$Si_6H_6(g)$ — THE LARGEST COMPUTATIONALLY PREDICTED ISOMERISM EFFECTS ON SYSTEM THERMODYNAMICS *

ZDENĚK SLANINA **

Max Planck Institut für Chemie (Otto Hahn Institut), Mainz (F.R.G.) ***

(Received 9 July 1990)

ABSTRACT

$Si_6H_6(g)$ has been studied as an equilibrium mixture of three isomers characterized by recent quantum chemical calculations, and it has been shown that the molar heat capacity term of this mixture can be enhanced by as much as 179.8 J K^{-1} mol^{-1} compared with the molar heat capacity of the ground state structure. This is the largest enhancement of heat capacity by isomeric interplay reported in the literature so far.

INTRODUCTION

Small silicon species with a few Si atoms have recently been subjected to relatively intensive theoretical studies [1–35], which is connected with the overall lively interest in this branch of chemistry [6]. In theoretical studies, it is not unusual to find several stationary points on studied hypersurface, all the points being relevant to the problem type given. The finding of this type of isomerism is due partly to the progress made in the development of automatic techniques for the location and characterization of these stationary points of hypersurfaces using analytically constructed energy gradients [36], and partly to the nature of the Si–Si bond itself. With suitable differences between the potential energy terms of these isomers and their rotational–vibrational motions, it is possible that sufficient amounts of these isomers will coexist at temperatures which, in principle, allow their observation. Their relative stability order may even be interchanged. Such interchanges in silicon-containing systems have also been described from compu-

---

tational studies [13,14,23,35]. These effects are most noticeable [35] in the Si_6H_6 isomeric system. In the light of recent interesting reports [37–40] concerning the possibility of fairly distinct enhancement of the heat capacity term by isomeric interplay alone, it seemed useful to investigate this in the Si_6H_6 system itself.

DESCRIPTION OF THE SYSTEM AND FORMULATION OF THE PROBLEM

The characterization of the Si_6H_6 system begins with computational studies [9,25] one of which [25] has postulated the existence of at least three Si_6H_6 isomers. In terms of the potential energy, the lowest lying (the global minimum) structure is hexasilaprismane with D_{3h} point group symmetry. The second is the silicon analogue of benzene, hexasilabenzene, whose potential energy was evaluated to be about 41 kJ mol^{-1} higher than that of the ground state structure. However, the symmetry of hexasilabenzene was found [25] to be lower than that of benzene: D_{3d} rather than D_{6h}. Finally, the third structure is hexasila-Dewar benzene with C_{2v} symmetry: it lies more than 100 kJ mol^{-1} higher than the second isomer, hexasilabenzene. As well as the energetics this study [25] provides structural and harmonic vibrational data for these isomers, except for hexasilabenzene for which there is only an incomplete set of vibrational frequencies. For our purposes, therefore, the frequencies of hexasilabenzene given in ref. 9 were used, with the two sets unscaled and scaled being used in conjunction. The scaling [9] was carried out with a factor of 0.9, the scaled set being taken as representing the true fundamental frequencies.

Using the structural and vibrational data of the isomers, their partition functions in the rigid rotor and harmonic oscillator (RRHO) approximation can be determined. Thus, the molar fractions of the isomers in their (generally n-membered) equilibrium mixture can be expressed [35,37–40]

$$w_i = \frac{q_i \exp\left(-\Delta H_{0,i}^{\ominus}/(RT)\right)}{\sum\limits_{j=1}^{n} q_j \exp\left(-\Delta H_{0,j}^{\ominus}/(RT)\right)} \tag{1}$$

where the terms $\Delta H_{0,i}^{\ominus}$ denote the ground-state energy difference between the ith and the isomer labelled with index 1. It is advantageous and usual to assign the latter isomer to the global minimum, i.e. to the structure with the lowest ground-state energy term, in this case hexasilaprismane. For testing purposes, the approximation admitting the vibrational motion alone was also considered as well as the usual RRHO approximation. These two approaches will be referred to as those with admitted and suppressed rotation, AR and SR treatments, respectively, the translational contribution being always cancelled out in eqn. (1). The SR treatment could be applied,

for example, to the approximation of isomers chemisorbed at a solid surface (provided that the problems of configurational factors connected with the arrangement of adsorption sites [41] are ignored).

Obviously, the molar thermodynamic characteristics of this equilibrium mixture of isomers will be different from those of the individual isomers. For this reason, the notions of overall and partial terms were introduced [37–40]. Consideration of the isomerism contributions to the values of thermodynamic quantities has also been introduced in terms of the differences between the molar thermodynamic term corresponding to the equilibrium isomeric mixture considered and the molar term corresponding to the isomer 1 [37–40]; these isomerism contributions are then denoted as relating to structure 1 as the reference species, $\delta_n X_1^{(iso)}$. Our attention is focused primarily on the contributions to enthalpy ($X = H$), entropy ($X = S$) and heat capacity at constant pressure ($X = C_p$). In the last case it is [37–40]

$$\delta_n C_{p,1}^{(iso)} = \sum_{i=1}^{n} w_i \, \Delta C_{p,i}^{\ominus} + \frac{1}{RT^2}\left\{ \sum_{i=1}^{n} w_i \left(\Delta H_i^{\ominus}\right)^2 - \left[\sum_{i=1}^{n} w_i \, \Delta H_i^{\ominus}\right]^2 \right\} \qquad (2)$$

where $\Delta C_{p,i}^{\ominus}$ denotes the differences in molar heat capacity between the ith and the first isomers, and $\Delta H_i^{\ominus}$ are the analogous differences in the enthalpy term (at a general temperature, in contrast to the $\Delta H_{0,i}^{\ominus}$ terms which effectively correspond to the absolute zero temperature).

RESULTS AND DISCUSSION

Figure 1 presents the temperature courses of the molar fractions, w_i. A distinct feature of these courses is the interchange of the relative stabilities of hexasilabenzene and hexasilaprismane (the third isomer appears to be insignificant throughout the temperature interval studied [35]). These interchanges are detailed in Table 1; for the scaled vibrational set [9], interchange occurs near room temperature in both the AR and SR approximations.

Figure 2 presents the temperature courses of the isomerism contribution to heat capacity related to hexasilaprismane as the reference structure, these courses being given for both vibrational sets of hexasilabenzene [9] and for both AR and SR approximations. In all four cases the isomerism contributions show extremal temperature courses with a distinct maximum lying at a temperature somewhat lower than that corresponding to the relative stability interchange, see Table 2. The values of the isomerism contributions to heat capacity found for the Si_6H_6 system are indeed high (the highest reported in the literature so far [37–40]); this is indicated by the comparison of the overall heat capacity term with its value for hexasilaprismane (Table 2). In terms of the AR approach, the isomerism contribution is 36.5 and 51.6% of
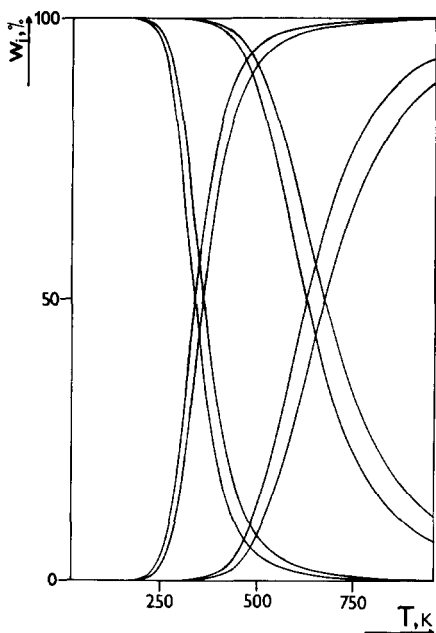
Fig. 1. Temperature evolution of molar fractions, w_i, of hexasilaprismane and hexasilabenzene in various approximations. The order of the equimolarity points reads from left: scaled and AR, scaled and SR, unscaled and AR, unscaled and SR (at low temperatures hexasilaprismane is always more stable while the third isomer, hexasila-Dewar benzene, is negligible, see Table 1).

the total $C_p^\ominus$ value for the unscaled and scaled vibrational set [9], respectively (at the temperature at which the maximum is reached for the $\delta_3 C_{p,1}^{(iso)}$ term).

Although the values of the isomerism contribution to heat capacity are lower in the SR approximation than in the AR approximation, the lowering is relatively small. This indicates the importance of the contributions of vibrational motion which are more different between the two isomers than are the rotational terms. The differences in vibrational frequencies of low

TABLE 1

Temperature positions of the relative stability interchanges between hexasilaprismane (D_{3h}) and hexasilabenzene (D_{3d}) in various approximations

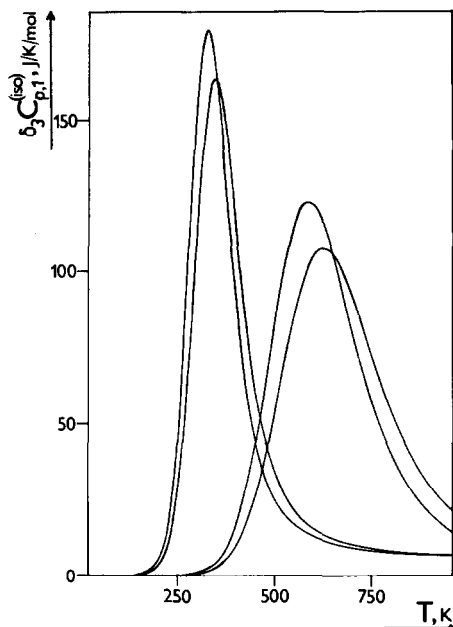| Approximation	T (K)	$w_{D_{3h}}$ (%)	$w_{D_{3d}}$ (%)	$w_{C_{2v}}$ [a] (%)
Unscaled and AR	627	50.0	50.0	4×10^{-9}
Unscaled and SR	675	50.0	50.0	7×10^{-9}
Scaled and AR	340	50.0	50.0	2×10^{-19}
Scaled and SR	360	50.0	50.0	1×10^{-18}

[a] Hexasila-Dewar benzene.

Fig. 2. Temperature evolution of the isomerism contribution, $\delta_3 C_{p,1}^{(iso)}$, to heat capacity (related to hexasilaprismane); the order of maxima reads from left: scaled and AR, scaled and SR, unscaled and AR, unscaled and SR (see Table 2).

TABLE 2

Positions of the maxima in the $\delta_3 C_{p,1}^{(iso)}$ term [a] and comparison with the corresponding overall term belonging to the equilibrium isomeric mixture [b]

Approximation	T (K)	$\delta_3 C_{p,1}^{(iso)}$ $(J\ K^{-1}\ mol^{-1})$	$C_p^{\ominus}$ $(J\ K^{-1}\ mol^{-1})$	$\delta_3 C_{p,1}^{(iso)}/C_p^{\ominus}$ (%)
Unscaled and AR	588	123	337	36.5
Unscaled and SR	627	108	292 [c]	36.9
Scaled and AR	328	180	348	51.6
Scaled and SR	347	164	305 [c]	53.8

[a] Related to hexasilaprismane as the reference isomer 1.
[b] Corresponding to 1 mol of hexasilaprismane, hexasilabenzene and hexasila-Dewar benzene.
[c] Both the rotational and translational contributions are suppressed.

values are particularly critical: these primarily compensate for the higher value of the $\Delta H_{0,i}^{\ominus}$ term.

CONCLUDING REMARKS

The present study is important as it demonstrates the possible high values of the isomerism contribution rather than predicting the precise values of the thermodynamic characteristics of the $Si_6H_6(g)$ system. This latter goal is

unattainable at present because the computational description of the stationary points of the hypersurface is insufficiently accurate [9,25]. Nevertheless it is clear that isomerism contributions can assume such high values that they could affect the presentation of data in thermodynamic tables (it would be desirable to give the overall terms as well as the partial ones), the comparison of theory and observation, or predictions of observed values.

Although the transition to partition functions of higher quality than RRHO also makes the isomerism contribution values more accurate, their importance is not diminished and nor are qualitative features such as the extremal temperature course observed with the $\delta_n C_{p,1}^{(iso)}$ term. Nevertheless, this treatment of isomerism effects is connected with a number of conceptual problems. The accessibility of conditions of thermodynamic equilibrium presupposes a reasonably high separation of the potential barriers. If, however, these barriers are too low, it could be difficult to distinguish the individual structures and to assign energy states to these structures. It seems relevant to mention here the studies [42–46] concerning the basic differences between symmetrical and asymmetrical double-minimum potentials with, for example, regard to tunnelling or state localization. These results strengthen the possibility of distinguishing structures separated by even relatively low barriers, presuming a distinct difference from the symmetrical double-well potential.

The applicability of eqn. (2), moreover, gives rise to questions concerning the limits of establishing thermodynamic equilibrium. It is presumed that thermodynamic equilibrium is established sufficiently fast to follow a temperature change. If w_i were unable to follow the temperature change sufficiently fast, the last term of eqn. (2) would be irrelevant. This rate of re-establishment of thermodynamic equilibrium must be understood with respect to the time scale of the technique used in the observation; see refs. 37–41.

A limiting case of the relatively rigid structures considered here is represented by the fluxional behaviour of systems which, at present, is studied in the case of clusters [47–51]. This limiting case indicates the importance of considering the entire potential energy hypersurface, rather than its isolated harmonic wells. Of course, so far the only computationally feasible alternative for the chemical systems exemplified by Si_6H_6 consists in the method presented, of weighting the contributions of individual local minima; this can be considered a particularly easy way of including hypersurface topology in thermodynamic values.

REFERENCES

1 R.A. Poirier and J.D. Goddard, Chem. Phys. Lett., 80 (1981) 37.
2 H. Lischka and H.-J. Köhler, Chem. Phys. Lett., 85 (1982) 467; 96 (1983) 690.
3 H.J. Köhler and H. Lischka, J. Am. Chem. Soc., 104 (1982) 5884.
4 R.S. Grev and H.F. Schaefer III, Chem. Phys. Lett., 119 (1985) 111.
5 K. Raghavachari, J. Chem. Phys., 83 (1985) 3520.
6 G. Raabe and J. Michl, Chem. Rev., 85 (1985) 419.
7 S. Nagase, T. Kudo and M. Aoki, J. Chem. Soc. Chem. Commun., (1985) 1121.
8 M.N. Glukhovtsev, B.Ya. Simkin and V.I. Minkin, Russ. Chem. Rev., 54 (1985) 54.
9 D.A. Clabo and H.F. Schaefer III, J. Chem. Phys., 84 (1986) 1664.
10 A. Sax and R. Janoschek, Angew. Chem. Int. Ed. Engl., 25 (1986) 651.
11 T. Dabish and W.W. Schoeller, J. Chem. Soc. Chem. Commun., (1986) 896.
12 D.A. Clabo and H.F. Schaefer III, J. Am. Chem. Soc., 108 (1986) 4344.
13 Z. Slanina, Thermochim. Acta, 97 (1986) 321.
14 Z. Slanina, Chem. Phys. Lett., 131 (1986) 420.
15 S. Nagase and T. Kudo, Organometallics, 6 (1987) 2456.
16 S. Nagase, M. Nakano and T. Kudo, J. Chem. Soc. Chem. Commun., (1987) 60.
17 S. Nagase, H. Teramae and T. Kudo, J. Chem. Phys., 86 (1987) 4513.
18 P.v.R. Schleyer, A.F. Sax, J. Kalcher and R. Janoschek, Angew. Chem. Int. Ed. Engl., 26 (1987) 364.
19 S. Collins, R. Dutler and A. Rauk, J. Am. Chem. Soc., 109 (1987) 2564.
20 P.v.R. Schleyer and R. Janoschek, Angew. Chem. Int. Ed. Engl., 26 (1987) 1267.
21 W.W. Schoeller, T. Dabisch and T. Busch, Inorg. Chem., 26 (1987) 4383.
22 A.F. Sax and J. Kalcher, J. Chem. Soc. Chem. Commun., (1987) 809.
23 Z. Slanina, Int. J. Thermophys., 8 (1987) 567.
24 S. Nagase and T. Kudo, J. Chem. Soc. Chem. Commun., (1988) 54.
25 A.F. Sax, J. Kalcher and R. Janoschek, J. Comput. Chem., 9 (1988) 564.
26 S. Nagase, T. Kudo and T. Kurakake, J. Chem. Soc. Chem. Commun., (1988) 1063.
27 J. Boatz and M.S. Gordon, J. Phys. Chem., 92 (1988) 3087.
28 B.F. Yates, D.A. Clabo and H.F. Schaefer III, Chem. Phys. Lett., 143 (1988) 421.
29 G. Ohanessian, P.C. Hiberty, J.-M. Lefour, J.-P. Flament and S.S. Shaik, Inorg. Chem., 27 (1988) 2219.
30 S. Nagase and M. Nakano, Angew. Chem. Int. Ed. Engl., 27 (1988) 1081.
31 R. Janoschek, Chem. Uns. Zeit, 22 (1988) 128.
32 S. Koseki and M.S. Gordon, J. Phys. Chem., 93 (1989) 118.
33 A.F. Sax and J. Kalcher, J. Comput. Chem., 10 (1989) 309.
34 B.F. Yates and H.F. Schaefer III, Chem. Phys. Lett., 155 (1989) 563.
35 Z. Slanina, Chem. Phys. Lett., 161 (1989) 175.
36 W.J. Hehre, L. Radom, P.v.R. Schleyer and J.A. Pople, Ab Initio Molecular Orbital Theory, J. Wiley, New York, 1986.
37 Z. Slanina, J. Phys. Chem., 90 (1986) 5908.
38 Z. Slanina, Int. Rev. Phys. Chem., 6 (1987) 251.
39 Z. Slanina, Thermochim. Acta, 128 (1988) 157.
40 Z. Slanina, J. Phys. Chem., 92 (1988) 5836.
41 Z. Slanina, Thermochim. Acta, 120 (1987) 207.
42 E.M. Fluder, Jr. and J.R. De La Vega, Chem. Phys. Lett., 59 (1978) 454.
43 E.M. Fluder and J.R. De La Vega, J. Am. Chem. Soc., 100 (1978) 5265.
44 J.H. Busch, E.M. Fluder and J.R. De La Vega, J. Am. Chem. Soc., 102 (1980) 4000.
45 J.R. De La Vega, J.H. Busch, J.H. Schauble, K.L. Kunze and B.E. Haggert, J. Am. Chem. Soc., 104 (1982) 3295.
46 J.R. De La Vega, Acc. Chem. Res., 15 (1982) 185.

47 R.S. Berry, in J. Hinze (Ed.), The Permutation Group in Physics and Chemistry, Springer–Verlag, Berlin, 1979.
48 R.S. Berry, in R.G. Woolley (Ed.), Quantum Dynamics of Molecules, Plenum Press, New York, 1980.
49 F.G. Amar and R.S. Berry, J. Chem. Phys., 85 (1986) 5943.
50 H.L. Davis, J. Jellinek and R.S. Berry, J. Chem. Phys., 86 (1987) 6456.
51 T.L. Beck, J. Jellinek and R.S. Berry, J. Chem. Phys., 87 (1987) 545.