Semi-empirical estimation of the thermodynamics of graphane; assessment of the graphite-graphane system for hydrogen storage and release; some potential formation reactions for graphane

Michael Jewess

The Long Barn, Harwell, Oxfordshire OX11 0DX, England

E-mail: michaeljewess@tiscali.co.uk

ABSTRACT

Graphane consists of macromolecular layers, each comprising CH units at the vertices of an indefinitely large 2-dimensional array of fused hexagons. Between the layers there are weak attractive van der Waals forces. Graphane has yet to be synthesized in pure bulk form. In order to facilitate the devising of improved syntheses of graphane, we here estimate the thermodynamic properties of graphane by semi-empirical methods. ΔH_f (CH, graphane) and S (CH, graphane) are estimated, respectively, as -8.8 ± 5 kJ mol^{-1} and 18 ± 4 J K^{-1} mol^{-1} at 298.15 K and 1 bar. This makes graphane thermodynamically unstable with respect to graphite and hydrogen gas at 298.15 K unless the pressure is raised above 1 bar, probably very considerably. (It is, however, believed that graphane, once formed, will survive indefinitely at 298.15 K and 1 bar – *ie* will be kinetically stable.)

Elevated temperature and use of a catalyst will probably be needed if high-pressure hydrogenation of graphite is to produce graphane at an appreciable rate, any increase in temperature needing to be offset by a further increase in pressure. The implications of this for the use of the graphite-graphane system for hydrogen storage and release are discussed.

The following reactions producing graphane *are* predicted to be thermodynamically favored at 298.15 K and 1 bar: addition polymerisation of acetylene; addition polymerisation of benzene; dehydrogenation of cyclohexene; the reaction of cyclohexene with graphite; and the reduction of graphite with formic acid.

I. INTRODUCTION

Graphane is an exciting new solid, on account of its structural simplicity, its potential for hydrogen storage, and its possible application in electronic and photonic devices. Sofo *et al*[1] predicted graphane's existence on the basis of *ab initio* calculations, while noting some previous experimental indications of its existence in impure form.[2] They calculated graphane's precise structure, binding energy, electronic band structure, and vibrational frequencies. Subsequently, Elias *et al*[3] synthesized small quantities of graphane from graphene and atomic hydrogen, and investigated it by transmission electron microscopy, Raman spectroscopy, and electrical conductivity measurements. However, pure bulk graphane has yet to be prepared, let alone single crystals of graphane which would allow definitive structural study.

Any synthetic route that can be forecast to be thermodynamically unfavorable is, of course, not worth pursuing. In addition, if one forecasts a route to be thermodynamically favorable, then one must still select for it conditions of temperature, pressure, and catalysis such that the formation reaction occurs at a significant rate but any thermodynamically favorable side-reactions do not. **The principal aim of this paper is to provide estimates of the thermodynamic properties of graphane which are reliable enough to guide experimenters seeking to synthesize pure bulk graphane.**

Another use of such estimates is in the assessment of the potential of the previously proposed use of the graphite – graphane system for hydrogen storage.

Sofo *et al*'s *ab initio* calculations suggest that graphane (of empirical formula CH) consists of indefinitely large macromolecular layers of fused six-membered carbon rings all in parallel chair conformations with one hydrogen atom attached to each carbon atom, the hydrogen atoms on any pair of adjacent carbon atoms being on opposite sides of each layer. This is highly plausible for these reasons:-[4]

(i)   It is well known that six-membered rings of sp^3-hybridized carbon atoms are unstrained from a mutually tetrahedral arrangement.

(ii)   Cyclohexane (molecular formula C_6H_{12}) is well known to be more stable in its chair conformation than in its boat conformation.

---

[1] J. O. Sofo, A. S. Chaudhari, and G. D. Barber, Phys. Rev. B **75**, 153401 (2007).

[2] A. D. Lueking, H. R. Gutierrez, D. A. Fonseca, D. L. Narayanan, D. Van Essendelft, P. Jain, and C. E. B. Clifford, J. Amer. Chem. Soc. **128**, 7758 (2006). These workers ball-milled anthracite coal with cyclohexene, and apparently obtained some hydrogenated graphite embedded in other materials.

[3] D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim, and K. S. Novoselov, Science **323**, 610 (2009). See also K. S. Novoselov, Phys. World **20** (8), 27 (August 2009).

[4] J. Clayden, N. Greeves, S.Warren, and P.Wothers, *Organic Chemistry*, 456-461 and 465-466 (Oxford University Press, 2001)
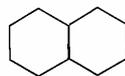
Of the two structural isomers of decalin[5] (molecular formula $C_{10}H_{18}$), *trans*-decalin is the more stable and comprises two fused parallel chairs.

The relationship of the cyclohexane molecule, the *trans*-decalin molecule, and the graphane macromolecule is shown in Figs. 1(a) to 1(c).

---

[5] The decalins are more properly known as the decahydronaphthalenes.
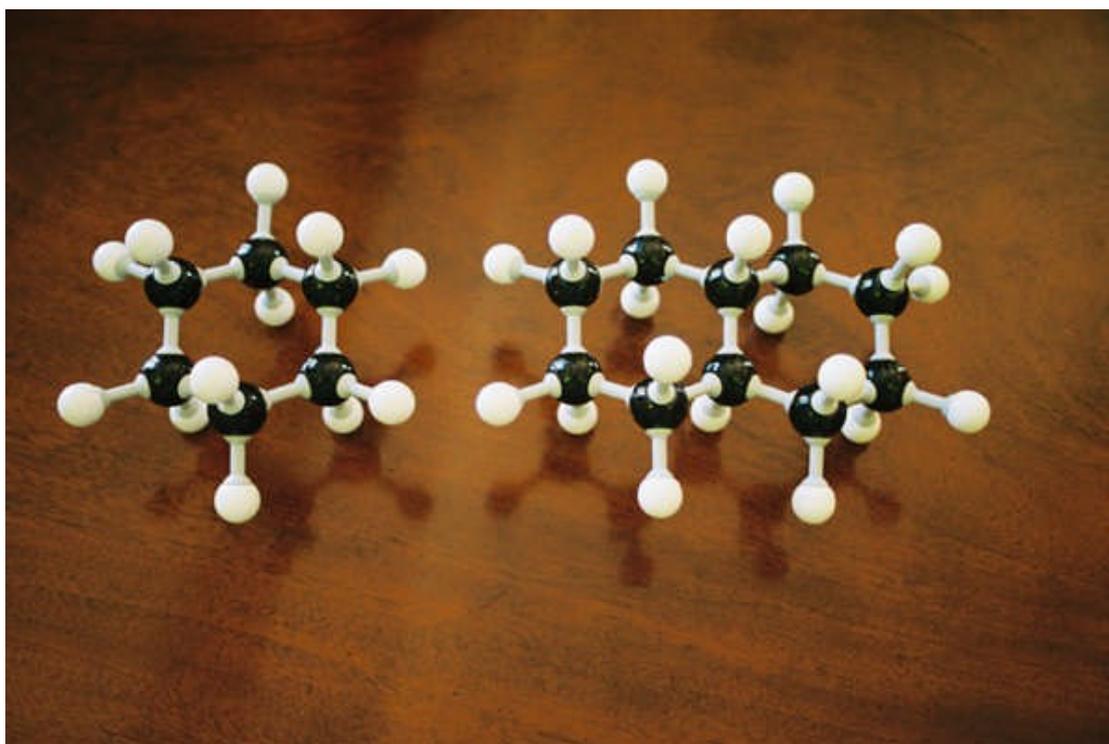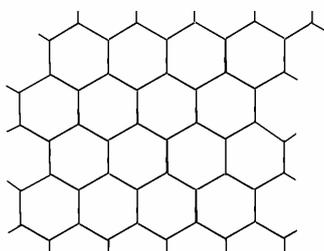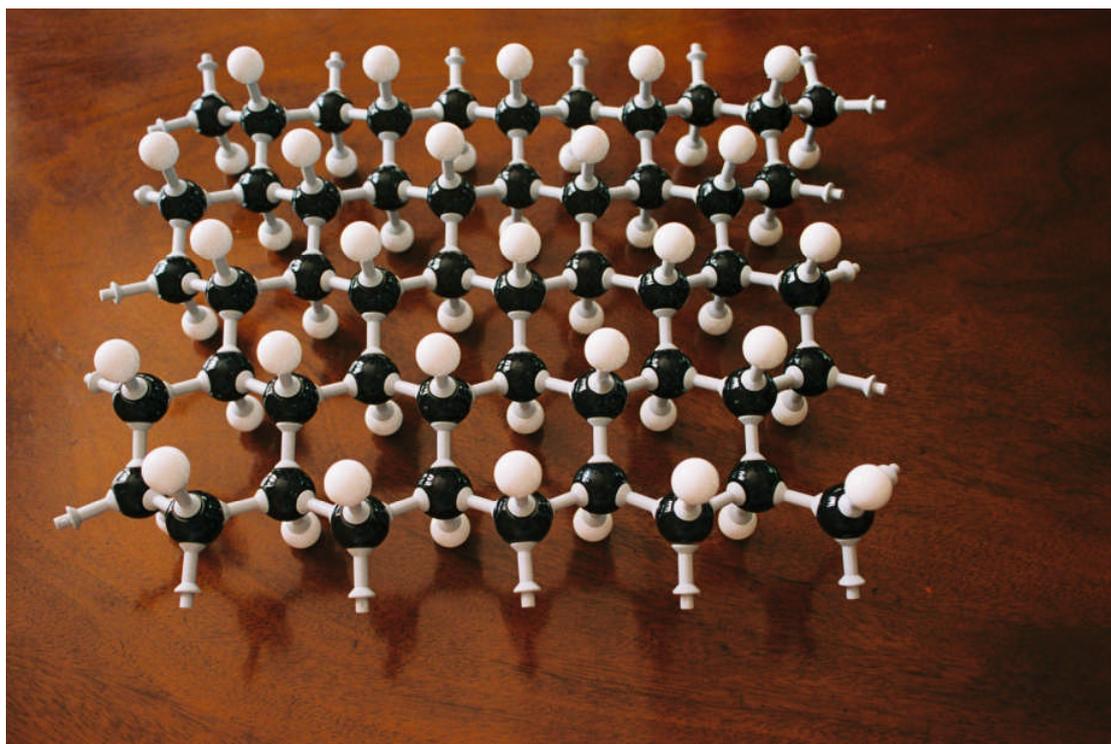
(a)   (b)

cont'd next page...

(c)

FIG. 1. Models of (a) cyclohexane chair, (b) *trans*-decalin with both rings in chair conformation, and (c) graphane according to Sofo *et al*, together with topological structural formulae in which, following convention, the carbon and hydrogen atoms are implied by the carbon-carbon bonds shown.

Sofo *et al* further propose that the graphane macromolecules are arranged in the crystal as parallel layers bonded by weak van der Waals forces (compare graphite, which consists of parallel planar graphene sheets).

In what follows, except when otherwise indicated, all thermodynamic properties are at 298.15 K and 1 bar (10^5 N m^{-2}) and all experimental thermodynamic data used in calculations are from the *CRC Handbook of Chemistry and Physics.*[6] All thermodynamic quantities are molar, and accordingly the subscript m is omitted for clarity. Chemical reactions are numbered, and are referred to in subscripts within mathematical equations (themselves not numbered), so ΔH_{reac1} is, for example, the molar enthalpy of reaction (1).

II. SEMI-EMPIRICAL ESTIMATION OF THE MOLAR ENTHALPY OF FORMATION OF GRAPHANE

Pauling[7] found many years ago that one may approximately compute unknown molar enthalpies of formation of compounds by adding empirical "bond molar enthalpies", even across the full gamut of organic compounds. The high accuracy of semi-empirical estimates within the restricted class of hydrocarbons was noted by Rossini *et al*,[8] implying that the additivity of C-C and C-H bond energies in that class is relatively accurate; this is as one would expect, because the electronic environment of each bond (*ie* the adjacent bonds) is similar in a way that would not be true in the generality of organic compounds (which may include electronegative atoms such as nitrogen, oxygen, and sulphur). This suggested to the author a semi-empirical approach towards estimating the molar enthalpy of formation of graphane (ie one-half of the molar enthalpy of reaction (9) below).

[Here is omitted what the author now considers to be unnecessary discussion, including Figure 2, Table I, reactions (1) to (3) with associated ΔH_{reac1}, ΔH_{reac2}, and ΔH_{reac3}, and footnotes 9 and 10.][10]

This approach views graphane as a layer of fused parallel chairs, which as we shall see allows the enthalpy of formation of graphane to be estimated from those of cyclohexane, cyclohexylcyclohexane, and *trans*-decalin, all of which are known.

As a first step, we imagine the formation of an indefinitely long macromolecular "tape" of fused chairs by the steps of reactions (4) to (6) (which use conventional topological structural formulae, but in which the

---

[6] *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide, 89th edition, pages 5-18 to 5-42 and 6-20 to 6-21 (CRC Press, 2008).
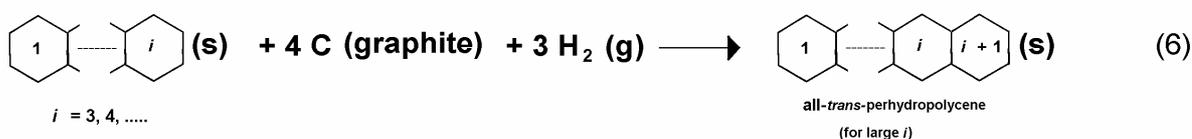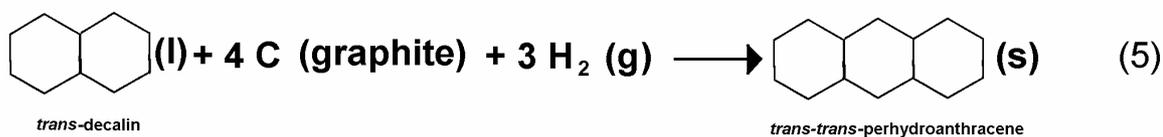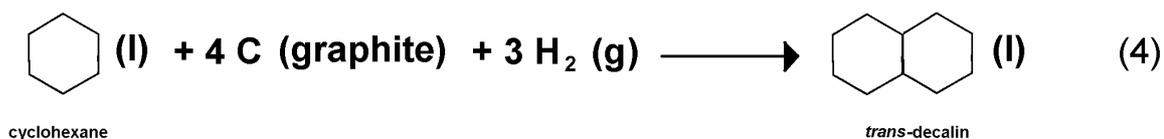[7] L. Pauling, *The nature of the chemical bond*, Chapter 3, 3rd edition (Cornell University Press, 1960).
[8] Quoted at page D-82 of the *CRC Handbook of Chemistry and Physics*, ed R. C. Weast, 59th edition (CRC Press, 1978).
[9] Footnote deleted.
[10] Footnote deleted.

cyclohexane rings are to be understood to be predominantly in chair form with all ring fusions are *trans*-). Reaction (4) can be imagined in space from the models of cyclohexane and *trans*-decalin in Fig. 1. The product of reaction (6) for indefinitely high *i* is depicted in Fig. 3. We refer to this (hypothetical) macromolecule as all-*trans*-perhydropolycene.

$$\text{(l)} + 4\text{ C (graphite)} + 3\text{ H}_2\text{ (g)} \longrightarrow \text{(l)} \qquad (4)$$

cyclohexane   *trans*-decalin

$$\text{(l)} + 4\text{ C (graphite)} + 3\text{ H}_2\text{ (g)} \longrightarrow \text{(s)} \qquad (5)$$

trans-decalin   *trans-trans*-perhydroanthracene

$$\boxed{1 \text{------} i}\text{ (s)} + 4\text{ C (graphite)} + 3\text{ H}_2\text{ (g)} \longrightarrow \boxed{1 \text{------} i\;\; i+1}\text{ (s)} \qquad (6)$$

i = 3, 4, ...   all-*trans*-perhydropolycene
                                                          (for large *i*)
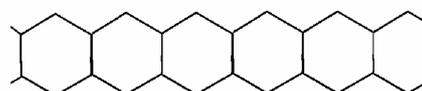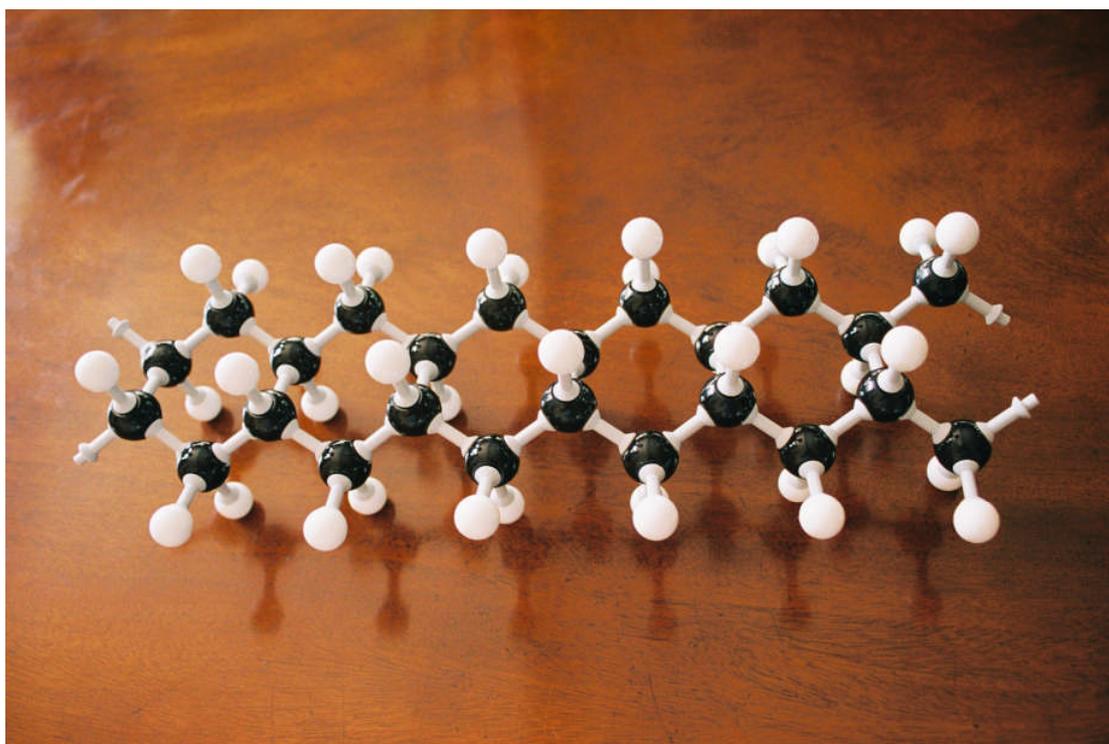
**FIG. 3.   All-t*rans*-perhydropolycene as a molecular model and topological structural formula.**

The molar enthalpy of reaction (4) is given by

$$\Delta H_{reac4} = \Delta H_f \ (trans\text{-}decalin,\ l) - \Delta H_f \ (cyclohexane,\ l).$$
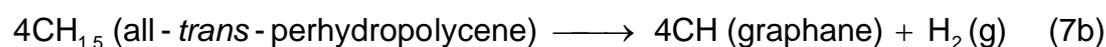
The two molar enthalpies of formation in this equation being known, we calculate ΔH_{reac4} = -74.2 kJ mol^{-1}. Moreover, the extremely close similarity of the bonds being broken and made in reactions (4) and (6), with no change of state in the hydrocarbon in either case, suggest that the molar enthalpy of reaction (6), ΔH_{reac6}, is very close to ΔH_{reac4} = -74.2 kJ mol^{-1}. And for large i+1 in reaction (6), we may take the empirical formula of all-$trans$-perhydropolycene to be $CH_{1.5}$ and its molar enthalpy of formation to be simply

$$\Delta H_f \ (all\text{-}trans\text{-}perhydropolycene,\ CH_{1.5}) = \Delta H_{reac6} / 4 \ = \ \Delta H_{reac4} / 4 =$$
$$-74.2 / 4 \ kJmol^{-1} = -18.6 \ kJmol^{-1}.$$

Now, all-$trans$-perhydropolycene is formally related to graphane by reaction (7a) in which pairs of CH_2 groups in adjacent all-$trans$-perhydropolycene macromolecules lose an H_2 molecule thereby forming the desired layer.

minus H$_2$ molecules

(7a)
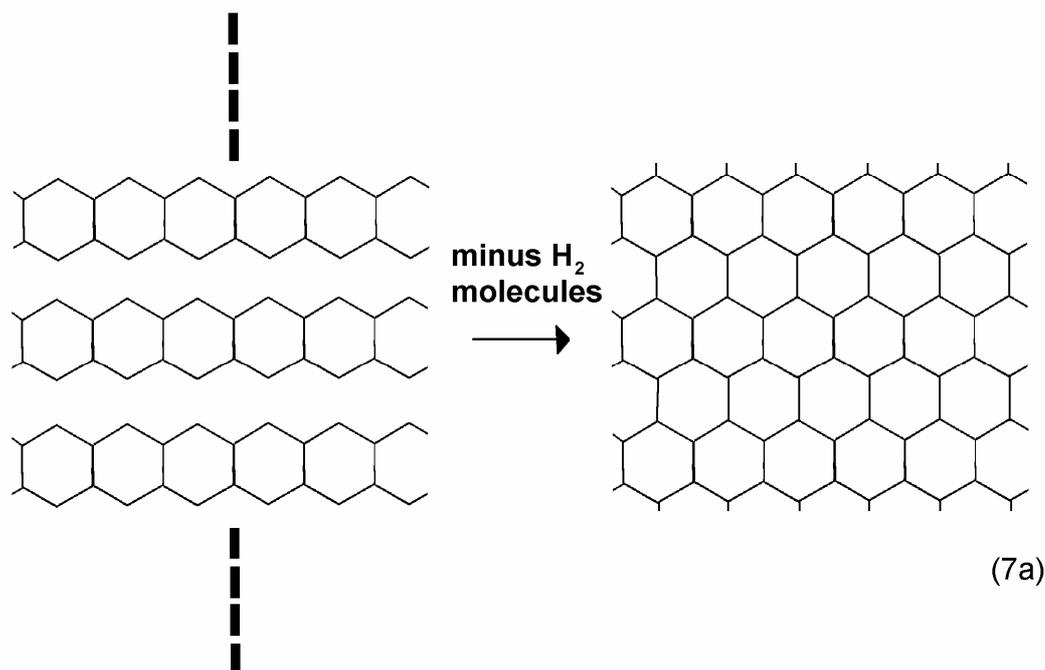
In empirical formulae, reaction (7a) is equivalent to

$$4CH_{1.5} \ (all\text{-}trans\text{-}perhydropolycene) \longrightarrow 4CH \ (graphane) + H_2 \ (g) \quad (7b)$$

It is reasonable to estimate the molar enthalpy of this reaction, ΔH_{reac7b}, as equal to ΔH_{reac8}, the molar enthalpy of the reaction

$$\text{cyclohexane} \quad (l) \longrightarrow \text{cyclocyclohexane} \ (l) \ + \ H_2 \ (g) \tag{8}$$
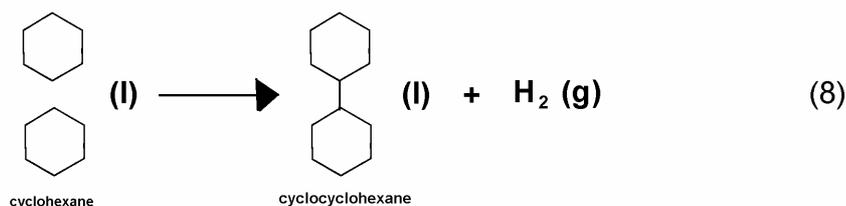
We know that

$$\Delta H_{reac8} = \Delta H_f \ (\text{cyclocyclohexane}, l) - 2 \ \Delta H_f \ (\text{cyclohexane}, l)$$

The two molar enthalpies of formation in this equation being known, we calculate ΔH_{reac8} = 39.1 kJ mol^{-1}. Further,

$$\Delta H_{reac7b} = 4 \ \Delta H_f \ (CH, \text{graphane}) - 4 \ \Delta H_f \ (CH_{1.5}, \text{all-}trans\text{-perhydropolycene}).$$

Putting ΔH_{reac7b} equal to ΔH_{reac8} and using the molar enthalpy of formation of per-*trans*-perhydropolycene obtained above, we obtain the desired result

$$\Delta H_f \ (CH, \text{graphane}) = \Delta H_f \ (CH_{1.5}, \text{all-}trans\text{-perhydropolycene}) + \Delta H_{reac8}/4 =$$
$$-18.6 + 39.1/4 \ \text{kJmol}^{-1} = -8.8 \ \text{kJ mol}^{-1}.$$

We have therefore estimated the molar enthalpy of formation graphane, $CH_{1.5}$, as -8.8 kJ mol^{-1}.

We estimate possible errors in this value as follows. It has been obtained by use of the known enthalpies of formation of liquid hydrocarbons to estimate the enthalpy of formation of high molecular weight solid hydrocarbons. If one estimates analogously the enthalpy of formation of the solid straight-chain hydrocarbon $C_{32}H_{66}$ from the enthalpies of formation of the liquid straight-chain hydrocarbons C_5H_{12} and C_6H_{12},[11] one obtains a value which is not negative enough by (only) 3.5 kJ mol^{-1} per carbon atom. Taking this analogy into account, and rounding, -

we estimate the molar enthalpy of formation graphane, $CH_{1.5}$, as - 8.8 ± 5 kJ mol^{-1}.

---

[11] In this case, the reactions analogous to reactions (4) to (6) involve sequential insertion, formally, of methylene groups, $-CH_2-$, instead of $-CH(CH_2)_2CH-$ groups.

III. COMPARISON OF THE ABOVE SEMI-EMPIRICAL ESTIMATE OF THE MOLAR ENTHALPY OF FORMATION OF GRAPHANE WITH THE *AB INITIO* BINDING ENERGY ESTIMATE OF SOFO *ET AL*

Sofo *et al* obtained by *ab initio* calculations a binding energy per atom in graphane, ignoring zero-point energies of vibration, of -0.15 eV, *ie* -0.30 eV per CH atom pair or -28.9 kJ mol⁻¹ per mole of graphane, CH. This we equate to the internal energy of formation, ΔU_f, *at the absolute zero of temperature*, if zero-point vibration is ignored. The principal factors distinguishing this from the to molar *enthalpy* of formation *at 298.15 K* are set out in the equation[12]

$$\Delta H_f \text{ (CH, graphane, 298.15K)} = -28.9 \text{ kJ mol}^{-1} +$$
$$(1/2)\, L h [f_{C-H} - (1/2)f_{H-H}] - (1/2)(7/2)\, R \times 298.15 \text{ K} +$$
$$\int_{0K}^{298.15 \text{ K}} [C_p(\text{graphane}) - C_p(\text{graphite})] \ dT.$$

in which –

the second term represents the difference in zero-point energy of the high-frequency vibrations involving the light hydrogen atoms, *L* and *h* being Avogadro's and Planck's constants and each *f* being the (stretching) vibrational frequencies of the respective bonds;

the third term represents the molar enthalpy of translation and rotation of half a mole of hydrogen molecules at 298.15 K; and

in the fourth term, each C_p represents the respective molar heat capacity at a constant pressure of 1 bar.

The second term we calculate as + 4.2 kJ mol⁻¹ for a C-H stretch at 2900 cm⁻¹ in graphane[13] and an H-H stretch in hydrogen at 4401 cm⁻¹.[14] The third term is -4.3 kJ mol⁻¹. The fourth term will not exceed + 5 kJ mol⁻¹ for any plausible $C_p - T$ functions for the two solids. We conclude that the result of Sofo *et al*'s *ab initio* calculation corresponds to ΔH_f (CH, graphane) at 298.15 K more negative than -24 kJ mol⁻¹, whereas above we have arrived at an estimate of -8.8 kJ mol⁻¹, very unlikely to be in error by even half the amount of the difference. This is not to deny the value of the *ab initio* approach for forecasting small differences in stability between very similar substances (*eg* as de Sofo *et al* do in preferring chair graphane as in Fig. 1(c) over a "boat" alternative) and for predicting other properties of a substance.

---

[12] Compare Pauling, *op. cit.*, footnote at page 81.

[13] According to I.L.Finar, *Organic Chemistry*, 84 (Longman, 6th edition, 1973), the stretch for tertiary C-H in branched-chain saturated hydrocarbons is at 2880 to 2900 cm⁻¹, and Sofo *et al*, ref. 1, predict two C-H stretches at around 2800 and at 2919 cm⁻¹ in graphane.

[14] Lide (ed.), *op. cit.*, page 9-105.

IV. ESTIMATION OF THE GIBBS MOLAR FREE ENERGY OF FORMATON OF GRAPHANE; IMPLICATIONS FOR SYNTHESIS OF GRAPHANE FROM GRAPHITE AND HYDROGEN AND FOR USE OF THE GRAPHITE – GRAPHANE SYSTEM FOR HYDROGEN STORAGE AND RELEASE

To obtain Gibbs free energies, which determine whether or not reactions are favorable at a given temperature and pressure, the absolute molar entropy of graphane now needs to be estimated. In this case, we use as reference compounds the 22 simple[15] organic compounds listed in ref. 6 which (i) have molecules of at least 20 atoms and (ii) are solid at 298.15 K and 1 bar. All these have absolute molar entropies of from 7.0 to 10.5 J K^{-1} mol^{-1} per mole of atoms (for example, octadecane has 56 atoms and an absolute molar entropy of 480.2 J K^{-1} mol^{-1} or 8.6 J K^{-1} per mole of atoms); the average is 9.2 J K^{-1} per mole of atoms. This average would imply a central estimate of 18.4 J K^{-1} mol^{-1} for the absolute molar entropy of graphane, S(graphane, CH). Taking the spread of results of which the average was taken, and rounding, -

we estimate absolute molar entropy of graphane, S(graphane, CH) as 18.4 ± 4 J K^{-1} mol^{-1}.[16]

The absolute molar entropies of graphite and hydrogen gas H_2 being 5.7 and 130.7 J K^{-1} mol^{-1} respectively, our central estimate gives a molar entropy of *formation* ΔS_f (CH, graphane) = (18.4 -130.7/2 – 5.7) = -52.7 J K^{-1} mol^{-1}.

The Gibbs free energy of formation of graphane is

$$\Delta G_f \text{ (CH, graphane)} = \Delta H_f \text{ (CH, graphane)} - T\Delta S_f \text{ (CH, graphane)}.$$

Using the above values for ΔH_f (CH, graphane) of -8.8 kJ mol^{-1} and ΔS_f (CH, graphane) of -52.7 J K^{-1} mol^{-1} and inserting T = 298.15 K, we obtain ΔG_f (CH, graphane) = 6.9 kJ mol^{-1}. On the worst assumption that the errors in our estimates of enthalpy and entropy are additive, -

we estimate the Gibbs free energy of formation of graphane ΔG_f (CH, graphane) = 6.9 ± 6.2 kJ mol^{-1} at 298.15 K.

Thus at 298.15 K and 1 bar, graphane is predicted to be thermodynamically *un*stable with respect to its elements. This does not mean that graphane, once formed, will not survive indefinitely under these conditions; rather it is expected to be kinetically stable, there being no kinetically feasible mechanism for conversion to the elements (just like other familiar hydrocarbons including benzene, ethylene, and acetylene).

---

[15] By "simple" is meant containing only C, H, N, and O atoms, and in particular not containing heavier atoms such as S atoms and/or not containing ions, either of which might affect the vibrational frequency spectrum appreciably.

[16] This spread, in terms of Gibbs free energy at 298.15 K and 1 bar, is less significant than the uncertainty in the estimate of the enthalpy of formation.

c:\documents and settings\user\my documents\backedup\science\s015hydrogengraphane\finpap\jewess10e.doc

Before, in Section V, investigating a range of possible synthetic routes for graphane, we shall first determine the conditions of temperature and pressure under which the reaction

$$2C \text{ (graphite)} + H_2 \longrightarrow 2CH \text{ (graphane)} \qquad\qquad (9)$$

is thermodynamically favorable. This is worthwhile for two reasons. First, reaction (9) may under such conditions be a possible way of preparing bulk samples of graphane for study. Secondly, a simple cycle for using graphite and graphane for hydrogen storage would involve the steps of (i) forming graphane from graphite and hydrogen at one temperature and pressure and (ii) driving off the hydrogen at higher temperature and/or lower pressure (which latter we already know would be thermodynamically permitted at 298.15 K and 1 bar).[17]

At 298.15 K and pressure p, reaction (9) has a Gibbs molar free energy of reaction, we use our central estimate of the Gibbs free energy of formation of graphane ΔG_f (CH, graphane) to obtain

$$\Delta G_{reac9} = 2 \times 6.9 \text{ kJ mol}^{-1} + \Delta G (H_2, p),$$

in which $\Delta G(H_2, p)$ is the difference at 298.15 K between the molar free energy of hydrogen at pressure p and at pressure 1 bar, the effect of pressure on the difference in G between the two solids being neglected. If we treat hydrogen as an ideal gas, then

$$\Delta G(H_2, p) = RT \ln (p/\text{bar})$$

(which is a good approximation at least up to 100 bar)[18], and we predict that at 298.15 K hydrogen gas will convert graphite to graphane, kinetics permitting, only at a pressure of exp [2 x 6.9/(298.15 x 8.314 x 0.001)] bar = 262 bar or more. Very likely, the reaction would proceed only slowly in the absence of a catalyst such as nickel metal,[19] which poses the problem of making the catalyst available between the "graphene" sheets that make up graphite; ball-milling of graphite with finely-divided catalyst suggests itself, or deposition of colloidal nickel.

Moreover, in order to get an appreciable reaction rate, even with a catalyst, it will almost certainly be necessary to raise the temperature. By elementary thermodynamics, ΔG_{reac9} changes with temperature at a rate equal to $-\Delta S_{reac9}$ *ie* (-2 x ΔS_f (CH, graphane)) or 105.4 (J mol^{-1})/K. If we (reasonably)

---

[17] A cycle for hydrogen storage also requires high yields in each of the two steps; the issue of side reactions, addressed in Section V below, is particularly significant.
[18] Ref. 6 at pages 6-20 to 6-21, with linear interpolation between 280 K and 300 K for $p = 100$ bar, gives the experimental $\Delta G(H_2, p)$ as 11.6 kJ mol^{-1}, compared with 11.4 kJ mol^{-1} for an ideal gas.
[19] I. Kagehira, Bull. Chem. Soc. Japan **6**, 241 (1931), used reduced nickel to hydrogenate aromatic hydrocarbons, which are related to graphite.

suppose that ΔS_f (CH, graphane) is approximately constant from 298.15 K over the 10 K range to 308.15 K, we see that the pressure required for graphane stability rises from 262 bar at 298.15 K to exp[(2 x 6.9+105.4 x 10 x 0.001)/(308.15 x 8.314 x 0.001)] bar = 329 bar. This emphasises the importance of finding a good catalyst so as to keep the temperature at which reaction (9) is performed as low as possible.

The effect on the above calculations of an error in our central estimate of 6.9 kJ mol^{-1} is that the pressure required for stability would be increased by a factor of 2.24 for every 1 kJ mol^{-1} of error in ΔG_f (CH, graphane) in a positive direction and reduced by a factor of 2.24 for every 1 kJ mol^{-1} of error in ΔG_f (CH, graphane) in a negative direction.

V. POSSIBLE SYNTHESES OF GRAPHANE FROM OTHER ORGANIC COMPOUNDS

The fact that graphane may be difficult to synthesize from its elements does not mean that it cannot be more readily synthesized from other starting materials; one just has to start with available materials that are *more* thermodynamically unstable with respect to the elements (and also make the graphane under conditions where the kinetics are such that thermodynamically favorable side-reactions do not predominate). Elias *et al*'s use of graphene and *atomic* hydrogen is an extreme example of this principle, but convenient preparation of graphane in bulk would require use of less exotic starting materials.

The favorability and unfavorability of reactions involving graphane can be calculated if the thermodynamic properties of the other compounds involved have been measured. Table II sets out some results.

TABLE II. Calculated molar enthalpies, entropies, and Gibbs free energies for various reactions at 298.15 K and 1 bar for reactions involving graphane. The coefficients in the reactions are chosen to achieve 2 CH on the right-hand side. ΔH_f (CH, graphane) and S (CH, graphane) were taken as -8.8 kJ mol^{-1} and 18.4 J K^{-1} mol^{-1} as estimated in Sections II and IV respectively.[20]

No	Reaction	$\Delta H/$ kJ mol^{-1}	$\Delta S/$ kJ mol^{-1}	$\Delta G/$ kJ mol^{-1}
(10)	2 C (graphite) + H$_2$ (g) $\longrightarrow$ 2 CH (graphane) [Discussed in Section IV, included here for comparison.]	-17.6	-105.3	13.8
(11)	acetylene C$_2$H$_2$ (g) $\longrightarrow$ 2 CH (graphane)	-245.0	-164.1	-196.1
(12)	(1/3) benzene C$_6$H$_6$ (l) $\longrightarrow$ 2 CH (graphane)	-34.0	-21.0	-27.7
(13)	(1/3) cyclohexene C$_6$H$_{10}$ (l) $\longrightarrow$ 2 CH (graphane) + (2/3) H$_2$ (g)	-4.8	52.4	-20.4
(14)	(1/5) cyclohexene C$_6$H$_{10}$ (l) + (4/5) C (graphite) $\longrightarrow$ 2 CH (graphane)	-9.9	-10.7	-6.7
(15)	(1/5) trans - decalin C$_{10}$H$_{18}$ (l) $\longrightarrow$ 2 CH (graphane) + (4/5) H$_2$(g)	28.5	88.4	2.2
(16)	(1/9) trans - decalin C$_{10}$H$_{18}$ (l) + (8/9) C (graphite) $\longrightarrow$ 2 CH (graphane)	8.0	2.3	7.3
(17)	(1/3) cyclohexane C$_6$H$_{12}$ (l) $\longrightarrow$ 2 CH (graphane) + H$_2$ (g)	34.5	99.3	4.9
(18)	(1/6) cyclohexane C$_6$H$_{12}$ (l) + C (graphite) $\longrightarrow$ 2 CH (graphane)	8.5	-3.0	9.4
(19)	2 methane CH$_4$ (g) $\longrightarrow$ 2 CH (graphane) + 3 H$_2$ (g)	131.6	56.3	114.8
(20)	(1/2) methane CH$_4$ (g) + (3/2) C (graphite) $\longrightarrow$ 2 CH (graphane)	19.7	-64.9	39.0
(21)	(1/2) cyclohexene C$_6$H$_{10}$ (l) + 2 C (graphite) $\longrightarrow$ (1/2) benzene C$_6$H$_6$ (l) + 2 CH (graphane)	26.2	4.8	24.8
(22)	formic acid HCO$_2$H (l) + 2 C (graphite) $\longrightarrow$ carbon dioxide CO$_2$ (g) + 2 CH (graphane)	13.9	110.2	-19.0

c:\documents and settings\user\my documents\backedup\science\s015hydrogengraphane\finpap\jewess10e.doc

The only syntheses considered in the Table which are predicted to be favorable at 298.15 K and 1 bar, allowing for an adverse error of 6.2 kJ mol^{-1} in ΔG_f (CH, graphane) at 298.15 K are the following:

reaction (11), addition polymerisation of acetylene;
reaction (12), addition polymerisation of benzene (see Figure 4);
reaction (13), dehydrogenation of cyclohexane; and
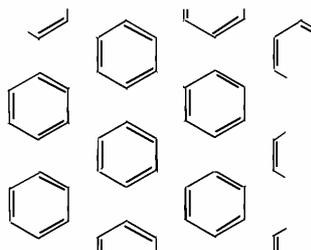reaction (22), the reduction of graphite by formic acid.

FIG. 4. Benzene molecules which on reorganisation of the carbon-carbon bonds (only) would form the structure of Fig. 1(c) according to reaction (13).

Catalysis might be advantageous or necessary for any or all of these four reactions. Reactions (11) to (13) would become less thermodynamically favorable with increased temperature but this would increase reaction rates (an especial reason for using a catalyst); while (22) would become more favorable both thermodynamically and kinetically with increased temperature. Reaction (11) would be favored thermodynamically by an increase in pressure; reaction (12) would be little influenced; and reactions (13) and (22) would be made less favorable.

Reactions (13) (and possibly (14), which is favorable at 298.15 K and 1 bar unless one assumes an adverse error of at least 3.3 kJ mol^{-1}) may explain the report in ref. 2 of the apparent synthesis of impure graphane by the (apparently uncatalyzed) ball-milling of cyclohexene with coal. The authors of that report describe cyclohexene as a "hydrogen donor", apparently implying that cyclohexene gives up hydrogen to graphite forming benzene and graphane (reaction (21) in Table II); but in fact reaction (21) is *not* predicted to be thermodynamically favorable at 298.15 K and 1 bar, unless one assumes a favorable error twice as large as 6.2 kJ mol^{-1}.[21]

The left-hand sides of those reactions in Table II which have a positive Gibbs free energy of reaction indicate products of possible side-reactions that may need to be guarded against by selection of conditions of reaction. In the

---

[21] Because cyclohexene and benzene are miscible, it would be more precise to add, "except at impractically low benzene concentrations in the liquid phase". The effect of any miscibility can be reasonably ignored in all the other reactions in Table II.

case of reaction (22), the decomposition of formic acid to hydrogen and carbon dioxide would have to be guarded against.

ACKNOWLEDGEMENTS