

## Hetero-trimers of HF and HCN: substantial isomerism effects on thermodynamics <sup>α</sup>

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### Abstract

The 2HF–HCN and HF–2HCN systems are treated as equilibrium isomeric mixtures of three isomeric structures each. The equilibrium is described in terms of partition functions supplied with recent ab initio structural, vibrational and energy data. There are relative stability interchanges present in both systems. The isomeric contribution to the standard heat capacity at constant pressure can form as much as 45% of the term. The relationship to observed characteristics is briefly discussed.

### INTRODUCTION

Recently, two interesting molecular complex systems were described [2] by calculations, namely the 2HF–HCN and HF–2HCN trimeric systems (both are related to the frequently treated [3–8] dimeric system HF–HCN). In this way, the rather limited experimental knowledge [9] was enhanced. The calculations revealed three different local energy minima on the potential energy hypersurface of each system. Such a molecular-complex isomerism has been proved [10–13] in some cases to have substantial consequences for thermodynamics. This study deals with the problem for both hetero-trimeric systems, giving particular attention to the heat capacity term.

### DESCRIPTION OF THE SYSTEMS

This report uses the results [2] obtained in SCF treatment with the D95 basis set [14]. A search for the hypersurface stationary points discovered [2]

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<sup>α</sup> Part LXVII in the series Multi-molecular clusters and their isomerism; for Part LXVI, see ref. 1.

TABLE 1

Survey of the D95 trimerization energetics for the 2HF–HCN and HF–2HCN systems

Process	$\Delta E_i$ <sup>a</sup> (kJ mol <sup>-1</sup> )	$\Delta H_{0,i}^\circ$ <sup>b</sup> (kJ mol <sup>-1</sup> )
2HF + HCN = HCN · (HF) <sub>2</sub>	-87.22	-68.13
= HF · HCN · HF	-66.92	-53.17
= (HF) <sub>2</sub> · HCN	-54.24	-43.55
HF + 2HCN = (HCN) <sub>2</sub> · HF	-76.54	-62.76
= HCN · HF · HCN	-74.10	-60.95
= HF · (HCN) <sub>2</sub>	-49.22	-42.22

<sup>a</sup> Potential energy change, see Ref. 2.<sup>b</sup> Ground state energy change (i.e., the enthalpy change at absolute zero temperature); vibrational frequencies of monomers according to ref. 15.

three local energy minima for the 2HF–HCN system: HCN · HF · HF [for short, HCN · (HF)<sub>2</sub>], HF · HCN · HF, and HF · HF · HCN [for short, (HF)<sub>2</sub> · HCN] structures, only the second being linear. In the HF–2HCN system also three local energy minima were found: HCN · HCN · HF [for short, (HCN)<sub>2</sub> · HF], HCN · HF · HCN and HF · HCN · HCN [HF · (HCN)<sub>2</sub>] species, all of them however possessing linear structure. Table 1 presents the potential energy changes  $\Delta E_i$  for the trimerizations. Among the associations of two HF and one HCN the HCN · (HF)<sub>2</sub> structure exhibits the deepest D95 potential energy minimum. The (HCN)<sub>2</sub> · HF structure shows the deepest minimum within associations of one HF and two HCN molecules (Table 1).

In addition to the potential energy changes  $\Delta E_i$ , Table 1 considers also the ground state energy changes  $\Delta H_{0,i}^\circ$  (i.e.,  $\Delta E_i$  terms corrected for zero-point harmonic vibrational motions). For the purpose the harmonic vibrational frequencies of the monomers [15] were employed (otherwise, this paper does not involve information on monomers). The order of structures in each triad is the same in the potential energy and ground state energy scales.

## COMPUTATIONAL OUTLINE

We shall follow temperature isomeric interplay in an  $n$ -membered set in terms of equilibrium mole fractions  $w_i$  of the individual structures. The equilibrium means equilibrium between the isomers; other types of thermodynamic equilibria are not important in our treatment. The isomers differ not only in the potential energy  $\Delta E_i$  or ground state energy  $\Delta H_{0,i}^\circ$ , but also in their rotational–vibrational (and possibly some other) motions. The motions are described by partition functions  $q_i$  of the individual isomers

[13,16]. In overall form, the isomeric mole fractions are given by

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

where  $R$  stands for the gas constant and  $T$  for temperature. Although the partition functions  $q_i$  in eqn. (1) can be of any quality in our case, with respect to the available data, the usual rigid rotor and harmonic oscillator approach [13] is applied.

Evaluation of the equilibrium mole fractions is the first logical step in studying isomeric thermodynamics. It was pointed out [17,18] that actually two classes of quantities should be considered for an isomeric system, viz. partial and overall. The standard partial terms  $\Delta X_i^\circ$  belong to the individual isomers. However, for description of the whole system, the standard overall terms  $\Delta X_T^\circ$  should be considered, into which all the isomers contribute accordingly. In addition to the partial and overall terms a third quantity has been introduced, namely, the so-called isomerism contributions to thermodynamic terms  $\delta X_1$  [17,18]

$$\delta X_1 = \Delta X_T^\circ - \Delta X_1^\circ \quad (2)$$

The values of  $\delta X_1$  generally depend on the choice of the reference isomer labelled by  $i = 1$ . It is convenient that the most stable species (in the low temperature region) should be chosen as the reference structure. We shall consider three thermodynamic terms  $X$ : enthalpy  $X = H$ , entropy  $X = S$ , or heat capacity at constant pressure  $X = C_p$ . It holds for  $X = C_p$

$$\delta C_{p,1} = \delta C_{p,w,1} + \frac{1}{RT^2} \left[ \sum_{i=1}^n w_i (\Delta H_i^\circ - \Delta H_1^\circ)^2 - (\delta H_1)^2 \right] \quad (3)$$

where  $\delta C_{p,w,1}$  is given by

$$\delta C_{p,w,1} = \sum_{i=1}^n w_i (\Delta C_{p,i}^\circ - \Delta C_{p,1}^\circ) \quad (4)$$

and the isomerism contribution to enthalpy reads

$$\delta H_1 = \sum_{i=1}^n w_i (\Delta H_i^\circ - \Delta H_1^\circ) \quad (5)$$

The  $\delta C_{p,1}$  term in eqn. (3) refers to the effects of changes in composition upon a corresponding temperature change; it is therefore called the relaxation isomerism contribution to heat capacity. The latter term is reduced to the so-called isofractional isomerism contribution to heat capacity  $\delta C_{p,w,1}$  (eqn. (4)) if  $w_i$  values are considered to be temperature independent (the situation is essentially reached in both high- and low-temperature limits).

## RESULTS AND DISCUSSION

Figure 1 presents the temperature evolution of the  $w_i$  terms in both three-membered isomeric systems. It is apparent that in both cases the ground state structure is the most stable one only up to some temperature threshold (specified in Table 2). In fact, in each system there are present all three possible temperature interchanges in relative stabilities. In the high temperature limit the species with the highest potential energy becomes relatively the most stable structure. A striking feature in the HF—2HCN system is the particularly low position of the first relative stability interchange. The two structures lower in potential energy [i.e.,  $(\text{HCN})_2 \cdot \text{HF}$  and  $\text{HCN} \cdot \text{HF} \cdot \text{HCN}$ ] interchange their relative stabilities even at 132 K.

Figures 2 and 3 present the temperature evolution of the isomerism contributions  $\delta X_1$  to enthalpy, entropy and heat capacity at constant pressure. In addition to the full, three-membered isomeric sets reduced sets are also considered which are created through neglecting the species highest in the potential energy. In view of the highest stability of the last-named species at high temperatures, there are substantial differences between the two types of isomerism contributions in the temperature region. It is worth noting in Fig. 2 that the two-component heat capacity terms are not necessarily lower than the three-component ones.

The temperature course of the  $\delta C_{p,1}$  terms exhibits a maximum (in the HF—2HCN system there are even two maxima). It is natural to ask if such a

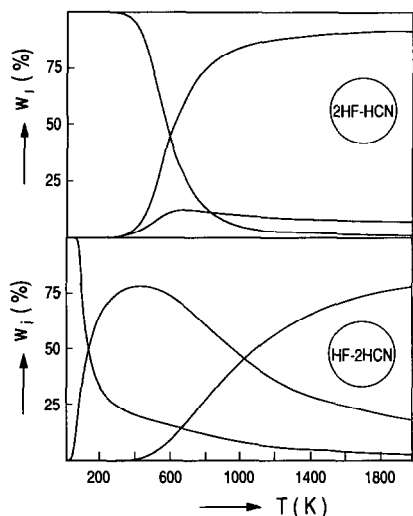


Fig. 1. Temperature dependences of the weight factors  $w_i$  in the 2HF—HCN (upper part) and HF—2HCN (lower part) isomeric sets. The order of the  $w_i$  curves at the highest temperature reads (from top to bottom)  $(\text{HF})_2 \cdot \text{HCN}$ ,  $\text{HF} \cdot \text{HCN} \cdot \text{HF}$ ,  $\text{HCN} \cdot (\text{HF})_2$  and  $\text{HF} \cdot (\text{HCN})_2$ ,  $\text{HCN} \cdot \text{HF} \cdot \text{HCN}$ ,  $(\text{HCN})_2 \cdot \text{HF}$ .

TABLE 2

Specification of the relative stability interchanges in the 2HF-HCN and HF-2HCN systems

System	$T$ (K)	$w_1^a$ (%)	$w_2^b$ (%)	$w_3^c$ (%)	$\delta C_{p,1}^d$ (J K <sup>-1</sup> mol <sup>-1</sup> )
2HF-HCN	348	97.4	1.3	1.3	16.4
	588	44.4	11.2	44.4	81.7
	833	11.3	11.3	77.5	21.2
HF-2HCN	132	50.0	50.0	$2 \times 10^{-6}$	8.5
	662	14.6	70.7	14.6	21.2
	1023	8.3	45.8	45.8	18.8

<sup>a</sup> The mole fraction of the HCN·(HF)<sub>2</sub> or (HCN)<sub>2</sub>·HF species in the equilibrium mixture with the other two related isomers.

<sup>b</sup> The mole fraction of the HF·HCN·HF or HCN·HF·HCN species in the equilibrium mixture with the other two related isomers.

<sup>c</sup> The mole fraction of the (HF)<sub>2</sub>·HCN or HF·(HCN)<sub>2</sub> species in the equilibrium mixture with the other two isomers.

<sup>d</sup> Isomerism contribution to heat capacity related to the species most stable in the very low temperature region, i.e., to HCN·(HF)<sub>2</sub> or (HCN)<sub>2</sub>·HF.

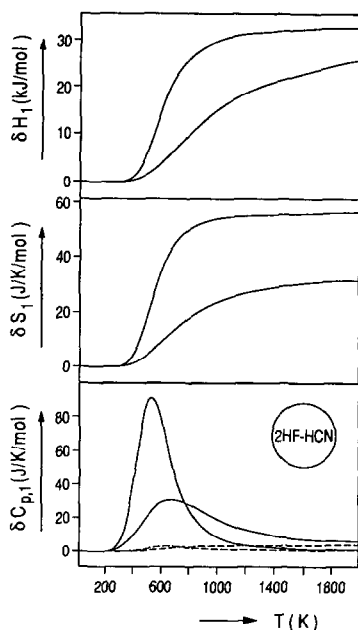


Fig. 2. Temperature dependences of the isomerism contributions to enthalpy  $\delta H_1$ , entropy  $\delta S_1$ , and heat capacity at constant pressure  $\delta C_{p,1}$  (relaxation term) or  $\delta C_{p,w,1}$  (isofractional term, dashed lines) in the two- [i.e., removing the (HF)<sub>2</sub>·HCN isomer] and three-membered 2HF-HCN isomeric system [the contributions are related to the HCN·(HF)<sub>2</sub> species as the reference structure].

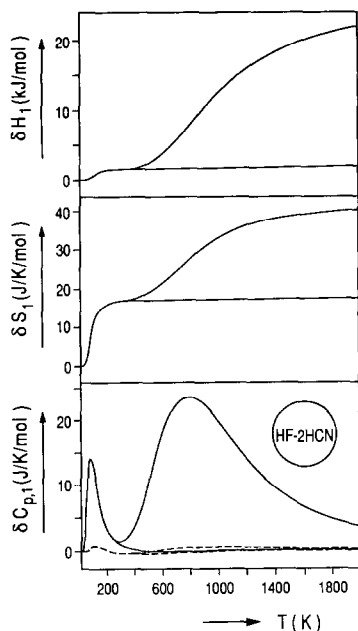


Fig. 3. Temperature dependences of the isomerism contributions to enthalpy  $\delta H_1$ , entropy  $\delta S_1$ , and heat capacity at constant pressure  $\delta C_{p,1}$  (relaxation term) or  $\delta C_{p,w,1}$  (isofractional term, dashed lines) of HF-2HCN isomeric system [the contributions are related to the  $(\text{HCN})_2 \cdot \text{HF}$  species as the reference structure]. In each related pair of curves the higher and lower curves refer to the three- and two-membered isomeric mixture, respectively [i.e., removal of the  $\text{HF} \cdot (\text{HCN})_2$  isomer].

maximum can be conserved and thus observed in experimentally accessible quantities. Figure 4 supplies an answer in terms of the standard molar heat capacity at constant pressure. While the temperature dependence for the pure isomer most stable at low temperatures (i.e., the partial  $C_{p,1}^\circ$  term) is smooth, the overall  $C_p^\circ$  term (i.e., equilibrium mixture of the three isomers) exhibits interesting irregularities. However, only in the 2HF-HCN system is the temperature maximum conserved. It should also be noted that in the low-temperature limit the heat capacity at constant pressure terms do not reach the rigorous zero value but the classical term  $4R$  instead. This is in fact a result [19] of our application of the conventional translational and rotational partition functions [13]. Although such wrong limiting behaviour can be corrected [19] this is not critical for our purposes.

Table 3 supplies a detailed specification of the temperature maxima related to heat capacity. In fact, three maxima can be considered (though all three are present only in the 2HF-HCN system): the maximum in the isomerism contribution to heat capacity  $\delta C_{p,1}$ , the maximum in the standard overall heat capacity at constant pressure  $C_p^\circ$ , or the maximum of the relative enhancement  $\delta C_{p,1}/C_p^\circ$  of the  $C_p^\circ$  term by interplay. The latter enhancement in the 2HF-HCN system reaches considerable values (up to

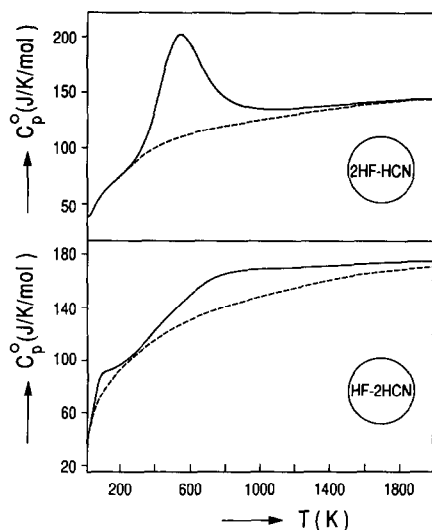


Fig. 4. Temperature dependences of the standard molar heat capacity at constant pressure for the pure isomer most stable at low temperatures [ $\text{HCN}\cdot(\text{HF})_2$  or  $(\text{HCN})_2\cdot\text{HF}$ ; the partial  $C_{p,1}^{\circ}$  term is the dashed line] and for the equilibrium mixture of the three isomers in the 2HF-HCN and HF-2HCN systems (i.e., the overall  $C_p^{\circ}$  term).

45.6%); this is quite close to the so far highest reported isomerism enhancement of heat capacity [20] (51.6%, although in the chemically completely different system  $\text{Si}_6\text{H}_6$ ).

In conclusion, let us mention that the quality of our approach can be further improved by an inclusion of corrections to anharmonicity and

TABLE 3

Characterization of some distinguished <sup>a</sup> points related to heat capacity of the 2HF-HCN and HF-2HCN isomeric systems

System	Type <sup>a</sup>	<i>T</i> (K)	<i>w</i> <sub>1</sub> <sup>b</sup> (%)	<i>w</i> <sub>2</sub> <sup>b</sup> (%)	<i>w</i> <sub>3</sub> <sup>b</sup> (%)	$\delta C_{p,1}^{\circ}$ ( $\text{J K}^{-1}$ $\text{mol}^{-1}$ )	$C_p^{\circ}$ ( $\text{J K}^{-1}$ $\text{mol}^{-1}$ )	$\frac{\delta C_{p,1}^{\circ}}{C_p^{\circ}}$ (%)
2HF-HCN	M: $\delta C_{p,1}$	530	60.6	9.4	30.0	91.4	200.6	45.5
	M: $C_p^{\circ}$	538	58.3	9.7	32.0	91.2	200.8	45.4
	M: %	524	62.5	9.1	28.4	91.2	200.1	45.6
HF-2HCN	M: $\delta C_{p,1}$	79	78.2	21.8	$5 \times 10^{-12}$	14.2	84.9	16.7
	M: $\delta C_{p,1}$	786	12.1	62.1	25.8	23.7	164.7	14.4

<sup>a</sup> I.e., maximum in the isomerism contribution to heat capacity  $\delta C_{p,1}^{\circ}$  (M:  $\delta C_{p,1}$ ), maximum in the standard overall heat capacity at constant pressure  $C_p^{\circ}$  (M:  $C_p^{\circ}$ ), or maximum of the relative enhancement  $\delta C_{p,1}^{\circ} / C_p^{\circ}$  of the  $C_p^{\circ}$  term by isomeric interplay (M: %).

<sup>b</sup> The mole fraction of the species in the equilibrium isomeric mixture, see Table 2.

<sup>c</sup> Isomerism contribution to heat capacity related to the species most stable in the very low temperature region, i.e., to  $\text{HCN}\cdot(\text{HF})_2$  or  $(\text{HCN})_2\cdot\text{HF}$  (see Table 2).

non-rigidity effects. Such corrections would certainly be desirable, although being precluded by computational demands. It should also be recognized that, in a real gas-phase mixture of HF and HCN, in addition to the trimers studied here, monomers and other clusters (e.g., dimers and tetramers) will take part. Nevertheless, the relative isomeric populations found within our isolated sets should be still transferable to the complex mixture.

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