International Journal of Thermophysics, Vol. 8, No. 5, 1987

The Relative Stability in and Thermodynamic Functions of the System of $Si_2H_4(g)$ Isomers: Comparison of Results from Two Different Evaluations of the System Energetics

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Received October 15, 1986

Thermodynamic consequences of the interplay of four recently found isomers of $Si_2H_4(g)$ are studied. The partition functions and energetics of the isomers are constructed on the basis of available quantum-chemical data, and the results from two different approximations of potential energy are compared. Substantial values of isomerism contributions to the overall thermodynamics of the system are pointed out, as well as their sensitivity to interisomer energetics.

KEY WORDS: isomers; mixtures, $Si_2H_4(g)$; statistical physics; thermodynamics.

1. INTRODUCTION

Recently, increasing attention has been paid to the thermodynamics of isomeric systems (e.g., Refs. 1–5), this being in connection with the development of experimental (cf. Refs. 1–3, 5–7) as well as theoretical (cf. Refs. 4, 8) techniques for isomer characterization. Particularly, it has been proved useful to evaluate standard thermodynamic terms both for individual isomers (partial terms) and for an equilibrium mixture of the isomers (total or overall terms). In the latter case all the isomers are considered as a group, as one pseudospecies, each isomer contributing to the total terms according to its weight factor. The weight factors can be evaluated [8]

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from the partition functions and energetics of the isomers, and molecular parameters for the evaluation can originate from observation [1–3, 5–7] as well as from theoretical calculations [4, 8].

Quantum-chemical calculations pointed out isomerism with several silicon-containing small molecules [9–15], the most abundant one with the Si_2H_4 system [9, 10]. The system was treated at the abinitio SCF level [9] and also with the inclusion of electron correlations by the CEPA-2 approach [10], and in both cases four different isomeric structures were found. The present article deals with the thermodynamic consequences of the isomerism in the $Si_2H_4(g)$ system.

2. OVERALL THERMODYNAMICS OF AN EQUILIBRIUM ISOMERIC MIXTURE

Let us consider the equilibrium mixture of n isomers of a given species in an ideal-gas phase. The isomer most stable within the group at a given temperature T is labeled by the index 1. The isomerizations of the most stable isomer to the ith one are described by the standard molar changes of enthalpy, ΔH_i°, entropy, ΔS_i°, and heat capacity, $\Delta C_{p,i}^\circ$ ($i = 1, 2, \ldots, n$; formally $\Delta H_1^\circ = \Delta S_1^\circ = \Delta C_{p,1}^\circ = 0$). Let us further denote the changes ΔH_i° at the absolute zero temperature as $\Delta HH_{0,i}^\circ$ and the corresponding changes in potential energy as ΔE_i (the difference between these in types of terms is just the energy of the zero-point motion). With q_i being the partition function of the ith isomer, theweight factor, w_i, of the isomer, characterizing the relative content of the isomer in the equilibrium mixture (i.e., mole fraction), is given by [8]

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

The weight factors given by Eq. (1) are of a rigorous nature within the Boltzmann statistics under the assumption of independence of motions of individual structures. However, with respect to the usual amount of information on the hypersurface stationary points available, the rigid-rotor and harmonic-oscillator approach (RRHO) has to be used for the evaluation of the partition functions q_i. Moreover, even a further simplified approximation of w_i is frequently used, viz., simple Boltzmann, configurational, or steric factors, w_i', based on mere potential energy terms, ΔE_i:

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

thus ignoring the effects of rotational-vibrational motions.

It is convenient to introduce [16, 17] isomerism contributions, $\delta X_1^{(\text{iso})}$, as the terms which must be added to the standard value of a thermodynamic function X related to the isomer 1, X_1°, in order to obtain the corresponding total term, X°, composed of the contribution of all isomers in their equilibrium mixture:

$$X^\circ = X_1^\circ + \delta X_1^{(\text{iso})} \tag{3}$$

These isomerism contributions (under the assumption of ideal behavior) do not depend on the other reactants and on the standard-state choice as well. Thus, they are just characteristics of the isomeric group, being widely transferable. In our connections, three thermodynamic quantities are considered: enthalpy ($X = H$), entropy ($X = S$), and heat capacity at constant pressure ($X = C_p$). It holds that

$$\delta H_1^{(\text{iso})} = \sum_{i=1}^{n} w_i \Delta H_i^\circ \tag{4}$$

$$\delta S_1^{(\text{iso})} = \sum_{i=1}^{n} w_i (\Delta S_i^\circ - R \ln w_i) \tag{5}$$

$$\delta C_{p,1}^{(\text{iso})} = \sum_{i=1}^{n} w_i \Delta C_{p,i}^\circ + \frac{1}{RT^2} \left\{ \sum_{i=1}^{n} w_i (\Delta H_i^\circ)^2 - \left[\sum_{i=1}^{n} w_i \Delta H_i^\circ \right]^2 \right\} \tag{6}$$

3. THE ISOMER SETS STUDIED

In the abinitio SCF calculations [9] in an extended basis set, four local energy minima were found on the system potential hypersurfaces, viz., the lowest singlet and triplet states of disilene (H_2Si–SiH_2) and silylsilylene (H_3Si–SiH), with ^1A_g, ^3B, and $^1A'$, $^3A''$, respectively, symmetries of electronic wave functions. The potential energy increases in the sequence $^1A'$, $^3A''$, ${}_1A_g$, and ^3B. In addition to the system energetics, structural as well as harmonic vibrational characteristics were also evaluated at the SCF level [9]. Later the energetics of the system was reevaluated [10] at a more sophisticated level of the CEPA-2 technique, enabling electron correlation energies to be included, too. In the latter approach, the $^1A'$ isomer is again the lowest one in the potential energy term, however, the stability order in the CEPA potential energy scale reads $^1A'$, ^1A_g, $^3A''$, and ^3B. The quantum-chemical data on Si_2H_4 available [9, 10] represent a complete information set enabling description of the system thermodynamics in the RRHO approximation (see, e.g., Refs. 18–20) of partition functions. In addition to the isomer system itself, the thermodynamics of the equilibrium

$$2H_2(g) + Si_2(g) \rightleftharpoons Si_2H_4(g) \tag{7}$$

is also valuated in the present article, and for the construction of the RRHO partition functions of both diatomics involved in Eq. (7), the molecular parameters from Ref. 18 were used.

4. RESULTS AND DISCUSSION

Generally, effects of temperature populations of rotational-vibrational states of isomers can change the isomer stability order following from the potential energy scale, and particularly, the stability order can be different at different temperatures. It is also the case for the $Si_2H_4(g)$ system. At the SCF level, there are [9] two such stability interchanges (^1A_g and ^3B at about 205 K and $^1A'$ and $^3A''$ at about 2235 K; see Fig. 1), however, there is no such interchange at the CEPA level (within the temperature interval presented in Fig. 1). The isomer most stable in the potential energy scale, $^1A'$, turns out to be more stabilized with the CEPA approach; however, above a temperature of about 810 K the remaining three structures represent increasingly more than 10% of the equilibrium mixture (with the SCF approach the same threshold temperature is about 460 K). It is also

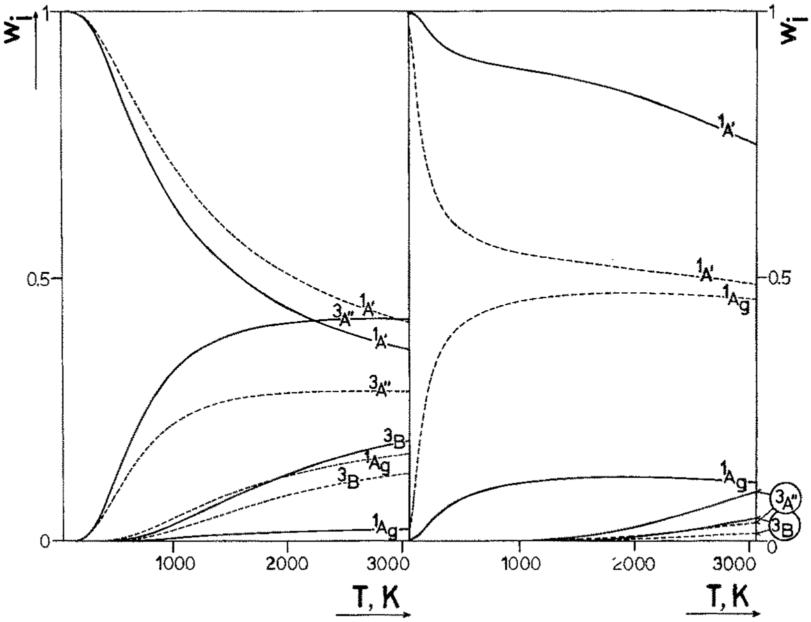

Fig. 1. Temperature dependences of weight factors, w_i [Eq. (1)], of the $Si_2H_4(g)$ isomers. (----) Simple Boltzmann factors; see Eq. (2). SCF [1] and CEPA results are given on the left and right, respectively.

Table I. Partial[a] and Total Standard[b] Changes of the Molar Heat Content Function, $\Delta(H_T^\circ - H_0^\circ)$, Entropy, ΔS_T°, and Heat Capacity at Constant Pressure, $\Delta C_{p,T}^\circ$, Terms for the Process $2H_2(g) + Si_2(g) \rightleftharpoons Si_2H_4(g)$

T	$\Delta(H_T^\circ - H_0^\circ)$ (kJ · mol^{-1})						ΔS_T° (J · K^{-1} · mol^{-1})						$\Delta C_{p,T}^\circ$ (J · K^{-1} · mol^{-1})					
					Total[c]						Total[c]						Total[c]	
(K)	$^1A'$	$^3A''$	^3B	^1A_g	SCF	CEPA	$^1A'$	$^3A''$	^3B	^1A_g	SCF	CEPA	$^1A'$	$^3A''$	^3B	^1A_g	SCF	CEPA
200	−8.72	−8.96	−8.80	−8.84	−8.69	−8.64	−198.1	−191.7	−196.2	−213.2	−197.9	−197.4	−35.18	−37.06	−34.86	−36.20	−34.28	−34.56
298.15	−11.69	−12.07	−11.65	−11.82	−11.44	−11.55	−210.3	−204.5	−207.9	−225.5	−209.3	−209.4	−25.52	−26.66	−23.73	−24.88	−21.96	−25.01
500	−15.28	−15.83	−14.86	−15.21	−13.93	−15.05	−219.8	−214.5	−216.5	−234.5	−216.0	−218.7	−11.33	−11.96	−9.61	−10.46	−4.71	−10.97
1500	−10.12	−11.23	−9.10	−10.29	−3.33	−9.20	−216.8	−212.1	−212.6	−231.6	−206.7	−215.0	14.79	14.38	14.93	14.29	18.57	17.01
3000	16.42	14.95	17.52	15.76	26.73	26.09	−204.6	−200.1	−200.4	−219.7	−192.9	−199.1	18.52	18.39	18.54	18.32	19.94	26.54

[a] $Si_2H_4(g)$ is represented by just one of the isomers $^1A'$, $^3A''$, ^3B, and ^1A_g.

[b] Standard state: an ideal gas at 1 atm = 101,325 Pa pressure.

[c] $Si_2H_4(g)$ is considered as the equilibrium mixture of the four isomers treated.

evident from Fig. 1 that the applicability of simple Boltzmann factors [Eq. (2)] instead of the weight factors given by Eq. (1) is poor, particularly so in the CEPA treatment.

With respect to the rather considerable differences in the weight factors w_i from SCF and CEPA energetics, one can expect rather pronounced differences in the thermodynamic terms from both these information sources. Indeed, at moderate and higher temperatures there are significant differences in the overall system thermodynamics, as documented in Table I for the total standard thermodynamic terms of reaction given by Eq. (7) and in Fig. 2 for the values of isomerism contributions (for simplicity, all isomerism contributions are related to the $^1A'$ structure throughout). The partial terms for reaction given by Eq. (7) presented in Table I are the same with both approaches, as structural and vibrational data of isomers are available only at the SCF level [9]. Thus, for the differences between

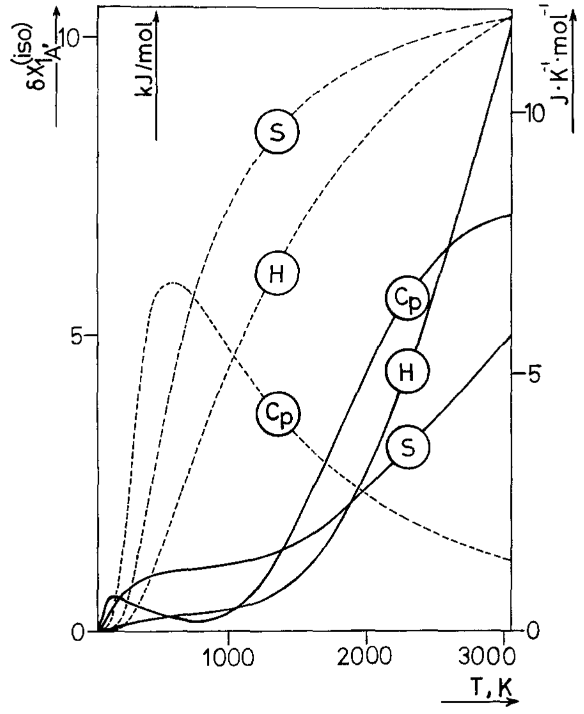

Fig. 2. Temperature dependences of isomerism contributions to the overall thermodynamics of the $Si_2H_4(g)$ system evaluated within the full, four-membered isomer set; SCF and CEPA values are represented by dashed and solid lines, respectively. See Table II for details.

overall terms the differences between the SCF and the CEPA energetics are exclusively responsible. The differences at higher temperatures are substantial for any of the three thermodynamic functions treated (Table I, Fig. 2); the differences in extreme behavior of the isomerism contribution to heat capacity for the SCF and CEPA energetic are particularly interesting (Fig. 2). Regardless of the description of energetics, the isomerism contributions to thermodynamic functions at elevated temperatures are certainly not negligible from a practical point of view, the values being comparable to or even higher than the frequently discussed anharmonicity/nonrigidity corrections to the RRHO model (cf. Ref. 19). Incidentally, let us mention that for the purpose of the Si_2H_4(g) thermodynamics prediction, the values from the CEPA approach should clearly be preferred, as the latter treatment is methodically more advanced.

So far all four isomers were considered, however, for methodical reasons it can be useful to follow the effects with smaller isomer sets, too, i.e., for $n = 3$ and even $n = 2$. In Table III the less stable structures are successively truncated. With the SCF approach, it is essential to consider the

Table II. Convergency Properties of Isomerism Contributions[a] to Standard Molar Enthalpy, $\delta_n H^{(\mathrm{iso})}_{1A'}$, Entropy, $\delta_n S^{(\mathrm{iso})}_{1A'}$, and Heat Capacity at Constant Pressure, $\delta_n C^{(\mathrm{iso})}_{p,1A'}$

T		$\delta_n H^{\mathrm{iso}}_{1A'}$		$\delta_n S^{(\mathrm{iso})}_{1A'}$		$\delta_n C^{(\mathrm{iso})}_{p,1A'}$	
(K)	Isomeric set[b]	SCF	CEPA	SCF	CEPA	SCF	CEPA
200	2	0.027	0.083	0.154	0.672	0.907	0.628
	3	0.027	0.083	0.154	0.673	0.907	0.628
	4	0.027	0.083	0.154	0.673	0.907	0.628
298.15	2	0.241	0.138	0.990	0.899	3.541	0.514
	3	0.241	0.138	0.991	0.899	3.558	0.514
	4	0.242	0.138	0.992	0.899	3.564	0.514
500	2	1.305	0.227	3.659	1.131	6.023	0.362
	3	1.343	0.227	3.747	1.131	6.515	0.362
	4	1.353	0.227	3.769	1.131	6.617	0.362
1500	2	4.520	0.318	7.721	1.269	1.259	−0.019
	3	6.571	0.793	9.816	1.645	3.629	1.660
	4	6.789	0.917	10.063	1.740	3.783	2.222
3000	2	5.401	0.281	8.166	1.253	0.267	−0.018
	3	9.994	6.510	11.486	4.147	1.393	4.979
	4	10.312	9.676	11.785	5.540	1.414	8.016

[a] Related to the ${}^1A'$ isomer; H terms in kJ·mol^{-1}, and S and C_p in J·K^{-1}·mol^{-1}.

[b] Isomer sets in SCF: (2) ${}^1A'$ and ${}^3A''$; (3) 2 and ${}^3B$; (4) 3 and ${}^1A_g$. Isomer sets in CEPA: (2) ${}^1A'$ and ${}^1A_g$; (3) 2 and ${}^3A''$; (4) 3 abd ${}^3B$.

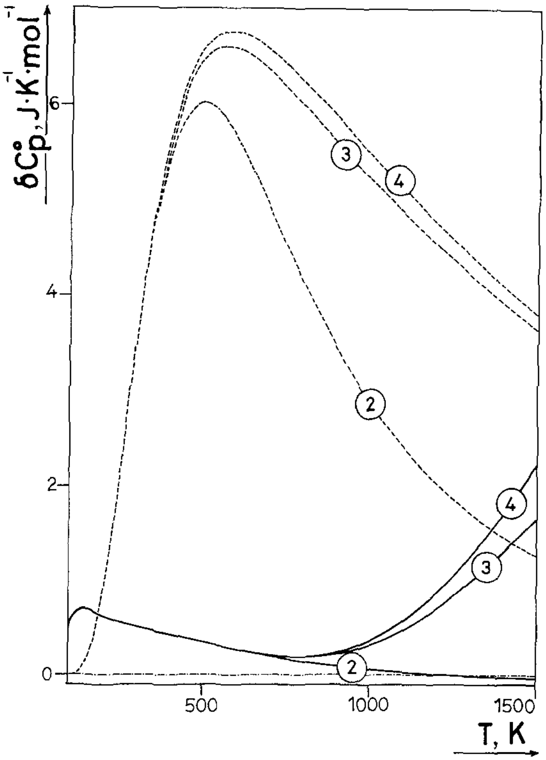

Fig. 3. Temperature dependences of isomerism contributions to the overall heat capacity of the $Si_2H_4(g)$ system evaluated within the four (4)-, three (3)-, and two (2)-membered isomer sets. SCF and CEPA values are represented by dashed and solid lines, respectively. The position of the zero is indicated by the dashed–dotted line.

other triplet state, ^3B, in addition to the structures $^1A'$ and $^3A''$, while the role of the fourth isomer, ^1A_g, is rather marginal. However, in the CEPA treatment even the fourth structure turns out to be significant for evaluation of the overall system thermodynamics at high temperatures. Finally, Fig. 3 documents that the interesting extreme behavior of the isomerism contribution to heat capacity is present in the truncated isomer sets as well (however, in the CEPA treatment above about 1250 K the $\delta 2C_{p,^1A'}^{(\mathrm{iso})}$ term falls to below zero).

5. CONCLUSIONS

It has been illustrated in the $Si_2H_4(g)$ isomeric system that the overall thermodynamics can be sensitive to the interisomer energetics. Regardless of the particular energy information used, the contribution of isomerism to the overall thermodynamics of Si_2H_4(g) is significant at moderate and higher temperatures; however, for predictive purposes the CEPA results are perferred.

The type of treatment presented is applicable to the conditions of full interisomer equilibrium only, and no attempt was made to clarify kinetic conditions for the establishment of equilibrium. Moreover, certain changes in the values reported can be caused by employing a more precise model for the partition functions q_i (i.e., beyond the RRHO model).

ACKNOWLEDGMENTS

Support from the Japan Society for the Promotion of Science is acknowledged, as well as the friendly, creative atmosphere and kind hospitality of Prof. Eiji Ōsawa and his group and the considerable help of Mr. Masatomo Togashi with computational aspects.

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