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REACTION COMPONENT ISOMERISM: Si_2H_4—AN INTERESTING, FOURFOLD CASE

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ABSTRACT

Relative stabilities of four local minima recently localized on the potential energy hypersurfaces of Si_2H_4 have been studied with respect to their dependence on temperature. Two interchanges in relative stabilities of the isomers with increasing temperature have been shown. This contributes to the difference (so far the most distinct of those described by quantum chemistry for chemical equilibria) between the thermodynamic characteristics of formation of the isomer, which is most stable at absolute zero, and those of formation of the whole isomeric system.

INTRODUCTION

Description of the quantum-chemical hypersurface of potential energy by localization and identification of its stationary points (e.g., refs 1-3) is applied to polyatomic systems of gradually increasing magnitude. Also, an increasingly frequent situation can be encountered (for a review, see ref. 4) in which several different local minima can be found at the potential hypersurface(s) for a single chemical species. This necessitates, at least for some types of observation, its result to be taken as a combination of contributions of all the isomeric structures taking part. In particular, in the theoretical study of equilibrium [5] and rate [6] processes with only theoretically recognized isomerism of the reaction component(s), it has become useful to evaluate, in addition to the partial thermodynamic terms connected with the individual isomers, the overall terms for which all the isomers are considered as a group.

Recent studies (e.g., refs 7 and 8) of relations on the ab initio hypersurfaces of Si_2H_4 proved [8] the existence of four local minima of different electronic wave function symmetries. Their relative stabilities have only been discussed so far in terms of the depths of the corresponding potential minima. In the light of our former findings (e.g., refs. 9 and 10) of interchanges of the relative stability of isomers with changing temperature, due to involvement of contributions of rotational–vibrational motions, it also appeared useful to carry out the respective examination of relations in the system [8] of Si_2H_4 isomers. Therefore, the aims of this communication are to study both the temperature dependence of relative stability of the four isomers in question and the consequences of this isomerism in the comparison of some types of experimental and theoretical thermodynamic characteristics of this system.

ISOMERIC STRUCTURES AND THEIR WEIGHTS

Ab initio calculations in the extended basis set, including polarization functions, which were carried out recently by Lischka and Köhler [8], provided structural, vibrational and energy information on the four Si_2H_4 isomers, viz. the lowest singlet and triplet states of disilene and silylsilylene with ^1A_g, ^3B, and $^1A'$, $^3A''$ symmetries, respectively, of the electronic wave function. Whereas structural optimization and vibrational analysis were carried out [8] in the $10s\ 6p\ 1d$ basis set for silicon, the energetics of these isomers were described in the $10s\ 6p\ 2d$ basis set for the atom. So far, these data represent the most extensive and best information set on Si_2H_4 isomers, and, therefore, they form the starting point for our further considerations (with the adoption of the recommendation [8] for describing frequencies of the normal vibrational modes of the ^1A_g planar structure). This information set enables a description of the thermodynamics of this system with the usual approach to the partition functions (cf., e.g., refs. 4 and 11), viz. the rigid rotor and harmonic oscillator (RRHO) approach.

In terms of the partition function of the i-th isomer, q_i (related to this isomer ground-state energy as the energy zero), and the difference, e_i, between the ground-state energy of the i-th isomer and a chosen reference substance, the weight factors, w_i, of the individual structures in the four-membered isomeric set are given [12] as follows

$$w_i = \frac{q_i \exp(-e_i/kT)}{\sum_{j=1}^{4} q_j \exp(-e_j/kT)} \tag{1}$$

These weight factors represent mole fractions of the individual isomers in the equilibrium mixture (w_i values do not depend [12] on the choice of the reference structure for adjustment of ground-state energies).

Figure 1 presents the course of the weight factors $w_{^1A_g}$, $w_{^3B}$, $w_{^1A'}$ and $w_{^3A''}$ over a broad temperature interval. Whereas at the lowest temperatures studied the clearly dominant structure is that lowest-lying in terms of potential (or ground state) energy, i.e., $^1A'$, increasing temperature increases the significance of the remaining three structures which represent more than 10% of the equilibrium mixture above a temperature of ~ 460 K. Above

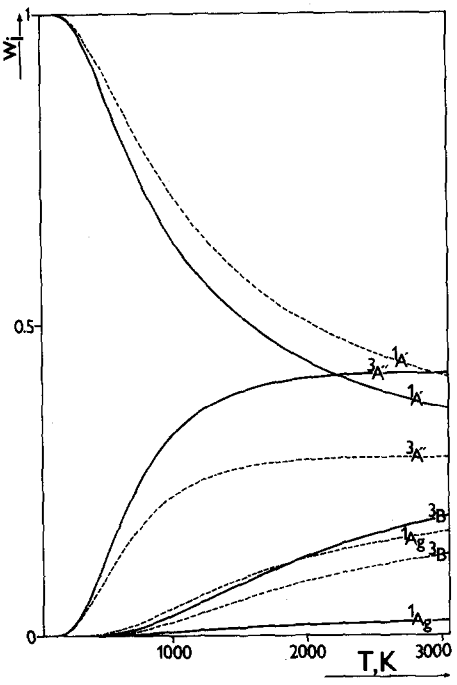

Fig. 1. Temperature dependence of weights, w_i, of the ^1A_g, ^3B, $^1A'$ and $^3A''$ isomers (- - - - - - simple Boltzmann factors).

~ 1580 K structure $^1A'$ already forms less than 50% of this mixture, and at the end of the interval studied it represents almost only one-third thereof. At ~ 2235 K an interchange is observed between relative stabilities of the isomers $^1A'$ and $^3A''$, so that above this temperature limit the latter structure (the lowest but one in terms of the potential or ground-state energy) represents the most stable isomer. The fact that (at a given temperature) the triplet state represents the thermodynamically most stable structure is not usual, but it is not unknown (for a trivial example see O_2). Another interesting factor is the interchange of relative stabilities of isomers ^1A_g and ^3B in the low-temperature region (~ 205 K). These results show (in analogy with a number of other isomers, cf. refs. 9 and 10) that, also within the Si_2H_4 system, the relative stability of the individual isomers represents no absolute characteristic readily deducible from their positions on the potential energy scale but depends on the choice of temperature. From Fig. 1 it also follows that simple Boltzmann or configurational factors (following from eqn. (1) by putting $q_i = 1$ and by transition from the ground-state energy to potential energy) would represent (except for low temperatures) only a very imperfect approximation of w_i. Finally, it is also clear that the $^1A'$ structure alone must not only be taken into account when evaluating various structure-dependent characteristics of this system at moderate and higher temperatures.

OVERALL ENTHALPY AND ENTROPY TERMS

If we want to predict the thermodynamics of an isomeric system as a whole or to interpret the results of observations which do not allow the individual isomers to be distinguished (e.g., pressure measurements, mass spectroscopy, and, according to experimental conditions, in principle, any other spectroscopy) or (at the present stage predominantly) to compare theoretical thermodynamic data with experimental values obtained from such observations, then we must replace the theoretical partial terms by overall terms, e.g., for the reaction

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

the four partial standard enthalpy and entropy terms, ΔH_i^0 and ΔS_i^0 ($i = {}^1A_g$, ${}^3B$, ${}^1A'$ or ${}^3A''$), must be replaced by the overall terms ΔH^0 and ΔS^0 according to the weighting relations [4]

$$\Delta H^0 = \sum_{i=1}^{4} w_i \Delta H_i^0 \tag{3}$$

$$\Delta S^0 = \sum_{i=1}^{4} w_i \left(\Delta S_i^0 - R \ln w_i \right) \tag{4}$$

However, for evaluation of the contributions of the remaining isomers to these overall values, in comparison with, e.g., the ${}^1A'$ structure, it is sufficient to consider the quantities [13]

$$\Delta H_{{}^1A'}^{(\mathrm{iso})} = \Delta H^0 - \Delta H_{{}^1A'}^0 \tag{5}$$

$$\Delta S_{{}^1A'}^{(\mathrm{iso})} = \Delta S^0 - \Delta S_{{}^1A'}^0 \tag{6}$$

with the information available [8] being sufficient for their calculation. Clearly enough, terms (5) and (6) are independent of the reactants in eqn. (2). Figure 2 presents the temperature dependences of these isomerism corrections. It can be seen that this correction of the H term exceeds the 1 kJ mol^{-1} limit at about 445 K, that of the TS term at about 405 K, whereas the value 1 kcal mol^{-1} is exceeded at about 945 and 695 K, respectively. At the highest temperature presented (3000 K) the correction of the enthalpy and TS terms is 10.3 and 35.4 kJ mol^{-1}, respectively. Hence, it follows that, at moderate and higher temperatures, application of the partial theoretical terms (corresponding, e.g., to the most stable structure on the potential energy scale), for the purpose of comparison with experimental values of overall nature, would lead to substantial inaccuracy. Isomerism corrections can obviously reach values comparable with, e.g., the contribution of the correlation energy term.

If characterization of the entropy of the reactants of reaction (2) is also carried out (in the RRHO approximation with the use of molecular parameters [14]), then transition from $\Delta S_{{}^1A'}^{(\mathrm{iso})}$ to ΔS^0 is possible, which allows

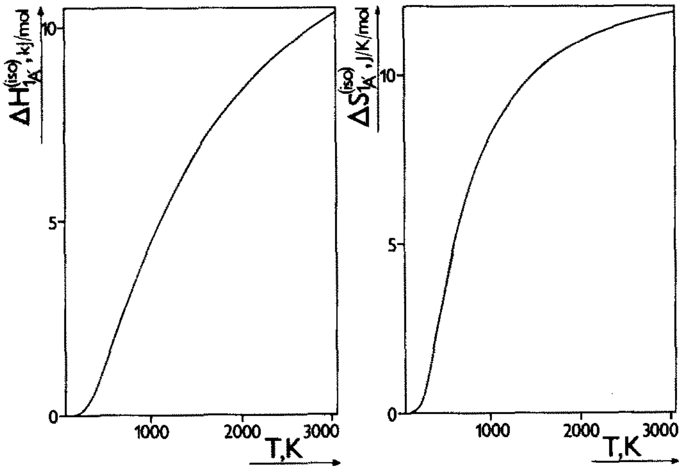

Fig. 2. Temperature dependence of isomerism corrections $\Delta H^{(\mathrm{iso})}_{^1A'}$ and $\Delta S^{(\mathrm{iso})}_{^1A'}$.

mutual relations of the overall term and all four partial standard entropy terms of reaction (2) to be evaluated (Fig. 3). These results represent a warning of the situation when the representing structure could be deduced

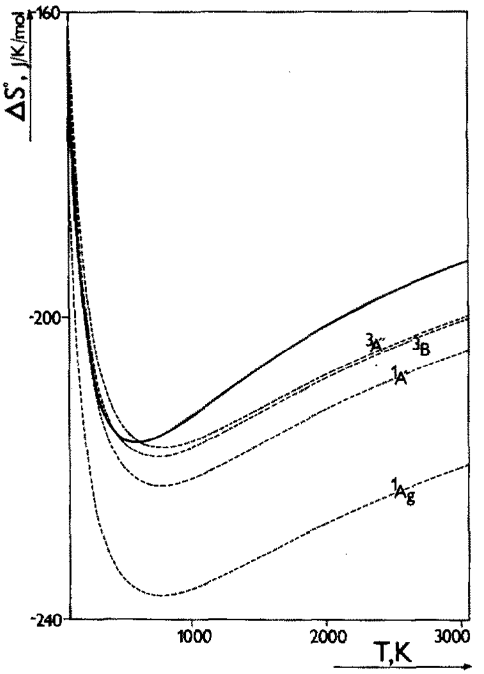

Fig. 3. Temperature dependence of the standard entropy change ΔS^0 of reaction (2) for the ^1A_g, ^3B, $^1A'$, and $^3A''$ isomers and for the overall process (———); the standard state is an ideal gas at 1 atm pressure (1 atm = 101 325 Pa).

TABLE 1

Comparison of $\Delta H_{A'}^{(\text{iso})}$ and $\Delta S_{A'}^{(\text{iso})}$ terms for two-, three- and four-membered isomeric sets

T (K)	Isomeric set [a]	$\Delta H_{A'}^{(\text{iso})}$ (kJ mol^{-1})	$\Delta S_{A'}^{(\text{iso})}$ (J K^{-1} mol^{-1})
298.15	2	0.241	0.990
	3	0.241	0.991
	4	0.242	0.992
500	2	1.305	3.659
	3	1.343	3.747
	4	1.353	3.769
1500	2	4.520	7.721
	3	6.571	9.816
	4	6.789	10.063
3000	2	5.401	8.166
	3	9.994	11.486
	4	10.312	11.785

[a] $2 = {}^1A', {}^3A''$; $3 = {}^1A', {}^3A'', {}^3B$; $4 = {}^1A', {}^3A'', {}^3B, {}^1A_g$.

from agreement of its respective theoretical (partial) term with the (overall) experimental term (because in our case, at various temperatures, ΔS^0 can coincide with different ΔS_i^0 values).

So far, we have not differentiated between the ${}^1A_g$, ${}^3B$ and ${}^3A''$ isomers, but we have taken them as one entire group. The results given in Table 1, which consider Si_2H_4 successively as a set of two, three and four structures, make it possible to evaluate the importance of these three isomers individually for calculation of the ΔH^0 and ΔS^0 terms. It is seen that, at moderate and higher temperatures, it is essential to consider the other triplet state, ${}^3B$, besides the ${}^1A'$ and ${}^3A''$ structures, whereas the effect of the fourth isomer, ${}^1A_g$, is of rather marginal importance.

CONCLUSIONS

The process studied (eqn. 2) represents the third case of chemical equilibrium with quantum-chemically recognized reaction component isomerism properly treated at the level of thermodynamic characteristics (for the first two cases, see refs. 4 and 15); so far, however, the role of isomerism is most distinct in process (2). Therefore, the results of the present article alone form a valuable illustrative example of the general concept of reaction component isomerism [4], which convincingly shows that multi-isomeric cannot be replaced by single-isomeric characteristics.

With respect to the comparison itself, between quantum-chemical information about the Si_2H_4 system and potential experimental data of overall nature, the following limitation must be taken into account. The strictly equilibrium conditions considered in our weighting need not be attained in experiment (the problem of kinetics of interisomer rearrangements, inclusive of singlet–triplet transitions), moreover, the temperature interval considered was obviously much too broad (cf. ref. 16). A certain improvement in the accuracy of the data, especially at higher temperatures, would be made on transition from the RRHO approximation to the model of anharmonic oscillator and non-rigid rotor, if, of course, the necessary data were available. The best approach would be to treat Si_2H_4 as one entire (non-rigid) system [17–19] using all the potential energy hypersurfaces involved. Nevertheless, the most desirable and obviously key correction with respect to prediction purposes is to consider the electron correlation (cf. ref. 8) which would provide a sufficiently reliable description of the interisomer energetics and, hence, our weight factors, w_i. Finally, the present results are also encouraging in relation to other isomeric silicon-containing systems, viz. the quite recently described protonated disilene [20].

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