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First steps towards a gas-phase acidity ladder for derivatized fullerene dications

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Abstract

C_{60}^{2+} can be derivatized by gas-phase ion/molecule reactions with polar hydrogen-bearing molecules. The adduct dications so produced may then undergo proton transfer to neutrals. The occurrence or absence of proton transfer as a secondary process gives information on the gas-phase acidity of the dicationic species $C_{60}\cdot(XH)_n^{2+}$. We have performed studies using a selected-ion flow tube at 294 ± 2 K and 0.35 ± 0.01 Torr, and have used the observed reactivity of such dicationic fullerene adducts to determine upper or lower limits to their apparent and absolute gas-phase acidities. We present also a rationale for assessing the proton-transfer reactivity of dications via the apparent gas-phase acidity of these species, rather than the traditional use of gas-phase basicities or proton affinities. We propose that further studies of proton transfer from polycharged fullerene adducts may provide considerable useful information to model the reactivity of polyprotonated proteins and other large molecular polycations which can now be produced by techniques such as electrospray ionization.

Keywords: dications; acidity; fullerenes; proton transfer; SIFT.

Introduction

The gas-phase reaction chemistry of molecular dications displays several features which differ from the reactivity of monocations. One of the most notable such features is an impediment to charge-separating reactions (for example, single charge transfer, proton transfer or hydride abstraction involving a dication and a neutral) which arises via the Coulombic repulsion between the initially-adjacent monocationic products of such a reaction [1,2]. This means, for example, that proton transfer from a dication to a neutral must be considerably exothermic in order to proceed efficiently, in sharp distinction to the generally observed facility of proton transfer from a monocation to a neutral [3]. We have recently discussed this effect in relation to the occurrence of proton transfer from $C_{60}\cdot NH_3^{2+}$ to NH_3 [4], and have also shown [2,5] how the existence of Coulombic repulsion barriers to charge transfer resolves the discrepancy between previously reported values of the second [6,7] and third [6,7(a)] ionization energies of C_{60}.

There is considerable information available upon the role of Coulombic repulsion in charge transfer reactions: the greater number of studies of dicationic charge transfer, rather than proton transfer, relates in part to the relative ease in generating dications capable of charge transfer (such dications may be atomic) rather than proton transfer (such dications must be molecular, and hence are more subject to fragmentation and more difficult to produce by conventional ionization

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techniques). While no direct experimental evidence exists to show conclusively the presence of a Coulombic repulsion barrier to proton transfer from a dication to a neutral, several reports have considered the effects of Coulombic repulsion upon deprotonation of dications and polycations. McGill and Radom [8,9] have performed high-level theoretical calculations upon proton loss from the small dications ClH^{2+}, $H_3NNH_3^{2+}$, $H_3PPH_3^{2+}$, MgH^{2+} and AlH^{2+}, and indicate that deprotonation in these systems is best viewed as a two-step process:

$$MH^{2+} \rightarrow [M^{2+} \cdots H]^{\neq} \rightarrow M^+ + H^+ \qquad (1)$$

This mechanism, which involves an avoided crossing (also interpreted as a barrier) between the states corresponding to $M^{2+} + H^{\cdot}$ and $M^+ + H^+$ at large separations, is relevant to systems in which $IE(M^+) > IE(H^{\cdot})$. (This criterion is met for many small dications but will not hold for larger dications, for example, $IE(C_{60}^{+\cdot}) = 11.39 \pm 0.05$ eV [2,7(c)], while $IE(H^{\cdot}) = 13.60$ eV). In another theoretical study, Bursey and Pedersen [10] have predicted substantial activation energy barriers to proton transfer from a diprotonated amine to NH_3 and to $(CH_3)_3N$.

Spears and Fehsenfeld [11] and Buckner and Freiser [12] have reported proton-transfer reactions of CaH_2O^{2+} and $NbCH_2^{2+}$ respectively: CaH_2O^{2+} transfers a proton efficiently to H_2O, while $NbCH_2^{2+}$ transfers a proton to CO (PA = 141.9 kcal mol^{-1} [13]) but not to CH_4 (PA = 132.0 kcal mol^{-1} [13]). The observations of $NbCH_2^{2+}$ reactivity were initially interpreted as indicating that proton transfer from this species is exothermic to CO and endothermic to CH_4, yielding $PA(NbCH^+) = 137 \pm 7$ kcal mol^{-1} [12]; subsequent reinterpretation [1] has provided a revised value of $PA(NbCH^+) = 103 \pm 30$ kcal mol^{-1} which suggests that both of these reactions are exothermic, but that proton transfer to CH_4 is not sufficiently exothermic to overcome the barrier to proton transfer arising from Coulombic repulsion.

McLuckey et al. [14] and Winger et al. [15] have studied proton-transfer reactions of multiply protonated cytochrome C with dimethylamine and with water. The reaction rate coefficients reported in the study of McLuckey et al. [14], for proton transfer from the ions $(M + nH)^{n+}$ ($n = 9$–15) to $(CH_3)_2NH$, did not exceed 3% of the expected collision rate. An additional effect of Coulombic repulsion reported in this study was to destabilize the protonation sites in multiply-protonated ions.

We have now studied several systems in which C_{60}^{2+} undergoes association with polar neutrals, [4,16,17,18] and in some of these systems proton transfer from the dicationic adduct to a polar neutral is observed. The occurrence or absence of proton transfer in such reactions offers information on the structure of the adduct and also indicates the relative strengths of different dicationic adducts as acids. An additional application of these studies of dicationic acidity is as a model for the much larger polyprotonated polycations of biomolecules which have recently been produced by electrospray ionization [14,15] and related techniques.

Terminology

We believe that it is more useful to talk about the gas-phase acidity (GA) of these dicationic adducts than to discuss the gas-phase basicity (GB) (or proton affinity (PA)) of the corresponding deprotonated monocation. In this case, the gas-phase basicity relates to the free energy of reaction of the process

$$H^+ + M^+ \rightarrow MH^{2+} \qquad (2)$$

$$GB(M^+) = -\Delta G^\circ$$

and the PA is defined in terms of the enthalpy change

$$PA(M^+) = -\Delta H^\circ_{298} = \Delta H^\circ_f(H^+) + \Delta H^\circ_f(M^+) - \Delta H^\circ_f(MH^{2+})$$

for the same process [13]. While the protonation of a neutral species M in the gas phase is not usually inhibited by barriers (proton transfer from a monocation to a neutral is almost always efficient when exoergic), protonation of M^+ is barrier-inhibited

— and so the calculated or bracketed value $GB(M^+)$ does not, in itself, reliably indicate the reactivity of the protonated species MH^{2+}. The GA of MH^{2+} is defined [19,20] as the free energy of reaction of

$$MH^{2+} \rightarrow M^+ + H^+ \tag{3}$$

$$GA(MH^{2+}) = \Delta G^\circ$$

and the corresponding enthalpic quantity is the enthalpy of deprotonation (HD) [20]

$$HD(MH^{2+}) = \Delta H_f^\circ(H^+) + \Delta H_f^\circ(M^+) - \Delta H_f^\circ(MH^{2+})$$

The quantities $GA(MH^{2+})$ and $HD(MH^{2+})$ are, in fact, the same as $GB(M^+)$ and $PA(M^+)$, respectively; however, for our purposes they have the advantage of describing the process of proton loss from a dicationic species, whereas GB and PA are defined in terms of proton addition to a monocation (a much less probable process). The historical use of acidities for proton transfer to an anion, and basicities/PAs for proton transfer from a cation, probably relates to the desire of researchers to quantify these reactions in terms of a property of a neutral molecule; the acidity of a dication cannot be directly related to a property of its parent neutral and therefore there seems no reason to use the basicity of the deprotonated species in this circumstance. Comparatively few experimental studies detailing proton transfer from dications have yet been performed [1,4,11,12]: hence, we feel that there is still the opportunity to adopt GA as a more sensible parameter for defining the ease of proton transfer from dicationic species.

An additional useful parameter, for which we propose the term "apparent gas-phase acidity", GA_{app}, takes into account the interaction between the two monocationic products of reaction (3). The apparent gas-phase acidity

$$GA_{app}(MH^{2+}) = GA(MH^{2+}) + \delta$$

includes consideration of a reverse activation barrier δ which will be discussed below. Figure 1 shows generalized reaction profiles for deprotonation of a dication, and provides an elucidation of the parameters discussed here. The apparent gas-phase acidity $GA_{app}(MH^{2+})$ is the quantity which is directly determinable from kinetic data in the present experiments; $GA(MH^{2+})$ must then be calculated by estimating the reverse activation barrier δ. While there are substantial uncertainties involved in this calculation as a result of the approximations made, GA for a dication is a thermodynamic quantity entirely analogous to the values of GA and GB relating to singly-charged species; many gas-phase basicity measurements, for example, are derived from kinetic measurements of the forward and reverse rate coefficients involved in the proton transfer equilibrium

$$XH^+ + Y \rightleftharpoons X + YH^+ \tag{4}$$

The measured rate coefficients for this equilibrium lead directly to the thermodynamic quantity ΔG°, which corresponds to the difference $GB(X) - GB(Y)$. In the present study, it is not possible to measure both forward and reverse rate coefficients in the "equilibrium"

$$MH^{2+} + X \rightleftharpoons M^+ + XH^+ \tag{5}$$

(since the influence of Coulombic repulsion would be to render the reverse reaction immeasurably slow even if exothermic), and so the acidity of the species MH^{2+} must be assessed by the technique of "bracketing". Many GA and GB values already in the literature [13] arise from bracketing studies; the factors influencing the reliability of such results should be considered also in interpreting the present data.

A detailed treatment of the reverse activation barrier δ should include the effects of Coulombic repulsion between the products (which acts to increase δ) as well as the dipole/dipole, ion/dipole and ion/induced dipole interactions (acting to decrease δ) between the product ions. Satisfactory treatment of the latter quantities is a complex matter and we have chosen to neglect these effects for the following reasons. Firstly, the calculation of the magnitude of these effects requires a detailed knowledge of the dipole moments and polarizabili-

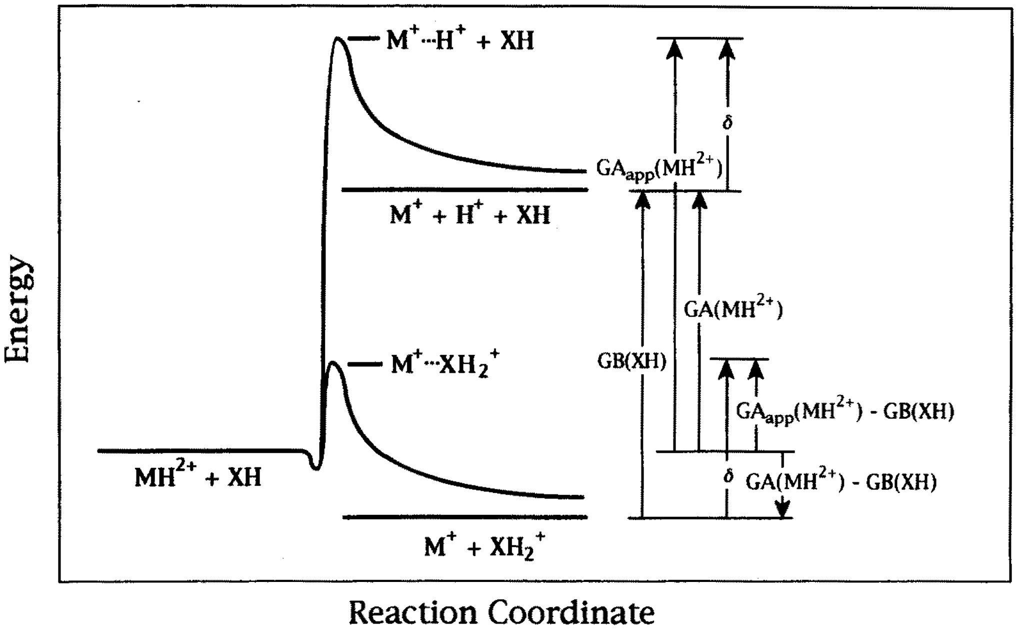


Fig. 1. Reaction profile and parameters involved in deprotonation of a dication MH^{2+}, and in the occurrence of proton transfer from such a species. The reaction profile shown is for the case that proton detachment from MH^{2+} is endoergic (which is believed to be so for all of the fullerene adduct dications discussed in the present study) and that proton transfer to a neutral XH is exoergic but inhibited by a barrier arising from Coulombic effects. Assumptions made in the present work are that the height of the threshold δ to proton transfer is well approximated by the Coulombic repulsion $q\phi$, between the monocation products, and that the reverse activation barrier δ is the same for proton transfer to XH as for proton detachment.

ties of the product ions — quantities which have not been experimentally determined and which (for the deprotonated fullerene adduct ions at least) are likely to require very lengthy theoretical calculation. Secondly, the results reported here provide some measure of the relative acidity of the dications in question, and (since the differences in size, molecular complexity and expected intercharge separation at point of proton transfer are comparatively small) it might be anticipated that the ion/induced dipole and other attractive interactions for all the proton-transfer reactions discussed here are approximately equal. If this is so, then the relative trend in GA_{app} values which we report is also a good indication of the relative GA values for these dications: appropriate consideration of attractive interactions between product ions may well necessitate adjustment of the GA values reported here (upwards, since consideration of attractive interactions will result in less positive values of δ), but the adjustment for all these $GA(MH^{2+})$ values is likely to be equal, or nearly so, in all cases. Finally, there is some theoretical support for using the Coulombic repulsion as a reasonable first approximation to the height of the barrier to proton transfer. Bursey and Pedersen [10] have reported semi-empirical MOPAC 6.1 (AMI) force field calculations upon the barrier-inhibited reactions

$$^{+}H_3NCH_2CH_2CH_2NH_3^{+} + NR_3 \rightarrow {}^{+}H_3N(CH_2)_3NH_2 + NR_3H^{+} \qquad (6)$$

for R = H and CH_3, and determined that the enthalpy of formation of the hydrogen-bonded ion pair $[^{+}H_3N(CH_2)_3NH_2 \cdots HNR_3^{+}]$ exceeded the sum of the enthalpies of formation of the products by more than three quarters of the expected Coulombic repulsion at this intercharge separation. The intercharge separations (7.70 and 8.80 Å respectively) assumed in the study of Bursey and Pedersen are very similar to the expected intercharge separations (8.4–10 Å) for the present system; it might, therefore, be expected in the reactions which we investigate here, that the magnitude of ion/induced dipole and other attractive interactions between the monocationic products should not exceed 25% of the expected Coulombic repulsion between these ions. In the calculations which follow, we have therefore used throughout the approximation that $\delta = q\phi_r$.

Experimental

The results reported here were obtained using a selected-ion flow tube which has been described previously [21,22]. Measurements were performed at 294 ± 3 K and at 0.35 ± 0.01 Torr unless otherwise indicated. Kinetic aspects of the results reported here, as well as of reactivity other than proton transfer, have been [4,16] or will be [18] discussed in detail elsewhere; here we concern ourselves exclusively with the occurrence or absence of proton transfer from the adducts of C_{60}^{2+} with various neutrals.

Results and discussion

Our results are detailed in Table 1. This lists the dicationic fullerene adducts for which the observed occurrence or absence of proton transfer is significant. We exclude from this list those instances where proton transfer was not observed because of possible competition from other efficient product channels (such as a collision-rate association process), since these reactions do not allow bracketing of the GA_{app} values of the species involved. Typical experimental data, depicting the reactivity of C_{60}^{2+} with butanone ($CH_3COCH_2CH_3$) (for which proton transfer is the predominant secondary reaction) and with propionitrile (CH_3CH_2CN (for which proton transfer is not detected from either the primary or secondary adduct)) are shown in Figs. 2 and 3.

Table 1 also lists upper or lower bounds to $GA_{app}(C_{60} \cdot (XH)_n^{2+})$ and $GA(C_{60} \cdot (XH)_n^{2+})$ for the dicationic species concerned. These values are determined in the following manner: if efficient proton transfer

$$C_{60} \cdot (XH)_n^{2+} + XH \rightarrow C_{60} \cdot (XH)_{n-1}X^+ + XH_2^+ \quad (7)$$

is seen, then $GA_{app}(C_{60} \cdot (XH)_n^{2+}) < GB(XH)$ and, by inference, $GA(C_{60} \cdot (XH)_n^{2+}) < GB(XH) - \delta$. Similarly, if proton transfer is not seen in the absence of possible competing channels, $GA_{app}(C_{60} \cdot (XH)_n^{2+}) > GB(XH)$ and $GA(C_{60} \cdot (XH)_n^{2+}) > GB(XH) - \delta$. The value for the Coulombic repulsion factor $q\phi_r$, necessary to determine δ and hence derive the GA value, is determined by assuming a dicationic structure featuring one charge localized upon the donor atom (O or N) and the other charge localized on the fullerene surface diametrically opposite this point. The fullerene cage diameter is taken as 7.0 Å [23] and a standard C–O (1.43 Å) or C–N bond length (1.48 Å) [24] is also assumed. This calculation is admittedly approximate, but a more rigorous treatment is not possible given the difficulties inherent in detailed ab initio determinations of the structures and charge distributions of species as large as those under consideration here. The uncertainty in the $GA_{app}(C_{60} \cdot (XH)_n^{2+})$ limits here is expected to be not substantially larger than the uncertainty in the GB(XH) values from which they are determined (typically $\pm$2–3 kcal mol^{-1}); the uncertainty in the $GA(C_{60} \cdot (XH)_n^{2+})$ limits is substantially larger (arguably $+15/-2$ kcal mol^{-1}), given the approximations inherent in assuming $\delta = q\phi_r$. We reiterate that more detailed consideration of attractive interactions affecting δ may revise upwards the GA values calculated here, but is likely to do so in a systematic manner.

For the instances where only upper limits to $GA_{app}(C_{60} \cdot (XH)_n^{2+})$ and $GA(C_{60} \cdot (XH)_n^{2+})$ are determined, lower limits can also be proposed based on the observation that the dicationic adducts are all detected despite the presence in the flow tube of helium buffer gas at 0.35 ± 0.01 Torr. If proton transfer to He does not occur, then $HD_{app}(C_{60} \cdot (XH)_n^{2+}) > PA(He)$ (42.5 kcal mol^{-1}) [13] and $HD(C_{60} \cdot (XH)_n^{2+}) > PA(He) - q\phi_r$. For all the dicationic adduct structures considered here, the Coulombic repulsion term $q\phi_r$ is less than the

TABLE 1

Observed proton-transfer reactivity of dicationic adducts $C_{60}\cdot(XH)_n^{2+}$ with neutrals XH, and inferred upper or lower bounds to gas-phase acidities for the species $C_{60}\cdot(XH)_n^{2+}$

$C_{60}\cdot(XH)_n^{2+}$	XH	GB(XH) [a]	React. [b]	GA_{app} [c]	GA [d]
$C_{60}\cdot NH_3^{2+}$	NH_3	195.6	P,A,F	< 196	< 157
$C_{60}\cdot(NH_3)_2^{2+}$	NH_3	195.6	P,F	< 196	< 163
$C_{60}\cdot CH_3NH_2^{2+}$	CH_3NH_2	205.7	P,A,F	< 206	< 167
$C_{60}\cdot(CH_3NH_2)_2^{2+}$	CH_3NH_2	205.7	P,F	< 206	< 173
$C_{60}\cdot C_2H_5NH_2^{2+}$	$CH_3CH_2NH_2$	208.5	P,A,F	< 209	< 170
$C_{60}\cdot(C_2H_5NH_2)_2^{2+}$	$CH_3CH_2NH_2$	208.5	P,F	< 209	< 176
$C_{60}\cdot(CH_3)_2NH^{2+}$	$(CH_3)_2NH$	212.8	P,F	< 213	< 174
$C_{60}\cdot CH_3OH^{2+}$	CH_3OH	174.1	P,F	< 175	< 135
$C_{60}\cdot C_2H_5OH^{2+}$	CH_3CH_2OH	180.2	P,F	< 181	< 141
$C_{60}\cdot HCOOH^{2+}$	HCOOH	171.0	P,F	< 171	< 132
$C_{60}\cdot CH_3COOH^{2+}$	CH_3COOH	181.7	P,A,F	< 182	< 143
$C_{60}\cdot(CH_3)_2CO^{2+}$	CH_3COCH_3	188.9	P,A,F	< 189	< 150
$C_{60}\cdot((CH_3)_2CO)_2^{2+}$	CH_3COCH_3	188.9	P,F	< 189	< 156
$C_{60}\cdot CH_3COC_2H_5^{2+}$	$CH_3COCH_2CH_3$	192.0	P,A,F	< 192	< 153
$C_{60}\cdot(CH_3COC_2H_5)_2^{2+}$	$CH_3COCH_2CH_3$	192.0	P,F	< 192	< 159
$C_{60}\cdot CH_3CN^{2+}$	CH_3CN	180.6	A,S	> 180	> 141
$C_{60}\cdot(CH_3CN)_2^{2+}$	CH_3CN	180.6	N	> 180	> 147
$C_{60}\cdot C_2H_3CN^{2+}$	CH_2CHCN	181.9	A,S	> 181	> 142
$C_{60}\cdot(C_2H_3CN)_2^{2+}$	CH_2CHCN	181.9	N	> 181	> 148
$C_{60}\cdot(C_2H_5CN)_2^{2+}$	CH_3CH_2CN	184.1	A,S	> 184	> 150
$C_{60}\cdot(n\text{-}C_3H_7CN)_2^{2+}$	$CH_3CH_2CH_2CN$	185.7	N	> 185	> 152
$C_{60}\cdot(i\text{-}C_3H_7CN)_2^{2+}$	$(CH_3)_2CHCN$	186.4	N	> 186	> 153

[a] Gas-phase basicity of the neutral XH (kcal mol^{-1}), according to the tabulation of Lias et al. [13].

[b] Reaction channels observed, and overall reaction efficiency. A, adduct formation; P, proton transfer; N, no reaction. F, fast ($> 1 \times 10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$); S, slow ($< 1 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$). Measured rate coefficients have been [4,16,17] or will be [18] reported elsewhere.

[c] Upper or lower limit to the apparent gas-phase acidity $GA_{app}(C_{60}\cdot(XH)_n^{2+})$ (kcal mol^{-1}) estimated from GB(XH) as detailed in the text. The uncertainty in this limit to $GA_{app}(C_{60}\cdot(XH)_n^{2+})$ is approximately equal to the uncertainty in GB(XH).

[d] Upper or lower limit to the gas-phase acidity $GA(C_{60}\cdot(XH)_n^{2+})$ (kcal mol^{-1}), estimated using $GA = GA_{app} - q\phi_r$. Approximations and assumptions inherent in this estimation are noted in the text. The Coulombic repulsion term $q\phi_r$ is calculated assuming an intercharge separation r derived from $d(C_{60}) = 7.0$ Å [23], $d(C\text{–}O) = 1.43$ Å and $d(C\text{–}N) = 1.48$ Å [24]. The approximate magnitude of $q\phi_r$ is, for single adducts, 39 kcal mol^{-1}, and for double adducts, 33 kcal mol^{-1}. The uncertainty in the limit to GA is approximately $+15/-2$ kcal mol^{-1}, as discussed in the text.

measured PA of helium; therefore, the failure to detect proton transfer from the dicationic adducts to helium indicates that $HD(C_{60}\cdot(XH)_n^{2+})$ (and, therefore, very probably $GA(C_{60}\cdot(XH)_n^{2+})$) is positive for all of these adducts. Proton detachment from any of these adducts is endothermic.

The tabulated results indicate a spread in gas-phase acidity values of at least 20 kcal mol^{-1} ($GA(C_{60}\cdot HCOOH^{2+}) < 132$ kcal mol^{-1}; $GA(C_{60}\cdot(i\text{-}C_3H_7CN)_2^{2+}) > 153$ kcal mol^{-1}) for the different dicationic adduct species studied. The actual range in values may, of course, be considerably greater: with the present experimental setup we are unable to vary the base XH with which a particular $C_{60}\cdot(XH)_n^{2+}$ may react. We are currently attempting to develop a method of injecting these $C_{60}\cdot(XH)_n^{2+}$ species directly into the flow tube. This would permit us to add a wide variety of target bases XH, and hence to bracket accurately the absolute GA_{app} values of the $C_{60}\cdot(XH)_n^{2+}$ species reported here.

In the absence of absolute values for the apparent gas-phase acidities of these species, some comments can still be made relating the structure of

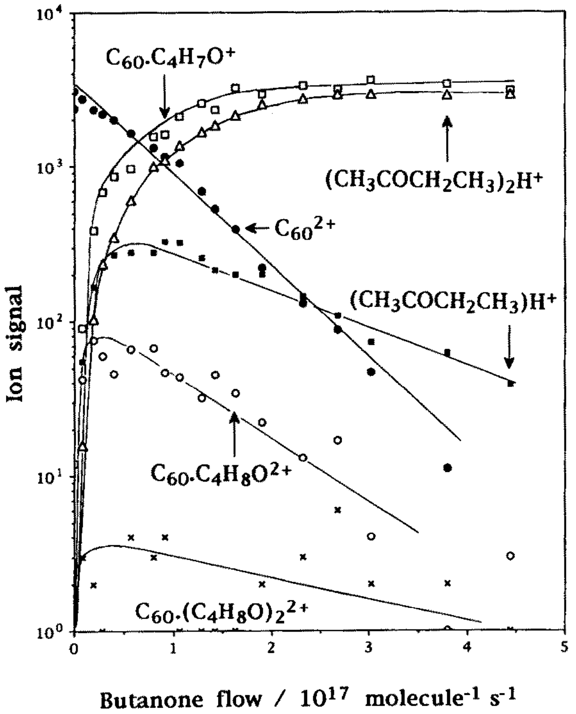


Fig. 2. Observed experimental data for the reaction of C_{60}^{2+} with 2-butanone ($CH_3COCH_2CH_3$) at 294 K and 0.35 ± 0.01 Torr. 2-Butanone was added as an 8.7 mol.% solution of $CH_3COCH_2CH_3$ in helium. The sole primary product channel is association ($k_1 = 1.2 \times 10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$); the dominant secondary product channel is proton transfer ($k_2 >> 1 \times 10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$). Formation of a proton-bound dimer of 2-butanone is also observed, as a tertiary process.

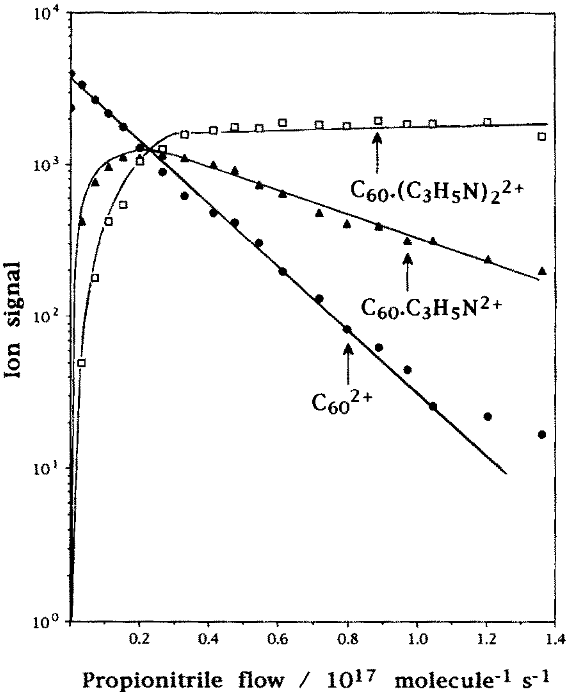
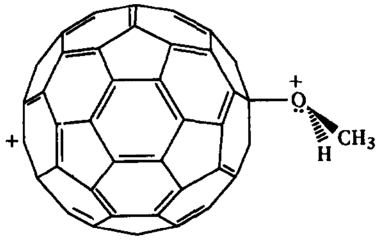


Fig. 3. Observed experimental data for the reaction of C_{60}^{2+} with propionitrile (CH_3CH_2CN) at 294 K and 0.35 ± 0.01 Torr. CH_3CH_2CN was added as a 1.6 mol.% solution of propionitrile in helium. The sole primary and secondary product channels seen are association ($k_1 = 2.5 \times 10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$; $k_2 = 2.2 \times 10^{-9}\,cm^3\,molecule^{-1}\,s^{-1}$). No proton transfer from $C_{60}(CH_3CH_2CN)_n^{2+}$ to CH_3CH_2CN was observed.

these adducts to their observed reactivity. Most adducts transfer a proton readily to the target base XH, suggesting a localization of charge in close proximity to at least one hydrogen atom. This can be easily comprehended for adducts formed from ammonia or from alcohols, since the structure which we have proposed for these species does involve a localization of charge upon the N or O atom, as typified by the methanol adduct **I**. Deprotonation of this species, which does not appear to require rearrangement, should be facile and is likely to produce a methoxylated fullerene cation **II** or **III**. It should be noted that other oxygen-ring isomers of **III** are also feasible, such as an O-methylated epoxide structure; we note that structure **III**, as shown, involves formation of two five-membered rings and might, therefore, be expected to be thermodynamically favoured over other structures featuring smaller and more strained rings.

A consideration of the structures of the adducts of C_{60}^{2+} with the various ketones and acids listed in Table 1, for which deprotonation to the parent neutral is observed, suggests that the charge upon the substituent is somewhat delocalized. Nucleophilic addition [8] of R–CO–R′ or R–CO–OR′ results in the formation of a C–O bond between the fullerene and the substituent, formally with the charge on O as shown in structure **IV**; however, other canonical forms such as **V–VII** are also feasible, and efficient proton loss suggests that these latter canonical forms significantly influence the overall resonance structure of the respective adducts. The



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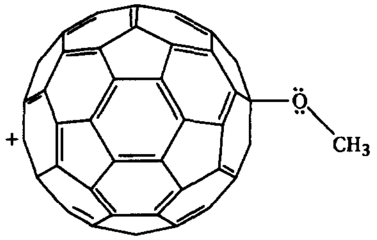

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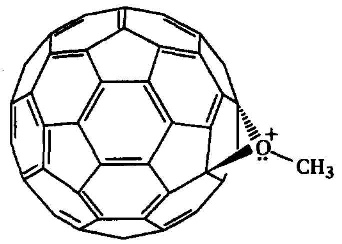

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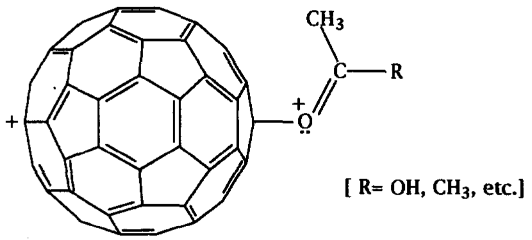

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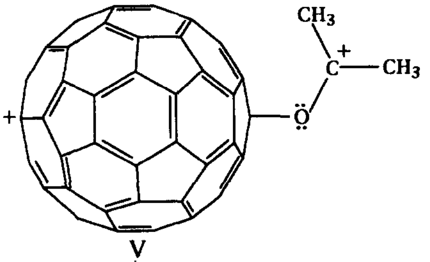

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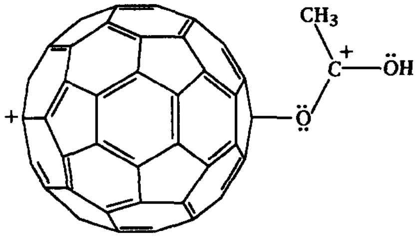
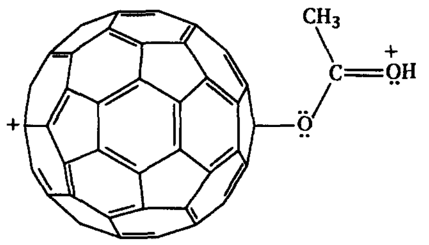


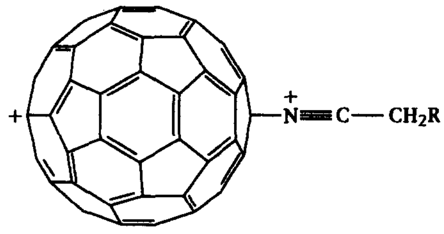
VI

observation of proton transfer from most $C_{60} \cdot (XH)_n^{2+}$ species to XH is also consistent with the observation of proton transfer from multiply-protonated cytochrome C to $(CH_3)_2NH$ [14] and to H_2O [15], despite the much higher GB values normally attributed to basic amino acid residues (e.g., GB(L-Lysine) = 222.5 kcal mol^{-1} [13]; GB(L-Histidine) = 224.1 kcal mol^{-1} [13]) than to dimethylamine (GB = 212.8 kcal mol^{-1} [13]) and to water (GB = 159.0 kcal mol^{-1} [13]). This can be rationalized in terms of the effects of Coulombic repulsion. Electrostatic interactions between the charges serve to destabilize the multiply-charged reactant as well as the initially-adjacent product ion pair; however, since the intercharge separation is less in the reactant polycation than in the initially-adjacent product ion pair, the destabilization of the reactant is greater than the destabilization of the product ion pair, and so the gas-phase acidity of the reactant polycation is reduced, permitting proton transfer to species of somewhat lower GB.

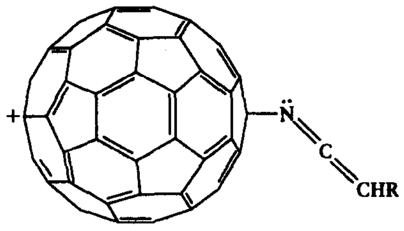
In contrast to our other observations of adduct reactivity, the lack of observed proton transfer from any of the nitrile adducts to their parent neutrals is consistent with the localization of charge upon the nitrogen atom as in **VIII**: well isolated from any hydrogen atoms. Proton loss from **VIII** requires considerable charge migration, and this process may be kinetically or thermodynamically inhibited. Alternatively, the absence of proton transfer in this system may reflect the expected high enthalpy of formation of the resulting deprotonated species, a ketene imine for which two possible structures (**IX** and **X**) are shown.



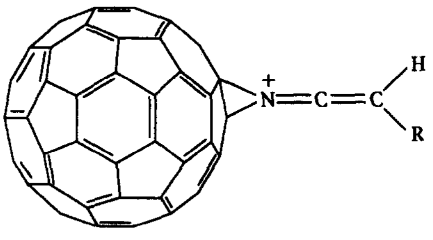
VII



VIII



IX



X

Table 2 allows a degree of comparison between the acidities of XH, $XH^{\cdot +}$, XH_2^+ and the dication adducts of XH under discussion. As can be seen, the upper or lower limits to GA($C_{60}\cdot(XH)_n^{2+}$) do not appear to correlate precisely to any trends within other acidity series. For example, the dicationic adducts of nitriles appear to be the weakest acids (high GA), yet neutral and ionized nitriles are substantially stronger acids than the alcohols CH_3OH and CH_3CH_2OH. Similarly, the acidity of the dicationic adducts is not simply dependent upon the acidity of the protonated species XH_2^+. A more detailed analysis of these trends in acidity does not seem warranted without more precise values of GA for the dicationic adducts.

Comparisons of the acidities of the fullerene adducts $C_{60}\cdot(XH)_n^{2+}$ with those of the dications XH^{2+}, while potentially being of substantial interest as a measure of the extent of charge stabilization by the fullerene, are possible only in very few instances. The acidities of the species NH_3^{2+} (GA(NH_3^{2+}) = − 67 kcal mol^{-1}, determined from IE($NH_3^{\cdot+}$) = 22.2 ± 0.3 eV [25]; a value of −62.9 kcal mol^{-1} has also been determined theoretically [26]) and $CH_2NH_3^{2+}$ (GA($CH_2NH_3^{2+}$) = − 65 kcal mol^{-1}, using AE($CH_2NH_3^{2+}$) − IE(CH_3NH_2) = 17.7 eV [27]) are, in fact, negative quantities, illustrating that proton detachment from these species is exothermic, albeit inhibited by substantial Coulombic barriers. This is in sharp contrast to the inferred acidities of the dicationic fullerene adducts $C_{60}\cdot NH_3^{2+}$ and $C_{60}\cdot CH_3NH_2^{2+}$; as we have argued above, the observation of these adducts in 0.35 Torr of helium indicates that GA > 0 kcal mol^{-1} for these species. Formation of a carbon–nitrogen bond (and, of course, a substantial increase in the separation of the two positive charges) thus

TABLE 2

A comparison of gas-phase acidities (kcal mol^{-1}) for XH, XH$^+$, XH_2^+, and upper or lower limits for $C_{60} \cdot (XH)_n^{2+}$ ($n = 1$ or 2)

X	GA				
	XH[a]	$XH^{\cdot +}$[b]	XH_2^+[c]	$C_{60} \cdot XH^{2+}$[d]	$C_{60} \cdot (XH)_2^{2+}$[d]
NH_3	396.0	187.6	195.6	<157	<163
CH_3NH_2	395.8	202.7	205.7	<167	<173
$CH_3CH_2NH_2$	391.7	198.7	208.5	<170	<176
$(CH_3)_2NH$	389.1	210.7	212.8	<174	–
CH_3OH	374.5	157.5	174.1	<135	–
CH_3CH_2OH	370.7	164.4	180.2	<141	–
HCOOH	338.2	–	171.0	<132	–
CH_3COOH	341.5	–	181.7	<143	–
CH_3COCH_3	361.9	–	188.9	<150	<156
$CH_3COC_2H_5$	363.2	–	192.0	<153	<159
CH_3CN	365.2	126	180.6	>141	>147
CH_2CHCN	364.4	–	181.9	>142	>148
CH_3CH_2CN	366.9	131	184.1	–	>150
n-C_3H_7CN	–	–	185.7	–	>152
i-C_3H_7CN	367.3	140	186.4	–	>153

[a] Obtained from ref. 19.

[b] Enthalpy of deprotonation calculated according to thermochemical values tabulated in ref. 19.

[c] Tabulated in ref. 13. By definition, GA(XH_2^+) = GB(XH).

[d] Determined in the present study.

provides a strong stabilizing influence (of at least 70 kcal mol^{-1}, and probably much higher) on the dication. This is also likely to be the case for dications of the other neutrals considered in this study, but the absence of experimental values of second ionization energies for the other species precludes further analysis of this notion.

It should also be noted that, for the secondary adducts especially, the geometry assumed in calculating the upper or lower limit to GA is that in which the two substituents are diametrically opposed to each other upon the fullerene cage. This case gives the lowest Coulombic repulsion between charges and is thus expected to be the lowest-energy double adduct isomer; however, several other isomers are also possible in which the two charges are somewhat closer together. For such isomers, the Coulombic component of GA_{app} will increase with decreasing charge separation. If this Coulombic component is reflected in the trend in GA for a series of isomeric double adducts, then the observed range in GA_{app} for the series of isomers should be small; however, if GA is essentially independent of the relative positions of the two substituents, then GA_{app} will increase with decreasing charge separation, since the barrier δ to proton transfer increases in this fashion. This consideration is expected to be a complicating factor in attempts to bracket the apparent gas-phase acidities of such secondary adducts, since it appears very difficult to envisage a method of selecting only one isomer of a possible range of secondary adducts.

Given the very recent proliferation in studies on proton transfer from large polycations [14,15], and the difficulties inherent in producing satisfactory signals of smaller molecular polycations, it seems possible that model systems involving polycharged fullerene adducts (which, as we have shown, can be produced in the gas phase with comparative ease) will provide considerable useful information to aid in comprehending proton transfer from polyprotonated proteins and similar species. In addition to numerous examples of adduct formation involving C_{60}^{2+}, we have also observed some examples of adducts involving $C_{60}^{\cdot+}$, $C_{60}^{3\cdot+}$, C_{60}^{4+} [16,18]. Systematic experimental or theoretical study of the acidity of adducts of the type $C_{60}\cdot(XH)_n^{m+}$ would yield information upon the dependence of proton transfer reactivity on charge state and nature and number of functional groups, for a system having (potentially) a very well-defined geometry. Information upon the effect of intercharge separation could be obtained via adducts from fullerenes of different sizes (C_{60}, C_{120}, and so on).

Conclusion

We have reported here upper or lower bounds to the apparent gas-phase acidities of several dicationic adducts of fullerenes with small organic neutrals. The observed proton-transfer reactivity of these adducts does not vary simply with the proton affinity of the substituent's parent neutral: rather, there is a clear dependence of acidity upon adduct structure. Most notably, the adducts of nitriles do not transfer a proton to the parent neutral, while all other classes of adducts are observed to undergo proton transfer. We have also proposed here that the quantity, the apparent gas-phase acidity, GA_{app}, of such dicationic species is a more useful measure of their ion/neutral reactivity than the gas-phase basicity or proton affinity of the corresponding deprotonated monocation.

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