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TEMPERATURE ISOMERIC INTERPLAY IN THE 2-PYRIDONE–2-HYDROXYPYRIDINE SYSTEM: THERMODYNAMICALLY CONSISTENT TREATMENT *

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ABSTRACT

The tautomeric system of 2-pyridone (P2) and 2-hydroxypyridine (HP2) is described by partition functions supplied with molecular parameters from recent advanced computations. In contrast to other isomeric systems studied within the approach, the simple Boltzmann factors represent here a reasonable approximation to isomeric relative populations derived from thermodynamically consistent (i.e., including rotational–vibrational motions if relevant) treatment. At moderate temperatures the HP2 structure clearly prevails; however, in the high temperature limit the P2 species also becomes significant. Its presence is manifested in the isomeric enhancement of heat capacity, which at ≈ 640 K reaches its maximum value of 3.1 $J\ K^{-1}\ mol^{-1}$. The relationship to interpretation or simulation of molecular spectra is discussed.

INTRODUCTION

Tautomeric equilibria are systems of great importance in organic and biological chemistry. The tautomerism of 2-pyridone (P2) and 2-hydroxypyridine (HP2) represents an interesting system studied intensively [1] by both experimental and theoretical means. A very recent study [2] complemented previous treatments [3–7] with an advanced evaluation (first-order correlation orbitals [8–11] and the coupled-cluster method at the CCSD + T(CCSD) level [12]) of the system energetics and, moreover, supplied harmonic vibrational frequencies for both species. In that study the P2–HP2 relative stabilities were evaluated [2] in terms of the simple Boltzmann

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factors. However, it was pointed out recently [13–15] for various isomeric systems that the latter factors (in spite of their rather frequent application; cf., e.g., Refs. 16–19) can be fairly poor approximation of the relative stabilities, as they do not reflect contributions from rotational–vibrational motions. Thus, the present report deals with the stability problem within a thermodynamically consistent scheme.

THE SYSTEM AND ITS COMPUTATIONAL TREATMENT

The optimum geometry of both species was found [2] to be planar, without any other additional symmetry elements. The HP2 species is, in terms of potential energy E, stabilized over the P2 species by ≈ 11.8 kJ mol^{-1}, while in terms of the ground-state energy (i.e., the standard enthalpy at absolute zero temperature, H_0°) the stabilization increases to ≈ 14.5 kJ mol^{-1}. Following the standard practice, the harmonic vibrational frequencies were scaled down in order to compensate for their computational overestimation. Although the latter, scaled, set is more reliable in this study, both scaled and the original (non-scaled) sets will be considered.

Relative stabilities in an equilibrium isomeric mixture are characterized by the mole fractions w_i of the individual isomers. In terms of the standard enthalpy changes (related to a common reference level, for example to the same set of dissociation products) at the absolute zero temperature, $\Delta H_{0,i}^\circ$, and the isomeric partition functions, q_i, the mole fractions are given [20–22] as follows

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

where n stands for the number of isomers (it can be proved [21] that the reference level is actually irrelevant, being cancelled exactly). Equation (1) was primarily designed for gas-phase conditions; however, it can (owing to cancellations between its numerator and denominator) be applied also to other environments, supposing the partition functions are adjusted accordingly. The weight factors (1) are principally different from the simple Boltzmann, configurational or steric factors [16–19]

$$w_i' = \frac{\exp[-\Delta E_i/(RT)]}{\sum_{j=1}^{n} \exp[-\Delta E_j/(RT)]} \tag{2}$$

the difference being manifested, for example, in the fact that the simple factors w_i' can never cross one another in spite of the well established possibility [14] of isomeric stability interchanges with changing temperature.

It is convenient to consider two well defined limiting situations: isolated individual isomeric species or their equilibrium isomeric mixture, and thus two categories of quantities (most generally, those quantities can be of any nature; however, we shall primarily discuss thermodynamic terms). With the individual (pure) isomers one can well consider the standard partial terms ΔX_i°. However, when dealing with the isomeric mixture, the standard overall terms ΔX_T°, in which all the isomers contribute accordingly, are to be employed. (In fact, the equilibrium isomeric mixture can be considered as one chemical pseudo-species.) Finally, it is convenient to consider a third type quantity too, viz. the isomerism contributions $\delta X_1^{(\mathrm{iso})}$ to thermodynamic terms

$$\delta X_1^{(\mathrm{iso})} = \Delta X_T^\circ - \Delta X_1^\circ \tag{3}$$

The latter terms are free of the contributions which are common to all the isomers, and hence the terms represent a useful tool for evaluation of isomeric interplay effects. As the values of $\delta X_1^{(\mathrm{iso})}$ generally depend on the choice of the reference isomer (labelled by $i = 1$) it is customary for the most stable species (in the low temperature region) to be chosen as the reference structure. Three terms will be considered in connection with eqn. (3): enthalpy H, entropy S, and heat capacity at constant pressure C_p. With the last term an interesting situation is encountered, as it can functionally be split [22] into two parts, viz. the isofractional ($\delta C_{p,w,1}^{(\mathrm{iso})}$, referring to the situation with temperature-independent terms w_i) and the relaxation ones (the latter reflecting the contribution to heat capacity owing to temperature changes of composition; cf. also Ref. 23).

RESULTS AND DISCUSSION

Figure 1 represents the course of w_i and w_i' terms evaluated within the scaled-frequency set in a broad temperature interval. In contrast to several other isomeric systems studied recently [14,15,22] the agreement of both types of terms is quite good (although at higher temperatures the HP2 species is slightly more stable than predicted by the simple Boltzmann factors). In other words, the contributions of rotational–vibrational motions to partition functions are sufficiently similar for both isomers in question. Table 1 demonstrates that cancellation in eqn. (1) results, too, in quite close values from the scaled and non-scaled approach. Nevertheless, the inclusion of rotational–vibrational contributions can be considered as significant when evaluating relative populations for more precise simulations of molecular spectra of our particular isomeric mixture at higher temperatures. For a general system, the use of the w_i terms instead of w_i' ones can be a necessity if a stability interchange is revealed at the w_i level of treatment.

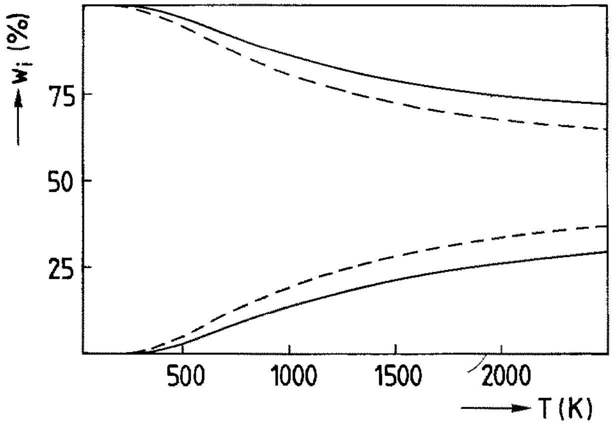

Fig. 1. Temperature evolution of the thermodynamically consistent mole fractions w_i (———) and the simple Boltzmann factors w_i' (— — —) of the components of the P2–HP2 isomeric system evaluated within the scaled vibration-frequency approach; the upper and lower pair of curves represent the HP2 and P2 isomer, respectively.

Figure 2 shows the course of the isomerism contributions $\delta X_1^{(\mathrm{iso})}$ to thermodynamics of the P2–HP2 system in the temperature interval from Fig. 1 evaluated in the scaled-frequency set [i.e., the isomerism contribution to the system enthalpy $\delta H_1^{(\mathrm{iso})}$, entropy $\delta S_1^{(\mathrm{iso})}$, and heat capacity $\delta C_{p,1}^{(\mathrm{iso})}$ related to the HP2 species as well as to the reference structure]. It is evident that at higher temperatures, in spite of a still relatively low population of the P2 species, the isomerism contributions are significant for a precise evaluation of the overall thermodynamic terms. As usual [14,15], a particularly interesting situation can be seen for the isomerism contribution to heat capacity. As the isofractional contribution is quite close to zero throughout

TABLE 1

The mole fractions [a] w_{HP2} and w'_{HP2} of the HP2 species in its equilibrium mixture with the P2 isomer at selected temperatures T

T (K)	w_{HP2} (%)		w'_{HP2} (%)
	Scaled [b]	Non-scaled [b]	
100	100.0	100.0	100.0
298.15	99.7	99.7	99.1
500	96.9	97.1	94.4
640 [c]	93.8	94.0	90.1
1000	85.9	86.1	80.5

[a] I.e., either the thermodynamically consistent terms w_i or the simple Boltzmann factors w_i'; clearly enough, $w_{\mathrm{HP2}} + w_{\mathrm{P2}} = w'_{\mathrm{HP2}} + w'_{\mathrm{P2}} = 100$.

[b] Non-scaled and scaled refer to the original and scaled set of vibrational frequencies [2], respectively.

[c] Temperature of the maximum in the $\delta C_{p,1}^{(\mathrm{iso})}$ term in the scaled approach; see Table 2.

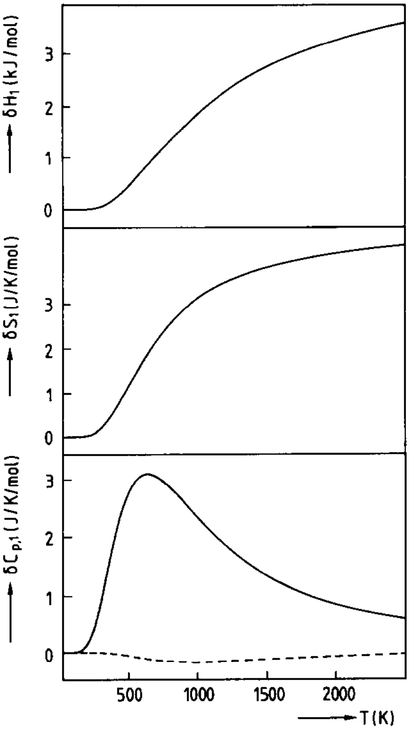

Fig. 2. Temperature evolution of the isomerism contributions (related to the HP2 species as the reference structure) $\delta X_1^{(\mathrm{iso})}$ to thermodynamic functions of the P2–HP2 isomeric system [$X = H$, S or C_p for enthalpy (top part), entropy (middle part), or heat capacity at constant pressure (the bottom part), respectively] evaluated within the scaled vibration-frequency approach. The dashed curve in the bottom part represents the isofractional contribution $\delta C_{p,w,1}^{(\mathrm{iso})}$.

the whole temperature interval studied, the total isomerism contribution is in fact determined by the relaxation part. The $\delta C_{p,1}^{(\mathrm{iso})}$ isomerism contribution exhibits a course with a maximum. Table 2 specifies the position of the

TABLE 2

Values of the isomerism contributions [a] $\delta X_1^{(\mathrm{iso})}$ to thermodynamic functions [b] of the P2–HP2 isomeric system at the temperature of the $\delta C_{p,1}^{(\mathrm{iso})}$ maximum

Approach [c]	T (K)	$\delta H_1^{(\mathrm{iso})}$	$\delta S_1^{(\mathrm{iso})}$	$\delta C_{p,1}^{(\mathrm{iso})}$
Scaled	640	0.849	1.86	3.09
Non-scaled	649	0.871	1.88	3.14

[a] Related to the HP2 species as the reference structure [i.e., the $\delta X_1^{(\mathrm{iso})}$ actually means $\delta X_{\mathrm{HP2}}^{(\mathrm{iso})}$].

[b] $X = H$, S or C_p for enthalpy (kJ mol^{-1}), entropy (J K^{-1} mol^{-1}) or heat capacity at constant pressure (J K^{-1} mol^{-1}), respectively.

[c] Non-scaled and scaled refer to the original and scaled set of vibrational frequencies [2], respectively (cf. Table 1).

maximum as well as the values of the other isomerism contributions at the temperature for both scaled and non-scaled sets, showing that the values from both data sources are quite close. The behaviour of isomeric enhancement of heat capacity found for the P2–HP2 pair agrees qualitatively with results reported for other isomeric systems; however, in its magnitude the enhancement is smaller at least by one order than most pronounced isomerism manifestations in the C_p term found so far [24].

There are several more general questions concerning the interplay of partial and overall terms. Depending on the nature of a particular experimental technique the former as well as the latter terms can be obtained. It is even possible to obtain both the terms within one technique using a suitably changed experimental organization. Thermodynamic characteristics are natural quantities to be considered as a subject of isomeric interplay; however, other quantities can also be considered from this point of view, for example rate parameters or spectra. The last mentioned case implies, on computational side, generation [2,25] of the spectra of the pure isomers as well as a superposition of them, i.e. their weighted average. Under conditions of thermodynamic inter-isomeric equilibrium our w_i weights represent a proper tool for the weighting [in some special situations when some degrees of freedom are preset (e.g., a nozzle expansion) the partition functions have to be modified accordingly]. Structural distinguishability is another major problem on the experimental side (limiting the fluxional behaviour [14,26]) in addition to the task of deciding the degree to which inter-isomer equilibrium has been established. In the fluxional limit, the theory should transfer from (isolated) minima to a pseudo- or super-species overlying all of them.

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NOTE ADDED IN PROOF

After acceptance of the article further related material was published [27].

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