

THERMODYNAMIC AND KINETIC CONSEQUENCES OF ISOMERIC INTERPLAY

ZDENĚK SLANINA *

*Department of Chemistry II, Faculty of Science, Hokkaido University, Nishi 8, Kita 10, Kita-ku,
Sapporo 060 (Japan)*

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ABSTRACT

This paper surveys situations where observational or theoretical means have discovered the presence of several isomeric structures in an equilibrium. The effects of this isomerism on the evaluation of thermodynamic (and also partly kinetic) quantities are studied. Particular attention is given to the coexistence of two (or more) isomeric structures of comparable stability. The convolutional and deconvolutional treatments described are important for the interpretation of the overall observed terms, the prediction of properties and the behaviour of complex mixtures as well as for theory–experiment comparisons.

INTRODUCTION

One of the first milestones [1a] in the creation of the molecular structure concept was that of chemical isomerism which is an unusually general and varied phenomenon. It has analogues in high (biological isomerism [1b]) as well as in low (atomic nucleus isomerism [1c]) levels of mass organization. The picture of isomerism is extended constantly by new findings (e.g. recently, phase isomerism [2]). The progress in observational techniques made it possible to reveal isomerism in very simple species [3]. Isomerism soon became an object of theoretical studies [4], which took place long before the establishment of quantum chemistry; Pólya's enumeration theorem [4c] represents the acknowledged summit [4b] of this early era. At present [5], theoretical chemistry is proving to be a full partner of experiment, and the many studies in isomeric chemistry represent an instructive example of cooperation between theory and experiment and make it possible to gain insight that is afforded independently by neither of these approaches. Recently, quantum chemical calculations have indicated possible isomerism even in the case of triatomic systems (e.g. CH_2 , HCN , O_3 , SiOH ,

* Permanent address: The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Máchova 7, CS-121 38 Prague 2, Czechoslovakia.

Si₃ [5a,6]; cf. also interstellar space studies [5d]). The mutually fruitful interaction with experiment continues.

CONCEPTUAL REMARKS AND BACKGROUND

A fundamental conceptual problem is that of distinguishability of isomeric structures [7]. The existence [7] of non-rigid or fluxional molecules makes it necessary to operatively view the isomerism [7b,c] (inclusive of the chirality [7e]) as a phenomenon whose observability depends on the conditions and methods of observation, so that three types of behaviour of an isomeric system can be considered: (i) distinctly defined, separable, individual species; (ii) coexisting, distinguishable but not separable isomers; (iii) a transition into fluxional behaviour without the possibility of differentiation of the individual components (in fact, a single system can, at a suitably chosen temperature and with a suitable observation technique, gradually exhibit all three types of behaviour [7b]). This property of isomers can be explained clearly in terms of total wave function [8]. The lowest-lying molecular wave function can exhibit a negligible amplitude everywhere except in one region of nuclear configurational space. However, on the other hand, it can also have non-negligible amplitude in several stability domains. Hence, there follows a retention of a certain unity among all the isomers even inclusive of those which are apparently entirely distinct. Therefore, the assignment of various eigenfunctions of the molecular Hamiltonian to a single species is only an approximation. In these terms it also appears that the more closely the isomers are investigated the less unique they appear to be. Nevertheless, in certain situations the uniqueness of isomers can represent a good and realistic approximation, which depends on the relative isolation of domains. If we go from total molecular wave function terms to the physically lower-lying description by potential hypersurface [9], we can discuss the isolation of domains in terms of separating potential barriers, considering of course both the transition over the barrier and tunnelling through the barrier. The symmetrical nature of the separating barrier [10] appears to be important for the evaluation of the problem of relative stability of isomers (the tunnelling can be drastically reduced on going from a symmetric to an asymmetric barrier of the same height). This fact also throws new light upon the problem of apparent stability of optical isomers [10b]. The description based on representation of potential hypersurfaces by their stationary (critical) points [11] remains, of course, the decisive means for the practical calculation treatment of problems of isomeric chemistry. At present, efficient optimization techniques are available for the location of the stationary points which, with analytically constructed potential gradients, work for practically all methodical levels, whether quantum chemical [11a] or molecular mechanical [11b], inclusive of advanced procedures for

evaluation of correlation effects [11c]. The properties of curvature of the hypersurface in the neighbourhood of stationary points are most often described in terms of second energy derivatives (in this connection, it is also possible to carry out the pertinent evaluation of the vibration spectrum). The second energy derivatives are a sufficient means for the differentiation of types of stationary points (the minima, transition states, higher types of stationary points) [11]. At present, there even takes place (at certain levels) a transition [11d] to analytically constructed second or even third potential derivatives (instead of the hitherto predominating numerical evaluation).

Although, so far, only rather simple systems (from the point of view of synthetic organic chemistry) have been investigated in terms of stationary points of the respective potential hypersurfaces, it is evident that, in general, we must presume a multiplicity of stationary points at these hypersurfaces. This was well documented by recent localization of the stationary points at the MINDO/3 hypersurface of the C_4H_4 system [12a]. Although the number of stationary points relevant for a given reaction can be considerably reduced on the basis of simple reasoning in terms of the potential energy (so that only the most stable structure, stabilomer [12b], need be considered; alternatively in very special classes of species, simple rigorous ordering rules can be derived [12c]), nevertheless, for a system of a certain size it will be quite typical that the investigation of the hypersurface will reveal a number of local energy minima of comparable stability, all of them representing the same species. Similarly, in the case of rate processes a number of different transition states can appear, all of them, nevertheless, acting as activated complexes within a reaction which is treated experimentally as a simple (concerted) one. The studies based on potential functions of molecular mechanics [13] have already shown the existence of tens to hundreds of stationary points in chemically or biochemically interesting systems. This isomerism problem was a substantial intermediate step between theory and experiment. In this connection it is possible to consider, for any structure-dependent characteristic, the effective overall averaged value of the characteristic composed of the contributions from all participating isomers. In particular, this is true of the standard and activation characteristics of reactions. Treatment of this type is important not only for adequate comparison of theory and experiment but also for mechanistic interpretations of the anomalies observed in the behaviour of these parameters and, finally, for the prediction of the behaviour of real systems.

EQUILIBRIUM OF n INTERCONVERTING ISOMERS

If a chemical equilibrium is established in a system of n isomers [14] as a consequence of their interconversions, then the populations of the isomers (i.e. their mole fractions), in terms of their partition functions q_i (constructed with respect to the ground state of the respective isomer as the reference

zero energy), and energy differences $\Delta H_{0,i}^\ominus$ between the ground state of the i th isomer and the most stable isomer (denoted with the index 1) are given as follows [14,15] (for the sake of completeness let us note that the referencing of energies to the most stable isomer is purely a matter of convention; the populations (also called weight factors) w_i do not depend on this choice of the reference isomer)

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

In terms of the Boltzmann statistics (the inter-isomer equilibria have not yet been studied in terms of the relevant quantal statistics, although the experiments carried out on matrices at very low temperatures could make this problem interesting), the weight factors * (eqn. (1)) have a rigorous nature under the presumption of independency of motions of individual isomers. Although this presumption is a natural consequence of the adoption of the representation of a hypersurface by its isolated stationary points, its plausibility, nevertheless, will depend on the separation of the individual local minima (here we encounter a certain inconsistency of the demands, because establishment of the inter-isomer equilibrium is, on the contrary, facilitated by easy interconversions). The partition function in eqn. (1) can be of any nature; however, the representation of a hypersurface by its stationary points usually leads to application of the rigid rotor and harmonic oscillator approximation. In this context it was pointed out [14d] that the correction factors between the numerator and denominator of eqn. (1) can be extensively cancelled out. The isomer populations according to eqn. (1) are mostly evaluated in the ideal gas phase [15].

The evaluation of the isomer populations is the basic prerequisite for the weighting of the isomer contributions to the overall values of the quantities observed in the experiment. A meaningful application of the equilibrium populations from eqn. (1) presumes that at the respective real situation the conditions of inter-isomer equilibrium will be attained. Attention here will be focused on the enthalpy (H), entropy (S), and heat capacity at constant pressure (C_p) terms for the isomerization of the first to the i th isomer, ΔH_i^\ominus , ΔS_i^\ominus , and $\Delta C_{p,i}^\ominus$, respectively (formally it is $\Delta H_1^\ominus = \Delta S_1^\ominus = \Delta C_{p,1}^\ominus = 0$). For studies of isomeric interplay it has proved useful to introduce the isomerism contribution terms, $\delta_n X_1^{(\text{iso})}$ [14c], which must be added to the

* Frequently an approximation (e.g. ref. 15) of w_i is used, viz. simple Boltzmann, configurational or steric factors, w'_i , based on mere potential energy terms (depths of minima), ΔE_i

$$w'_i = \exp(-\Delta E_i/RT) / \sum_{j=1}^n \exp(-\Delta E_j/RT)$$

(partial) value of the standard quantity belonging to the 1 isomer in order to obtain the corresponding overall values belonging to the whole equilibrium group of isomers. For the three thermodynamic functions in question we have [14c]

$$\delta_n H_1^{(\text{iso})} = \sum_{i=1}^n w_i \Delta H_i^\ominus \quad (2)$$

$$\delta_n S_1^{(\text{iso})} = \sum_{i=1}^n w_i (\Delta S_i^\ominus - R \ln w_i) \quad (3)$$

$$\delta_n C_{p,1}^{(\text{iso})} = \sum_{i=1}^n w_i \Delta C_{p,i}^\ominus + \frac{1}{RT^2} \left\{ \sum_{i=1}^n w_i (\Delta H_i^\ominus)^2 - \left[\sum_{i=1}^n w_i \Delta H_i^\ominus \right]^2 \right\} \quad (4)$$

An agreeable feature of these isomerism contribution terms is that they are independent of the reactants (and of the choice of the standard state) and are devoid of terms which are identical for all the isomers (e.g. the translational contributions). Hence these contributions can be treated as the standard thermodynamic functions of individual chemical species (in particular it would be possible to suggest a reorganization of tables of thermodynamic functions in the case of isomeric substances—the presentation of both the partial terms belonging to the individual isomers and the isomerism contributions, would enable the evaluation of the thermodynamic function belonging to the equilibrium isomeric mixture). It is, of course, obvious that the isomerism contributions, in contrast to w_i , depend on the choice of the reference isomer (if we abandon the particular choice of the most stable isomer).

An equilibrium isomeric mixture differs from a general gas mixture in that the populations of components cannot be arbitrarily chosen but are unequivocally given by eqn. (1) as a result of the isomer interconversions. The temperature dependence of the weight factors w_i is also precisely defined by eqn. (1). This is manifested in the isomerism contribution to the heat capacity. In contrast to a general gas mixture (i.e. non-reacting components), the differentiation of eqn. (2) must also take into account the temperature derivative of w_i , which is the reason for the second and the third summations in eqn. (4). These are naturally missing in the analogous formula for a general gas mixture. If, however, eqn. (4) is to be relevant in relation to experiment, then the inter-isomer equilibrium (at a temperature change) must be established more rapidly than would follow from the time scale of the observation technique used for the measurement of heat capacity.

EXAMPLES OF CHEMICAL EQUILIBRIA WITH ISOMERISM OF A COMPONENT

In very small systems the isomerism is not realized as several local minima within a single hypersurface but rather as minima at several hyper-

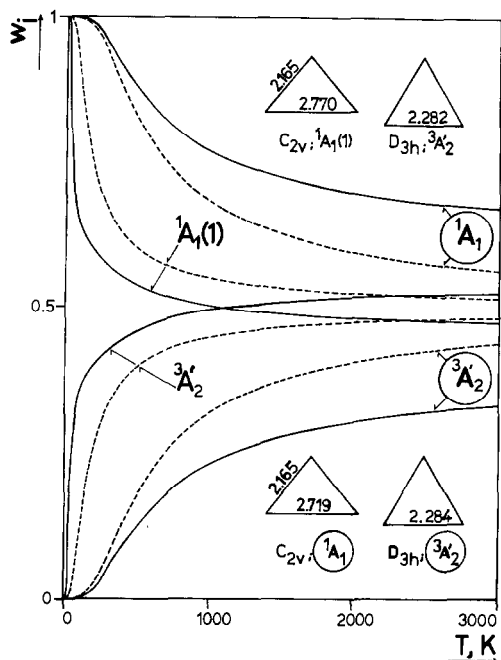


Fig. 1. Temperature dependence of weight factors (mole fractions) for two low-lying isomers of $\text{Si}_3(\text{g})$ evaluated using molecular parameters from ref. 6b (${}^1A_1(1)$ and ${}^3A_2'$) and from ref. 6c (1A_1 and ${}^3A_2'$) (circles); ---, denotes simple Boltzmann factors; bond lengths in 10^{-10} m.

surfaces. This is also the case for the $\text{Si}_3(\text{g})$ system for which advanced ab initio studies [6b,c] proved the existence of two low-lying energy minima with different symmetries of electronic wave function [6b] (${}^1A_1(1)$ (or 1A_1 [6c]) and ${}^3A_2'$) and two energetically high-lying minima. The energy difference of the low-lying isomers between the two studies [6b,c] is about 1 kcal mol^{-1} which leads to substantial differences in the weight values w_i (Fig. 1). It is also obvious that the simple Boltzmann factors [15] which neglect the effects of rotational-vibrational motions represent only a poor approximation of w_i . Table 1 shows that, at high temperatures, the fourth isomer (located about 51 kcal mol^{-1} above the lowest-lying minimum [6b]) also contributes to the values of the isomerism contribution terms (eqns. (2)–(4)). Similarly it was shown for ethanal [14c] that its less stable isomer (ethenol [16]) can contribute substantially to the overall thermodynamics.

The $C_m(\text{g})$ aggregates were studied [17] at several methodical levels; the MINDO/2 treatment [17a] for $m = 4$ leads to three local minima. Table 2 illustrates the weighting of the contributions to the equilibrium formation of these aggregates over graphite. From the data presented, it is obvious that the inclusion of the isomerism contributions is desirable for the proper confrontation of theory with the observed data.

The ab initio SCF [18a] and CEPA [18b] calculations for $\text{Si}_2\text{H}_4(\text{g})$ proved the existence of four local minima with different symmetries of electronic

TABLE 1

Comparison of isomerism contributions $\delta_n X_1^{(iso)}$ to enthalpy (H), entropy (S) and heat capacity (C_p) for two-, three- and four-membered sets of $\text{Si}_3(\text{g})$ isomers at 3000 K

Isomeric set ^a	$\delta_n H_1^{(iso)}$ (kJ mol ⁻¹)	$\delta_n S_1^{(iso)}$ (J K ⁻¹ mol ⁻¹)	$\delta_n C_{p,1}^{(iso)}$ (J K ⁻¹ mol ⁻¹)
2	0.817	6.461	0.029
3	4.423	7.891	6.302
4	4.433	7.894	6.328

^a Reference 6b; 1: $^1A_1(1)$; 2: $1\&^3A_2'$; 3: $2\&^3A_2$; 4: $3\&^1A_1'$.

TABLE 2

Partial and overall MINDO/2 standard enthalpy ΔH^\ominus and entropy ΔS^\ominus terms of $4\text{C}(\text{s}) \rightleftharpoons \text{C}_4(\text{g})$ equilibrium [15a] at 2400 K

Process ^a	ΔH^\ominus (kJ mol ⁻¹)	ΔS^\ominus (J K ⁻¹ mol ⁻¹)
$4\text{C}(\text{s}) \rightleftharpoons \text{C}_4(\text{g}; D_{2h})$	904.1	210.2
$4\text{C}(\text{s}) \rightleftharpoons \text{C}_4(\text{g}; D_2)$	952.2	213.6
$4\text{C}(\text{s}) \rightleftharpoons \text{C}_4(\text{g}; T_d)$	1301.5	205.5
$4\text{C}(\text{s}) \rightleftharpoons \text{C}_4(\text{g}; \text{overall})$	909.9	213.6

^a Point group of symmetry of a particular isomer is indicated in parentheses (see ref. 17a).

wave function (Fig. 2); the one with the lowest potential energy exhibits the $^1A'$ symmetry in both evaluations. Nevertheless, the differences between the energetics of the higher-lying isomers for the SCF and CEPA approaches lead to considerably different pictures of the isomeric interplay [18c] (Fig. 3) (it is, of course, clear that for prediction purposes the CEPA data must be

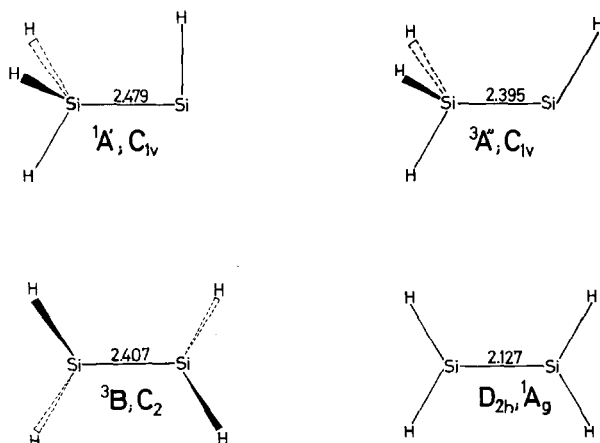


Fig. 2. Schemes of minima found on ab initio SCF hypersurfaces [18a] of Si_2H_4 (cf. Fig. 1).

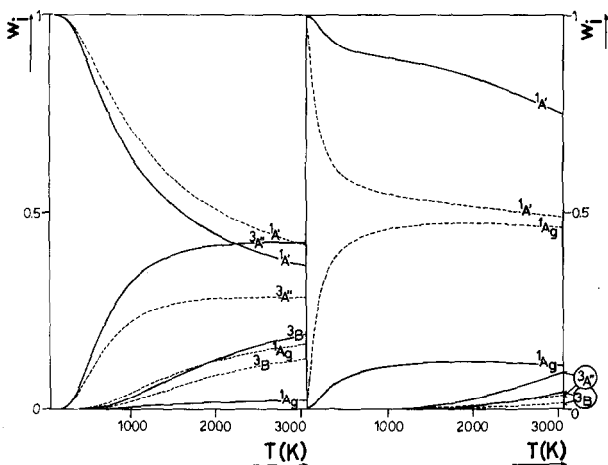


Fig. 3. Temperature dependence [18c] of weights w_i of the $\text{Si}_2\text{H}_4(\text{g})$ isomers (cf. Fig. 2): ---, simple Boltzmann factors; left, SCF [18a]; right, CEPA [18b].

preferred). Also it is confirmed that the inclusion of rotational-vibrational motions is essential, and the simple Boltzmann factors [15] would be an insufficient simulation of the weights (eqn. (1)). The isomerism contributions (eqns. (2)–(4)) attain remarkably high values (Fig. 4). A comparison of the isomerism contributions to heat capacity of the two-, three- and four-membered isomer sets (Fig. 5) shows a relatively slow convergence and therefore

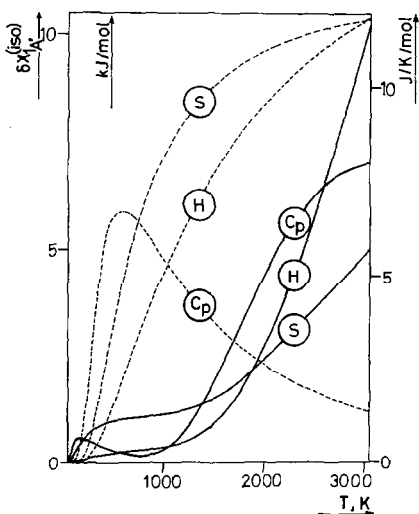


Fig. 4. Temperature dependences [18c] of isomerism contributions, $\delta_4 X_4^{(\text{iso})}$, to enthalpy, entropy and heat capacity of $\text{Si}_2\text{H}_4(\text{g})$ ($X = H, S, C_p$) related to the $1A'$ isomer (cf. Fig. 2; full line: CEPA [18b]; broken line: SCF [18a]).

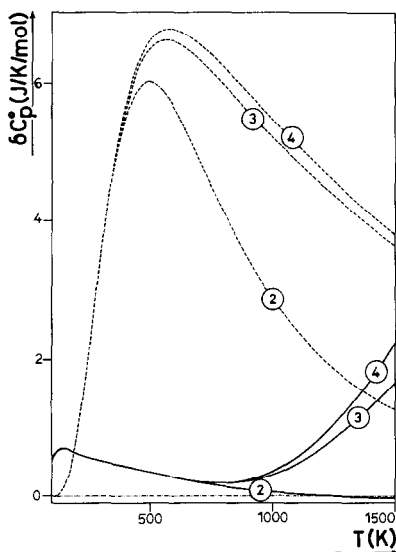


Fig. 5. Temperature dependences of $\delta_n C_{p,A}^{(iso)}$ of $\text{Si}_2\text{H}_4(\text{g})$ evaluated within four- (4), three- (3), and two-membered (2) isomer set (cf. Fig. 4 for details; the position of zero is indicated by the broken and dotted line).

it is also necessary to consider higher-lying structures at higher temperatures.

In a series of papers [14b] Alberty studied the isomerism contributions to the thermodynamics of higher hydrocarbons, especially the effects on the standard overall Gibbs free energy of formation, ΔG_f^\ominus . He compared (Table 3) this contribution with the limiting term $-RT \ln n$ and showed that their difference is directly proportional to the latter limit. This behaviour enabled a prediction of overall thermodynamics of higher alkanes, which is of practical importance in a number of cases, particularly for the calculation of the composition of complex equilibrium mixtures.

TABLE 3

Examples [14b] of isomerism contributions ^a, $\delta_n G_1^{(iso)}$, to standard Gibbs energy of alkane isomer groups at 900 K

Carbon atom content	n^b	$\delta_n G_1^{(iso)}$ (kJ mol ⁻¹)	$\delta_n G_1^{(iso)} /$ ($-RT \ln n$)
5	3	-7.28	0.88
7	9	-11.76	0.71
9	35	-16.95	0.63
10	75	-20.13	0.62

^a Related to the corresponding normal alkane. ^b Number of isomers.

MULTI-PARTICLE CLUSTERS

The examples already presented of the treatment of the isomerism of a reaction component show that this approach is especially justified when isomers of comparable stability coexist; the experimentally measured effects correspond to the whole equilibrium group of isomers. These conditions are well fulfilled by atomic and molecular clusters. As an example we can take $(\text{CO}_2)_2(\text{g})$ for which the ab initio calculations [19a] proved the existence of two local minima: parallel (P) and T form (Fig. 6). The temperature dependence [19b] of w_i of the two structures shows a rather dramatic interchange in relative stability at about 230 K (Fig. 6). This crossing point lies quite near to the normal sublimation point of $\text{CO}_2(\text{s})$ at which the calculated composition is 59% P and 41% T. The partial and overall standard thermodynamic terms of dimerization of $\text{CO}_2(\text{g})$ are presented in Fig. 7 and, again, they indicate the considerable differences between the two types of terms.

There exist in the literature several experimental pieces of evidence [20] for the isomerism of complexes in the gas phase. We could ask whether the effects of isomerism on thermodynamic terms could be applied to the

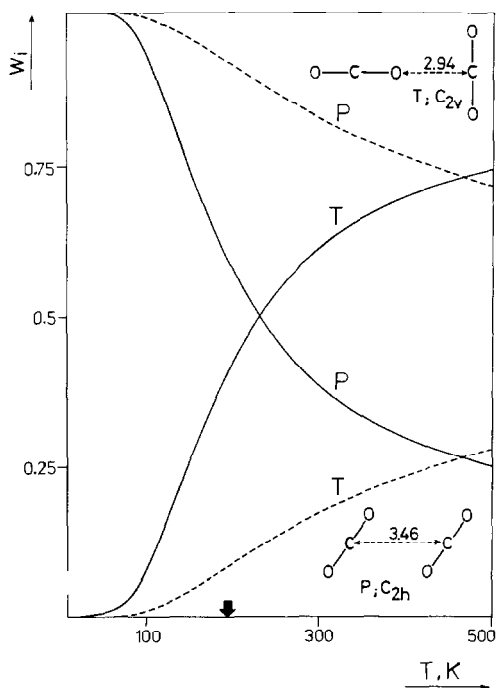


Fig. 6. Temperature dependences [19b] of weights w_i within the $(\text{CO}_2)_2(\text{g})$ isomeric system: ---, simple Boltzmann factors; the arrow indicates the normal sublimation point of CO_2 (cf. Fig. 1).

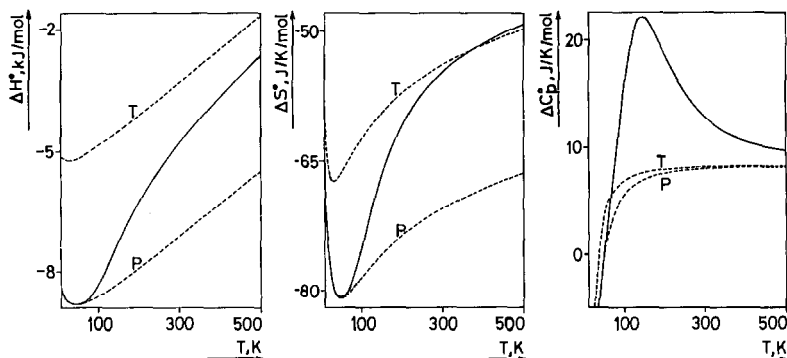


Fig. 7. Temperature dependences [19b] of the standard enthalpy, entropy and heat capacity changes for the partial (cf. Fig. 6) and overall (—) dimerizations of $\text{CO}_2(\text{g})$.

discovery of isomerism. In this context [21a] the standard heat capacity changes ΔC_p^\ominus , of the formation of five dimers [19,21b] were examined (for which isomerism was indicated by the theoretical analysis of their potential hypersurfaces). It was found that, if the isomerism is connected with a fast interchange of relative stability of the isomers in some temperature region, then a distinct extreme of the temperature dependence curve of the ΔC_p^\ominus term can be expected in that temperature region. This represents an interesting suggestion for experimental observation, although the technique for sufficiently accurate measurement of the ΔC_p^\ominus term is not available as yet.

Water associates [22a] hold a distinct position among molecular clusters. Whereas no isomerism could be proved with the water dimer and trimer [22], the higher oligomers exhibited ample forms [5c,22c]. So, for example, in the set of three isomeric tetramers [22c] there is an interchange of relative stability with increasing temperature [14e]. Hence it is not surprising that the isomerism contributions to the overall thermodynamic terms of tetramerization are distinct (Table 4). For a study of very large clusters it is necessary to turn to simple empirical potentials [23], and in studies of this type enormous numbers of isomers can be found [23a]. For clusters of these dimensions, isomerism becomes a critically important factor of stabilization. For example, for a cluster of 49 atoms it was shown [23b] that the effects of isomerism lead to an increase in the population of the clusters by three orders of magnitude.

* Here, we arbitrarily refer to the heat capacity at constant pressure; however, there would be no principal difference with the constant volume regime.

TABLE 4

Illustration of the weighting [14e] on enthalpy and entropy terms^a of formation of water tetramers (H₂O)₄(g) at 400 K

w_i ^b	ΔH_i^\ominus ^c	ΔH^\ominus ^d	ΔS_i^\ominus ^c	ΔS^\ominus ^d
0.624	-77.36	-74.69	-335	-324
0.297	-73.01		-330	
0.078	-59.79		-308	

^a In kJ mol⁻¹ and J K⁻¹ mol⁻¹, respectively. ^b Pyramid, S₄ cyclic, and asymmetric cyclic (H₂O)₄ [22c]. ^c Here, partial water tetramerization terms. ^d The overall term.

The problems of isomerism of the clusters serving for models of heterogeneous catalysis and sorption, are methodologically close [24]. Thermodynamically consistent treatment of some processes has been presented [24b].

ISOMERISM OF ACTIVATED COMPLEXES

The relation between isomerism and rate processes has already been treated within the known Curtin-Hammett principle [25a], but we shall concentrate on the isomerism in the activated complex itself. From the point of view of relations between the activated complexes on going from reactant(s) to product(s), we can differentiate between parallel (each complex acts on its own reaction path) and sequential (activated complexes on a single common reaction path) isomerism. The parallel isomerism can be (thanks to the equilibrium hypothesis) transformed simply [25b] to the treatment applied to equilibria. Table 5 gives an illustration of the chair-boat inversion of cyclohexane which, according to the MINDO/2 study [25c], can proceed by two parallel reaction paths with activated complexes of different symmetry. Parallel isomerism can also be expected with interconversions of molecular complexes. This is, for example, the case of the auto-isomerizations of water dimers which, according to the study [22d], can be realized through three parallel activated complexes. Figure 8 shows the mutual relations of the partial and overall activation parameters of this rate process.

TABLE 5

Partial [25c] and overall [25b] activation enthalpies and entropies of cyclohexane isomerization^a C₆H₁₂(g; D_{3d}) → C₆H₁₂(g; D₂) at 298 K

Activation process	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J K ⁻¹ mol ⁻¹)
C _s	26.36	25.02
C ₂	26.78	28.62
Overall	26.60	32.75

^a That is, the chair to boat interconversion.

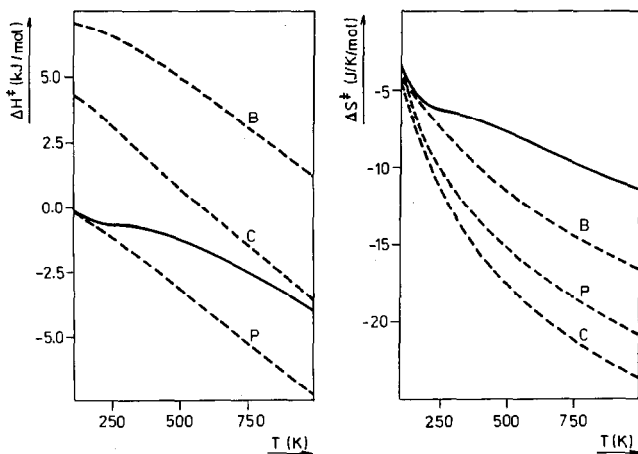


Fig. 8. Temperature dependences [22d] of activation enthalpy ΔH^\ddagger and entropy ΔS^\ddagger for the water dimer interconversion through planar-linear (P), closed (C) and bifurcated (B) transition state and for the overall activation process (—).

The simplest case of sequential isomerism is represented by one local minimum separating two activated complexes on the reaction path from reactants to products. This case is described within the unified statistical theory [26a]. A simplified approach has been applied recently [26b] to the Cope rearrangement of 1,5-hexadiene which, according to the MINDO results [26c], proceeds through a cyclic intermediate * separating two cyclic activated complexes. As compared with the weighting of the contribution of isomeric activated complexes in the parallel situation, the sequential arrangement exhibits a substantially new feature—a time dependence of the overall activation terms [26b]. Nevertheless, it should be noted in conclusion that a proper treatment of combined parallel and sequential isomerism in complex reaction systems, as that encountered recently for the relatively simple reaction system C_4H_4 [12a], is still a problem.

CONCLUDING REMARKS

The existing examples of the isomerism of reaction components show that a replacement of multi-configurational characteristics by single-configurational ones is generally untenable in spite of its being widespread. Before it is possible to turn to the treatment of these phenomena in terms of the whole potential hypersurface (or even molecular wave function), the descrip-

* However, an intermediate existence has not been proved in ab initio MC SCF calculations [26d].

tion will be developed within the representation of the hypersurface by its stationary points. At this latter level it will be desirable, inter alia, to attain a better description of the rotational-vibrational motions of the individual isomers [27a], to involve the coupling of motions between the individual structures up to the limiting situation of fluxional behaviour [27b], or to elaborate the criteria testing the attainment of inter-isomer equilibria in observations [27c].

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