable at close reactant separations. With regard to the dielectric polarizability  $\epsilon_r$ , we have assumed a value of 1.0 while studies on various multiply protonated species in the gas phase have recommended values for  $\epsilon_r$  of  $1.01 \pm 0.07$  for diprotonated diaminoalkanes [24],  $<1.2$  for the diprotonated peptide gramicidin S [9], and  $2.0 \pm 0.2$  for multiply protonated cytochrome *c* ( $M + nH$ ) $^{n+}$ ,  $n = 3-15$  [10]. Given the near-unity values reported for  $\epsilon_r$  for the diprotonated diaminoal-

kanes and gramicidin S (species that are in a similar charge state to the fullerene adduct ions, and with similar intercharge separations estimated by molecular modelling [9, 10]), we believe that our choice of  $\epsilon_r = 1.0$  is reasonable.

It should be noted that the barrier  $\delta$  is not simply the sum,  $V'_3$ , of the Coulombic repulsions between the positive charge on the protonated atom and each of the charges on the fullerene cage, although this sum is expected to be the major component of  $\delta$ . The barrier  $\delta$  also contains a component  $V''_2$  [43], which arises from the distortion of the charge distribution upon the dicationic product ion  $C_{60}X^{2+}$  by the proximity of the monocationic product ion  $XH_2^+$ . For charge transfer from  $C_{60}^{3+}$  to various neutrals [45, 46], we have determined a value of  $V''_2 = 0.32$  eV, and we use this value in the present work also. Other components present in  $\delta$  include attractive ion/dipole and ion/induced dipole interactions, although these are expected to be substantially outweighed by repulsive Coulombic terms, and in our experience (for the well-categorized example of partial charge transfer from  $C_{60}^{2+}$  to a neutral X [40]) these attractive interactions can be neglected without a grave loss of accuracy.

The thermochemical data derived from these reaction studies is clearly not definitive: we are unable to determine anything other than an upper or lower limit to the GA of the respective tricationic adducts. It is certainly desirable, if these adduct ions are to be of use as "model systems," to tie down their thermochemistry more rigorously: however, it is not easy to see how this could be done. We believe that the fullerene-adduct bond is generally much too weak to survive such a process as triple ionization within an electron-impact ion source, even if it were possible to produce the neutral adducts by chemical synthesis, while the tendency of  $C_{60}^{3+}$  to react efficiently with virtually all neutrals precludes a "bracketing" study involving sequential introduction of two neutrals, XH and Y, into the reaction region. (Such a strategy may, however, be appropriate to the adducts of the less reactive  $C_{60}^{2+}$ , and we are currently attempting a study to determine the occurrence or absence of proton transfer in various reactions of the type 9



where Y is a neutral with which  $C_{60}^{2+}$  does not react measurably.)

In the absence of more detailed thermochemical data on  $C_{60}XH^{3+}$ , it is still possible to draw some conclusions from the present results.

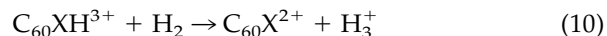
Studies on multiply protonated biomolecules [4, 5, 7, 9–11, 14, 16] have indicated that the tendency for proton donation to a reactant neutral depends upon the degree of protonation  $n$  of the species  $MH_n^{n+}$ , with  $GA_{app}$  decreasing as  $n$  increases. In the context of the present study, it should be noted that the systems

$C_{60}XH^{2+}$  and  $C_{60}XH^{3+}$  differ in their degree of ionization rather than their degree of protonation. Nevertheless, in both  $C_{60}XH^{2+}$  and  $C_{60}XH^{3+}$  the possible sites of deprotonation are identical (barring gross structural differences between the dicationic ions and their tricationic analogs), and we would therefore expect a similar trend to that evident in the studies on multiply protonated biomolecules. Although the nature of the results obtained from our SIFT studies—namely, determination only of an upper or lower limit to  $GA_{app}$ —prevents us from identifying more than a handful of examples, we can point to  $C_{60}(CH_3CN)^{n+}$  as an instance where the tricationic adduct is clearly more acidic than the dicationic adduct: on the basis of the Coulombic effects for the respective proton-transfer reactions, we can assume that the difference in the gas-phase acidities of  $C_{60}(CH_3CN)^{2+}$  and  $C_{60}(CH_3CN)^{3+}$  is more than 42 kcal mol<sup>-1</sup>. It is likely that the GAs of other dicationic and tricationic adducts also differ by a similar degree, although our data does not allow us to verify this. It is notable, perhaps, that the tricationic adduct  $C_{60}(C_2H_4)^{3+}$  is observed [34] to transfer a proton to the parent hydrocarbon, whereas none of the several dicationic adducts of hydrocarbons exhibits such a proton transfer mode ( $C_2H_4$  itself does not measurably add to  $C_{60}^{2+}$ , and so a more direct comparison is not possible).

We have also observed substantial differences in the reactivity of the dicationic adduct  $C_{60}XH^{2+}$  and the corresponding “deprotonated tricationic adduct”  $C_{60}X^{2+}$ . For example, none of the deprotonated adducts  $C_{60}X^{2+}$ , resulting from the chemistry initiated by the reaction of  $C_{60}^{3+}$  with alcohols or with carboxylic acids, are seen to exhibit proton transfer to the parent neutral XH [31, 33], whereas such proton transfer is seen from  $C_{60}XH^{2+}$  for these classes of compounds. This observation can be rationalized on structural grounds, because the hydroxyl group contains the only acidic hydrogen in the ROH or RCOOH molecules: deprotonation of this site; a lack of further deprotonation from  $C_{60}X^{2+}$  is consistent with the structures that we have ascribed for the  $C_{60}XH^{n+}$  adducts. In contrast, further proton transfer is seen from  $C_{60}NH_2^{2+}$  to  $NH_3$  [30], and from  $C_{60}OH^{2+}$  [formed by alkyl cation transfer from  $C_{60}O(H)R^{3+}$  in the reaction chemistry initiated by  $C_{60}^{3+} + ROH$ ] to the alcohols  $C_2H_5OH$ ,  $n$ - $C_3H_7OH$ , and  $i$ - $C_3H_7OH$  [31]. We have suggested [30] that the  $C_{60}NH_2^{2+}$  adduct possesses a “bridging N” structure, and a similar bridged structure (e.g., a protonated epoxide) may also account for the evident acidity of  $C_{60}OH^{2+}$ . Incidentally, the occurrence of proton transfer from  $C_{60}OH^{2+}$  to  $C_2H_5OH$  provides upper limits for  $GA_{app}$  (<181 kcal mol<sup>-1</sup>) and  $GA$  (<141 kcal mol<sup>-1</sup>) for this dication: note that  $GA(C_{60}OH^{2+})$  cannot greatly exceed  $GA(C_{60}H^{2+})$ , for which we have determined a value of  $124 \pm 8$  kcal mol<sup>-1</sup> [29].

It is worth noting that the upper limits to  $GA$ , determined for those tricationic adducts that do undergo proton transfer to the parent neutral, are all very low: for comparison, the gas-phase basicity of  $H_2$  is 94.6

kcal mol<sup>-1</sup> [41]. Therefore, for most (if not all) of the adducts featured in Table 2, the reaction



is estimated to be exothermic—although the large Coulombic term  $\delta$  makes it quite likely that this proton transfer reaction would not measurably occur for these adducts. Indeed, measurements of reaction 10 for  $XH = C_2H_4$ ,  $CH_3CN$ , and  $CH_3COOH$  indicated no reaction,  $k < 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, at room temperature and 0.35 torr of helium.

Studies on the apparent gas-phase acidities of multiply protonated peptide ions have indicated that  $GA_{app}$  depends only weakly upon the degree of protonation: for example, the trend in  $GA_{app}([M + nH]^{n+})$  values for bovine ubiquitin is for an increase in  $GA_{app}$  with decreasing  $n$ , with  $GA_{app} = 205.0 \pm 5.7$  kcal mol<sup>-1</sup> for  $n = 13$  to  $GA_{app} = 224.0 \pm 5.3$  kcal mol<sup>-1</sup> for the most abundant isomer for  $n = 4$  [16]. Although this appears consistent with our observation that the majority of adducts  $C_{60}XH^{n+}$  that undergo proton transfer to XH for  $n = 3$  also undergo proton transfer to XH for  $n = 2$ , it appears at variance with the finding that many of the species  $C_{60}X^{2+}$  (which result from the proton transfer reaction of  $C_{60}XH^{3+} + XH$ ) do *not* undergo further proton transfer with XH. This distinction underscores our interpretation that, although the peptide polycations are genuinely polyprotonated, most of the fullerene tricationic adducts cannot properly be considered as multiply protonated species. Another difference between our results and those involving polyprotonated biomolecules is that the derivatized fullerene trications  $C_{60}XH^{3+}$  feature substantially larger reverse activation energy barriers to proton transfer than those reported elsewhere [9–11, 13, 14] for multiply protonated peptides or proteins. This distinction appears to be a consequence of the structural rigidity of the fullerene skeleton, which facilitates a greater degree of charge crowding (and which may offer less charge shielding, as diagnosed by the dielectric polarizability  $\epsilon_r$ ) than is possible in more flexible structures of comparable mass-to-charge ratio. Notwithstanding these differences, the fullerene adduct ions do have several features (such as comparative structural inflexibility and simplicity of functionalization) that are useful attributes for a class of “model” gas-phase polycations. In future studies, we intend to bracket more closely the gas-phase acidities of the dicationic adducts  $C_{60}XH^{2+}$ , and to employ molecular modeling methodologies on the energetics of proton transfer from the dicationic and tricationic adducts to the parent neutral XH.

## Conclusions

The adducts of  $C_{60}^{3+}$  with various small, hydrogen-bearing neutrals XH are found to be, in general, highly reactive with respect to proton transfer to the parent

neutral. These observations allow the establishment of upper limits to  $GA_{app}$  and to  $GA$  for these tricationic adducts. In some instances, a clear difference in the proton-transfer reactivity of  $C_{60}XH^{2+}$  and  $C_{60}XH^{3+}$  is apparent. Derivatized fullerene polycations have a great potential as models of more complex polycations such as multiply protonated protein molecules: the extreme rigidity of the fullerene cage, and the simplicity of the functionalizing species  $XH$ , ensure that the site of protonation and the interchange separation in the reactant can be determined with a higher degree of confidence than is typically possible for large, multiply charged species. We hope to exploit these advantages in further experimental and theoretical studies on these systems.

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