$(NH_4)_3C_{60}$: A New C_{60} Superconductor?

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The enthalpy of formation (ΔH_f) of the ionic solid $(NH_4^+)_3C_{60}^{3-}$ is assessed. The solid is found to be stable with respect to the standard state reactants ($N_2(g)$, $H_2(g)$, and $C_{60}(s)$), with a ΔH_f of -1.82 eV/mol. For comparison, this enthalpy of formation is less than the enthalpy of formation of, e.g., K_3C_{60} (-6.27 eV/mol). There are several attractive features of $(NH_4^+)_3C_{60}^{3-}$ as a new ionic solid and potential superconductor, *if it can be synthesized*. It is well-known that the size of the NH_4^+ cation is almost exactly the same as that of Rb^+. Among the M_3C_{60} superconductors, Rb_3C_{60} has the second highest superconducting transition temperature, with $T_c = 28$ K, which suggests that the T_c of a superconducting $(NH_4)_3C_{60}$ *could* be higher than yet achieved for C_{60} superconductors, of which $Cs_3C_{60}(s)$ has the highest T_c of 40 K. There is a 28% relative mass change when the NH_4^+ countercation is replaced by $^{15}ND_4^+$, which is a much larger relative change than can be achieved with the alkali metal atoms, which is important for study of the isotopic substitution effect on T_c. There is also the possibility of unique dynamics in which the ammonium ion rotates in the lattice; the presence of a molecular ion, rather than an atomic ion, could play a role in the mechanism of superconductivity, if the solid is superconducting. Finally, alternative methods to produce such an ammonium salt of C_{60}, such as electrosynthesis or direct synthesis in liquid ammonia, would be required in contrast to the method of the production of M_3C_{60} (M = alkali atom) based on vapor phase transport of M via sublimation in sealed tubes.

Introduction

When the interstitial sites of fcc $C_{60}(s)$ are doped with alkali atoms, superconducting solids can be formed.[1] Examples include $M_3C_{60}(s)$ (M = K, Rb, and various mixtures of alkali atoms)[1] and $M_5C_{60}(s)$ (M = Ca).[2] Such solids have been synthesized in a variety of ways, for example, mixing by sublimation in a sealed glass tube,[3] reaction in liquid ammonia,[4] and electrosynthesis.[5] The highest T_c superconductor is Cs_3C_{60}, for which a T_c of 40 K has recently been measured.[6] C_{60}-based superconductors are of interest for a variety of reasons, including the desire to understand in detail the mechanism of superconductivity; M_3C_{60} (M = alkali) are isotropic solids, in contrast to the highly anisotropic "high T_c" cupric oxide systems. Also, there is the possibility of achieving higher T_c values.

Like all the fullerenes, C_{60} is very electronegative, with an electron affinity of 2.65 eV;[7] to date, all C_{60}-based superconductors are based on doping of interstitial sites with very electropositive elements. In some sense, one might suggest that the highest T_c has in fact been achieved with admixtures of the electropositive elements, because scientists have tried many possibilities;[1] however, note comments in ref 8 about the new class of binary alkali $M_2Na_lC_{60}$ or $M_1Na_2C_{60}$ (M = Rb, Cs). For example, the alkali and alkaline earth groups have been extensively studied. The highly electropositive lanthanides have been suggested as possible superconductors,[9] but little synthesis effort has been expended on them. This is largely due to the very high temperatures required to achieve significant fluxes of lanthanide atoms (with the exception of the elements Sm, Eu, and Yb, which behave more like alkaline earths and have in fact been the subject of recent studies);[10,11] the typical method of production of M_xC_{60} by sublimation of M (vapor phase transport) is therefore very difficult. With the caveat that the high melting point, higher boiling point lanthanide elements deserve experimental effort, we may ask: Has the periodic table been "exhausted" as far as electropositive elements, and if so

are there are alternatives for formation of ionic solids that have interstitial sites occupied by a new type of cation?

A worthwhile exercise has been calculation by a Born−Haber (B−H) thermodynamic cycle of the enthalpy of formation, ΔH_f of (assumed) ionic solids such as $(M^{+1})_6C_{60}^{-6}$ (M = alkali) (see ref 12 for an extended discussion of the method of the B−H cycle calculation). Recent differential scanning calorimetry measurements by Chen et al. for ΔH_f of M_6C_{60} (M = Na, K, Rb, Cs)[13] agree to within a few percent (Na, Rb) and within 10% (K, Cs) with the values obtained from the B−H cycle calculation. This close agreement suggests that the M_6C_{60} solids *are* in fact ionic solids with essentially full transfer of six electrons to C_{60}, a conclusion suggested by photoemission spectra of K-doped C_{60} thin films,[14] electrical conductivity measurements,[15] and LDA calculations.[16]

The close agreement between experimental and B−H cycle calculated ΔH_f for these M_6C_{60} solids also shows that the calculation of ΔH_f with the B−H cycle is essentially quantitatively correct. There is strong indirect evidence from experiment[1,14] that the M_3C_{60} solids (M = Na, K, Rb, Cs) are also completely ionic and therefore of the form $(M^{+1})_3C_{60}^{-3}$; these conclusions are supported by the B−H cycle treatment (close agreement of calculated and experimental lattice constants, calculated and experimental stability trends between M_3C_{60} and M_6C_{60}, and calculated and experimental zero-pressure bulk modulus values), which *assumed* full electron transfer from M to C_{60};[12] this picture is also strongly supported by extensive LDA calculations of the M_3C_{60} solids.[1,16] ΔH_f values have not yet been experimentally determined for the M_3C_{60} solids (M = alkali); however, the very close agreement between the B−H calculated and experimentally determined ΔH_f for the M_6C_{60} solids *very strongly suggests* that the calculated B−H cycle ΔH_f values for the M_3C_{60} solids are also correct to a few percent or so. This serves as an important assumption in the analysis of the ΔH_f of $(NH_4^+)_3C_{60}^{3-}$ presented below, and I have therefore outlined the basis for this assumption in such detail. It is worth noting as an aside that the ΔH_f of M_3C_{60} could likely be

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accurately determined by exploiting the "titration" or "back reaction" of M_6C_{60} with C_{60} to yield M_3C_{60}. The enthalpies of formation of M_6C_{60} and C_{60} are now known, so measurement of the enthalpy change for the reaction

$$M_6C_{60} + C_{60} \rightarrow M_3C_{60}$$
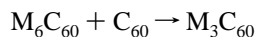
would yield the ΔH_f of M_3C_{60}.

Results and Discussion

Fifty years ago Bleick used the method of Born and Mayer to calculate the lattice energy, U, of the ammonium halides NH_4X (X = Cl, Br, I) with the assumption of a fully ionic crystal, that is, $NH_4^+X^-$.[17] He obtained from use of his calculated U and a B–H cycle, for each NH_4X, derived values for the proton affinity (PA) of NH_3, which are (in kcal/mol) 206.3 (Cl), 206.6 (Br), and 206.2 (I). The extremely close agreement for the derived proton affinity from each cycle for these three different halogens demonstrated that the lattice energy calculations were accurate and that the ammonium halide crystals indeed were ionic. The proton affinity of NH_3 has since been determined to be 204 kcal/mol.[18]

In his lattice energy calculations, Bleick needed to calculate the repulsive potential $B(R_0)$, and to do so he needed the ionic radii. He noted that the lattice distances of the NH_4X (in the NaCl, i.e., rock salt structure) were almost identical to those of RbX; at the time of his calculation, ionic radii were available for Rb^+ but not for NH_4^+. Bleick assumed that the ionic radius of NH_4^+ was identical to that of Rb^+, and his assumption is strongly supported by the internal consistency of the treatment (mentioned in the paragraph above) and also by modern data: the value presented for the ionic radius of NH_4^+ is identical to that of Rb^+ and is 1.48 Å.[19]
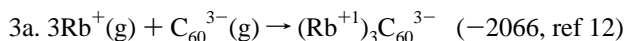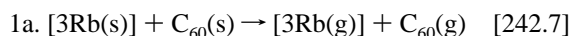
Thus, although NH_4^+ is isoelectronic with Na^+, it is identical in size to Rb^+. The bulk moduli, B_0 (units: GPa) of NH_4Cl (18.5) and NH_4Br (16.6) are closer to those of KCl (16.7) and KBr (14.3) than to those of RbCl (16.2) and RbBr (13.8).[20] However, care is needed in comparing these numbers, because the B_0 values for NH_4Cl and NH_4Br are for the CsCl low-temperature structure, whereas the values for the alkali halide salts are all for the NaCl crystal structure. That the structural change influences the crystal stiffness can be seen by comparing the trends in B_0 for a series of alkali chlorides: NaCl (25.8 GPa), KCl (18.2), RbCl (16.2), CsCl (16.7);[21] the Na, K, and Rb halides all crystallize in the NaCl structure and can be converted to the CsCl structure with pressure. The NH_4X (X = Cl, Br, I) all have the CsCl structure at low temperature and the less dense NaCl structure at high temperature. The obvious break in the monotonic decrease in B_0 values between RbCl and CsCl suggests that a naive assumption of the ion being more similar to K^+ than to Rb^+ in its compressibility is incorrect. In any case the compressibility of NH_4^+ is close to that of both K^+ and Rb^+.

The bulk modulus of an ionic crystal, if available, is normally used to fit the energy terms in the Born–Mayer calculation of the lattice energy.[17] Bleick assumed a repulsive parameter that is identical for all the alkali atoms (standard method, as discussed in ref 12) and with an identical radius as Rb^+ for the NH_4^+, obtained the correct enthalpy of formation of NH_4X (X = Cl, Br, I) and proton affinity of NH_3.[17] In our previous B–H cycle treatment of the M_3C_{60} and M_6C_{60} solids, only the bulk modulus of K_3C_{60} was used as a constraint to obtain the repulsive parameter; ΔH_f of all other M_3C_{60} and M_6C_{60} solids were calculated on the basis of this constraint.[12] Note that the formation enthalpies of K_3C_{60}, Rb_3C_{60}, and Cs_3C_{60} as calculated

with this approach are (per alkali atom) -2.09, -2.12, and -2.10 eV, respectively.[12] Placing the compressibility of the NH_4^+ ion as "closer to K^+ or closer to Rb^+" is therefore of secondary importance in a treatment of the lattice energy, and I have outlined the issue at this length to demonstrate that one does not need *a priori* knowledge of the bulk modulus of $(NH_4)_3C_{60}$ to obtain a good estimate of the lattice energy. However, the reader may wish to speculate on the influence of pressure, where the "hardness" of the countercation may eventually make an important contribution.
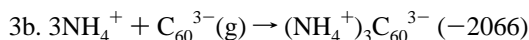
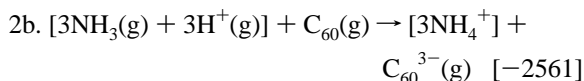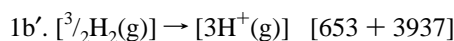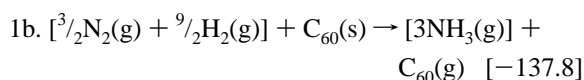**Estimation of the ΔH_f of $(NH_4^+)_3C_{60}^{3-}$.** On the basis of the discussions above, it is clear that an excellent estimate for ΔH_f of $(NH_4^+)_3C_{60}^{3-}$ can be made using, but modifying, the B–H cycle calculated for $(Rb^{+1})_3C_{60}^{3-}$. The modification is straightforward and involves replacement of the steps where Rb(s) is converted to Rb^+(g), with the steps involving formation of NH_4^+(g) from N_2(g) and H_2(g). The full cycle for Rb_3C_{60} is shown in steps la–3a and the cycle for $(NH_4)_3C_{60}$ is shown in steps lb–3b. Numbers in brackets and parentheses are in kilojoule energy units.[22]

Rb_3C_{60}:

1a. $[3Rb(s)] + C_{60}(s) \rightarrow [3Rb(g)] + C_{60}(g)$ [242.7]

2a. $[3Rb(g)] + C_{60}(g) \rightarrow [3Rb^+(g)] + C_{60}^{3-}(g)$ [1209.3]

3a. $3Rb^+(g) + C_{60}^{3-}(g) \rightarrow (Rb^{+1})_3C_{60}^{3-}$ (−2066, ref 12)

$\Delta H_f\, Rb_3C_{60} = -613.7$ kJ $= -6.36$ eV (ref 12)

$(NH_4)_3C_{60}$:

1b. $[^3/_2N_2(g) + {}^9/_2H_2(g)] + C_{60}(s) \rightarrow [3NH_3(g)] +$
$\qquad\qquad\qquad C_{60}(g)$ [−137.8]

1b′. $[^3/_2H_2(g)] \rightarrow [3H^+(g)]$ [653 + 3937]

2b. $[3NH_3(g) + 3H^+(g)] + C_{60}(g) \rightarrow [3NH_4^+] +$
$\qquad\qquad\qquad C_{60}^{3-}(g)$ [−2561]

3b. $3NH_4^+ + C_{60}^{3-}(g) \rightarrow (NH_4^+)_3C_{60}^{3-}$ (−2066)

$\Delta H_f\, (NH_4)_3C_{60} = -176$ kJ $= -1.82$ eV

The energy changes related to formation of the countercation *only* are shown in brackets (the energy changes for C_{60} are the same in each cycle) in eqs la–3a and lb–3b.

On the basis of the discussions above about the strong similarity, in ionic crystals, of the ionic radius and hardness (from bulk modulus data) of NH_4^+ to Rb^+ and of the calculated lattice energies of NH_4X (X = Cl, Br, and I) and RbX(X = Cl, Br, and I), *the lattice energies in steps 3a and 3b are assumed to be the same.* The difference in ΔH_f between Rb_3C_{60} and $(NH_4)_3C_{60}$ is then the difference in ΔH_f of three NH_4^+(g) from N_2(g) and H_2(g), and of ΔH_f of three Rb^+(g) from Rb(s), relative to the ΔH_f of Rb_3C_{60}. As shown above, ΔH_f of $(NH_4)_3C_{60}$ is negative and therefore stable with respect to the constituents in their standard states.

Can $(NH_4)_3C_{60}$ Be Made? Kadish and co-workers have made C_{60}-based superconductors such as Cs_3C_{60} by electrosynthesis.[5] This is one method that could possibly synthesize $(NH_4)_3C_{60}$.

A New C$_{60}$ Superconductor?

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An important question is, what is the likelihood of proton transfer from NH$_4^+$ to C$_{60}^{n-}$ ($n = 0$, 1, 2, 3) during synthesis attempts? The proton affinity (which is by definition a "gas phase" value) of C$_{60}$ has been bracketed by observation of proton transfer to C$_{60}$ from MH$^+$ for M = NH$_3$ (PA = 204 kcal/mol), but not for M = hexamethylbenzene (PA = 207 kcal/mol).[23] Note that an obvious correlation has never been made between *gas phase* proton affinities and proton transfer energetics *in solution or in solids*. For example, it is well known that proton transfer between NH$_3$ and HCl occurs readily in the bulk, with precipitation of the ionic salt NH$_4$Cl; however, the dimer between monomers in the gas phase is not NH$_4^+$Cl$^-$(g), but rather a H-bonded dimer with orientation H$_3$N···HCl.[24] Thus the slightly larger proton affinity of C$_{60}$ compared with that of NH$_3$ should not be taken as any sort of argument that (NH$_4$)$_3$C$_{60}$ cannot be made. In fact, Zhou et al. have studied C$_{60}^-$ in ammonia solutions and state that "addition of strong acid (NH$_4^+$) did not affect the cyclic voltammogram behavior, indicating lack of protonation of the radical anion in this solvent".[25]

Although not the main point of this paper, we point out one significant aspect of the electrochemical measurements by Zhou et al., which is that they showed that, on the time scale of the electrochemical measurement, proton transfer from NH$_4^+$ to C$_{60}^-$ does not occur. This result means that it is likely that the remarkable polymeric chains observed for M$_1$C$_{60}$ (M = Na, K, Rb, Cs)[26] can also be observed with countercation M$^+$ replaced by NH$_4^+$. Either electrosynthesis or synthesis in liquid ammonia looks to be a useful method for production of NH$_4$C$_{60}$; the author feels that the dynamics of an ammonium ion trapped between neighboring C$_{60}$ monoanions and comparison of the NH$_4$C$_{60}$ linear polymer formed with that of M$_1$C$_{60}$ (M = Na, K, Rb, Cs) make synthesis attempts worthwhile.

Cliffel and Bard also recently studied proton transfer to the mono- and dianion of C$_{60}$ in dichlorobenzene solution and concluded that C$_{60}^-$ is a weak base but that C$_{60}^{2-}$ is a fairly strong base, capable of deprotonating relatively weak acids like benzoic acid.[27] This suggests that electrochemical production of C$_{60}^{3-}$ in the presence of NH$_4^+$ may be difficult. In this regard, we may consider the possibility of synthesizing (NH$_4$)$_3$C$_{60}$ by step wise replacement of (say) Rb in (Rb)$_3$C$_{60}$ by NH$_4^+$. Mixed salts of type (M)$_2$NH$_4$C$_{60}$ or M(NH$_4$)$_2$C$_{60}$ (M = Na, K, Rb, Cs) are also possibilities. The ΔH_f of these ionic solids, if they can be made, will lie between the ΔH_f of M$_3$C$_{60}$ and that of (NH$_4$)$_3$C$_{60}$ and will therefore all be more stable than (NH$_4$)$_3$C$_{60}$; the ΔH_f value of M$_x$(NH$_4$)$_{3-x}$C$_{60}$ can be estimated quite accurately[28] by

$$\Delta H_f = x(\Delta H_f)(M_3 C_{60}) + (3-x)\Delta H_f((NH_4)_3 C_{60}) \quad (4)$$

For example, the ΔH_f of Rb$_3$C$_{60}$ is -6.4 eV, and those of (Rb)$_2$NH$_4$C$_{60}$ and Rb(NH$_4$)$_2$C$_{60}$ are -4.9 and -3.3 eV, respectively. As stated above, the ΔH_f of (NH$_4$)$_3$C$_{60}$ is calculated to be -1.8 eV.

Ziebarth and co-workers recently suggested that metathesis reactions which exploit the relative solubilities of M$_3$C$_{60}$ (M = alkali) and LX (L = countercation, X = halide anion) in liquid ammonia may be a method of incorporation of larger countercations into the lattice;[29] for example, KRb$_2$C$_{60}$ has been synthesized by reaction of 3 equiv of RbCl with K$_3$C$_{60}$ in liquid ammonia. The liquid ammonia synthesis approach was also recently used by Palstra and coworkers to synthesize (Cs)$_3$C$_{60}$, whereas vapor phase transport by sublimation of Cs in sealed capillary tubes had not allowed synthesis of (Cs)$_3$C$_{60}$.[6] Another possibility may be cation transfer by intimate contact of an ionic solid involving C$_{60}$ (for example, Rb$_3$C$_{60}$) and a simple ammonium halide salt.

Conclusions

A number of similarities have been noted between ammonium halide and rubidium halide salts; these similarities support the assumption that the lattice energy of ionic solids (Rb)$_3$C$_{60}$ and (NH$_4$)$_3$C$_{60}$ is the same. The enthalpy of formation of (NH$_4$)$_3$C$_{60}$ is calculated to be -1.8 eV/mol, which demonstrates that (NH$_4$)$_3$C$_{60}$ is stable with respect to the standard state reactants but less stable than Rb$_3$C$_{60}$, for which $\Delta H_f = -6.3$ eV/mol. Although (NH$_4$)$_3$C$_{60}$ is stable with respect to the standard state reactants, proton transfer may occur to the di- or trianion of C$_{60}$, which would make synthesis impossible. Three techniques seem relevent for attempting synthesis of (NH$_4$)$_3$C$_{60}$: electrosynthesis, synthesis in liquid ammonia, and solid/solid ion exchange reaction. Direct reaction may not work and an indirect method involving stepwise replacement of alkali countercations in, for example, Rb$_3$C$_{60}$, may succeed.

Independent from success or failure of synthesis of (NH$_4$)$_3$C$_{60}$, it is likely that the remarkable polymeric chains observed for M$_1$C$_{60}$ (M = Na, K, Rb, Cs) can also be observed with countercation M$^+$ replaced by NH$_4^+$. Either electrosynthesis or synthesis in liquid ammonia looks to be a useful method for production of NH$_4$C$_{60}$. Synthesis of NH$_4$C$_{60}$ may also provide insight into how to produce (NH$_4$)$_3$C$_{60}$ or M$_x$(NH$_4$)$_{3-x}$C$_{60}$.

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