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A computational evaluation of the CO_2–HCN associating system thermodynamics: considerable low temperature isomerism manifestations [α,β]

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Abstract

The CO_2–HCN system is studied as a superspecies composed of the linear OCO·HCN and T-shaped $O_2C\cdot NCH$ structures. The temperature interplay of both structures is treated in terms of partition functions supplied with parameters from recent computational data. The linear species (though lower in potential energy) can even become less stable than the T-shaped structure in the region of low or medium temperatures. The relative-stability interplay is also observed in the temperature behaviour of isomerism contributions to thermodynamic functions. The isomerism contribution to heat capacity exhibits a temperature maximum at very low temperatures with maximum height less than or equal to 7 J K^{-1} mol^{-1}. The temperature maximum is not conserved in the corresponding overall terms, although some irregularities also exist in their temperature course.

INTRODUCTION

Cluster isomerism has become the subject [1–10] of experimental studies (or even an essential factor in some of them), although primary interest in the phenomenon originally started from the theoretical side [11–15]. From research activities employing both means it has become clear that isomerism represents a rather frequent feature of gas-phase molecular complexes, with significant consequences for the interpretation and understanding of experimental observations. However, various types of experimental arrangements can differ substantially in the degree to which they reach conditions of inter-isomer equilibrium, i.e. the conditions which are most convenient for computational description. This communication adopts the equilibrium con-

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[α] Dedicated to professor Georg Zundel on the occasion of his 60th birthday.

[β] Part LXIV in the series Multi-Molecular Clusters and their Isomerism (see ref. 1 for Part LXIII).

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ditions and deals with the thermodynamic consequences of isomerism in the molecular complex [16–18] CO_2–HCN, thus continuing the approach of our recent report [19].

THE CO_2-HCN ASSOCIATING SYSTEM

There are two significant structures [18] representing the CO_2–HCN associating system (i.e. two local energy minima): the linear OCO · HCN and the T-shaped O_2C · NCH species. In the linear isomer, both monomeric units are connected by the O–H hydrogen bond. The T-shaped complex is formed by an interaction between the C and N atoms of the monomers. Altogether four energy approximations were applied [18] to geometry-optimization treatment, viz. the self-consistent field (SCF) treatments in the split-valence STO/4-31G (coded here as 4-31G) [20], the double-zeta D95 (D95) [21], and the extended STO/6-31G**(6-31G**) [22] basis sets, in the last case also combined with the MP2 perturbation treatment (MP2) [23]. However, the sensitivity of geometrical parameters (in contrast to potential energy) to a particular choice of approximation is small. Thus, for our purposes, just one set of geometry parameters was selected, namely that originating from the most sophisticated approximation, i.e. MP2. The optimized structure of the T-shaped isomer was slightly adapted in order to conform to the supposed [16,17] C_{2v} point group of symmetry (the small computational distortion [18] of the symmetry is most probably a calculational artefact).

In terms of the four energy approximations, the linear OCO · HCN isomer is always located lower than the T-shaped O_2C · NCH structure, although in the D95 treatment the two structures are nearly isoenergetic (see

TABLE 1

Survey of the energetics [18] of formation of the OCO·HCN (linear) and O_2C·NCH (T-shaped) complexes

Treatment	Dimerization to OCO·HCN		Dimerization to O_2C·NCH	
	ΔE_t [a]	$\Delta H^\circ_{0,t}$ [b]	ΔE_t [a]	$\Delta H^\circ_{0,t}$ [b]
4-31G	−13.56	−10.46	−12.66	−10.39
D95	−14.45	−11.54	−14.44	−11.92
6-31G**	−8.83	−6.69	−7.37	−5.82
MP2:4-31G	−11.03	−7.93	−9.89	−7.62
MP2:D95	−11.03	−8.12	−9.89	−7.37
MP2:6-31G**	−11.03	−8.89	−9.89	−8.35

[a] Potential energy change (kJ mol^{-1}).

[b] Ground state energy change, i.e. the enthalpy change at absolute zero temperature (kJ mol^{-1}).

Table 1 for a survey). In Table 1 the potential energy changes ΔE_i connected with the associations

$$CO_2(g) + HCN(g) = OCO \cdot HCN(g) \tag{1}$$

$$CO_2(g) + HCN(g) = O_2C \cdot NCH(g) \tag{2}$$

are presented, i.e. the monomers are taken as a common reference level.

In addition to geometry and energetics, harmonic vibrational frequencies are also available [18] in the above-mentioned three SCF approaches (although not in the correlated MP2 treatment). Hence the harmonic vibrational contributions to the zero-point energy yielding the ground state energy changes (or the standard enthalpy changes at zero temperature) for reactions (1) and (2), $\Delta H^\circ_{0,i}$, can be considered. In order to evaluate such terms also in the MP2 treatment, three additional mixed approaches to the $\Delta H^\circ_{0,i}$ terms are considered, viz. by combining the MP2 potential energy with each of the SCF vibrational sets (coded as MP2 : 4-31G, MP2 : D95 and MP2 : 6-31G**). With one exception (D95) the linear structure OCO · HCN remains the lower one in the $\Delta H^\circ_{0,i}$ scale (Table 1). Nevertheless, no final conclusion on the relative stabilities of the species can be made before an adequate consideration [14,15] of the temperature excitations of rotational–vibrational motions of the individual structures.

COMPUTATIONAL

The rotational–vibrational motions can be considered through the isomeric partition functions q_i. It holds [14,15] for the mole fractions in an n-membered isomeric equilibrium set (i.e. inter-isomeric equilibrium is required) that

$$w_i = \frac{q_i \exp[-\Delta H^\circ_{0,i}/(RT)]}{\sum\limits_{j=1}^{n} q_j \exp[-\Delta H^\circ_{0,j}/(RT)]} \tag{3}$$

where R is the gas constant and T the temperature. If we completely neglect the rotational–vibrational motions (i.e. $q_i = 1$, and the $\Delta H^\circ_{0,i}$ terms are replaced by ΔE_i ones), the simple Boltzmann factors w_i' result. The rotational–vibrational partition functions q_i are for our purposes constructed in the usual approximation [14] of rigid rotor and harmonic oscillator (RRHO).

It has become customary [24,25] for isomeric systems to consider two limiting situations with the standard thermodynamic terms X° (in this study, for enthalpy, $X = H$; for entropy, $X = S$, and for heat capacity at constant pressure, $X = C_p$). Those are either standard partial terms ΔX_i° for isolated individual isomeric species or the overall terms ΔX°_T belonging to the equilibrium isomeric mixture. Moreover, a third type of quantity is also considered, viz. the isomerism contributions δX_1 to the thermodynamic terms related to the structure labelled 1 as a reference species (the structure 1 is usually selected as the species most stable in the low temperature region):

$$\delta X_1 = \Delta X_T^\circ - \Delta X_1^\circ \tag{4}$$

Detailed formulae are available in refs. 24 and 25. An interesting situation is encountered with the heat capacity term, as two different quantities can be relevant to the term. The full $\delta C_{p,1}$ term, considering the effects of changes in composition upon a temperature change accordingly, is called [24,25] the relaxation isomerism contribution to heat capacity. However, an auxiliary term $\delta C_{p,w,1}$ is also employed [24,25], being based on an assumption of temperature independent w_i mole fractions and thus called the isofractional isomerism contribution to heat capacity. (The latter term becomes rigorous for a mixture of species with no interconversion possible, i.e. a mixture of ideal gases in the very original sense with the w_i factors in fact arbitrary but fixed.)

RESULTS AND DISCUSSION

The calculations were carried out side by side for the six treatments listed in Table 1. Figure 1 presents the temperature evolution of the mole fractions w_i. The striking twofold crossing in the 4-31G approach is interesting from the methodological point of view [19]; it is actually the first event of such type observed in a two-component system. Moreover, there is a stability

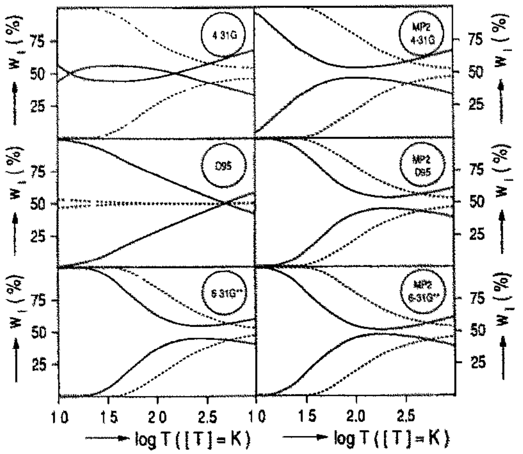

Fig. 1. Temperature dependences of the weight factors w_i (solid lines) and simple Boltzmann factors w_i' (broken lines) for CO_2–HCN isomers. The higher curves in the low temperature region belong to the linear OCO·HCN isomer (with one exception: the w_1 term in the D95 treatment belongs to the T-shaped O_2C·NCH structure); the particular treatment is indicated in the circle (cf. Table 1).

TABLE 2

Specification of distinguishable temperature points [a] of the equilibrium interplay of the OCO·HCN (linear) and O_2C·NCH (T-shaped) complexes

Treatment	Type of point [a]	T (K)	w_1 [b] (%)	$\delta C_{p,1}$ [c] (J K^{-1} mol^{-1})
4-31G	$\delta C_{p,1}$ maximum	4.4	83.5	6.99
4-31G	Equimolarity	13.5	50.0	−1.30
4-31G	$\delta C_{p,1}$ maximum	36.7	43.8	−1.28
4-31G	Equimolarity	157	50.0	−1.74
D95	$\delta C_{p,1}$ maximum	30.4	90.8	2.18
D95	Equimolarity	472	50.0	2.43
6-31G**	$\delta C_{p,1}$ maximum	37.6	90.0	5.58
6-31G**	Closest approach	281	55.2	−1.71
MP2:4-31G	$\delta C_{p,1}$ maximum	12.4	91.4	5.79
MP2:4-31G	Closest approach	111	53.9	−1.73
MP2:D95	$\delta C_{p,1}$ maximum	29.3	90.8	5.75
MP2:D95	Closest approach	226	54.7	−1.75
MP2:6-31G**	$\delta C_{p,1}$ maximum	24.5	88.7	5.83
MP2:6-31G**	Closest approach	195	51.0	−1.91

[a] Point of equimolarity, point of the closest mutual approach of the two-species relative stabilities, or the maximum in isomerism contribution to heat capacity $\delta C_{p,1}$ [c].

[b] The mole fraction of the linear OCO·HCN isomer (in the D95 treatment, the T-shaped structure) in its equilibrium mixture with the T-shaped O_2C·NCH species (in the D95 treatment, the linear structure).

[c] Isomerism contribution to heat capacity related to the species more stable in the very low temperature region (the T-shaped isomer in the D95 treatment, otherwise the linear structure).

crossing also in the D95 approximation. In the remaining four cases another type of distinguishable temperature point can be observed, namely a point of closest mutual approach of both w_i curves, i.e. the point of the highest degree of coexistence of both isomers (for a precise specification of both types of distinguishable temperature points, see Table 2). Incidentally, the simple Boltzmann factors w_i' represent rather poor estimates of the w_i terms.

Particular attention has recently been paid [24,25] to the isomerism contribution to heat capacity and its extremum course. Figure 2 deals with the $\delta C_{p,1}$ and $\delta C_{p,w,1}$ terms in the CO_2–HCN system. In all six treatments considered the $\delta C_{p,1}$ term exhibits a temperature course with a maximum (in the 4-31G treatment two local maxima are actually present). It should be noted that the isofractional isomerism contribution $\delta C_{p,w,1}$ possesses substantially lower values in the regions of the relaxational-term maximum. Table 2 again gives a precise specification of the distinguishable temperature-point positions. Clearly enough, all the temperature maxima in the isomerism contribution to heat capacity appear at quite low temperatures, namely, all are located below (or even substantially below) a temperature

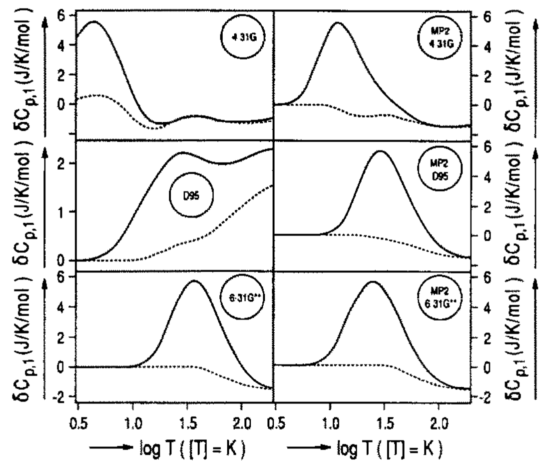

Fig. 2. Temperature dependences of the isomerism contributions $\delta C_{p,1}$ (solid lines) related to the species more stable in the low temperature region (i.e. with the exception of the D95 treatment, the linear OCO·HCN isomer; cf. Fig. 1); the broken lines indicate the corresponding isofractional $\delta C_{p,w,1}$ components.

threshold of 40 K. This indicates the reliability of the RRHO model application.

The isomerism contributions to thermodynamic terms are interesting correction quantities; however, they cannot be directly measured. Therefore, Fig. 3 presents temperature dependences of the standard enthalpy, entropy and heat capacity at constant pressure terms for reactions (1) and (2) (i.e. the partial terms ΔX_i^0) as well as the corresponding overall terms $\Delta X_{\mathrm{T}}^{\circ}$ related to the equilibrium isomeric mixture (pseudospecies) CO_2–HCN formation (for illustrative purposes the MP2 : 4-31G treatment was chosen). It is apparent from the plots that in some temperature regions there can be really significant differences between the overall and any of the partial terms. However, the local maximum present in the $\delta C_{p,1}$ term is still not conserved in the overall $\Delta C_{p,\mathrm{T}}^{\circ}$ standard change. In order to extract the monomeric contributions, we can follow the standard heat capacity terms for the dimeric species themselves. Figure 4 compares the standard heat capacity at constant pressure C_p° for the equilibrium CO_2–HCN isomeric mixture and for the sole linear OCO · HCN isomer evaluated in the MP2 : 4-31G approach. Although there are interesting variations in the temperature behaviour of both species, a temperature maximum does not appear. After all, the isomerism contribution $\delta C_{p,1}$ in the CO_2–HCN system is rather modest compared with the highest values so far observed for a cluster system [25].

In this article, plots of logarithmic temperature scales have been used in order to make low temperature features more visible (as most interesting events take place in the system at low temperatures). Thus, some propor-

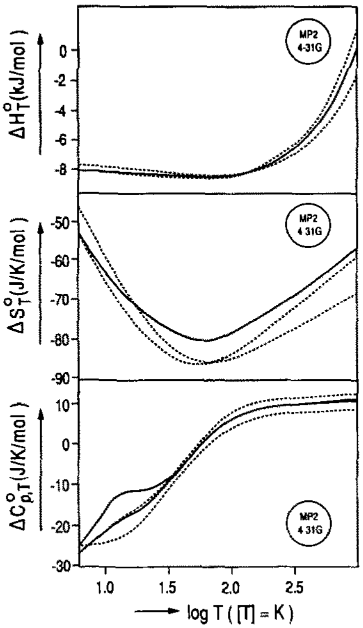

Fig. 3. Temperature dependences of the partial (broken lines) and overall (solid lines) standard enthalpy ΔH_T° (top), entropy ΔS_T° (middle), and heat capacity at constant pressure $\Delta C_{p,T}^\circ$ (bottom) changes for CO_2(g) and HCN(g) associations evaluated in the MP2:4-31G approach; the other solid line with heat capacity dependence represents the isofractional overall term.

tions are changed compared with the usual linear scales. Incidentally, Figs. 3 and 4 recall the problem of the low temperature behaviour of the conventional partition functions [26,27]. For example, the conventionally used terms for translational and rotational contributions to heat capacity do not exhibit the proper limit for vanishing temperature, which is seen also in the plots. Although it is not of particular practical importance, the problem should be paid some attention for conceptual reasons (as was done in the free internal rotation case using the direct summation technique [28]).

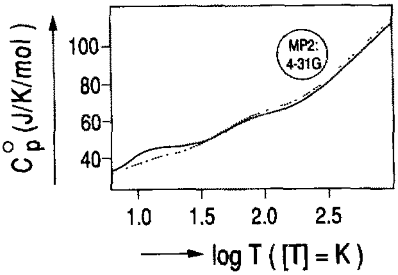

Fig. 4. Temperature dependences of the standard heat capacity at constant pressure C_p° for the equilibrium CO_2–HCN isomeric mixture (the solid line) and for the sole linear OCO·HCN isomer (the broken line) evaluated in the MP2:4-31G approach.

In conclusion, isomeric interplay was proved to be important for the evaluation and understanding of the thermodynamic terms of the CO_2–HCN system. The qualitative conclusion should remain valid also for more sophisticated evaluations of the system parameters and/or partition functions.

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