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Fullerene C_{50} isomers: temperature-induced interchange of relative stabilities

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Abstract

The species C_{50} is treated as a system composed of three local energy minima (D_{5h}, D_3 and C_{2v}) found in recent modified neglect of diatomic overlap (MNDO) calculations. Although the D_{5h} species corresponds to the deepest minimum it is the most stable structure only up to about 1390 K. Beyond this temperature the D_3 species becomes relatively more populous.

INTRODUCTION

The fullerenes C_n have recently been established [1–3] as a new class of molecules; namely, polyhedral, purely carbonaceous species with $n \geqslant 20$. Although originally research was concentrated on the now famous C_{60} and C_{70} aggregates [4–7] other fullerenes also have been isolated [8]. On the theoretical side, the most comprehensive fullerene study has so far been supplied by semiempirical quantum-chemical methods [9,10]. Isomerism has been recognized as a substantial feature of fullerenes, and separation energetics have been calculated for several systems [9–12]. Temperature effects on relative stabilities have been considered for fullerenes of different size [13,14], but not yet for species with the same number of carbon atoms. In this paper the relative stability in the C_{50} system is treated on the basis of recent modified neglect of diatomic overlap (MNDO) results [9,10].

THE C_{50} ISOMERS

Three structures of minimum energy were found in the MNDO study [9,10], each of them being built from pentagonal and hexagonal rings.

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These polyhedra belong to the point groups D_{5h}, D_3 and C_{2v}. The D_{5h} structure has the lowest heat of formation; the D_3 and C_{2v} isomers have heats of formation some 30 kJ mol^{-1} and 1600 kJ mol^{-1} higher respectively (for schemes of the structures see ref. 9). It is assumed that the D_{5h} and D_3 species are indeed the two lowest energy isomers. However, there can be probably several other high energy structures in addition to the C_{2v} isomer, which thus serves as an example. The calculated MNDO geometries, energetics, and unscaled harmonic frequencies of these isomers form the input for the present report.

CALCULATIONS

In some stages of fullerene preparation very high temperatures can be reached. In the first approach, an equilibrium thermodynamic treatment can be employed for understanding inter-isomeric relationships. At 0 K the lowest energy species represents the thermodynamically stable species in a set of n isomers. At any finite temperature all species are present, although their relative populations can vary considerably with temperature, the feature being exemplified by various cluster systems [15–18]. Let us introduce mole fractions w_i of the components in the n-membered isomeric equilibrium mixture. If we consider the rotational–vibrational motions, then in terms of the ground state energy changes $\Delta H^\circ_{0,i}$ (i.e. the standard enthalpies at 0 K) and the isomeric partition functions q_i, the mole fractions are given by [19,20]

$$w_i = \frac{q_i \exp[-\Delta H^\circ_{0,i}/(RT)]}{\sum_{j=1}^{n} q_j \exp[-\Delta H^\circ_{0,j}/(RT)]} \tag{1}$$

where R is the gas constant and T the temperature. There is also a practical simplification of eqn. (1) — the so-called simple Boltzmann, configurational or steric factors [21]:

$$w_i' = \frac{\exp[-\Delta E_i/(RT)]}{\sum_{j=1}^{n} \exp[-\Delta E_j/(RT)]} \tag{2}$$

where ΔE_i denote the potential energy terms, i.e. all contributions from the rotational–vibrational motions are neglected in the simplification. Partition functions q_i from eqn. (1) are, with respect to the available data, of the usual rigid rotor and harmonic oscillator quality [19]. It should be noted that in the present study the MNDO heats of formation are converted from 298 to 0 K before applying eqn. (1).

The presence of several isomeric structures leads [19,20] to overall, many-component thermodynamic terms ΔX°_T (in addition to partial, onecomponent terms ΔX°_i). It is convenient to visualize the isomerism effects by means of so-called isomerism contributions [19,20] to thermodynamic terms, δX_1, which do not depend on the standard state

$$\delta X_1 = \Delta X^\circ_T - \Delta X^\circ_1 \tag{3}$$

Commonly, the most stable species (in the low temperature limit) is chosen as the reference structure labelled $i = 1$. This paper deals with the enthalpy ($X = H$), entropy ($X = S$), or heat capacity at constant pressure ($X = C_p$); for a definition of the terms see refs. 19 and 20. The heat capacity case is particularly interesting as, in addition to the full, exact (relaxation) term $\delta C_{p,1}$, a simplified term neglecting the temperature dependency of w_i is considered ($\delta C_{p,w,1}$, isofractional term). The heat capacity results as a temperature derivative of the enthalpy and thus, in an isomeric situation, products of enthalpy and w_i are to be differentiated. Hence, quotients $\mathrm{d}w_i/\mathrm{d}T$ appear which are missing for mixtures free of any chemical reaction. The relaxation term is reduced to the isofractional part in both high and low temperature limits.

RESULTS AND DISCUSSION

Figure 1 presents the temperature evolution of the w_i and w_i' terms in a wide temperature interval. Effectively, the system behaves like a two-component mixture: populations of the C_{2v} species are negligible throughout. The simple Boltzmann factors do not represent a good approximation of the exact w_i terms. The most interesting feature of the w_i temperature dependence is the relative stability crossing between the D_{5h} and D_3 structures at about 1390 K (Table 1). With respect to the temperature of

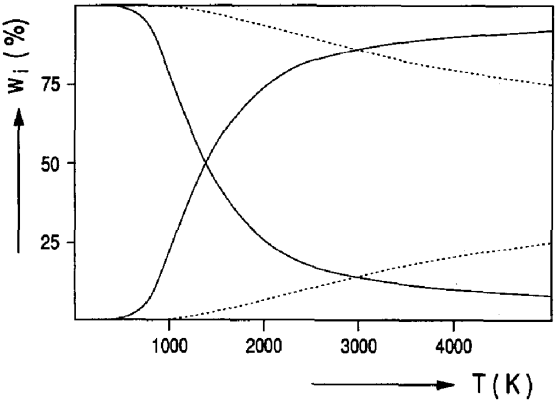

Fig. 1. Temperature dependences of the weight factors w_i and simple Boltzmann factors w_i' (broken lines) for the D_{5h} (decreasing curves) and D_3 C_{50} isomers (the C_{2v} population cannot be seen within the scale).

TABLE 1

Specification of some distinct points [a] in the temperature interplay of the D_{5h}, D_3 and C_{2v} isomers of C_{50}

Type [a]	T (K)	$w_{D_{5h}}$ [b] (%)	w_{D_3} [b] (%)	$w_{C_{2v}}$ [b] (%)	$\delta C_{p,1}$ [c] (J K^{-1} mol^{-1})	$C°_p$ J K^{-1} mol^{-1})	$\delta C_{p,1}/C°_p$ (%)
Crossing	1390	50.0	50.0	8×10^{-57}	24.9	1135	2.2
$\delta C_{p,1}$ maximum	1110	69.3	30.7	1×10^{-71}	29.9	1082	2.8
$\delta C_{p,1}/C°_p$ maximum	1070	72.5	27.5	1×10^{-74}	29.7	1069	2.8

[a] Point of two-isomer equimolarity (crossing), maximum in the isomerism contribution to heat capacity $\delta C_{p,1}$, or maximum in the relative enhancement $\delta C_{p,1}/C°_p$ of the $C°_p$ term by isomeric interplay.

[b] The mole fraction of the species in the equilibrium isomeric mixture.

[c] Isomerism contribution to heat capacity related to the species most stable in the low temperature region, i.e. to the D_{5h} isomer.

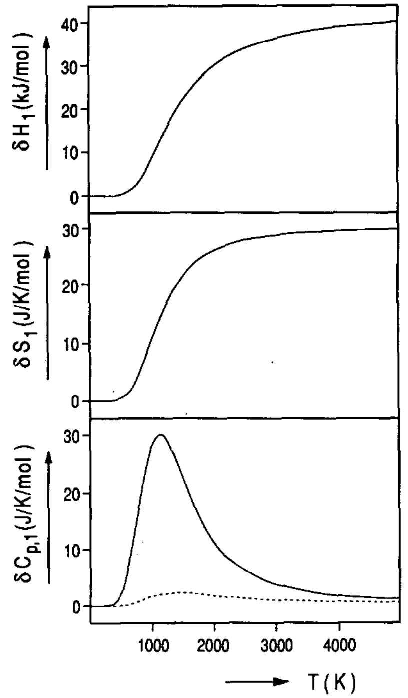

Fig. 2. Temperature evolution of the isomerism contributions (related to the D_{5h} species as reference structure) δX_1 to thermodynamic functions of the C_{50} isomeric system [$X = H$, S or C_p for enthalpy (top), entropy (middle), or heat capacity at constant pressure (bottom) respectively; the broken line in the bottom part represents the isofractional contribution $\delta C_{p,w,1}$].

carbon evaporation this is still a relatively low temperature; for example, the normal sublimation point of graphite was estimated [22,23] as 4100 K, and the temperature of carbon vapor [22] varied between 1800 and 2700 K. Hence, from the thermodynamic equilibrium point of view, the D_3 species should be preferentially formed in the high temperature region.

Figure 2 presents the temperature evolution of the isomerism contributions to the thermodynamics for the isomeric C_{50} system related to the D_{5h} species as the reference species. Features exhibited by the isomerism contributions resemble those already reported for other isomeric cluster systems [19,20]. The behavior of the heat capacity term is most interesting. The full (relaxation) term exhibits a clear temperature maximum, which is not present in the sole isofractional term. This maximum occurs close to the relative stability crossing (Table 1). Although the absolute value of the isomerism contribution to the heat capacity is quite substantial, the maximum itself does not appear in the temperature dependence of the overall standard heat capacity C°_{p} of the equilibrium isomeric C_{50} mixture. This is because of the extremely high $C^{\circ}_{p,i}$ values for large carbon aggregates, which cause the isomerism contributions to remain below 3% of the overall value (Table 1).

Finally, let us mention that the D_3 species could also be treated as an enantiomeric pair (i.e. not as just one of the enantiomers); this option for fullerenic systems is being studied elsewhere [24].

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