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Proton Transfer from a Fullerene Dication: Bracketing the Gas-Phase Acidity of $C_{60}H^{\bullet 2+}$

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Abstract: Several gas-phase ion–molecule reactions of the hydrogenated fullerene dication $C_{60}H^{\bullet 2+}$ (produced by the reaction of $C_{60}{}^{\bullet 3+} + C_3H_8$) have been studied using a SIFT apparatus at 0.35 ± 0.01 Torr and 294 ± 2 K. Proton transfer from $C_{60}H^{\bullet 2+}$ to the neutrals CH_2CHCN, CH_3OH, CH_3NO_2, HCOOH, $CH_2(CN)_2$, H_2CO, and HCN has been observed but was not detected in reactions of $C_{60}H^{\bullet 2+}$ with several other neutrals. The occurrence of efficient proton transfer to neutrals having a gas-phase basicity (GB) value >170 kcal mol^{-1} and failure to proton transfer with neutrals having GB < 163 kcal mol^{-1} is used to bracket the gas-phase acidity of $GA(C_{60}H^{\bullet 2+}) = 124 \pm 8$ kcal mol^{-1}, when consideration is taken of the effects of Coulombic repulsion between the product ions. The reactivity of $C_{60}H^{\bullet 2+}$ is compared to that of $C_{60}{}^{2+}$ and thermochemical data are derived for $\Delta H_f{}^\circ(C_{60}H^{\bullet 2+})$, $IE(C_{60}H^+)$, the hydrogen-atom affinity of $C_{60}{}^{2+}$, and the hydride affinity of $C_{60}{}^{\bullet 3+}$.

Introduction

Proton transfer, from a monocation to a neutral species or from a neutral to an anion, is one of the most widely-studied types of ion–molecule reactions in the gas phase,[1,2] and there exists a substantial database of thermochemical information derived from such studies.[3,4] The occurrence of proton transfer from a dication to a neutral has received considerably less study, due largely to the difficulty of generating and studying molecular dications using available techniques. Previous reports of proton transfer reactions of the type

$$XH^{2+} + Y \rightarrow X^+ + YH^+ \qquad (1)$$

have concerned the observation of proton transfer from $Ca{\cdot}H_2O^{2+}$ to H_2O[5] and from $NbCH_2{}^{2+}$ to CO but not to CH_4.[6] Recently, the development of electrospray ionization (ESI) and similar techniques has permitted the generation and study of multiply-protonated proteins and other large molecules, and proton transfer from these polycations to neutrals such as CH_3NH_2[7] and H_2O[8] has been reported.

Theoretical treatments of proton loss from dications[9,10] have suggested that most such processes can be viewed as hydrogen-atom loss, followed by charge transfer at larger separations—though this model is disfavored if $IE(X^+) < IE(H^\bullet)$, as is the case for $X = C_{60}$. It has long been understood,[11,12] though perhaps not widely known, that the energetics of charge-separating reactions of multiply-charged ions (e.g. charge transfer, hydride abstraction, proton transfer) are influenced by the occurrence of Coulombic repulsion between the product ions. To be efficient, a charge-separating reaction must have an exothermicity in excess of the reverse activation barrier which arises from the Coulombic repulsion between the product ions at their closest separation.[13,14]

We have embarked upon a systematic study of the gas-phase ion–molecule reactivity of fullerenes.[14–28] In previous reports,[14,25,26] we have used the occurrence or absence of charge transfer, from $C_{60}{}^{2+}$ and from $C_{60}{}^{\bullet 3+}$ to a variety of neutrals, to address the discrepancy between earlier values of $IE(C_{60}{}^{\bullet +})$ and to recommend a value of $IE(C_{60}{}^{2+}) = 15.6 \pm 0.5$ eV. We have noted the occurrence of rapid proton transfer from $C_{60}{\cdot}NH_3{}^{2+}$ to NH_3,[17] and we have also used the occurrence or absence of proton transfer, from a variety of fullerene dicationic adducts $C_{60}{\cdot}XH^{2+}$ to the neutral XH, to loosely estimate the gas-phase acidities of these dications.[22] Here we report the results of a bracketing study of proton transfer from the prototypical hydrogenated fullerene dication $C_{60}H^{\bullet 2+}$ to a variety of neutrals.

Experimental Section

All measurements were performed at 294 ± 2 K and a helium buffer gas pressure of 0.35 ± 0.01 Torr, using a selected-ion flow tube (SIFT)

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which has been described previously.[29] $C_{60}H^{\bullet 2+}$ was generated from $C_{60}^{\bullet 3+}$ (produced by 100 eV electron bombardment of a mixture of C_{60} vapor and argon, in a conventional electron-ionization source) by the reaction of $C_{60}^{\bullet 3+}$ with C_3H_8, discussed below. H_2CO and HCN was prepared according to the methods of Spence and Wild[30] and Melville and Gowenlock,[31] respectively. Other neutrals were commercially obtained and were of high stated purity (>99%). Malononitrile, $CH_2(CN)_2$, was added to the tube as a stream of helium vapor saturated with malononitrile, using a method which we have previously used for naphthalene.[32] Other reactant neutrals were admitted to the flow tube either as a pure gas or, for neutrals having low vapor pressure, as a dilute (1–10%) mixture in high-purity (>99.995%) helium. Rate coefficients reported here are estimated to have an uncertainty of ±30% unless specified otherwise.

Results and Discussion

$C_{60}H^{\bullet 2+}$ was formed in the flow tube by the reaction[33]

$$C_{60}^{\bullet 3+} + C_3H_8 \rightarrow C_{60}H^{\bullet 2+} + C_3H_7^{+} \quad [0.9] \qquad (2a)$$

$$\rightarrow C_{60}^{2+} + C_3H_8^{\bullet +} \quad [0.1] \qquad (2b)$$

for which we have measured a rate coefficient of $k = 4.2 \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹.[26] $C_{60}H^{\bullet 2+}$ is observed to undergo a further, but much slower, hydride abstraction with C_3H_8:

$$C_{60}H^{\bullet 2+} + C_3H_8 \rightarrow C_{60}H_2^{\bullet +} + C_3H_7^{+} \qquad (3)$$

($k = 1.5 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹). This is, incidentally, almost identical to the rate coefficient which we have measured for the H^- abstraction reaction of $C_{60}^{2+} + C_3H_8$.[18] The very low rate coefficient for reaction 3 compared to reaction 2 permits the complete conversion of $C_{60}^{\bullet 3+}$ to $C_{60}H^{\bullet 2+}$ and C_{60}^{2+} upon addition of sufficient C_3H_8 to the flow tube. The reaction of $C_{60}H^{\bullet 2+}$ with various neutrals was investigated by addition of the neutral in question to the flow tube, 25 cm downstream from the inlet used to introduce C_3H_8. The results obtained are summarized in Table I.

Typical experimental data, for the reaction of $C_{60}H^{\bullet 2+}$ with CH_3NO_2, is shown in Figure 1. There is significant curvature in the decay of the $C_{60}H^{\bullet 2+}$ ion signal, as plotted against the CH_3NO_2 flow. This curvature was evident in all of the $C_{60}H^{\bullet 2+}$ reactions surveyed here, with the exception of those with i-C_4H_{10}, C_3H_8, $NO^\bullet$, and those compounds with which $C_{60}H^{\bullet 2+}$ was observed not to react. The unreactive component of the $C_{60}H^{\bullet 2+}$ ion signal is attributed to C_{60}^{2+} (produced by reaction 2b), which cannot be resolved from $C_{60}H^{\bullet 2+}$ in the high-mass-range mode used in these experiments, but whose presence is indicated by the observed formation of the companion product ion $C_3H_8^{\bullet +}$ in reaction 2. (The low-mass-range mode does permit unit mass resolution—making possible the assignment of product channels of $C_{60}H^{\bullet 2+} + X$ due to proton transfer, charge transfer, or hydride abstraction—but it is capable only of detecting ions having m/z < 200.) The rate coefficients listed in Table I have been determined by subtracting the "background" signal due to C_{60}^{2+} from the total reactant ion signal, as depicted in Figure 1.

Table I. Rate Coefficients and Product Distributions for Reactions of $C_{60}H^{\bullet 2+}$ with Various Neutrals

reactant	products	k_{obs}[a]	k_c[b]	GB(X)[c]	IE(X)[d]
CH_2CHCN	$C_{60}^{\bullet +} + CH_2CHCNH^+$	7.0	4.51	181.9	10.91
CH_3OH	$C_{60}^{\bullet +} + CH_3OH_2^+$	1.9	2.92	174.1	10.85
CH_3NO_2	$C_{60}^{\bullet +} + CH_3NO_2H^+$	1.2	3.73	171.7	11.02
HCOOH	$C_{60}^{\bullet +} + HCOOH_2^+$	3.2	2.27	170.4	11.33
$CH_2(CN)_2$	$C_{60}^{\bullet +} + NCCH_2CNH^+$	0.45[e]	3.64	167.4	12.70
H_2CO	$C_{60}^{\bullet +} + H_2COH^+$	0.34	3.48	164.3	10.87
HCN	$C_{60}^{\bullet +} + HCNH^+$	0.14	4.23	163.8	13.60
H_2S	$C_{60}H_2^{\bullet +} + HS^+$	0.008	2.26	162.8	10.45
CS_2	none	<0.001	1.68	158.0[f]	10.07
C_2H_4	none	<0.001	1.86	155.6	10.51
i-C_4H_{10}	$C_{60}H_2^{\bullet +} + C_4H_9^+$	0.015	1.84	155.5	10.57
C_2H_2	none	<0.001	1.78	146.1	11.40
C_3H_8	$C_{60}H_2^{\bullet +} + C_3H_7^+$	0.0015	1.90	142.0	10.95
CO	none	<0.001	1.28	133.9[g]	14.01
$NO^\bullet$	$C_{60}H^+ + NO^+$	0.015	1.18	119.0[g]	9.26
O_2	none	<0.001	1.06	95.0	12.06

[a] Observed effective bimolecular rate coefficient at 294 ± 2 K and 0.35 ± 0.01 Torr of helium, in units of 10^{-9} cm³ molecule⁻¹ s⁻¹. [b] ADO collision rate coefficient in units of 10^{-9} cm³ molecule⁻¹ s⁻¹, calculated according to the method of Su and Bowers.[34] [c] Gas-phase basicity of the reactant neutral in kcal mol⁻¹, as given in the tabulation of Lias et al.[3] [d] Ionization energy of the reactant neutral in eV, as given in the tabulation of Lias et al.[4] [e] Direct determination of this rate coefficient was not possible since malononitrile was added as a saturated solution in helium vapor: the vapor pressure of $CH_2(CN)_2$ at 294 ± 2 K has not been determined. The reaction of $Ar^{\bullet +} + CH_2(CN)_2$ was also studied using the same method to introduce malononitrile: $Ar^{\bullet +}$ was generated in the ion source by electron impact upon argon, and the rate coefficient for the charge-transfer reaction of $Ar^{\bullet +} + CH_2(CN)_2$ is anticipated to be equal to the calculated ADO collision rate coefficient[34] by analogy with the rate coefficients for reaction of $Ar^{\bullet +}$ with other polyatomic molecules.[35] The rate coefficient shown here for $C_{60}H^{\bullet 2+}$ was obtained by a comparison of the decays in the $C_{60}H^{\bullet 2+}$ and $Ar^{\bullet +}$ ion signals with added $CH_2(CN)_2$ and has an estimated uncertainty of +100%/−50%. [f] Re-evaluated as given in ref 4. [g] Re-evaluated as given in ref 36.

The reaction series shown in Table I appears to be that of a reasonably well-behaved proton transfer system. Efficient proton transfer ($k_{obs} \sim k_c$) is seen to all the neutrals X having GB(X) ≥ 170.4 kcal mol⁻¹; inefficient proton transfer ($k_{obs} < k_c$) is noted for $CH_2(CN)_2$ (GB = 167.4 kcal mol⁻¹), H_2CO (GB = 164.3 kcal mol⁻¹), and HCN (GB = 163.8 kcal mol⁻¹); and proton transfer does not occur ($k_{obs} < 0.001k_c$) for all the neutrals having GB(X) ≤ 162.8 kcal mol⁻¹. These results bracket the "apparent gas-phase acidity",[22] GA_{app}, of $C_{60}H^{\bullet 2+}$ as 166 ± 4 kcal mol⁻¹. As we have discussed elsewhere,[22] the absolute gas-phase acidity $GA(C_{60}H^{\bullet 2+})$ can be determined from this using the relation

$$GA(XH^{2+}) = GA_{app}(XH^{2+}) - \delta \qquad (4)$$

where δ is a reverse activation barrier to the occurrence of proton transfer. A rigorous treatment of δ should include consideration of ion/dipole, ion/induced dipole and, to a lesser extent, dipole/induced dipole interactions as well as a consideration of the Coulombic repulsion expected between the initially adjacent monocationic products. However, we contend that as a first approximation δ can be taken as equal to the Coulombic repulsion $q\phi_r$ expected between point charges at an intercharge separation r. Bursey and Pedersen[37] have performed semiempirical MOPAC6.1 (AMI) force field calculations upon the species involved in the reaction

$$^{+}H_3NCH_2CH_2CH_2NH_3^{+} + NR_3 \rightarrow {}^{+}H_3NCH_2CH_2CH_2NH_2 + NR_3H^{+} \qquad (5)$$

and have determined that the enthalpy of formation of the hydrogen-bonded ion pair $[^{+}H_3N(CH_2)_3NH_2\cdots HNR_3^{+}]$ exceeds the sum of the enthalpies of formation of the separated product ions by 77% (for R = H) and 92% (for R = CH_3) of the expected Coulombic repulsion at the calculated intercharge separation. This calculation therefore provides some theoretical support for assuming that $q\phi_r$ does not greatly exceed δ. We assume here,

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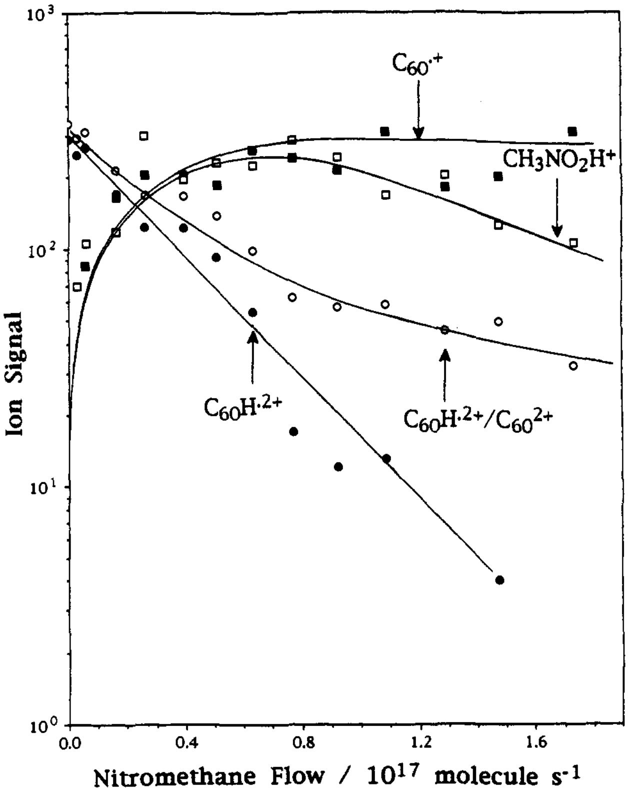

Figure 1. Experimental data for the reaction of $C_{60}H^{\cdot 2+}$ with nitromethane, CH_3NO_2, at 294 ± 2 K and 0.35 ± 0.01 Torr. As detailed in the text, approximately 15% of the monitored $C_{60}H^{\cdot 2+}/C_{60}^{2+}$ ion signal (hollow circles) is unresolved C_{60}^{2+}, which reacts slowly ($k = 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1})[28] by association with CH_3NO_2. Subtraction of 15% of the initial ion signal yields the corrected ion signal (filled circles) which shows the reaction of $C_{60}H^{\cdot 2+}$ with CH_3NO_2 by proton transfer, with an observed rate coefficient of 1.2×10^{-9} cm^3 molecule^{-1} s^{-1}. The primary products of this reaction, $C_{60}^{\cdot +}$ and $CH_3NO_2H^+$, are also shown: the reduction in $CH_3NO_2H^+$ ion signal intensity, visible at large CH_3NO_2 flows, arises from a subsequent addition reaction with CH_3NO_2 to form the proton-bound dimer, $(CH_3NO_2)H^+$ (*m/z* 123). This secondary product signal was detected but was not monitored due to the low overall signal intensity.

as we have elsewhere,[14,22,25,26] that charge-separating reactions involving multiply-charged fullerene ions occur only upon a close approach of the neutral X to the fullerene polycation. The Coulombic effects expected for proton transfer from $C_{60}H^{\cdot 2+}$ are likely to be very similar to those affecting charge transfer from C_{60}^{2+}, and so we assume an intercharge separation, at the point of proton transfer, of 8.0 ± 0.7 Å[25,26] giving rise to a Coulombic repulsion component of $q\phi_r = 1.80 \pm 0.16$ eV (42 ± 4 kcal mol^{-1}). This yields GA($C_{60}H^{\cdot 2+}$) = 124 ± 8 kcal mol^{-1}, from which a number of other thermochemical quantities can be tabulated (see Figure 2) given the known thermochemistry of C_{60} and its ionized and protonated forms.

The values shown in Figure 2 have been obtained as follows. $\Delta H_f°$(C_{60}, crystalline, 298 K) has been determined as 545.0 ± 3.2 kcal mol^{-1} by Beckhaus et al.[38] and as 578.9 ± 3.3 kcal mol^{-1} by Steele et al.[39] The latter value yields $\Delta H_f°$(C_{60}, g, 298 K) = 635 ± 6 kcal mol^{-1},[39] and a similar calculation using the value of Beckhaus et al. gives $\Delta H_f°$(C_{60}, g, 298 K) = 601 ± 6 kcal mol^{-1}. Both of these thermodynamic determinations (which lie near the middle of a range of calculated theoretical values encompassing $\Delta H_f°(C_{60})$ = 286–973 kcal mol^{-1})[40] involve repeated and reproducible measurements of the combustion of C_{60} in a bomb calorimeter: the discrepancy between the two results presumably indicates a systematic error in one of the experiments. In the present study, we have adopted the gas-phase value of Steele et al. ($\Delta H_f°(C_{60})$ = 635 ± 6 kcal mol^{-1}) rather than the earlier determination of Beckhaus et al., although we concede that there is, at present, insufficient basis to establish which of the two results is more accurate. Our intent in selecting an enthalpy of formation for gas-phase, neutral C_{60} is largely to set a scale of enthalpies of formation of the gas-phase ions which can be generated from C_{60} (since $\Delta H_f°$ for these ions cannot at present be derived independently from any other known thermodynamic parameters), and any subsequent revision of $\Delta H_f°(C_{60})$ will necessarily indicate adjustment, by an equal amount, of the ionic enthalpies of formation presented in Figure 2.

Other thermochemical values used here are IE(C_{60}) = 7.61 ± 0.02 eV,[41] AP(C_{60}^{2+}/C_{60}) = 19.00 ± 0.03 eV,[42] IE(C_{60}^{2+}) = 15.6 ± 0.5 eV,[26] PA(C_{60}) = 205.5 ± 1.5 kcal mol^{-1},[43] and GA($C_{60}H^{\cdot 2+}$) = 124 ± 8 kcal mol^{-1} as reported in the present work. $\Delta H_f°$ values for the various C_{60}^{n+} species are, therefore, obtained as $\Delta H_f°(C_{60}^{\cdot +}) = \Delta H_f°(C_{60}) + IE(C_{60})$; $\Delta H_f°(C_{60}^{2+}) = \Delta H_f°(C_{60}) + AP(C_{60}^{2+}/C_{60})$; and $\Delta H_f°(C_{60}^{\cdot 3+}) = \Delta H_f°(C_{60}) + AP(C_{60}^{2+}/C_{60}) + IE(C_{60}^{2+})$. $\Delta H_f°(C_{60}H^+)$ has been calculated from PA(C_{60}), since this quantity equals $\Delta H°$ for the reaction

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

Calculation of $\Delta H_f°(C_{60}H^{\cdot 2+})$ requires a determination of $\Delta H°$ for the reaction

$$C_{60}H^{\cdot 2+} \rightarrow C_{60}^{\cdot +} + H^+ \qquad (7)$$

$\Delta G°$ for this reaction is GA($C_{60}^{\cdot 2+}$), determined above. The entropy change for reaction 7 is expected to be equal, to a good approximation, to $\Delta S_{trans} + \Delta S_{rot}$, the sum of the changes in translational and rotational entropy. At 298 K, $T\Delta S_{trans}$ = 7.7 kcal mol^{-1}; $T\Delta S_{rot}$ = 2.4 kcal mol^{-1} assuming that the charge upon $C_{60}^{\cdot +}$ is effectively delocalized and $C_{60}^{\cdot +}$ therefore possesses the same rotational symmetry number as C_{60} ($\sigma(C_{60}^{\cdot +}) = 60$), and that the hydrogen atom in $C_{60}H^{\cdot 2+}$ is bonded to a specific carbon atom ($\sigma(C_{60}H^{\cdot 2+}) = 1$). From these quantities, $\Delta H°$ = 134 ± 8 kcal mol^{-1} can be obtained for reaction 7, leading to $\Delta H_f°(C_{60}H^{\cdot 2+})$ = 952 ± 9 kcal mol^{-1}. The ionization energy of $C_{60}H^+$ can be obtained as $\Delta H_f°(C_{60}H^{\cdot 2+}) - \Delta H_f°(C_{60}H^+)$. Values for hydride affinities and hydrogen atom affinities have been obtained from the $\Delta H_f°$ values shown in Figure 2, and from $\Delta H_f°(H^-)$ = 145 kcal mol^{-1} and $\Delta H_f°(H^\cdot)$ = 52.10 kcal mol^{-1}.[4] Since the $\Delta H_f°$ values in Figure 2 are all expressed relative to $\Delta H_f°(C_{60})$ = 545 kcal mol^{-1}, all uncertainties are also relative and ignore any uncertainty in $\Delta H_f°(C_{60})$ itself: any future revision of the enthalpy of formation of C_{60} will result in alteration, by an identical amount, of the enthalpies of formation of these ionized fullerene species.

We note that $C_{60}H^{\cdot 2+}$ is a substantially stronger acid than $C_{60}H^+$, even after consideration of the Coulombic effects which act to destabilize $C_{60}H^{\cdot 2+}$: that is, GA($C_{60}H^+$) − GA($C_{60}H^{\cdot 2+}$) > $q\phi_r$. This is consistent with the trend in IE(C_{60}) and IE($C_{60}^{\cdot +}$), which differ by a quantity (3.78 ± 0.07 eV = 87.2 ± 1.6 kcal mol^{-1}) substantially greater than the Coulombic repulsion ($q\phi_r$ = 2.06 eV = 47.5 kcal mol^{-1}) expected for two charges separated by the diameter of C_{60} ($d(C_{60})$ = 7.0 Å).[44] A possible rationalization for this additional destabilization is that the two charges are not independent. Coulombic repulsion constrains the two charges to remain more-or-less as far from each other

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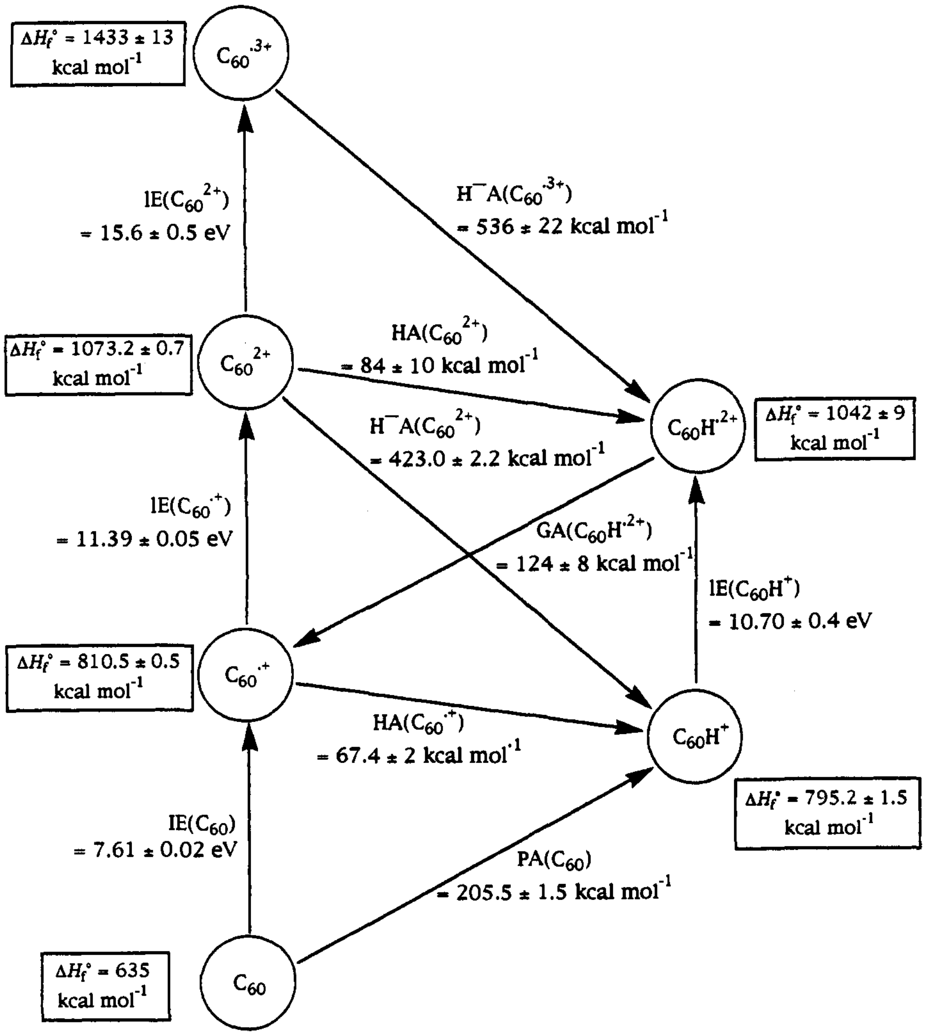

Figure 2. Thermochemical data relating to ionization and protonation of C_{60} (HA = hydrogen atom affinity; $H^{-}A$ = hydride affinity; GA = gas-phase acidity; PA = proton affinity). All heats of formation are calculated relative to the value $\Delta H_f^\circ(C_{60})$ = 635 kcal mol^{-1}, determined by Steele et al.[39] Uncertainties in $\Delta H_f^\circ(C_{60})$ are disregarded in this scheme, since such uncertainties do not affect the relative uncertainties in the other thermodynamic quantities shown.

as possible: thus, although the charge pair may be delocalized to some extent, the position of each charge is directed by the other. As a result, the delocalization energy associated with C_{60}^{2+} and $C_{60}H^{\bullet 2+}$ may be substantially less than the delocalization energy of $C_{60}^{\bullet +}$ and $C_{60}H^{+}$.

We have observed addition reactions of C_{60}^{2+} with a wide variety of neutrals.[16,18,21,23] Aside from proton transfer (which is not a product channel accessible to C_{60}^{2+}!) there is a general similarity in the reactivity of C_{60}^{2+} and $C_{60}H^{\bullet 2+}$, and it might be anticipated that the addition chemistry of $C_{60}H^{\bullet 2+}$ would follow that of C_{60}^{2+}. However, if it is assumed that $C_{60}H^{\bullet 2+}$ will not add efficiently to those neutrals with which C_{60}^{2+} does not form adducts, the prospects for association reactions of $C_{60}H^{\bullet 2+}$ appear meager. Of all the neutrals to which C_{60}^{2+} has been observed to add detectably,[16,18,21,23] the weakest base is HCOOH (GB = 171.0 kcal mol^{-1})[3]—to which rapid proton transfer occurs from $C_{60}H^{\bullet 2+}$, as shown in Table I. It appears, therefore, that association of $C_{60}H^{\bullet 2+}$ with various neutrals will not occur except in competition with proton transfer. In other reactions of fullerene dications which have exhibited competition between proton transfer and association,[17,22] proton transfer is invariably the dominant product channel: this pattern is also likely to be evident in the reaction chemistry of $C_{60}H^{\bullet 2+}$.

Previous studies of fullerene ion chemistry have indicated that the dication $C_{60}H^{\bullet 2+}$ can be formed by the reaction of C_{60}^{2+} with atomic hydrogen[15]

$$C_{60}^{2+} + H^{\bullet} \rightarrow C_{60}H^{\bullet 2+} \qquad (8)$$

and by hydride abstraction reactions of $C_{60}^{\bullet 3+}$—for example, reaction 2 employed in this study. We have also conjectured previously that reaction 8 may be efficient within interstellar clouds and circumstellar shells, environments which are expected to contain significant abundances of atomic hydrogen and fullerenes[45,46] (including fullerene dications).[19,47] The observed high efficiency of proton transfer from $C_{60}H^{\bullet 2+}$ to neutrals of GB > 170 kcal mol^{-1} suggests that proton transfer from $C_{60}H^{\bullet 2+}$ will be a viable loss mechanism for fullerene dications in interstellar environments. However, the comparatively low interstellar abundance of neutrals having GB > 170 kcal mol^{-1} indicates that subsequent hydrogenation reactions such as

$$C_{60}H^{\bullet 2+} + H^{\bullet} \rightarrow C_{60}H_2^{2+} \qquad (9)$$

(which appears to be efficient under the conditions attainable with our SIFT apparatus)[16] are likely to compete effectively with proton transfer as a loss mechanism for $C_{60}H^{\bullet 2+}$. The reaction chemistry of these more highly hydrogenated fullerene dications is, in the absence of viable experimental methods for producing $C_{60}H_2^{2+}$, a subject for further investigation. By analogy with the

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reaction chemistry of $C_{60}H^{\bullet 2+}$ discussed here, we anticipate that these more highly hydrogenated ions should readily proton transfer but should not undergo addition with many molecules.

We believe that the occurrence of proton transfer from various dicationic fullerene adducts may provide valuable information on the comparative acidities of various proton-bearing groups within multiply-charged ions. We have shown that it is possible to generate a wide variety of dicationic fullerene adducts, bearing various functional groups attached to the fullerene skeleton. These comparatively simple and durable fullerene ions seem well suited to the requirements of a system for modeling the reaction chemistry of larger and more complex multiply-charged cations such as polyprotonated proteins.

Conclusion

The reaction chemistry of $C_{60}H^{\bullet 2+}$ with several neutrals has been assessed. Product channels observed are charge transfer, hydride abstraction and, in the majority of reactions studied, proton transfer. The occurrence of proton transfer is believed to be inhibited by an activation energy barrier arising from the interaction between the product ions which is modeled here by Coulombic repulsion. For this reason, the occurrence or absence of proton transfer from $C_{60}H^{\bullet 2+}$ to a neutral molecule of known GB does not directly indicate the gas-phase acidity of the dication $C_{60}H^{\bullet 2+}$. Nevertheless, the proton transfer reactions of $C_{60}H^{\bullet 2+}$ appear to be "well behaved" in the sense that the observed efficiency of proton transfer decreases consistently with the basicity of the reactant neutral. Rapid proton transfer (occurring at close to the collision rate coefficient) is observed to neutrals having GB > 170 kcal mol^{-1}; no proton transfer is seen with neutrals having GB < 163 kcal mol^{-1}; and proton transfer occurring at substantially less than the collision rate is seen for neutrals having 163.8 kcal mol^{-1} < GB < 167.4 kcal mol^{-1}.

Our observations of $C_{60}H^{\bullet 2+}$ reactivity, considered in conjunction with the expected contribution of Coulombic repulsion between the product ions, enable an estimation of the thermochemistry of $C_{60}H^{\bullet 2+}$. We recommend a value for the gas-phase acidity, $GA(C_{60}H^{\bullet 2+}) = 124 \pm 8$ kcal mol^{-1}. This value, in combination with previously reported thermochemical values for C_{60}^{2+}, $C_{60}^{\bullet 3+}$, and $C_{60}H^{+}$, also permits calculation of the hydride affinity, $H^{-}A(C_{60}^{\bullet 3+}) = 536 \pm 22$ kcal mol^{-1}, the hydrogen atom affinity, $HA(C_{60}^{2+}) = 84 \pm 10$ kcal mol^{-1}, and the ionization energy, $IE(C_{60}H^{+}) = 10.7 \pm 0.4$ eV. None of these values have been obtained previously.

We expect that further studies of dicationic fullerene adduct acidity will yield valuable information on the comparative acidities of various proton-bearing functional groups within multiply-charged cations. Such information could serve as the basis for a model of the proton-transfer reactivity of larger and more complex proton-bearing, multiply-charged species such as polyprotonated proteins.

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