

**(NH<sub>4</sub>)<sub>3</sub>C<sub>60</sub>: A New C<sub>60</sub> Superconductor?****R. S. Ruoff***Molecular Physics Laboratory, SRI International, Menlo Park, California 94025**Received: October 1, 1995; In Final Form: January 19, 1996*<sup>⊗</sup>

The enthalpy of formation ( $\Delta H_f$ ) of the ionic solid  $(\text{NH}_4^+)_3\text{C}_{60}^{3-}$  is assessed. The solid is found to be stable with respect to the standard state reactants ( $\text{N}_2(\text{g})$ ,  $\text{H}_2(\text{g})$ , and  $\text{C}_{60}(\text{s})$ ), with a  $\Delta H_f$  of  $-1.82$  eV/mol. For comparison, this enthalpy of formation is less than the enthalpy of formation of, e.g.,  $\text{K}_3\text{C}_{60}$  ( $-6.27$  eV/mol). There are several attractive features of  $(\text{NH}_4^+)_3\text{C}_{60}^{3-}$  as a new ionic solid and potential superconductor, *if it can be synthesized*. It is well-known that the size of the  $\text{NH}_4^+$  cation is almost exactly the same as that of  $\text{Rb}^+$ . Among the  $\text{M}_3\text{C}_{60}$  superconductors,  $\text{Rb}_3\text{C}_{60}$  has the second highest superconducting transition temperature, with  $T_c = 28$  K, which suggests that the  $T_c$  of a superconducting  $(\text{NH}_4)_3\text{C}_{60}$  *could* be higher than yet achieved for  $\text{C}_{60}$  superconductors, of which  $\text{Cs}_3\text{C}_{60}(\text{s})$  has the highest  $T_c$  of 40 K. There is a 28% relative mass change when the  $\text{NH}_4^+$  counteranion is replaced by  $^{15}\text{ND}_4^+$ , 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  $\text{C}_{60}$ , such as electrosynthesis or direct synthesis in liquid ammonia, would be required in contrast to the method of the production of  $\text{M}_3\text{C}_{60}$  ( $\text{M} = \text{alkali atom}$ ) based on vapor phase transport of  $\text{M}$  via sublimation in sealed tubes.

**Introduction**

When the interstitial sites of fcc  $\text{C}_{60}(\text{s})$  are doped with alkali atoms, superconducting solids can be formed.<sup>1</sup> Examples include  $\text{M}_3\text{C}_{60}(\text{s})$  ( $\text{M} = \text{K, Rb, and various mixtures of alkali atoms}$ )<sup>1</sup> and  $\text{M}_5\text{C}_{60}(\text{s})$  ( $\text{M} = \text{Ca}$ ).<sup>2</sup> Such solids have been synthesized in a variety of ways, for example, mixing by sublimation in a sealed glass tube,<sup>3</sup> reaction in liquid ammonia,<sup>4</sup> and electrosynthesis.<sup>5</sup> The highest  $T_c$  superconductor is  $\text{Cs}_3\text{C}_{60}$ , for which a  $T_c$  of 40 K has recently been measured.<sup>6</sup>  $\text{C}_{60}$ -based superconductors are of interest for a variety of reasons, including the desire to understand in detail the mechanism of superconductivity;  $\text{M}_3\text{C}_{60}$  ( $\text{M} = \text{alkali}$ ) 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,  $\text{C}_{60}$  is very electronegative, with an electron affinity of 2.65 eV;<sup>7</sup> to date, all  $\text{C}_{60}$ -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;<sup>1</sup> however, note comments in ref 8 about the new class of binary alkali  $\text{M}_2\text{Na}_i\text{C}_{60}$  or  $\text{M}_1\text{Na}_2\text{C}_{60}$  ( $\text{M} = \text{Rb, Cs}$ ). For example, the alkali and alkaline earth groups have been extensively studied. The highly electropositive lanthanides have been suggested as possible superconductors,<sup>9</sup> 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);<sup>10,11</sup> the typical method of production of  $\text{M}_x\text{C}_{60}$  by sublimation of  $\text{M}$  (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

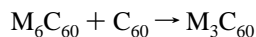
are there alternatives for formation of ionic solids that have interstitial sites occupied by a new type of cation?

A worthwhile exercise has been calculation by a Born–Haber (B–H) thermodynamic cycle of the enthalpy of formation,  $\Delta H_f$  of (assumed) ionic solids such as  $(\text{M}^+)_6\text{C}_{60}^{-6}$  ( $\text{M} = \text{alkali}$ ) (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  $\Delta H_f$  of  $\text{M}_6\text{C}_{60}$  ( $\text{M} = \text{Na, K, Rb, Cs}$ )<sup>13</sup> 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  $\text{M}_6\text{C}_{60}$  solids *are* in fact ionic solids with essentially full transfer of six electrons to  $\text{C}_{60}$ , a conclusion suggested by photoemission spectra of K-doped  $\text{C}_{60}$  thin films,<sup>14</sup> electrical conductivity measurements,<sup>15</sup> and LDA calculations.<sup>16</sup>

The close agreement between experimental and B–H cycle calculated  $\Delta H_f$  for these  $\text{M}_6\text{C}_{60}$  solids also shows that the calculation of  $\Delta H_f$  with the B–H cycle is essentially quantitatively correct. There is strong indirect evidence from experiment<sup>1,14</sup> that the  $\text{M}_3\text{C}_{60}$  solids ( $\text{M} = \text{Na, K, Rb, Cs}$ ) are also completely ionic and therefore of the form  $(\text{M}^+)_3\text{C}_{60}^{-3}$ ; these conclusions are supported by the B–H cycle treatment (close agreement of calculated and experimental lattice constants, calculated and experimental stability trends between  $\text{M}_3\text{C}_{60}$  and  $\text{M}_6\text{C}_{60}$ , and calculated and experimental zero-pressure bulk modulus values), which *assumed* full electron transfer from  $\text{M}$  to  $\text{C}_{60}$ ;<sup>12</sup> this picture is also strongly supported by extensive LDA calculations of the  $\text{M}_3\text{C}_{60}$  solids.<sup>1,16</sup>  $\Delta H_f$  values have not yet been experimentally determined for the  $\text{M}_3\text{C}_{60}$  solids ( $\text{M} = \text{alkali}$ ); however, the very close agreement between the B–H calculated and experimentally determined  $\Delta H_f$  for the  $\text{M}_6\text{C}_{60}$  solids *very strongly suggests* that the calculated B–H cycle  $\Delta H_f$  values for the  $\text{M}_3\text{C}_{60}$  solids are also correct to a few percent or so. This serves as an important assumption in the analysis of the  $\Delta H_f$  of  $(\text{NH}_4^+)_3\text{C}_{60}^{3-}$  presented below, and I have therefore outlined the basis for this assumption in such detail. It is worth noting as an aside that the  $\Delta H_f$  of  $\text{M}_3\text{C}_{60}$  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



would yield the  $\Delta H_f$  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,  $NH_4^+X^-$ .<sup>17</sup> 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.<sup>18</sup>

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.<sup>19</sup>

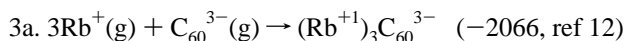
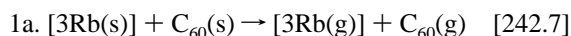
Thus, although  $NH_4^+$  is isoelectronic with  $Na^+$ , it is identical in size to  $Rb^+$ . The bulk moduli,  $B_0$  (units: GPa) of  $NH_4Cl$  (18.5) and  $NH_4Br$  (16.6) are closer to those of  $KCl$  (16.7) and  $KBr$  (14.3) than to those of  $RbCl$  (16.2) and  $RbBr$  (13.8).<sup>20</sup> However, 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);<sup>21</sup> 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.<sup>17</sup> 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  $NH_3$ .<sup>17</sup> 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;  $\Delta H_f$  of all other  $M_3C_{60}$  and  $M_6C_{60}$  solids were calculated on the basis of this constraint.<sup>12</sup> 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.<sup>12</sup> 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 counteraction may eventually make an important contribution.

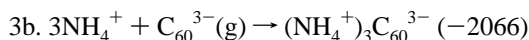
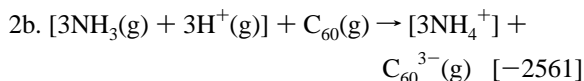
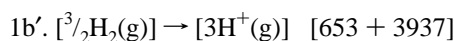
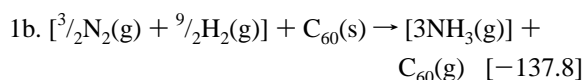
**Estimation of the  $\Delta H_f$  of  $(NH_4^+)_3C_{60}^{3-}$ .** On the basis of the discussions above, it is clear that an excellent estimate for  $\Delta H_f$  of  $(NH_4^+)_3C_{60}^{3-}$  can be made using, but modifying, the B–H cycle calculated for  $(Rb^+)_3C_{60}^{3-}$ . The modification is 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 1a–3a and the cycle for  $(NH_4)_3C_{60}$  is shown in steps 1b–3b. Numbers in brackets and parentheses are in kilojoule energy units.<sup>22</sup>

$Rb_3C_{60}$ :



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

$(NH_4)_3C_{60}$ :



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

The energy changes related to formation of the counteraction *only* are shown in brackets (the energy changes for  $C_{60}$  are the same in each cycle) in eqs 1a–3a and 1b–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  $NH_4X$  ( $X = Cl, Br, \text{ and } I$ ) and  $RbX$  ( $X = Cl, Br, \text{ and } I$ ), *the lattice energies in steps 3a and 3b are assumed to be the same*. The difference in  $\Delta H_f$  between  $Rb_3C_{60}$  and  $(NH_4)_3C_{60}$  is then the difference in  $\Delta H_f$  of three  $NH_4^+(g)$  from  $N_2(g)$  and  $H_2(g)$ , and of  $\Delta H_f$  of three  $Rb^+(g)$  from  $Rb(s)$ , relative to the  $\Delta H_f$  of  $Rb_3C_{60}$ . As shown above,  $\Delta H_f$  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 electro-synthesis.<sup>5</sup> This is one method that could possibly synthesize  $(NH_4)_3C_{60}$ .

An important question is, what is the likelihood of proton transfer from NH<sub>4</sub><sup>+</sup> to C<sub>60</sub><sup>n-</sup> (n = 0, 1, 2, 3) during synthesis attempts? The proton affinity (which is by definition a "gas phase" value) of C<sub>60</sub> has been bracketed by observation of proton transfer to C<sub>60</sub> from MH<sup>+</sup> for M = NH<sub>3</sub> (PA = 204 kcal/mol), but not for M = hexamethylbenzene (PA = 207 kcal/mol).<sup>23</sup> 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<sub>3</sub> and HCl occurs readily in the bulk, with precipitation of the ionic salt NH<sub>4</sub>Cl; however, the dimer between monomers in the gas phase is not NH<sub>4</sub><sup>+</sup>Cl<sup>-</sup>(g), but rather a H-bonded dimer with orientation H<sub>3</sub>N...HCl.<sup>24</sup> Thus the slightly larger proton affinity of C<sub>60</sub> compared with that of NH<sub>3</sub> should not be taken as any sort of argument that (NH<sub>4</sub>)<sub>3</sub>C<sub>60</sub> cannot be made. In fact, Zhou et al. have studied C<sub>60</sub><sup>-</sup> in ammonia solutions and state that "addition of strong acid (NH<sub>4</sub><sup>+</sup>) did not affect the cyclic voltammogram behavior, indicating lack of protonation of the radical anion in this solvent".<sup>25</sup>

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<sub>4</sub><sup>+</sup> to C<sub>60</sub><sup>-</sup> does not occur. This result means that it is likely that the remarkable polymeric chains observed for M<sub>1</sub>C<sub>60</sub> (M = Na, K, Rb, Cs)<sup>26</sup> can also be observed with counteraction M<sup>+</sup> replaced by NH<sub>4</sub><sup>+</sup>. Either electrosynthesis or synthesis in liquid ammonia looks to be a useful method for production of NH<sub>4</sub>C<sub>60</sub>; the author feels that the dynamics of an ammonium ion trapped between neighboring C<sub>60</sub> monoanions and comparison of the NH<sub>4</sub>C<sub>60</sub> linear polymer formed with that of M<sub>1</sub>C<sub>60</sub> (M = Na, K, Rb, Cs) make synthesis attempts worthwhile.

Cliffel and Bard also recently studied proton transfer to the mono- and dianion of C<sub>60</sub> in dichlorobenzene solution and concluded that C<sub>60</sub><sup>-</sup> is a weak base but that C<sub>60</sub><sup>2-</sup> is a fairly strong base, capable of deprotonating relatively weak acids like benzoic acid.<sup>27</sup> This suggests that electrochemical production of C<sub>60</sub><sup>3-</sup> in the presence of NH<sub>4</sub><sup>+</sup> may be difficult. In this regard, we may consider the possibility of synthesizing (NH<sub>4</sub>)<sub>3</sub>C<sub>60</sub> by step wise replacement of (say) Rb in (Rb)<sub>3</sub>C<sub>60</sub> by NH<sub>4</sub><sup>+</sup>. Mixed salts of type (M)<sub>2</sub>NH<sub>4</sub>C<sub>60</sub> or M(NH<sub>4</sub>)<sub>2</sub>C<sub>60</sub> (M = Na, K, Rb, Cs) are also possibilities. The ΔH<sub>f</sub> of these ionic solids, if they can be made, will lie between the ΔH<sub>f</sub> of M<sub>3</sub>C<sub>60</sub> and that of (NH<sub>4</sub>)<sub>3</sub>C<sub>60</sub> and will therefore all be more stable than (NH<sub>4</sub>)<sub>3</sub>C<sub>60</sub>; the ΔH<sub>f</sub> value of M<sub>x</sub>(NH<sub>4</sub>)<sub>3-x</sub>C<sub>60</sub> can be estimated quite accurately<sup>28</sup> by

$$\Delta H_f = x(\Delta H_f)(M_3C_{60}) + (3 - x)\Delta H_f((NH_4)_3C_{60}) \quad (4)$$

For example, the ΔH<sub>f</sub> of Rb<sub>3</sub>C<sub>60</sub> is -6.4 eV, and those of (Rb)<sub>2</sub>NH<sub>4</sub>C<sub>60</sub> and Rb(NH<sub>4</sub>)<sub>2</sub>C<sub>60</sub> are -4.9 and -3.3 eV, respectively. As stated above, the ΔH<sub>f</sub> of (NH<sub>4</sub>)<sub>3</sub>C<sub>60</sub> is calculated to be -1.8 eV.

Ziebarth and co-workers recently suggested that metathesis reactions which exploit the relative solubilities of M<sub>3</sub>C<sub>60</sub> (M = alkali) and LX (L = counteraction, X = halide anion) in liquid ammonia may be a method of incorporation of larger counteractions into the lattice;<sup>29</sup> for example, KRb<sub>2</sub>C<sub>60</sub> has been synthesized by reaction of 3 equiv of RbCl with K<sub>3</sub>C<sub>60</sub> in liquid ammonia. The liquid ammonia synthesis approach was also recently used by Palstra and coworkers to synthesize (Cs)<sub>3</sub>C<sub>60</sub>, whereas vapor phase transport by sublimation of Cs in sealed capillary tubes had not allowed synthesis of (Cs)<sub>3</sub>C<sub>60</sub>.<sup>6</sup> Another possibility may be cation transfer by intimate contact of an ionic solid involving C<sub>60</sub> (for example, Rb<sub>3</sub>C<sub>60</sub>) 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)<sub>3</sub>C<sub>60</sub> and (NH<sub>4</sub>)<sub>3</sub>C<sub>60</sub> is the same. The enthalpy of formation of (NH<sub>4</sub>)<sub>3</sub>C<sub>60</sub> is calculated to be -1.8 eV/mol, which demonstrates that (NH<sub>4</sub>)<sub>3</sub>C<sub>60</sub> is stable with respect to the standard state reactants but less stable than Rb<sub>3</sub>C<sub>60</sub>, for which ΔH<sub>f</sub> = -6.3 eV/mol. Although (NH<sub>4</sub>)<sub>3</sub>C<sub>60</sub> is stable with respect to the standard state reactants, proton transfer may occur to the di- or trianion of C<sub>60</sub>, which would make synthesis impossible. Three techniques seem relevant for attempting synthesis of (NH<sub>4</sub>)<sub>3</sub>C<sub>60</sub>: 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 counteractions in, for example, Rb<sub>3</sub>C<sub>60</sub>, may succeed.

Independent from success or failure of synthesis of (NH<sub>4</sub>)<sub>3</sub>C<sub>60</sub>, it is likely that the remarkable polymeric chains observed for M<sub>1</sub>C<sub>60</sub> (M = Na, K, Rb, Cs) can also be observed with counteraction M<sup>+</sup> replaced by NH<sub>4</sub><sup>+</sup>. Either electrosynthesis or synthesis in liquid ammonia looks to be a useful method for production of NH<sub>4</sub>C<sub>60</sub>. Synthesis of NH<sub>4</sub>C<sub>60</sub> may also provide insight into how to produce (NH<sub>4</sub>)<sub>3</sub>C<sub>60</sub> or M<sub>x</sub>(NH<sub>4</sub>)<sub>3-x</sub>C<sub>60</sub>.

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