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THERMODYNAMICS OF MOLECULAR ELECTRONICS AGENTS: THE SIGNIFICANCE OF HIGHLY MOBILE ISOMERIC EQUILIBRIA *

ZDENĚK SLANINA

The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, CS-18223 Prague 8-Kobylisy (Czechoslovakia)

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ABSTRACT

The possible application of computational thermodynamics in relation to the design of bistable conformational systems for use in molecular electronics has been analysed. The search for these systems has revealed some conflicting requirements, namely, the relatively easy conversion of one structure into the other and vice versa, with the isomerisation equilibrium constants close to unity, but, at the same time, the need for both isomers to be sufficiently different to enable their easy differentiation. Using the example of the interconversions in the Si_6H_6 system characterised by means of recent theoretical calculations, the formulation and verification of the design criteria have been demonstrated using the computational approach.

INTRODUCTION

A substantial role in molecular electronic concepts is played by bistable or multistable molecules which represent a potential switch [1–4], enabling the storage of information. It is expected [5–7] that, in this switching at molecular levels, various types of conformational changes could be used, e.g. intramolecular hydrogen transfer, *cis–trans* isomerisation, charge transfer or dimerisation. The requirements of molecular electronics in the search for suitable systems overlap with endeavours in the chemical syntheses of organic species of very specific functionality. Concepts of computer design of syntheses and molecular engineering are constructed for both these purposes. Hence, in the search for structures with suitable or even optimum properties for applications in molecular electronics, it also becomes possible to adopt the prediction approaches of computational chemistry [8–11]. The present report deals with some (essentially thermodynamic) criteria which should be fulfilled by bistable systems.

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* Dedicated to Academician Josef Říman, the former President of the Academy, on the occasion of his 65th birthday.

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GENERAL REASONING

The conformational changes applicable to storage of information must exhibit a relatively easy conversion between two isomeric forms in both directions, i.e. reversibility of the conformational change. The stability of both isomers with regard to their decomposition into other products is also important, as well as the rates of mutual interconversions of both isomers. In order to evaluate such factors, one can use the values of the corresponding equilibrium and rate constants, which need not contradict the fact that molecular electronics, in principle, is applicable to individual molecules (although it seems more likely that it will work with their sets, e.g. arrays on supporters, to ensure a reliable reproducibility). With these conditions, of course, the problem of reaching thermodynamic equilibrium is irrelevant; nevertheless the equilibrium (and rate) constants do represent useful complex terms into which various molecular parameters (important for evaluation of the applicability of the system to molecular electronics) are transformed.

Let us consider a bistable conformational system

$$A = B \tag{1}$$

which is (in a condensed manner) characterised by the equilibrium constant K of this isomerisation (1). At present it is possible to evaluate this equilibrium constant by purely computational means [12–14], namely on the basis of statistical mechanics supplied by the molecular data from quantum-chemical or molecular-mechanical calculations. These structural, energy, and vibrational characteristics of the system (1) are deduced from potential energy hypersurfaces, particularly from the closest regions to the local energy minima of A and B. This is the starting point for a priori, non-empirical design considerations.

Let us separate the standard Gibbs energy change, $\Delta G_T^{\ominus}$, corresponding to process (1), into the standard enthalpy and entropy changes, $\Delta H_T^{\ominus}$ and $\Delta S_T^{\ominus}$, in the usual way

$$\Delta G_T^{\ominus} = \Delta H_T^{\ominus} - T\Delta S_T^{\ominus} \tag{2}$$

The requirement for easy transitions between the isomers A and B can be viewed from both the kinetic and the thermodynamic standpoints. In reaction rate terms, this means sufficiently high values for the rate constants of the mutual interconversions of the isomers. In the thermodynamic approach, these easy transitions can be expressed as comparable populations of each isomer, i.e.

$$K \approx 1 \tag{3}$$

or

$$\Delta G_T^{\ominus} \approx 0 \tag{4}$$

for the region of working temperature of the bistable system being considered. However, for the storage and retrieval of information, it is necessary that both isomers are sufficiently different. This difference is primarily manifested in the entropy term. Thus it follows that the standard term $\Delta S_T^\ominus$ should be sufficiently different from zero

$$|\Delta S_T^\ominus| \gg 0 \tag{5}$$

With regard to condition (4), after application of (5), a similar condition follows for the enthalpy term

$$|\Delta H_T^\ominus| \gg 0 \tag{6}$$

From the results of the above paragraph, it is possible to formulate the temperature course of the equilibrium constant, K, with respect to temperature (R is the gas constant)

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H_T^\ominus}{RT^2} \tag{7}$$

According to relation (6), it then follows from eqn. (7) that the equilibrium constant K will show a relatively considerable temperature dependence, at least in the region of the working temperature of the bistable system (1). This conclusion can also be reached by another argument. Whereas at the working temperature the stabilities of A and B are comparable, only one of these isomers will predominate at absolute zero (i.e. it will be either $K = 0$ or $K = \infty$). Hence, on going from absolute zero to the working temperature, K must change from 0 or ∞ to a value near to 1, whence the conclusion concerning the distinct temperature-dependence of K follows once again.

Thus, the above analysis shows that from the standpoint of information storage, it is useful to concentrate on systems in which, at the working temperature (most often room temperature), the equilibrium constant of interconversion of both forms in the bistable system is close to unity, the entropy terms of the two forms being, however, sufficiently different. These systems will then exhibit a distinct temperature-dependence of K in the neighbourhood of the working point. Furthermore, sufficiently rapid interconversion is also required. Thus, it follows that highly mobile equilibria both in the rate and temperature senses, are potentially useful areas of investigation.

ILLUSTRATION OF THE GENERAL REASONING ON A MODEL ISOMERIC SYSTEM Si_6H_6

Isomeric systems containing hydrogen bonds [15–17] can serve as examples of highly mobile equilibria. In these systems, the equimolarity of both isomers involved often prevails even at low temperatures. The potential

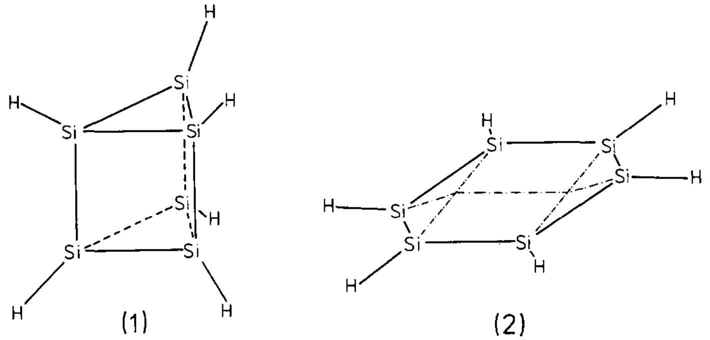

Fig. 1. Schemes of hexasilaprismane (1) and hexasilabenzene (2); (1) and (2) belong to D_{3h} and D_{3d} point groups of symmetry, respectively [20].

barriers for the transitions between these isomers are low, which also ensures sufficiently fast kinetics for these interconversions. In fact, it was found, in according with the previous analysis, that these equilibria about the equimolarity point are usually also distinctly thermally mobile. However, equilibria of the mobile type considered can also be sought in more typical organic systems. For instance, a distinct temperature-dependence of relative equilibrium concentrations was found [18] for isomeric diamantan-1- and -4-ols.

In the present context, we shall focus attention on the isomeric system Si_6H_6. Theoretical studies [19,20] of the potential hypersurface of this system showed the existence of three local minima. Of these, the two energetically lowest-lying isomers, namely hexasilaprismane with D_{3h} symmetry and hexasilabenzene with D_{3d} symmetry, have particular significance in the present context (Fig. 1). In the potential energy term, hexasilabenzene was approximately 41 kJ mol^{-1} higher than hexasilaprismane. More than 100 kJ mol^{-1} above this hexasilabenzene, there was a third isomer, hexasila-Dewar benzene with C_{2v} symmetry. Although a detailed description of the reaction coordinates for the interconversion of the D_{3h} and D_{3d} structures is not known at present, it can be expected that it could be a simple concerted process connected with a reasonably high potential barrier. This is indicated by the considerable non-rigidity of the hexasilabenzene skeleton manifested in three ring-deforming modes with very low frequencies [20].

Using computational data from the literature [19,20], the complete information required for a statistical-thermodynamic description of the stabilities of both the lowest-lying isomers can be acquired. (We have adopted the so-called scaled set of vibrational frequencies of hexasilabenzene from ref. 19.) The partition functions q_i of both these structures were constructed in the rigid rotor and harmonic oscillator approximation [12]. If $\Delta H_0^{\ominus}$ denotes the difference in the ground-state energies between hexasilabenzene ($i = 2$)

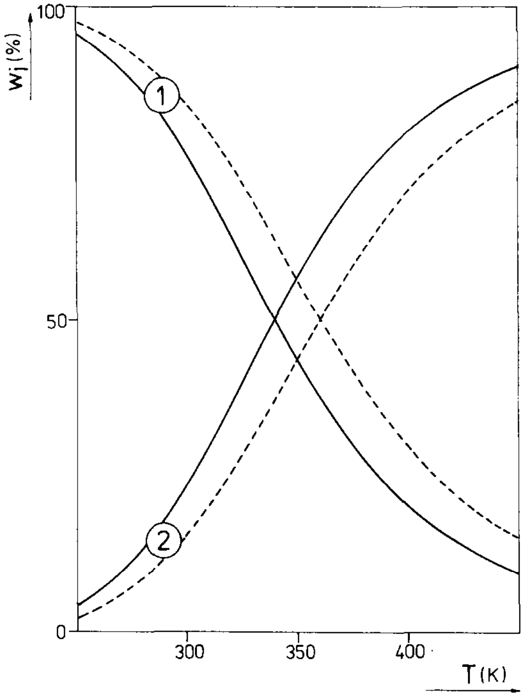

Fig. 2. Temperature dependences of calculated mole fractions w_i of hexasilaprismane (1) and hexasilabenzene (2) in their equilibrium mixture; the solid and dashed lines represent the treatment with full consideration of rotational motion and its neglecting, respectively.

and hexasilaprismane ($i = 1$) (i.e. the enthalpy term for reaction (1) at absolute zero), then eqn. (8) can be written for the mole fraction w_1 of hexasilaprismane in its equilibrium mixture with hexasilabenzene [12–14]

$$w_1 = \frac{q_1}{q_1 + q_2 \exp(-\Delta H_0^{\ominus}/(RT))} \tag{8}$$

These mole fractions can be evaluated for two limiting situations of rotational motion—either its full admission or its full suppression (so that only the intramolecular vibrations are present in the system).

Figure 2 presents the temperature dependences of the w_1 and w_2 terms for both approaches to rotational motion. From the temperature course of the w_1 and w_2 mole fractions presented, it can be seen that, although hexasilaprismane is predominant at the lowest temperatures, further temperature increase results in rapid converging of the relative stabilities of the two isomers. The equimolar ratio is attained just above room temperature. The courses are qualitatively identical for both the descriptions of rotation; quantitatively, suppression of rotation somewhat delays the attainment of equimolarity. Table 1 shows the values of the $\Delta H_T^{\ominus}$ and $\Delta S_T^{\ominus}$ terms at room temperature and at the point of equimolarity. Although in the system

TABLE 1

Calculated thermodynamic data for isomerisation[a] of hexasilaprismane (1) to hexasilabenzene (2)

Temperature T (K)	Mole fractions		Enthalpy change $\Delta H_T^\ominus$ (kJ mol^{-1})	Entropy change $\Delta S_T^\ominus$ (J K^{-1} mol^{-1})
	w_1 (%)	w_2 (%)		
298.15	77.4	22.6	24.73	72.71
	(85.3)	(14.7)	(24.73)	(68.34)
339.5	50.0	50.0	25.38	74.77
360.4	(50.0)	(50.0)	(25.68)	(71.24)

[a] Treated as an ideal system. Results are presented for full admission of rotational motion and for its full suppression (in parentheses).

under consideration equimolarity is attained at a temperature higher than room temperature, it is clear that small changes in the system (substitution) could make it possible to affect this temperature in a desirable direction.

From the illustrative example given, it is obvious that intramolecular vibrational motions play a critical role in the levelling of relative stabilities. In this case, it is exactly this interplay of vibrational motions which enables hexasilabenzene to overcome the unfavourable difference in the potential energy term relatively soon. There are convenient relationships between the vibration frequencies of both structures; in hexasilabenzene these are the low-lying frequencies which have no counterparts in hexasilaprismane. These easily populated low-frequency vibrations are, therefore, primarily responsible for the fairly rapid increase in the relative population of hexasilabenzene. This compensation mechanism, however, does not operate with hexasila-Dewar benzene which is sparsely populated at room temperature; its mole fraction in the equilibrium mixture with both the more stable structures would be only about 3×10^{-22} and 8×10^{-23}% for the approaches with the admitted and suppressed rotation, respectively.

CONCLUDING REMARKS

It has been shown that the demands made on bistable systems applicable to the storage of information indicate the potential importance of highly mobile isomeric systems. The accompanying feature of these systems, besides their mobility in the reaction-rate sense, is the mobility of their equilibria with respect to temperature. This paper indicates the significance of vibrational motions as a factor which can compensate even relatively high differences in potential energy. Simple systems of the type already considered are readily described at present by means of computational chemistry, which creates conditions favourable for applications of approaches of a priori molecular design of agents with required parameters. This study also suggests that silicon compounds may present another potential source of bistable systems because of their relatively ample isomerism even when combined with very simple species. This reasoning is, however, based on a purely thermodynamic approach. A further study should also deal with the time needed for switching between the two states of a bistable system and, thus, with details of the interconversion mechanism.

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