

Linear versus cyclic (HCN)₃: a computational–thermodynamic study *

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Abstract

The trimer of HCN is treated as an equilibrium mixture of two species, linear and cyclic, using a partition-function treatment supplied with recent computed parameters. The linear isomer, which is favoured in potential energy by about 3 kJ mol^{-1} , is always the prevailing structure. The highest inter-isomeric coexistence degree is reached at about 630 K when the linear form represents 91% of the equilibrium mixture. Isomerism contributions to enthalpy, entropy and heat capacity exhibit an interesting temperature course with a maximum. Several exact thermodynamic inter-relations are demonstrated on the system.

INTRODUCTION

Oligomers of HCN represent a relatively frequently computed system [1–5]. The trimer (HCN)₃ exhibits an interesting structural feature, namely, isomerism; there are two local energy minima, linear and cyclic [1,3,5]. Such a feature is of course important for relating calculations to the available observed (HCN)₃ information [6–8]. Such cluster isomerism of other systems has been the subject of considerable interest, both theoretical and experimental (see, for example, refs. 9–11). Particularly, it has been demonstrated that proper inclusion of rotational–vibrational motions can have substantial thermodynamic consequences. Thus, the present paper deals with the relative-stability problem of the (HCN)₃ isomers within a thermodynamically consistent scheme.

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TABLE 1

Survey of the formation energetics [5] for (HCN)₃ complexes

Association of 3 HCN to	ΔE_i^a (kJ mol ⁻¹)	$\Delta H_{0,i}^0$ ^b (kJ mol ⁻¹)
Linear isomer	-42.3	-34.9
Cyclic isomer	-39.3	-33.2

^a The ACPF potential-energy change [5].^b Ground-state energy state, i.e. the enthalpy change at absolute zero.

THE SYSTEM AND ITS COMPUTATIONAL TREATMENT

The (HCN)₃ system was described [5] in the averaged coupled pair approximation (ACPF) and two local energy minima were found, linear (*C*_{∞v}) and cyclic (*C*_{3h}) structures. The linear species is slightly more stabilised in terms of potential-energy changes upon HCN trimerization ΔE_i (*i* = 1 denotes the linear isomer) over the other species by about 3 kJ mol⁻¹. The difference is even further reduced after addition of the zero-point energy corrections, i.e. after transfer to the ground-state energy (or enthalpy at absolute zero temperature) changes $\Delta H_{0,i}^0$. The system energetics are surveyed in Table 1.

Let us consider an *n*-membered equilibrium isomeric mixture described by the mole fractions *w_i* of the individual isomers. In terms of the enthalpy changes at absolute zero $\Delta H_{0,i}^0$ and the isomeric partition functions *q_i*, the mole fractions are expressed [10–12]

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

The partition functions can be of any nature; however, typically they are constructed in the rigid-rotor and harmonic-oscillator (RRHO) approximation [10]. The RRHO weight factors (eqn. (1)) are principally different from the simple Boltzmann, configurational or steric factors [13–16]

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

in which the rotational–vibrational motions are completely neglected.

If the isomeric relative stabilities are known, the system thermodynamics can be evaluated. It is convenient to consider two well defined, limiting situations: sole, isolated individual isomeric species or their equilibrium mixture. This introduces two categories of thermodynamic term [17–20]. With the individual (pure) isomers the standard partial terms ΔX_i^0 are to be considered. However, when dealing with the isomeric mixture the standard overall terms ΔX_T^0 , in which all the isomers contribute accordingly, are to be

used instead. (Clearly enough, the equilibrium isomeric mixture can be understood as one chemical pseudo-species.) Finally, it is useful to consider also a third type of quantity, namely, the isomerism contributions δX_1 to thermodynamic terms [18,20]

$$\delta X_1 = \Delta X_T^0 - \Delta X_1^0 \quad (3)$$

The latter terms are free of the contributions which are common to all the isomers. The values of δX_1 however generally depend on the choice of the reference isomer (labelled by $i = 1$). Thus, it is customary for the species most stable in the low temperature region to be selected 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 latter term an interesting situation is met as two different terms can be considered [21]. If the w_i factors are treated as temperature independent then the so called isofractional [21] $\delta C_{p,w,1}$ term results. More generally, the relaxation isomerism contribution to heat capacity $\delta C_{p,1}$ respects temperature changes of composition accordingly [21]. Most frequently the isofractional part is nearly negligible in comparison with the full, relaxation term.

RESULTS AND DISCUSSION

Figure 1 presents temperature dependences of the RRHO mole fractions w_i and the simple Boltzmann factors w_i' for both components of the $(\text{HCN})_3$ system. The temperature dependence of the w_i terms is quite moderate while for w_i' factors it is more pronounced. In terms of the RRHO weights w_i the linear species in the whole temperature interval considered prevails over the cyclic one, the content of the former always being higher than 90%. A very

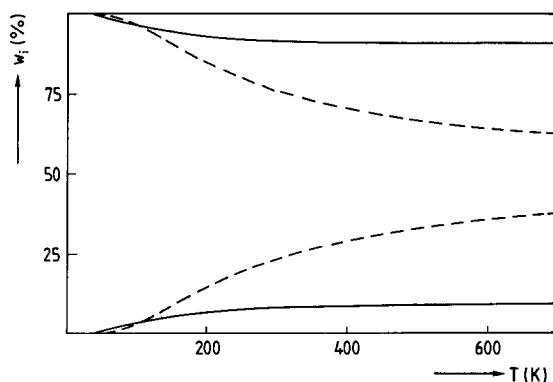


Fig. 1. Temperature evolution of the RRHO mole fractions w_i (solid lines) and the simple Boltzmann factors w_i' (dashed lines) of the components of the linear/cyclic $(\text{HCN})_3$ isomeric system; the upper and lower pair of related curves represent the linear and cyclic isomer, respectively.

TABLE 2

Values of the linear-structure mole fraction ^a w_1 and of the isomerism contributions ^b δX_1 to thermodynamic functions of the linear/cyclic (HCN)₃ isomeric system at some distinguished temperature points

Significance of the point	T (K)	w_1 (%)	δH_1 (kJ mol ⁻¹)	δS_1 (J K ⁻¹ mol ⁻¹)	$\delta C_{p,1}$ (J K ⁻¹ mol ⁻¹)
Min. w_1 ^c	627	91.0	1×10^{-6}	0.785	-0.275
Max. δH_1	218	92.8	0.071	0.945	-5×10^{-6}
Max. δS_1	218	92.8	0.071	0.945	-5×10^{-6}
Max. $\delta C_{p,1}$	68.8	98.3	0.023	0.475	0.767

^a For the cyclic-structure mole fraction in equilibrium with the linear ones $w_2 = 1 - w_1$.

^b $X = H, S$ or C_p for enthalpy, entropy or heat capacity at constant pressure, respectively; the contributions are related to the linear isomer as the reference species.

^c That is, maximum in w_2 ^a.

careful examination of the w_i curves can show that there is in fact a minimum and maximum on the w_1 and w_2 dependency, respectively, both being reached at exactly the same temperature (as follows from differentiation of the equation $w_1 + w_2 = 1$). The particular temperature value is about 627 K and the linear and cyclic species represent about 91% and 9%, respectively, of their equilibrium mixture at the temperature (see Table 2). In this particular temperature point the curves w_1 and w_2 approach one another most closely. It was suggested [22] that such point be described as the point of highest isomeric coexistence. Moreover, an interesting rigorous theorem was proved [22] in this connection. In the point of the highest coexistence the isomerism contribution to enthalpy (vide infra) equals zero.

In Fig. 2 temperature evolution of the isomerism contributions (related to the linear species as the reference structure) δX_1 to thermodynamic functions (enthalpy H , entropy S , and heat capacity C_p) of the linear/cyclic (HCN)₃ isomeric system are given. The values are rather small compared with the highest values reported so far [11,18,20] for other systems. (Incidentally, with the isomerism contribution to enthalpy, its zero value at a non-zero temperature is indicated in Fig. 2 as evidence of the above mentioned rule [22] concerning the highest coexistency point (see Table 2).) However, their temperature dependences exhibit a uniform feature; in all three cases there is a temperature maximum. For the isomerism contribution to heat capacity the isofractional part is (at lower temperatures) a quite negligible component of the full relaxation term. However, the relaxation isomerism contribution itself is still too small to be significantly felt in the overall heat capacity term at any temperature.

Table 2 specifies the distinguished temperature points in the linear/cyclic (HCN)₃ isomeric interplay (the highest coexistence and temperature maxima in the isomerism contributions to thermodynamic functions). There is a striking coincidence in the position of the maximum for isomerism contribu-

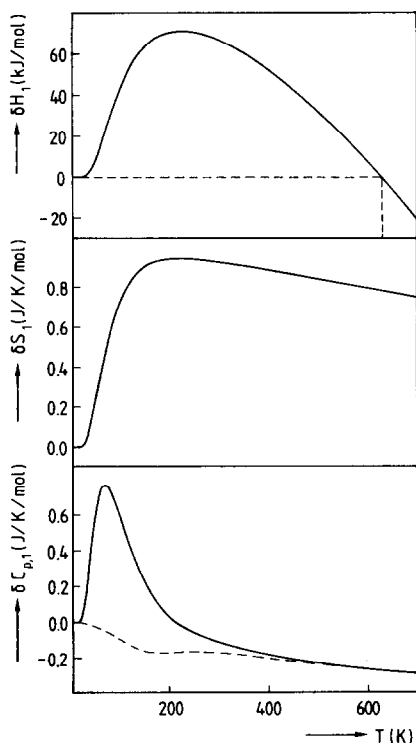


Fig. 2. Temperature evolution of the the isomerism contributions (related to the linear species as the reference structure) δX_1 to thermodynamic functions of the linear/cyclic $(\text{HCN})_3$ isomeric system ($X = H, S$ or C_p for enthalpy (top part), entropy (middle part), or heat capacity at constant pressure (bottom part), respectively); the dashed lines in the top part indicate the maximum-coexistence point while the dashed curve in the bottom part represents the isofractional contribution $\delta C_{p,w,1}$.

tion to enthalpy and entropy. In fact, it is a particular illustration of another rigorous general rule recently proved [23] for isomeric interplay. The rule says that if the isomerism contribution to enthalpy and/or entropy exhibits a temperature extremum then both terms assume it at precisely the same temperature. Moreover, the related $\delta C_{p,1}$ term exactly equals zero at that temperature (the rules follow [23] from differentiation properties of enthalpy and entropy terms). Table 2 and Fig. 2 document the rule validity.

In spite of quite small energy separation between the linear and cyclic isomers of $(\text{HCN})_3$ the linear species prevails throughout. The behaviour is a result of interplay between rotational (moments of inertia, symmetry numbers) and especially vibrational (harmonic vibrational frequencies) parameters of both structures. In particular, very low vibrational frequencies of the linear species are systematically lower than those belonging to the cyclic species. Previous experience suggests [11,18,20] that if the ordering relation were opposite a relative stability interchange could be expected. Finally, the RRHO description of the system motions is an approximation, the use of

which is imposed by computational difficulties. A further improvement of the values reported can be thus expected [24] when an evaluation of corrections to the RRHO model becomes feasible.

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