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The effects of temperature on the relative stabilities of five complexes of 4-hydroxypyridine and water

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Abstract

The relative stabilities of five isomeric complexes of 4-hydroxypyridine with water have been computed. Description of the isomers is based on ab initio SCF calculation, with energetics corrected by the second-order perturbation treatment. The relative stabilities are evaluated in terms of partition functions constructed from the calculated dimeric parameters. A possibility of relative stability interchange is pointed out in the higher temperature region. However, the overall heat capacity of the system can be enhanced by the isomeric interplay by 7%, at most.

INTRODUCTION

Tautomeric systems containing hydroxypyridine(s) have frequently been studied owing to their importance in organic chemistry and biochemistry [1–11]. The formation of various molecular complexes in the tautomeric systems is entirely expected. The complexes can be recognized in molecular spectra, and even their isomerism can be evidenced. A very natural example of such complexes are complexes with water, primarily heterodimers with a water molecule.

This study deals with the heterodimers between 4-hydroxypyridine and water, and evaluates the temperature dependences of their relative stabilities.

DIMERS OF 4-HYDROXYPYRIDINE AND WATER

The search for energy minima was carried out by ab initio SCF treatment in 6-31++G** basis set; numerical details are presented elsewhere [12]. Harmonic vibrational analysis followed the geometry optimization, serving

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TABLE 1

The relative MP2/6-31++G** potential energy ΔE and ground-state energy $\Delta H_0^{\ominus}$ terms[a] for the dimers of 4-hydroxypyridine with water

Dimer[b]	Symmetry	ΔE/kJ mol^{-1}	$\Delta H_0^{\ominus}$/kJ mol^{-1}
HOH	C_s	0.0	0.0
HN	C_s	6.76	6.67
HO	C_s	18.42	16.75
OO	C_s	19.79	20.89
ON	C_{2v}	22.96	22.41

[a] See ref. 12 for computational details. [b] See Fig. 1.

a useful test of the stationary point type. Finally, the energetics was refined for the SCF optimal structures by means of the second-order perturbation treatment (Table 1).

The geometry optimization revealed five different isomeric complexes; in three of them, the hydroxy (**H**) form is present, while in the remaining two, the oxo (**O**) form is present (Fig. 1). The ground-state structure is represented by a non-planar species with a hydrogen bond between the –OH group and the oxygen atom of water (**HOH**). The second lowest structure is planar and possesses a hydrogen bond between the N atom of 4-hydroxypyridine and water (**HN**), being followed by another planar hydroxy form, however with the OH group involved in the hydrogen bond (**HO**). Complexes with the oxo form are somewhat higher in energy. The planar structure with the hydrogen bond towards the O atom (**OO**) possesses lower energy than the last, non-planar species with the NH moiety participating in the hydrogen bond with water (**ON**).

THE RELATIVE STABILITY COMPUTATION

Although a real reaction mixture can be quite complex, we can still deal with a selected equilibrium subsystem, a mixture of the five isomeric complexes. For the heterodimer relative stabilities themselves, we can avoid consideration of all the other species. Under reasonably acceptable conditions, the ratios of the heterodimer concentrations are independent of the concentrations of all other possible species.

The relative populations w_i of n different isomers in their equilibrium mixture can be expressed [13] in molecular terms in the form

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

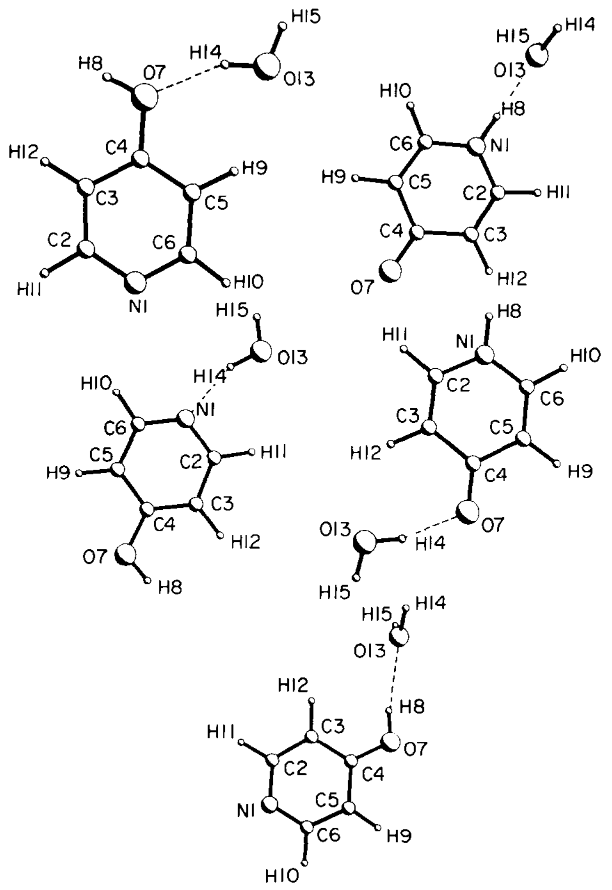

Fig. 1. Minimum energy structures of the complexes of 4-hydroxypyridine with water: **HOH** (bottom), **HN** (middle, left), **OO** (middle, right), **HO** (top, left), and **ON** (top, right).

where q_i denote partition functions of the isomers and $\Delta H^{\ominus}_{0,i}$ their ground-state energies (potential energy terms ΔE_i corrected for zero-point vibrations). A simplified treatment is offered by means of the so-called simple Boltzmann configurational or steric factors:

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

based on the sole potential energy differences. However, the factors (2) cannot exhibit a relative-stability temperature interchange.

The partition functions are constructed in the usual approach of the rigid-rotor and harmonic-oscillator approximation, as no higher description of the motions is technically possible at present (through eqn. (1) itself permits any vibrational-rotational correction).

TABLE 2

The simple Boltzmann factors[a] w_i' for the dimers of 4-hydroxypyridine with water at selected temperatures T

T/K	w_i' in %				
	HOH	**HN**	**HO**	**OO**	**ON**
100	99.97	0.03	2×10^{-8}	5×10^{-9}	1×10^{-10}
200	98.31	1.69	2×10^{-3}	7×10^{-4}	1×10^{-4}
250	96.25	3.73	0.01	7×10^{-3}	2×10^{-3}
300	93.66	6.24	0.06	0.03	9×10^{-3}
350	90.79	8.91	0.16	0.10	0.03
400	87.82	11.52	0.35	0.23	0.09
500	81.88	16.12	0.98	0.70	0.33
688[b]	71.61	21.98	2.86	2.25	1.29
750	68.61	23.22	3.58	2.87	1.73
1000	58.53	25.97	6.39	5.41	3.70

[a] $w_1' + w_2' + w_3' + w_4' + w_5' = 100\%$. [b] Temperature of equimolarity of the **HOH** and **HN** species in the thermodynamically consistent weight factors w_i, see Table 3.

RESULTS AND DISCUSSION

Table 2 presents the temperature evolution of the simple Boltzmann factors w_i' for the five-membered isomeric set. The **HOH** species remains the most stable throughout, though the **HN** structure approaches it in a high-temperature limit. The Boltzmann factors for the other three structures remain rather low in the studied temperature interval. However, without evaluating the thermodynamically consistent terms w_i, one cannot say how good or bad approximations of the latter quantities the simple w_i' terms are in a particular situation.

In contrast to the simple Boltzmann terms, the proper weight factors w_i, eqn. (1), exhibit a relative-stability interchange, see Table 3: 688 K, the second local minimum, **HN**, becomes more populated than the supposed global minimum **HOH**. The increase of w_i with temperature for two of the remaining three structures is also more pronounced than indicated by the simple Boltzmann factors. Although the temperature of the **HOH/HN** relative-stability interchange is rather high, the **HN** structure already exhibits a significant population at room temperature.

The presence of several isomeric forms brings [13] some changes to the thermodynamic functions of the overall equilibrium isomeric mixture (in comparison with the partial values connected with the most stable species). The heat capacity term is known to be substantially influenced by the phenomenon. Table 4 studies this case. The isomerism contribution to the heat capacity exhibits the usual temperature maximum, although its height

TABLE 3

The weight factors[a] w_i for the dimers of 4-hydroxypyridine with water at selected temperatures T

T/K	w_i in %				
	HOH	**HN**	**HO**	**OO**	**ON**
100	99.89	0.11	4×10^{-7}	2×10^{-9}	2×10^{-10}
200	94.07	5.92	0.01	6×10^{-4}	2×10^{-4}
250	87.78	12.12	0.09	7×10^{-3}	2×10^{-3}
300	80.87	18.77	0.31	0.03	0.01
350	74.16	24.91	0.78	0.10	0.05
400	68.01	30.13	1.52	0.22	0.13
500	57.58	37.60	3.72	0.65	0.45
688[b]	43.67	43.67	9.15	1.91	1.60
750	40.30	44.29	10.97	2.36	2.08
1000	30.69	43.87	17.32	4.05	4.07

[a] $w_1 + w_2 + w_3 + w_4 + w_5 = 100\%$. [b] Temperature of equimolarity of the **HOH** and **HN** species.

is a rather modest 10.7 J mol^{-1} K^{-1}. The highest relative isomeric enhancement reaches about 7.2%. The enhancement is significant even below room temperature.

Our evaluation of the relative dimeric populations represents one of the first attempts of its kind and hence, various improvements can be suggested. The treatment should be refined by the inclusion of anharmonicity effects. Also, the relative energetics can be further improved by the inclusion of higher-order contributions. The treatment is based on an equilibrium assumption which should be satisfied by real systems. The computational scheme deals with a gas-phase situation but one can expect a cancellation in eqn. (1) concerning possible solvent effects, at least to some degree. Hence,

TABLE 4

Specification of two distinguished points[a] in the isomeric enhancement of the heat capacity of the dimers of 4-hydroxypyridine with water

Type[a]	T/K	$\delta C_{p,1}$[b]/ J mol^{-1} K^{-1}	$\delta C_{p,1}/C_p^\ominus$ in %	$C_p^\ominus$/ J mol^{-1} K^{-1}
$\delta C_{p,1}$ maximum	506	10.66	5.28	200.0
$\frac{\delta C_{p,1}}{C_p^\ominus}$ maximum	248	9.00	7.17	125.4

[a] Maximum in the isomerism contribution to the heat capacity $\delta C_{p,1}$, or maximum in the relative enhancement $\delta C_{p,1}/C_p^\ominus$ of the $C_p^\ominus$ term. [b] Isomerism contribution to heat capacity related to the species most stable in the low-temperature region, i.e. to the **HOH** isomer.

the computational predictions of the relative stabilities should, even at this level of sophistication, be directly applicable to experimental conditions.

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