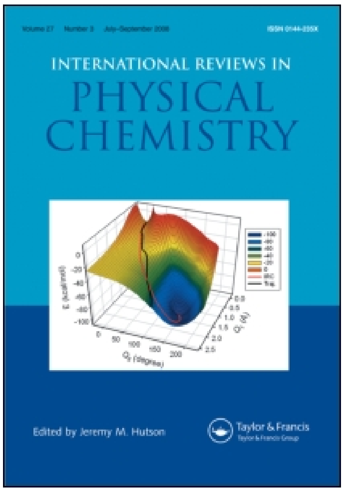

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Equilibrium isomeric mixtures: potential energy hypersurfaces as the origin of the overall thermodynamics and kinetics

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Equilibrium isomeric mixtures: potential energy hypersurfaces as the origin of the overall thermodynamics and kinetics†

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Potential energy hypersurfaces are now most frequently represented by the location and characterization of their stationary (critical) points. Model studies have demonstrated that hundreds of stationary points can be present on some potential hypersurfaces of chemical interest. Any structure-dependent observed quantity can thus have a convolutional nature, being composed of contributions of relevant stationary points. This article focuses on equilibrium and rate processes; it deals with situations in which component of an equilibrium is represented by a group of several different local energy minima and/or when several different saddle points serve as activated complexes in a single rate process. Particular attention is paid to the case where two or more isomeric structures of comparable stability coexist, the isomers being indistinguishable under observational conditions. Evaluations of overall, convolutional standard and/or activation reaction terms based on the stationary-point hypersurface representation are discussed with emphasis on theory–observation comparisons, experiment interpretation, and prediction of behaviour.

1. Introduction

More that 150 years after the introduction of the notion of isomerism into chemistry by Berzelius (1830) the concept is still a subject of strong experimental (Mislow and Bickart 1976/77, Eliel 1976/77, Ōki 1984) as well as theoretical (Minkin *et al.* 1981, Slanina 1981 b, Mislow and Siegel 1984, Knop *et al.* 1985) interest. New types of isomerism are being recognized (for example, phase isomerism described by Cozzi *et al.* (1981) and Kawada and Iwamura (1981)), and even very simple compounds (e.g., ClO_2 (Benson and Buss 1957), N_2O_4 (Bolduan and Jodl 1982), H_2SO_4 (Kuczkowski *et al.* 1981), or glycine (Suenram and Lovas 1980)) are observed (or supposed) to exhibit isomerism. The process of discovery is assisted considerably by theoretical approaches well equipped at present for the indication of new isomers (again, examples of very simple, even triatomic, systems are available, for example O_3 (Wright 1973, Karlström *et al.* 1978), Si_3 (Grev and Schaefer 1985, Raghavachari 1985), or SiOH (Frenking and Schaefer 1985)). The discovery of a number of small, chemically bizarre isomers has recently resulted from studies of interstellar space species (for a review, see Green and Herbst (1979)). The development of the concept of isomerism has always been intimately connected with the understanding of the concept of molecular structure. (Incidentally, the classical concept of molecular structure has recently been the subject of a vigorous reanalysis (for surveys see Woolley (1976, 1978, 1986), Wilson (1979),

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† Dedicated to the late Professor Massimo Simonetta.

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Claverie and Diner (1980), Bader and Nguyen-Dang (1982)). As with molecular structure (Benfey 1957, Berry 1960 a, Muetterties 1965), it has been accepted that a definition of isomerism cannot be given (Mislow and Bickart 1976/77, Eliel 1976/77) in the absence of defined experimental criteria of the conditions and methods of observation. Thus, isomers are now considered (Rouvray 1974, Dugundji *et al.* 1978) as individual chemical species that display at least some differing physicochemical properties and are stable for periods of time long in comparison with the times during which measurements of their properties are performed.

The prevailing theoretical approach to chemical phenomena has been that of the potential energy hypersurface. The concept of the potential hypersurface is a consequence of the separation of the nuclear and electronic motions as suggested by Born and Oppenheimer (1927) (cf. also Özkan and Goodman (1979), Murrell *et al.* (1984)). The phenomenon of isomerism can be interpreted straightforwardly in terms of the potential hypersurface as the occurrence of more than one local minimum within one hypersurface (or set of hypersurfaces). The feasibility of transitions between minima (as well as the possibility of distinguishing individual structures in an observation) is determined by the heights of the barriers separating the adjacent minima and by the temperature (and possibly also by quantum-mechanical tunnelling and transition probabilities between hypersurfaces). However, the hypersurface approach, as well as the related quantum-chemical picture of isomerism, are simplifications. Therefore there has been an interest in a rigorous quantum-mechanical interpretation of isomerism (Berry 1960 b, Woolley 1976, Aronowitz 1978, Harris and Stodolsky 1978, 1981). In terms of total molecular wavefunctions Aronowitz (1978) has shown that uniqueness of isomers is only an approximation but it is, nevertheless, well established provided that the change in wavefunction with time is sufficiently slow. Concisely speaking, the more closely we examine isomers, the less unique these species become. However, the distinguishability can sometimes be a good approximation because of the relative isolation of isomer domains. Thus, the quantum-mechanical interpretation of isomerism can include both the possibility of distinct isomers as well as the representation of a species by several stability regions.

Theoretical studies in isomer chemistry are overwhelmingly carried out through the stationary point representation of hypersurfaces to avoid the tedious, or even practically impossible, generation of a whole hypersurface. The stationary (or critical) points are the hypersurface points with zero first energy derivatives with respect to nuclear coordinates (McIver and Komornicki 1972, Mezey 1977, Murrell 1977, Ermer 1976, Ōsawa and Musso 1982, 1983, Masamune *et al.* 1986, Pople *et al.* 1979, Camp *et al.* 1983, Fox *et al.* 1983, Schaefer and Yamaguchi 1986). Among these points, local minima and transition states (or activated complexes) with either no, or just one, imaginary frequency within the theoretically generated harmonic vibrational spectrum, are especially important in the interpretation of chemical reactivity. The computational treatment for the stationary points location and characterization is essentially the same for both quantum-chemical (McIver and Komornicki 1972, Mezey 1977, Murrell 1977) and molecular-mechanical (Ermer 1976, Ōsawa and Musso 1982, 1983, Masamune *et al.* 1986) energy functions, analytical energy derivatives being used widely, even at the most sophisticated level of *ab initio* correlated wavefunctions (Pople *et al.* 1979, Camp *et al.* 1983, Fox *et al.* 1983, Schaefer and Yamaguchi 1986).

A systematic investigation of a potential energy hypersurface often reveals several different local energy minima, all representing the same species in an experiment and/or several different transition states corresponding to the activated complexes (ACs) in a single rate process. Potential energy criteria can sometimes prove† that it is only one structure which plays an important role (the useful notion of the *stabilomer*, i.e. the most stable isomeric structure, has been introduced in that connection by Godleski *et al.* (1981)). However, it may also happen that two or more isomeric structures of comparable stability coexist and, moreover, are indistinguishable under some conditions of observation. In this case it has proved useful to consider various structure-dependent observed parameters as average values resulting from contributions of all the isomers in play. In particular, the evaluation of reaction characteristics (both standard and activation values) of processes whose components have been shown by theoretical analysis to be mixtures of isomers, has recently been studied for several classes of processes of current interest. The results have turned out to be important for evaluation, interpretation, or prediction of behaviour of the isomeric mixtures and for a proper comparison of the theoretical and observed reaction characteristics. These topics are the subject of the present review.

2. A simple, two-state model

Let us start with a very simple system with just two energy levels separated by an energy difference, *e*, which can serve as a model of two highly similar isomers. When passing from the more stable isomer alone to an equilibrium mixture of both isomers, the enthalpy, entropy and heat capacity increase as shown in figure 1 in terms of reduced quantities. With increasing temperature, enthalpy and entropy terms increase up to the value $\frac{1}{2}e$ and $R \ln 2$, respectively, in comparison with the more stable isomer (as usual, R denotes the gas constant). The temperature dependence of the difference

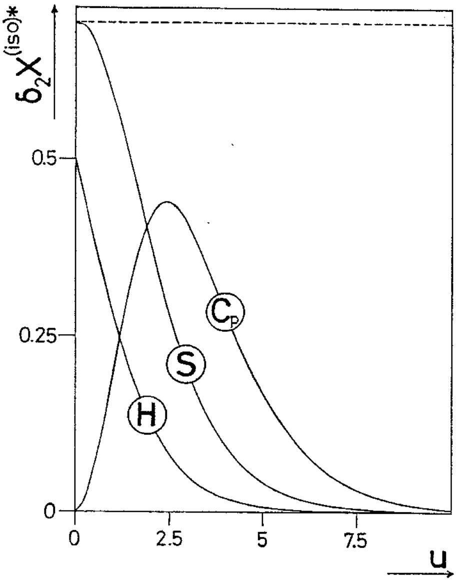

Figure 1. Reduced, dimensionless isomerism contributions (Slanina 1986 b), $\delta_2 X^{(iso)*}$, to enthalpy, entropy, and heat capacity ($X = H, S, C_p$) evaluated within a simple model consisting of two states separated by energy e; $u = e/(kT)$; --- position of the ln 2 term.

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† Surprisingly enough, simple, rigorous rules can be derived for the potential-energy ordering of some isomers, as proved quite recently by Mezey (1984, 1985).

between the heat capacity† of the isomeric mixture and that of the more stable isomer shows a course with a maximum (Slanina 1986 b).

In contrast to the simple model, in a real situation more than two isomers can be involved, each having its own specific set of energy levels. Moreover, the isomer stability order can be interchanged by a change in temperature. Consequently, the picture of isomeric interplay can be more complex.

3. Equilibrium of *n* isomers

In view of a large number of (mostly) computational discoveries of isomerism in a component of a chemical reaction, it has become useful to consider (Slanina 1975 a) a new class of generalized gas-phase chemical equilibria, i.e. equilibria in which, most generally, each component is a mixture of isomers. While such complex equilibria certainly exist, in contemporary practice a special case, isomerism in only one reaction component, is frequently met (Lielmezs and Bondi 1965, Heatley 1972, Frankiss 1974, Slanina 1975 b, 1979 a, 1981 a, Chen *et al.* 1975, Compton 1977, Hald and Rasmussen 1978, Hollenstein *et al.* 1980, Blandamer *et al.* 1982, Durig and Compton 1980, Durig *et al.* 1980 a, b, Durig and Gerson 1981, Compton and Murphy 1981, Alberty 1983, 1985). Experimental observations of processes of these types usually yield overall, effective, multi-configuration thermodynamic values to which each isomer contributes; theoretical treatment, however, leads primarily to partial, single-configuration terms.

The gap between these two approaches can be overcome by a weighting of the partial terms. Let us consider a reaction just one component of which is an equilibrium mixture of, say, n isomers. Consequently, there are n different alternatives of the reaction, each being connected with just one of these isomers. These individual alternatives are connected with partial standard molar changes of enthalpy ΔH_i°, entropy ΔS_i°, and heat capacity $\Delta C_{p,i}^\circ$, $(i=1,2,\ldots,n)$. Let us further denote the changes ΔH_i° at the absolute zero of temperature as $\Delta H_{0,i}^\circ$. With q_i being the partition function of the ith isomer, the weight factor, w_i, of the isomer, characterizing the relative content of the isomer in the equilibrium mixture, is expressed by (Slanina 1979 a):

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

The weight factors (1) are of a rigorous nature‡ within the Boltzmann statistics under the assumption of independence of motions of individual structures. However, because of limitations on the amount of information on the hypersurface stationary points that is usually available, the rigid-rotor and harmonic-oscillator approaches are used for the evaluation of the partition functions q_i.

The weighting treatment for a quantity ΔX° can be simply sketched by a general relation:

$$\Delta X^\circ=f(\Delta X_i^\circ, w_i, T) \tag{2}$$

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† Here, we arbitrarily refer to the heat capacity at constant pressure; however, there would be no difference in principle with the constant-volume regime.

‡ Frequently, an approximation 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:

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

thus ignoring effects of rotational-vibrational motion.

It is illustrated (Slanina 1984 b, c) for $X = C_p$ in equations (3) and (4)

$$\Delta C_p^\circ = \Delta C_{p,w}^\circ + \frac{1}{RT^2}\left\{\sum_{i=1}^{n} w_i(\Delta H_i^\circ)^2 - \left[\sum_{i=1}^{n} w_i \Delta H_i^\circ\right]^2\right\} \tag{3}$$

$$\Delta C_{p,w}^\circ = \sum_{i=1}^{n} w_i \Delta C_{p,i}^\circ \tag{4}$$

Partial and overall changes (2) are related to a particular, given reaction. However, the isomerism contribution terms, $\delta X_1^{(\mathrm{iso})}$, can be introduced (equation (5)) as the value to be added to the partial term ΔX_1°,

$$\Delta X^\circ = \Delta X_1^\circ + \delta X_1^{(\mathrm{iso})} \tag{5}$$

in order to obtain the overall change ΔX° (the index 1 is usually assigned to the most stable structure). Clearly, these isomerism contributions (under the assumption of ideal behaviour) do depend neither on the other reactants, nor on the standard state choice. They are thus characteristics of the isomeric group and are widely transferable.

It may seem that the equilibrium isomeric mixture is no more than a special case of a general gaseous mixture. However, there is a difference in principle. The equilibrium in the former case is established through chemical reactions (isomerizations). Consequently, the weight factors or mole fractions of isomers in equilibrium are not random numbers but well defined quantities (equation (1)). Moreover, the weight factors are temperature dependent as is clearly seen in, for example, equation (3). A mixture of non-reacting components would obey a simple equation of the type (4). The second term in equation (3) arises just as a consequence of the fact that w_i of the individual reacting components is temperature dependent. However, equation (3) is valid only under equilibrium conditions. From the observational point of view, two limiting situations can be distinguished for an isomeric mixture. If the time scale (Benfey 1957, Berry 1960 a, b, Muetterties 1965, Woolley 1976, Harris and Stodolsky 1978, 1981) of the technique used for C_p° measurement is sufficiently long compared to the time scale of the w_i changes with temperature, then the overall term from equation (3) is measured. If, on the contrary, the technique used in the heat capacity measurement did not leave enough time for the w_i to change with respect to the temperature change, then the heat capacity of the mixture would effectively be measured at fixed, frozen w_i values, leading to the overall term from equation (4) only. However, a deeper discussion of equilibrium re-establishment requires a knowledge of the kinetic factors in each particular case.

4. Chemical equilibria

Let us try to illustrate isomeric interplay with the formation of carbon atom aggregates C_n(g). The aggregates have been studied at several theoretical levels (Pitzer and Clementi 1959, Slanina and Zahradník 1977, Whiteside *et al.* 1981 a, b, Kroto *et al.* 1985, Haymet 1985, Klein *et al.* 1986). The MINDO/2 calculations (Slanina and Zahradník 1977) demonstrated the existence of at least two isomeric structures for $n = 4$–7 (figure 2). The weighting for the formation of three isomers of C_4 above graphite is surveyed in table 1. In the TS scale the isomerism contribution to entropy exceeds the value of 8 kJ/mol; the contribution to enthalpy is about 6 kJ/mol. Thus, inclusion of the isomerism contribution is important for a correct comparison of MINDO/2 results with the observed thermodynamic data.

The existence of vinyl alcohol (ethenol) has been confirmed both experimentally by Saito (1976) and theoretically by Rodwell *et al.* (1980). The evaluation (Slanina 1984 b)

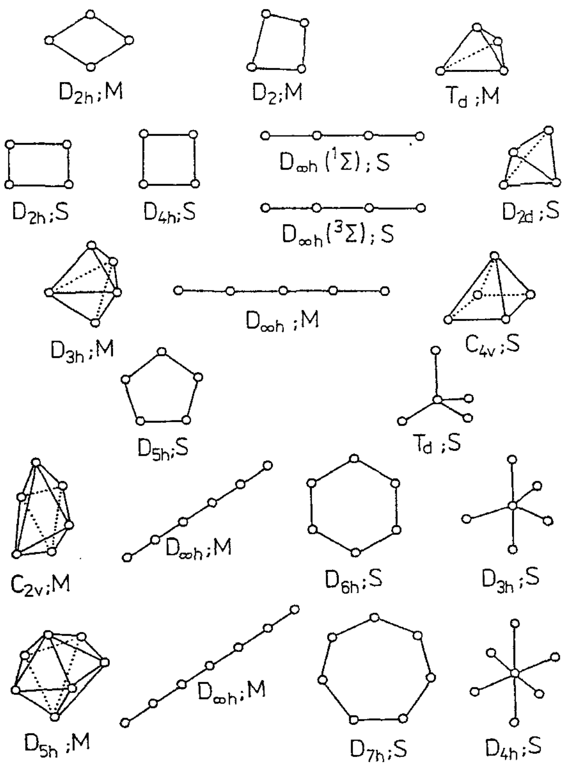

Figure 2. Schemes of stationary points found (Slanina and Zahradník 1977) on the MINDO/2 hypersurfaces of C_n. M, minimum; S, saddle point.

Table 1. Partial and overall MINDO/2 standard enthalpy ΔH° and entropy ΔS° terms of $4C(s) \rightleftharpoons C_4(g)$ equilibrium at 2400 K.

Process†	ΔH° (kJ/mol)	ΔS° (J/K/mol)
$4C(s) \rightleftharpoons C_4(g; D_{2h})$	904·1	210·2
$4C(s) \rightleftharpoons C_4(g; D_2)$	952·2	213·6
$4C(s) \rightleftharpoons C_4(g; T_d)$	1301·5	205·5
$4C(s) \rightleftharpoons C_4$(g; Overall)	909·9	213·6

† See figure 2; according to Slanina and Zahradník (1977).

of the weight factor of ethenol in equilibrium mixture with ethanal has shown that at a temperature of 1500 K the ethenol content should not exceed 5%. Nevertheless even this small population contributes significantly to the equilibrium thermodynamics of the gas-phase C_2H_4O system (table 2). The largest effects were observed with the isomerism contribution to the heat capacity term. A distinct difference between the results from equations (3) and (4) is noteworthy.

A third example concerns the formation (Lischka and Köhler 1982, 1983, Köhler and Lischka 1982, Slanina 1986 a) of $Si_2H_4(g)$. Recent theoretical studies of the hypersurfaces of this system carried out by Lischka and Köhler (1982) proved the existence of four local minima each with different electronic wavefunction symmetry

Table 2. Isomerism contributions† $\delta H^{(\mathrm{iso})}_{\mathrm{CH_3CHO}}$, $\delta S^{(\mathrm{iso})}_{\mathrm{CH_3CHO}}$, $\delta C^{(\mathrm{iso})}_{p,\mathrm{CH_3CHO}}$ to the standard molar enthalpy, entropy, and heat capacity terms of gas-phase ethanal with respect to the presence of ethenol at 1500 K.

$\delta H^{(\mathrm{iso})}_{\mathrm{CH_3CHO}}$ (kJ/mol)	$\delta S^{(\mathrm{iso})}_{\mathrm{CH_3CHO}}$ (J/K/mol)	$\delta C^{(\mathrm{iso})}_{p,\mathrm{CH_3CHO}}$‡ (J/K/mol)	$\delta C^{(\mathrm{iso})}_{p,w,\mathrm{CH_3CHO}}$§ (J/K/mol)
1·629	1·453	3·263	0·122

† According to Slanina (1984 b, c).
‡ Equation (3).
§ Equation (4).

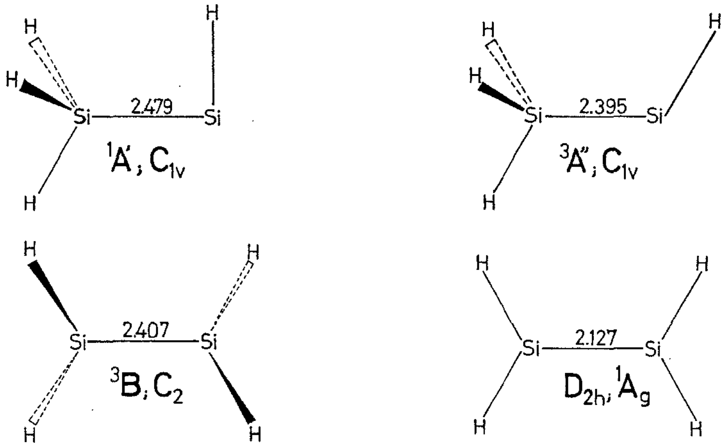

Figure 3. Schemes of minima found on *ab initio* SCF hypersurfaces (Lischka and Köhler 1982) of Si_2H_4; Si–Si bond lengths in 10^{-10} m.

(figure 3). In the *ab initio* SCF potential energy scale, silylsilylene $^1A'$ turns out to be the most stable structure (Lischka and Köhler 1982). However, the evaluation (Slanina 1986 a) of the weight factor (1) shows that actually this isomer is predominant only at low temperatures (figure 4). Already around a temperature of 460 K the remaining three structures form more than 10% of the equilibrium mixture, and above about 1580 K the $^1A'$ isomer represents less than 50% thereof. A further rise in temperature finally causes an interchange in the relative stabilities of the isomers $^1A'$ and $^3A''$. These pronounced changes in the weight factors are reflected in the significant values of the isomerism contributions (figure 5). For example, at the highest temperature considered the isomerism contribution to the TS term is greater than 35 kJ/mol. The Si_2H_4 system permits the investigation of the convergence properties of the weighting treatment with increasing *n* (table 3). It is apparent that at moderate and higher temperatures the contribution of the other triplet state is important, too, and that only the ^1A_g structure has a marginal role. Finally, electron correlation will not be negligible (Köhler and Lischka 1982), and further refinements of the Si_2H_4 weights can be expected.

5. Formation of atomic and molecular clusters

The application of the weighting treatment is especially desirable in situations where at least two isomers of comparable stability coexist and can be studied under

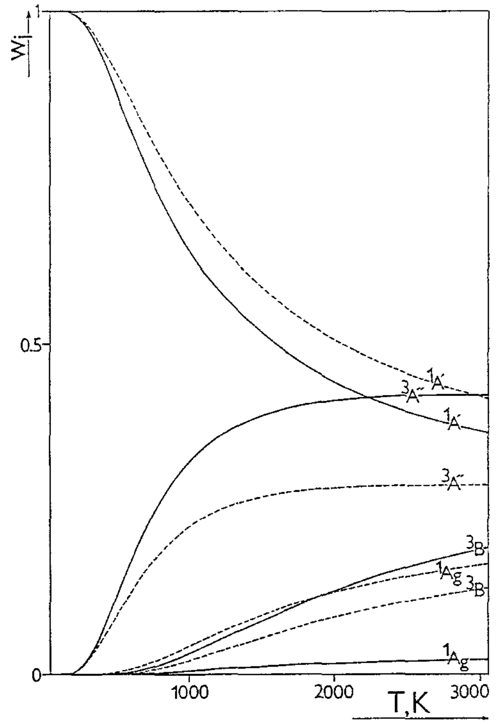

Figure 4. Temperature dependences (Slanina 1986a) of weights w_i of the $Si_2H_4(g)$ isomers (see figure 3); --- simple Boltzmann factors.

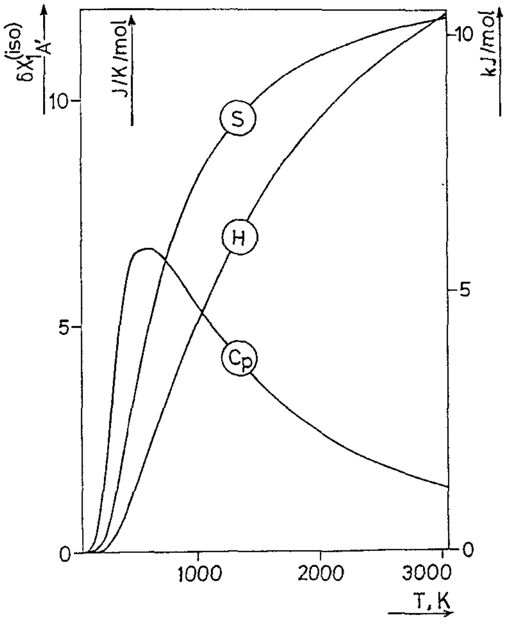

Figure 5. Temperature dependences of isomerism contributions, $\delta X^{(iso)}_{^1A'}$ $(X = H, S, C_p)$, to enthalpy, entropy, and heat capacity of $Si_2H_4(g)$ related to the $^1A'$ isomer (see figure 3).

Table 3. Isomerism contributions† to the heat capacity of Si_2H_4(g) at 1000 K.

Isomeric set‡	$\delta C^{(iso)}_{p,{}^1A'}$§ (J/K/mol)	$\delta C^{(iso)}_{p,w,{}^1A'}$¶ (J/K/mol)
$^1A'$; $^3A''$	2·861	−0·197
$^1A'$; $^3A''$; ^3B	5·213	−0·176
$^1A'$; $^3A''$; ^3B; ^1A_g	5·461	−0·178

† Related to the $^1A'$ isomer‡.
‡ See figure 3.
§ Equation (3).
¶ Equation (4).

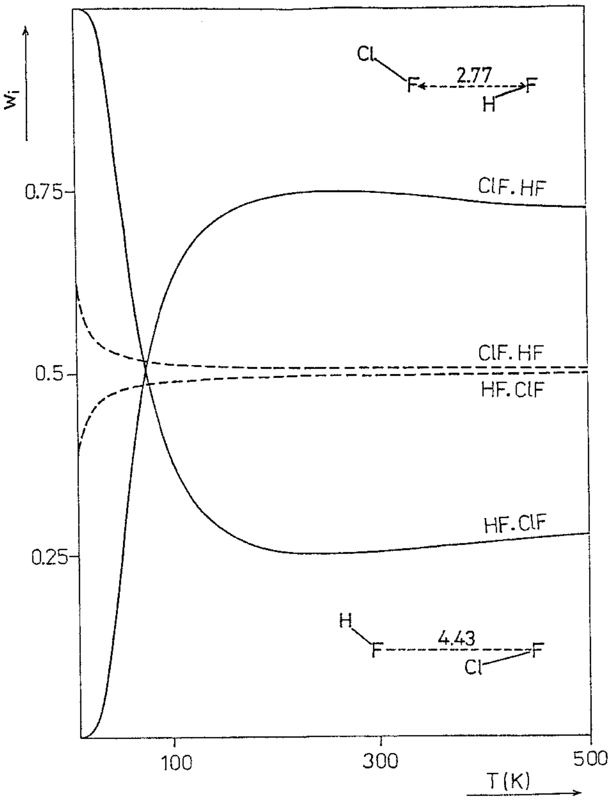

Figure 6. Temperature dependences (Slanina 1982 b) of weights w_i within the HF–ClF(g) isomeric system; --- simple Boltzmann factors (cf. figure 3).

experimental conditions ensuring thermodynamic equilibrium though not allowing us to discern the isomers in the observation. These conditions are generally well fulfilled for isomeric clusters of atoms and/or molecules. The recently studied system HF–ClF serves as an example (figure 6). The weight factors (Slanina 1981 c, 1982 b, c, 1983 c) of two different local energy minima found by Umeyama *et al.* (1977) exhibit an interesting interchange of relative stability explaining why only the non-hydrogen-bonded structure was observed in the experiment (Janda *et al.* 1976, Novick *et al.* 1976).

Incidentally, the simple Boltzmann factors work even worse here than was the case with Si_2H_4 (cf. figure 3).

Another nice example of a two-isomer system represents $(CO_2)_2$ composed (Brigot *et al.* 1977, 1982) of so-called parallel (P) and T forms (figure 7). Whereas in the region of the lowest temperatures the structure P is entirely dominant, at about 230 K the equilibrium mixture becomes equimolar. At the normal sublimation point of $CO_2(s)$ the composition of the equilibrium gas phase has been predicted to be 59% P and 41% T (Slanina 1983 d, 1985). The thermodynamics of this system formation is presented in figure 8. The isomerism corrections at some temperatures represent a substantial contribution to the overall terms. With the overall ΔC_p° term there exists a well defined maximum in the low-temperature region. Such a maximum is a general attribute of isomeric systems and its occurrence could, under carefully selected conditions, be used for an experimental proof of isomerism.

It is obvious that the magnitude of the isomerism corrections will, in general, increase with increasing magnitude of the cluster system. However, knowledge in this respect is rather limited. Table 4 presents the interplay (Slanina 1979 b) of three isomeric water tetramers described in the EPEN potential by Owicki *et al.* (1975) at a temperature slightly above the normal boiling point.

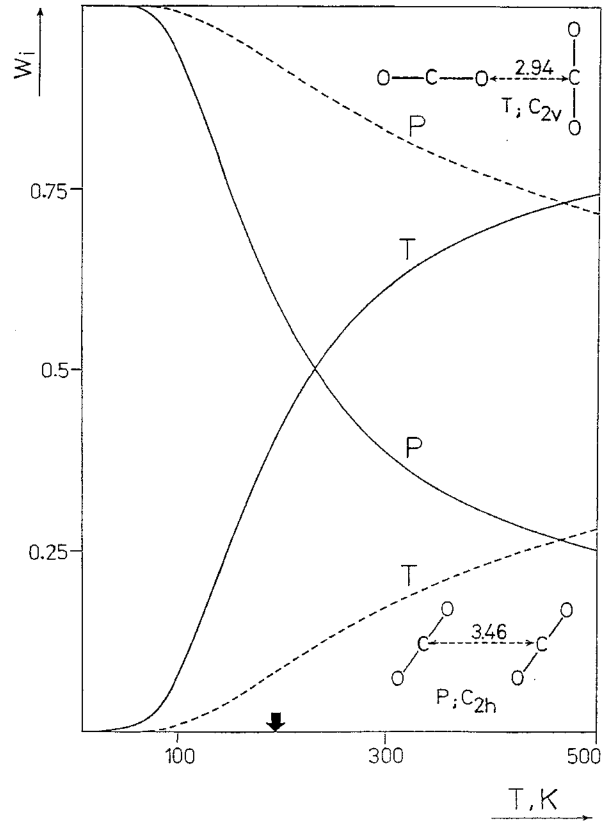

Figure 7. Temperature dependences of weights (Slanina 1983 d) w_i within the $(CO_2)_2(g)$ isomeric system, --- simple Boltzmann factors; the arrow indicates the normal sublimation point of CO_2 (cf. figure 3).

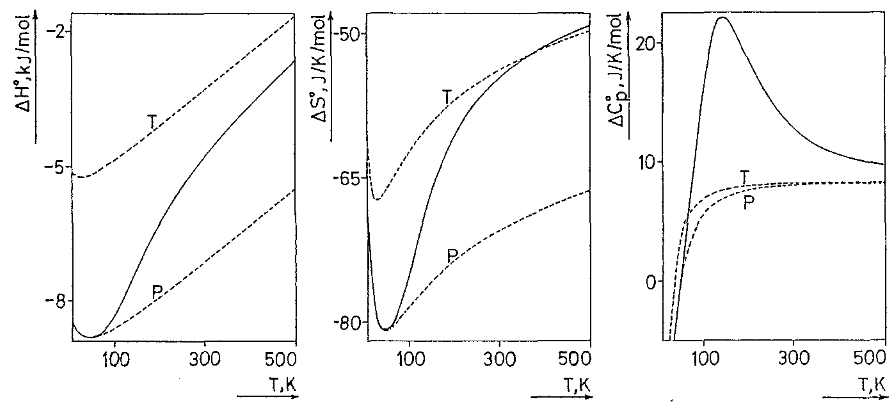

Figure 8. Temperature dependences (Slanina 1983 d) of the standard enthalpy, entropy, and heat capacity changes for the partial (see figure 7) and overall (——) dimerizations of $CO_2(g)$.

Table 4. Illustration of the weighting (Slanina 1979 b) on enthalpy and entropy terms of formation of water tetramers $(H_2O)_4(g)$ at $T = 400$ K.

w_i†	ΔH_i° (kJ/mol)	ΔH°‡ (kJ/mol)	ΔS_i° (J/K/mol)	ΔS°‡ (J/K/mol)
0·624	−77·36	−74·69	−335	−324
0·297	−73·01		−330	
0·078	−59·79		−308	

† Pyramid, S_4 cyclic, and asymmetric cyclic $(H_2O)_4$ (Owicki *et al.* 1975).
‡ The overall term.

However, to obtain information on the isomerism of large clusters, quantum-chemical methods have to be replaced by very simple phenomenological potentials (Burton 1972, 1973, McGinty 1972, Slanina 1975 c, 1977 b, 1981 d, Bauer and Frurip 1977, Hoare and Pal 1971, Kaelberer *et al.* 1976, Kaelberer and Etters 1977, Etters and Kaelberer 1977, Hoare 1979, Natanson *et al.* 1983, Berry *et al.* 1984 a, b). Figure 9 surveys a portion of the total of 988 isomers found by Hoare (1979) for 13 particles governed by the Lennard-Jones potential. Similarly, Burton (1972) estimated for 49-atom clusters that inclusion of the configurational effects may lead to an increase in the cluster concentration by up to three orders of magnitude. It is apparent that the rather common belief in the possibility of replacing multi-configuration thermodynamics by sole partial terms derived from the deepest potential minimum is not justified in such situations.

Let us mention finally that results obtained for gas-phase clusters are also valid for the isomerism of clusters used as models in theoretical studies of heterogeneous catalysis and sorption. In the literature (Slanina 1982 a, 1983 b, f, 1984 d, e) examples are available of a consistent treatment of the latter isomerism.

6. Activated-complex isomerism

Computational studies of hypersurfaces have recently indicated the possible role of the isomerism of a reaction component in rate processes. An example is the isomerism

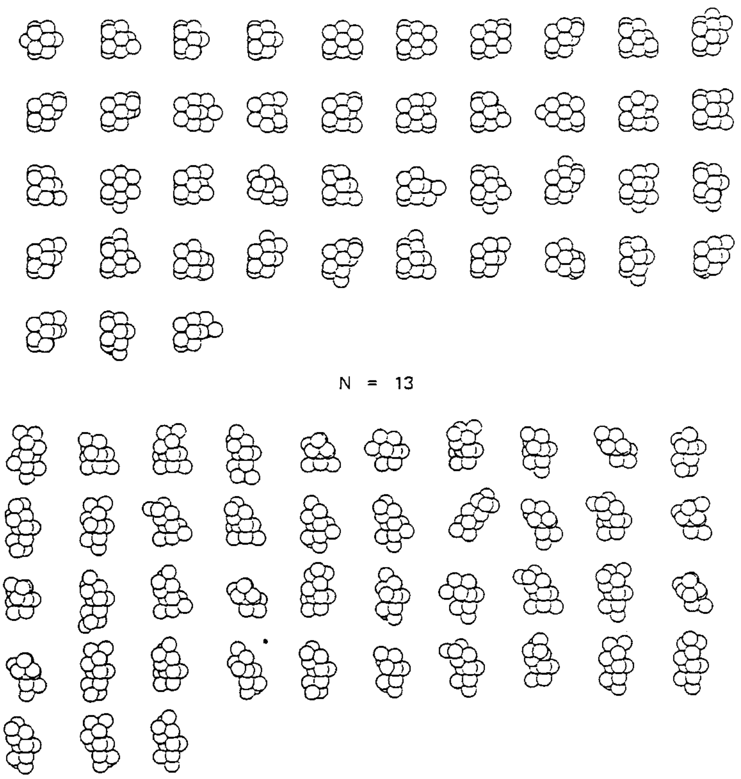

Figure 9. 86 isomers from the total of 988 Lennard-Jones clusters (Hoare 1979) of $N=13$ particles.

of reactants or products in the sense of the Curtin (1954)–Hammett (1970) principle. Another interesting case is that of isomerism in the activated complex (AC) itself. Two different types can be distinguished, either parallel or sequential isomerism, depending on whether the isomeric ACs act on different, parallel pathways or simultaneously on a common pathway between reactants and products.

The equilibrium hypothesis embedded in the principles of the AC theory allows a reduction (Slanina 1977 c) of the parallel isomerism treatment to a straightforward application of the above results for equilibria. For example, according to the MINDO/2 study by Komornicki and McIver (1973) the chair–boat inversion of cyclohexane is realized through two different parallel ACs of C_s and C_2 symmetry. There are (Slanina 1977 c) quite pronounced differences between the overall entropy term and any of the partial activation entropy terms for this interconversion (table 5). Another rather common example of the parallel AC isomerism is the *cis–trans* isomerization around a $-N=N-$ bond which can proceed either via inversion or rotation mechanisms; figure 10 presents the kinetics (Slanina 1977 a, 1978) of *cis–trans* isomerization of $N_2F_2(g)$. Two parallel ACs of C_s and C_1 symmetries are in play and, again, the entropy term is more influenced by the isomerism. Incidentally, with $n^{\neq}$ parallel ACs the overall activation entropy can exceed the highest partial entropy term by $R \ln n^{\neq}$.

The sequential AC isomerism represents a more complex problem; its simplest case involves a single local minimum separating two activated complexes lying on a

Table 5. Partial† and overall‡ activation enthalpies and entropies of cyclohexane isomerization§ $C_6H_{12}(g; D_{3d}) \rightarrow C_6H_{12}(g; D_2)$ at 298 K.

Activation process	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (J/K/mol)
C_s	26·36	25·02
C_2	26·78	28·62
Overall	26·60	32·75

† Komornicki and McIver (1973).
‡ Slanina (1977 c).
§ i.e., the chair–boat interconversion.

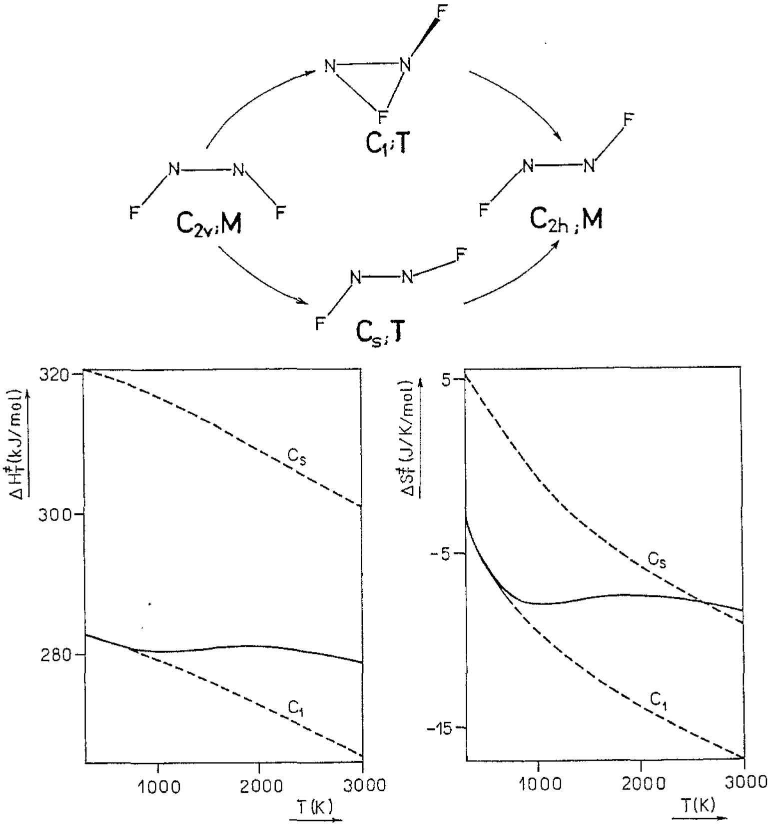

Figure 10. Temperature dependences (Slanina 1978) of activation enthalpy and entropy changes for the partial (through C_s or C_1 ACs) and for the overall (——) kinetics of the *cis–trans* isomerization of $N_2F_2(g)$. M, minimum; T, transition state.

common path from the reactants to the products. The kinetic consequences of this type of isomerism have recently been illustrated (Slanina 1982 d, 1983 a, e, g, 1984 a) with the Cope rearrangement of 1,5-hexadiene. According to MINDO results (Komornicki and McIver 1976, Dewar *et al.* 1977), the rearrangement proceeds via a cyclic intermediate and two cyclic ACs as well.† In contrast to the weighting of parallel AC contributions,

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† However, an intermediate existence has not been proved in more recent *ab initio* MC SCF calculations by Osamura *et al.* (1984).

the overall activation terms with the sequential AC isomerism are time-dependent (Slanina 1982 d, 1983 a, e, g, 1984 a), and this time dependence can be very strong. The theory for just one intermediate has been developed along two lines—the practical approach (Slanina 1982 d, 1983 a, e, g, 1984 d), and the more sophisticated form of a unified statistical theory (Miller 1976, Pollak and Pechukas 1980, Chesnavich *et al.* 1981, Garrett *et al.* 1981). The findings in this simplest case indicate that a whole series of unstable, rapidly interconverting, hardly distinguishable intermediates could manifest their presence by a remarkable time behaviour of the measured overall rate characteristics.

7. Concluding remarks

The phenomenon of reaction component isomerism can be considered to be a rather general feature of more complex chemical processes. However, this isomerism has so far been identified (or even consistently treated) only rather exceptionally in theoretical studies. It may be a result of the fact that, at present, quantum-chemical studies deal with relatively small systems and that such isomerism is frequently not assumed *a priori*, so that the search is limited to a single structure. Existing examples of complete investigations indicate convincingly that the simulation of multi-isomer reaction characteristics by those corresponding to a single structure should no longer be generally considered as acceptable. The phenomenon represents a possible field for cooperation and complementarity between theory and experiment. With the theoretical approach, however, several points require further development, for example a better description of the rotational-vibrational motion of isomers (Shin 1977, Le Roy 1979, Tennyson and van der Avoird 1982, 1984, Bernstein and Wormhoudt 1984), the problem of the coupling of motions between individual isomers including non-rigid, fluxional behaviour (Berry 1979, 1980 a, b, Berry *et al.* 1983) in some isomeric systems, or the question of attaining equilibrium conditions in real systems (Andresen *et al.* 1984). Through such advances an 'infinite-time limit' in the description in terms of whole potential hypersurfaces or even of total molecular wavefunctions can be approached more closely.

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