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C_2Si_2 as an equilibrium four- or eight-membered isomeric set [α]

Zdeněk Slanina [1]

Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Mainz (Germany)

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Abstract

The C_2Si_2 system, characterized by using recent ab initio data, has been studied computationally and treated as an equilibrium set of either four or eight isomers. It has been shown that relative populations of these isomers are markedly temperature sensitive, as manifested by substantial values of the terms for isomerism contributions to values of thermodynamic functions. A pronounced temperature maximum of such contributions to the heat capacity term has been characterized. The representation of thermodynamic functions of C_2Si_2 as an equilibrium mixture of isomers is discussed.

INTRODUCTION

Isomer enumerations [1–4] show the possibility of ample isomerism for even relatively small systems. If under given conditions at least a portion of these structures can coexist or even form an equilibrium mixture, then it is no longer formal to consider the corresponding isomeric mixtures in theory. This fact has led to studies of the thermodynamics of those mixtures [5–9] which are noteworthy because the component equilibrium populations are controlled by isomerization reactions. So far only a few organic isomeric systems [10–22], most often rotamers, have been studied from this standpoint. In computational studies it is advantageous to characterize [23,24] the individual isomers by means of the terms of partition functions and inter-isomeric energetics. The molecular parameters necessary for such a treatment are available (at present, in a complete set) from quantum-chemical or

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[α] Dedicated to the memory of Academician František Šorm (1913–1980), the former President of the Academy.

[1] Permanent address and address for request of reprints: J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, CS-18223 Prague 8-Kobylisy, Czechoslovakia.

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molecular-mechanical studies rather than from observation. A recent ab initio treatment [25] provides a characterization of the C_2Si_2 isomeric set which is sufficient to allow a study of isomerism effects on the thermodynamics of this system.

OUTLINE OF COMPUTATIONS

The mole fractions, w_i, of components of an equilibrium n-membered isomeric mixture in the gas phase are given in terms of their partition functions, q_i, by the relation [9]

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

where $\Delta H^\circ_{0,i}$ denotes the ground state energies related to a common energy level, e.g. to the ground state energy of the isomer with the lowest value of this term (by convention this isomer is assigned the index 1).

It is useful [9,26,27] to introduce two types of quantities for the values of standard thermodynamic functions X° of an isomeric mixture: the partial quantities belonging to the isomer 1 (i.e. that with the lowest ground state energy) and the overall quantities corresponding to the equilibrium mixture of isomers taken as a single pseudospecies. The differences between these two quantities represent the so-called isomerism contributions [9], $\delta_n X_1^{(\mathrm{iso})}$, to the values of thermodynamic function X° related to the isomer 1 as the reference structure. Thus, for example, for the usual three thermodynamic

functions($\delta_n H_1^{(\mathrm{iso})} = \sum_{i=1}^{n} w_i \, \Delta H_i^\circ$

$$\delta_n S_1^{(\mathrm{iso})} = \sum_{i=1}^{n} w_i (\Delta S_i^\circ - R \ln w_i) \tag{3}$$

$$\delta_n C_{p,1}^{(\mathrm{iso})} = \delta_n C_{p,w,1}^{(\mathrm{iso})} + \frac{1}{RT^2}\left[\sum_{i=1}^{n} w_i (\Delta H_i^\circ)^2 - \left(\delta_n H_1^{(iso)}\right)^2\right] \tag{4}$$

where $\delta_n C_{p,w,I}^{(\mathrm{iso})}$ is the so-called isofractional isomerism contribution to heat capacity

$$\delta_n C_{p,w,1}^{(\mathrm{iso})} = \sum_{i=1}^{n} w_i \, \Delta C_{p,i}^\circ \tag{5}$$

and ΔX_i° denotes the standard change of thermodynamic function along the isomerization of the first to the nth isomer (specifically it is $\Delta H_1^\circ = \Delta S_1^\circ = \Delta C_{p,1}^\circ = 0$). The isofractional term (eqn. (5)) results [9,26,27] from suppression of the temperature dependence of w_i, i.e. of the term in the square brackets in eqn. (4) (while the full term (4) is called the relaxation isomerism contribution).

THE SYSTEM DESCRIPTION

A published report [25] presents the localization of stationary points at the 3-21G and 6-31G* ab initio self-consistent field (SCF) potential hypersurfaces of the C_2Si_2 system. Eight of these stationary points were proved (by means of harmonic vibrational analysis) to be local energy minima (for a survey, see Table 1). These eight energy minima represent four low lying singlet states and four triplet states. The energetics of these eight isomers were, for the 6-31G* structures, evaluated using the second-order Møller–Plesset perturbation theory (MP2/6-31G*) and, moreover, for the four lowest lying isomers, also in terms of the fourth-order perturbation theory MP4/6-31G*.

From the results in ref. 25, two different C_2Si_2 isomeric sets can be derived: (i) an eight-membered set with geometries obtained in terms of the 6-31G* basis, energetics in terms of MP2/6-31G*, and harmonic vibration frequencies in terms of 3-21G, (ii) a four-membered set with geometries from the 6-31G* basis, energetics from MP4/6-31G*, and harmonic vibration frequencies from calculations on the 6-31G* basis. In the following text these two isomeric sets will be studied side by side.

RESULTS AND DISCUSSION

The extent of information available [25] about molecular parameters of the C_2Si_2 system allows a construction of the partition functions q_i from relation (1) in the usual approximation [23,24] of rigid rotor and harmonic oscillator. Figure 1 presents a survey of courses of mole fractions, w_i, for both isomeric sets considered ((i) and (ii)) in a broad temperature interval. In the region of low and moderate temperatures the predominant isomer is

TABLE 1

Survey of C_2Si_2 isomeric sets and their energetics [a]

Species [a]	Electronic state	Point group of symmetry	Relative potential energy (kJ mol^{-1})	
			MP2/6-31G*	MP4/6-31G*
5s	^1A_g	D_{2h}	0.0	0.0
6s	$^1A'$	C_s	48.5	35.6
1t	$^3\Sigma_g^-$	$D_{\infty h}$	66.9	47.7
1s	$^1\Sigma_g^+$	$D_{\infty h}$	100.0	71.5
6t	$^3A''$	C_s	140.2	
3t	$^3B_1$	C_{2v}	235.1	
5t	$^3B_{3u}$	D_{2h}	243.5	
7s	^1A_g	D_{2h}	353.5	

[a] According to ref. 25.

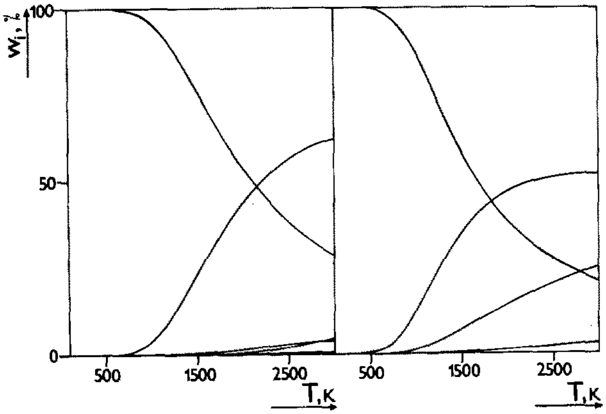

Fig. 1. Temperature evolution of the w_i terms in the eight- (left) and four-membered (right) $C_2Si_2(g)$ isomeric sets. The order of isomers at the right (high temperature) limit reads (from the top): eight-membered set—6s, 5s, 6t, 1t, 1s (3t, 5t, 7s cannot be recognized in the figure); four-membered set—6s, 1t, 5s, 1s.

the ^1A_g structure. Its content decreases below 90% only at about 1200 K and 930 K for the eight- and four-membered sets, respectively. At 2000 K, however, this isomer represents only 53.9% and 38.2% in the sets (i) and (ii), respectively. In this temperature region the order of relative stabilities of the ^1A_g and $^1A'$ structures is reversed, the other structures being also relatively more significant than they are at low temperatures. Another change in the order of relative stabilities is observed in the eight-membered set at about 2900 K, when the $^3A''$ isomer becomes the third most populated structure, thus replacing the $^3\Sigma_g^-$ structure.

Figure 2 presents the temperature courses of the isomerism contributions (related to the ^1A_g isomer as the reference structure) to the enthalpy, entropy

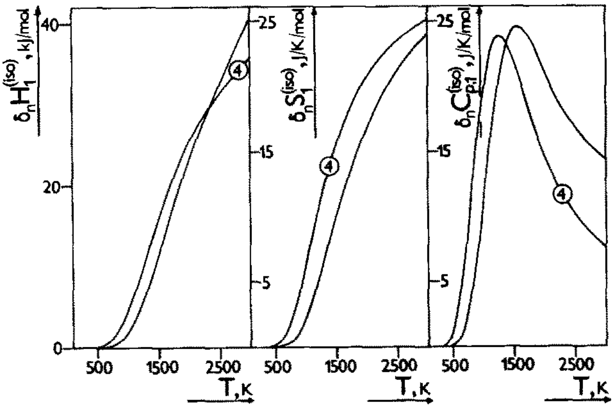

Fig. 2. Temperature evolution of the isomerism contributions $\delta_n X_1^{(iso)}$ (cf. Tables 2 and 3) to enthalpy ($X = H$), entropy ($X = S$), and heat capacity ($X = C_p$) for the four- ④ and eight-membered isomeric sets of $C_2Si_2(g)$.

and heat capacity terms for both isomeric sets considered. Obviously, at higher temperatures these corrections represent significant (clearly non-negligible) contributions to the values of thermodynamic functions. The difference between the overall term and the partial term corresponding to the ^1A_g isomer can be substantial at some temperatures. This fact shows that in comparisons of observed and calculated data, account must be taken of the type of quantity (partial or overall) that was measured in the observation, and the comparison of theory with experiment must be adapted to it.

If $n > 2$, then it is possible to study the convergence properties of the $\delta_n X_1^{(iso)}$ terms. This means gradual generation of the isomerism contributions within the isomeric sets recursively formed by always leaving out the highest lying structure (in terms of the ground state energy). This produces the series $\delta_n X_1^{(iso)}$, $\delta_{n-1} X_1^{(iso)}$, $\delta_{n-2} X_1^{(iso)}, \ldots, \delta_2 X_1^{(iso)}$. Tables 2 and 3 provide an illustration of these convergence properties, for both the isomeric sets considered, at three selected temperatures. With increasing temperature, also the contribution of the highest lying isomer becomes distinct.

TABLE 2

Convergence properties of the isomerism contributions[a] $\delta_n X_1^{(iso)}$ to enthalpy ($X = H$), entropy ($X = S$) and heat capacity ($X = C_p$) for the eight-membered (MP2/6-31G*) isomeric set of C_2Si_2(g)

T (K)	n	$\delta_n H_1^{(iso)}$ (kJ mol^{-1})	$\delta_n S_1^{(iso)}$ (J K^{-1} mol^{-1})	$\delta_n C_{p,1}^{(iso)}$ (J K^{-1} mol^{-1})
1000	2	2.003	2.349	11.372
	3	2.025	2.373	11.559
	4	2.026	2.373	11.562
	5	2.026	2.374	11.566
	6	2.026	2.374	11.566
	7	2.026	2.374	11.566
	8	2.026	2.374	11.566
2000	2	21.987	15.946	17.768
	3	22.847	16.508	18.939
	4	22.904	16.541	19.076
	5	23.511	16.888	21.106
	6	23.512	16.889	21.115
	7	23.512	16.889	21.117
	8	23.512	16.889	21.117
3000	2	33.447	20.745	6.819
	3	35.424	21.761	7.883
	4	35.686	21.876	8.142
	5	40.470	23.860	14.143
	6	40.546	23.889	14.337
	7	40.562	23.895	14.377
	8	40.562	23.895	14.378

[a] Related to the ^1A_g isomer as the reference structure.

TABLE 3

Convergence properties of the isomerism contributions[a] $\delta_n X_1^{(\mathrm{iso})}$ to enthalpy ($X = H$), entropy ($X = S$) and heat capacity ($X = C_p$) for the four-membered (MP4/6-31G*) isomeric set of C_2Si_2(g)

T (K)	n	$\delta_n H_1^{(\mathrm{iso})}$ (kJ mol^{-1})	$\delta_n S_1^{(\mathrm{iso})}$ (J K^{-1} mol^{-1})	$\delta_n C_{p,1}^{(\mathrm{iso})}$ (J K^{-1} mol^{-1})
1000	2	4.449	5.561	16.687
	3	5.034	6.246	19.915
	4	5.050	6.263	20.050
2000	2	19.559	16.400	9.447
	3	24.885	20.344	13.758
	4	25.498	20.742	14.666
3000	2	25.399	18.849	3.459
	3	34.418	24.304	6.765
	4	35.974	25.085	7.689

[a] Related to the ^1A_g isomer as the reference structure.

TABLE 4

Temperature maxima in the relaxation isomerism contribution to heat capacity[a] $\delta_n C_{p,1}^{(\mathrm{iso})}$ for the eight- and four-membered isomeric sets of C_2Si_2(g)

n	T (K)	$\delta_n C_{p,w,1}^{(\mathrm{iso})}$ [b] (J K^{-1} mol^{-1})	$\delta_n C_{p,1}^{(\mathrm{iso})}$ (J K^{-1} mol^{-1})
8 (MP2/6-31G*)	1563	−0.047	24.511
4 (MP4/6-31G*)	1254	0.161	23.751

[a] Related to the ^1A_g isomer as the reference structure.

[b] Isofractional contribution to heat capacity.

TABLE 5

Transformation of the maximal course of the $\delta_n C_{p,1}^{(\mathrm{iso})}$ term into the behaviour of the total standard[a] heat capacity at constant pressure C_p° for both isomeric sets of C_2Si_2(g)

T (K)	$n = 8$ (MP2/6-31G*)		$n = 4$ (MP4/6-31G*)	
	$C_{p,{}^1A_g}^{\circ}$ [b]	C_p° [c]	$C_{p,{}^1A_g}^{\circ}$ [b]	C_p° [c]
1100	79.280	94.809	78.474	100.947
1200	79.856	98.901	79.161	102.768
1300	80.314	102.074	79.709	103.369
1400	80.685	104.209	80.154	103.092
1500	80.988	105.364	80.519	102.258
1600	81.239	105.709	80.822	101.125
1700	81.449	105.459	81.077	99.870
1800	81.626	104.821	81.292	98.609

[a] Heat capacity terms (J K^{-1} mol^{-1}); ideal gas–standard state choice irrelevant.

[b] Partial term belonging to the structure of the lowest ground state energy (^1A_g).

[c] Overall term for the equilibrium isomeric mixture.

Figure 2 shows an interesting qualitative feature—the extreme course (namely, with a maximum) of temperature dependence of the relaxation isomerism contribution to the heat capacity, $\delta_n C_{p,1}^{(\mathrm{iso})}$. Table 4 gives precise coordinates of this maximum. These maxima are relatively quite high, even though they do not exceed the greatest values for this type of maximum so far reported [27]. From Table 4 it is also obvious that the value of the isofractional contribution $\delta_n C_{p,w,}^{(\mathrm{iso})}1$ is in this case virtually negligible as compared with the $\delta_n C_{p,1}^{(\mathrm{iso})}$ value. The course with a maximum can be quite well conserved when going from the isomerism contribution to the overall heat-capacity values (currently obtained by observation), too, and thus it can also serve as a diagnostic means to prove the presence of isomerism (Table 5).

CONCLUDING REMARKS

The C_2Si_2 system represents the most extensive set of isomers submitted to this type of investigation so far. In accordance with earlier findings [8,9] it has been shown that the structure with the lowest ground state energy need not be the most stable one at all temperatures. On the contrary, changes in the order of relative stabilities of the individual members of an isomeric set are possible. The isomeric interplay allows creation of a new type of quantities, the overall quantities, which can differ distinctly from the partial values belonging to the individual isomers, e.g. the isomer with the lowest ground state energy. However, the overall terms are applicable only to situations where the inter-isomer equilibrium has been established. In the sense of this paper, every chemical species can be considered [8] to represent an isomeric mixture, even though for only some species will such consideration not be formal at low and moderate temperatures. From the standpoint of the form of conventional tables of values of thermodynamic functions, the effects of isomerism at the highest temperatures (considered as standard for tabulation) can even generally appear significant and hence non-negligible for most species. Then it becomes meaningful to tabulate two types of quantities, the partial and overall ones. Alternatively, it is possible to tabulate the values of partial terms for the isomer with the lowest ground-state energy and the values of isomerism contributions related to this isomer.

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