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ISOMERISM AND THERMODYNAMICS OF THE HF(g) AND HCl(g) ASSOCIATION *,**

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ABSTRACT

The thermodynamics of the association of HF(g) and HCl(g) leading to formation of two isomeric complexes HF·HCl and HCl·HF have been studied. This computational study makes use of the molecular parameters from quantum-chemical calculations. The evaluation of the thermodynamics has been carried out for full harmonic vibrational partition function and, simultaneously, for treating torsional vibration as free internal rotation. The characterisation of the latter motion is connected with a study of the effect of choice of the free internal-rotational axis. Attention is also paid to the interplay of both isomeric structures which are present at comparable concentrations at modest and higher temperatures even though the HF·HCl structure is relatively more populated.

INTRODUCTION

Together with the general intensive interest in the properties and behaviour of atomic and molecular complexes, clusters, there has recently been increasing interest in the thermodynamics of their formation [1–18] (predominantly, of course, only in the gas phase at present). A typical feature of such species is their isomerism (recognised, so far, mostly by theoretical means). This has new and interesting thermodynamical consequences and, hence, determines the nature of the planning and organisation of the observation.

The present communication focusses on the HF–HCl system [19] belonging to the growing family of small, halogen-atom-containing complexes [20–28]. As with other members of this class, two-fold isomerism was recognized in this particular system [19]. The present communication is an evaluation of the system thermodynamics with a proper treatment of the latter-mentioned phenomenon.

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* Dedicated to the memory of Academician Jaroslav Heyrovský (1890–1967).

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Two local energy minima were found on the potential hypersurface of the HF–HCl system [19], namely the structures $HF \cdot HCl$ and $HCl \cdot HF$. For structural characterisation of these quasi-linear structures (the hydrogen bond formed deviates by less than 10° from the F–Cl axis), the present study makes use of the uniform SCF ($+VP^s$ $(2d)^s$ basis set) set of geometry parameters [19]. The six harmonical vibrational frequencies of both isomers were evaluated on the same methodical level [19]; the descriptions of the structural and vibrational patterns of both monomeric units were carried out to the same extent [19]. In order to ensure a realistic determination of the potential energy change, ΔE_i, during the association reactions

$$HF(g) + HCl(g) = HF \cdot HCl(g) \tag{1}$$

$$HF(g) + HCl(g) = HCl \cdot HF(g) \tag{2}$$

the SCF data [19] corrected at the MP2 level for the electron correlation was used and, at the same time, subtraction of the so-called BSSE term was carried out. Table 1 presents the ΔE_i terms along with the values after the correction for zero-point vibrational energy, i.e. the ground-state energy changes or enthalpy changes at the absolute zero temperature, $\Delta H_{0,i}^{\ominus}$. In both energy scales, the $HF \cdot HCl$ isomer is slightly favoured.

In describing internal systemic motions, it is useful to distinguish two approaches differing in the technique of treatment of the torsional motion in complexes: either this torsional motion is treated like the five remaining vibrational motions in terms of harmonical vibrations, i.e. the treatment of harmonic torsion, HT, or this sixth degree of freedom is treated as internal rotation (IR), taken, in accordance with the relations in weak molecular complexes, as free internal rotation. The differences between these two approaches are already manifested at the level of the $\Delta H_{0,i}^{\ominus}$ terms (Table 1), but the relations between these HT and IR approximations are predomi-

TABLE 1

Potential energy [a] ΔE_i and ground-state energy [b] $\Delta H_{0,i}^{\ominus}$ changes upon formation of $HF \cdot HCl$ and $HCl \cdot HF$ complexes

Process	ΔE_i (kJ mol^{-1})	$\Delta H_{0,i}^{\ominus}$ (kJ mol^{-1})	
		HT [c]	IR [c]
$HF(g) + HCl(g) = HF \cdot HCl(g)$	−10.25	−6.16	−6.63
$HF(g) + HCl(g) = HCl \cdot HF(g)$	−10.00	−4.96	−5.44

[a] Evaluated [19] in the $+VP^s(2d)^s + MP2$ approach with the BSSE subtraction.

[b] The standard enthalpy change at absolute zero temperature.

[c] The HT and IR denote the treatment considering and omitting, respectively, one of the six harmonic vibrational frequencies, i.e. harmonic-torsional versus free internal-rotational motion.

nantly studied in terms of standard changes of enthalpy, entropy, and heat capacity at constant pressure in processes (1) and (2). In terms of the HT approach, the partition functions necessary for these thermodynamic purposes are constructed in terms of the usual approximation [14–17] of rigid rotor and harmonic oscillator (RRHO). In the case of IR treatment, the situation concerning the partition functions of free rotation is more varied. Because incorrect limiting behaviour of the expression conventionally used for this partition function has recently been indicated [29,30], a series of approximations with the correct limiting behaviour has been suggested [29–35]. Some of these approximations work with closed-form formulae [29–33] (these were extended by an, in a sense, even more sophisticated formula suggested by Pan [36] on the basis of the Korsch semi-classical approximation [37,38]). Nevertheless, the technique of direct summation [34,35] appears to be the most reliable, and this was also used in the context of this work. The governing parameter for this partition function is the reduced moment of inertia, I_{red}, evaluated by the standard procedure [14] from structural data.

The primary results in the description of the thermodynamics of formation of the HF–HCl system are the so-called partial thermodynamic terms [15–17]. For the purposes of studies of isomeric thermodynamics [39,40], however, it is useful to introduce the so-called overall terms [15–17,40] connected with the equilibrium mixture of the existing isomers. In our particular case, this means their correspondence to the total process

$$\mathrm{HF(g) + HCl(g) = HF\text{–}HCl(g)} \qquad (3)$$

where, on the right-hand side, there is the pseudo-species HF–HCl, formed by an equilibrium mixture of both the isomers produced in processes (1) and (2). The overall terms corresponding to the total process (3) were derived from the partial terms by the weighting treatment presented earlier [15–17,40]. In this weighting scheme, the mole fractions (weight factors) w_i of both isomers in their equilibrium mixture (i denotes either 1 and 2 or HF · HCl and HCl · HF) play an important intermediate role.

RESULTS AND DISCUSSION

The effect of geometry-parameter values from various quantum-chemical approximations on values of moments of inertia is usually small. Nevertheless, there is an aspect of this which has not so far been given attention in this context and which could be important, namely the choice of internal-rotational axis and its influence on the I_{red} values. Whereas for normal sufficiently rigid chemical species this choice is clear, this need not be the case with weak molecular complexes. In ref. 14, the adopted choice for complexes of the studied type was the axis defined by two heavy atoms (the

TABLE 2

Reduced moment of inertia I_{red} for HF·HCl and HCl·HF species, compared with the isomeric pair [a] HF·ClF and ClF·HF, and the influence of the internal–rotational axis choice

Internal–rotational axis	$I_{red} \times 10^{39}$ (g cm^2)			
	HF·HCl	HCl·HF	HF·ClF	ClF·HF
According to ref. 14 [b]	0.00506	0.00217	0.00662	0.00282
Intermolecular bond [c]	0.00458	0.00215	0.00638	0.00257

[a] Geometry parameters of 4-31G quality [14].

[b] The F–Cl, Cl–F, F–F and F–F line for HF·HCl, HCl·HF, HF·ClF and ClF·HF species, respectively.

[c] The F–H, Cl–H, F–Cl and F–H line for HF·HCl, HCl·HF, HF·ClF and ClF·HF species, respectively (the two atoms in the defining pairs always belong to the different molecular sub-units of the complex).

calculations concerned I_{red} of the isomeric pair HF · ClF and ClF · HF [24]). For consistency, this choice was adopted here in the same form as it was introduced in the literature. Nevertheless, one can suggest that it would be equally meaningful to choose the hydrogen or analogous bond in these complexes for the internal-rotational axis. Table 2 compares the I_{red} values for both these choices of internal-rotational axis in the HF–HCl and HF–ClF systems as examples. It can be seen that the differences resulting from the choice of axis are insignificant from the standpoint of a statistical-thermodynamical treatment. This is connected with the above-mentioned small deviations from linearity in these quasi-linear species. This quasi-linearity, however, has a significant consequence: the relatively small I_{red} values (cf. ref. 14), which represents the poor applicability of the conventional partition function of free internal rotation.

Table 3 presents a survey of the temperature evolution of the mole fractions w_i of the HF · HCl and HCl · HF isomers in their equilibrium gas-phase mixture (of course, $w_1 + w_2 = 1$). The overall picture is the same in both treatments. At the lowest temperatures studied, the predominant structure is that exhibiting the lower energy content (both ΔE_i and $\Delta H_{0,i}^{\ominus}$) i.e. the HF · HCl isomer. However, with increasing temperature the relative populations of both isomeric structures rapidly approach each other, although over the whole temperature interval studied, the structure which predominates at the lowest temperatures is always somewhat more stable. The decrease in the relative stability of the HF · HCl isomer is at first somewhat faster in the IR treatment; then, however, lower values are exhibited by the HT treatment. In principle, however, there is no distinct difference between the results of both approaches except that the w_1 values systematically decrease in the HT treatment within the temperature interval studied, whereas in the IR approach they exhibit a shallow local minimum.

The data [19] adopted in the present work suffer from an uncertainty connected with the difficulties which can occur during assignment of the

TABLE 3

Temperature dependence of the weight factors [a], w_i, in the equilibrium mixture of the HF·HCl(g) and HCl·HF(g) isomers

T (K)	HT [b]		IR [b]	
	w_1 (%)	w_2 (%)	w_1 (%)	w_2 (%)
20	99.9	0.1	99.9	0.1
50	92.1	7.9	91.9	8.1
100	74.6	25.4	74.1	25.9
150	66.2	33.8	65.9	34.1
200	62.3	37.7	62.6	37.4
250	60.3	39.7	61.5	38.5
298.15	59.1	40.9	61.5	38.5
300	59.1	40.9	61.5	38.5
400	57.8	42.2	62.5	37.5
500	57.2	42.8	63.6	36.4
750	56.5	43.5	65.1	34.9
1000	56.2	43.8	65.5	34.5

[a] Mole fractions; $i=1$ or 2 denotes the HF·HCl or HCl·HF isomer, respectively.

[b] See Table 1; the IR approach uses I_{red} derived within the internal-rotational axis according to ref. 14.

simple motional (pictorial) characterisation to normal vibrational modes. The reference cited adopts a characterisation convention in which the torsional motion is not explicitly considered. For simplicity, this last motion type mentioned was identified, for the purposes of the present study, with the lowest frequency in the given set of six frequencies [19] (although it is known that the torsional frequency need not necessarily be the lowest in such a set of frequencies [25]). Hence, with this reservation, the HT and IR procedures yield very close results at the level of w_i terms. This is clearly supported by the form of the expressions [15–17] for the weight factors w_i which enables extensive cancelling of parent terms between the numerator and denominator.

Table 4 presents a survey of the temperature courses of partial and overall standard thermodynamic terms (enthalpy, $\Delta H_x^{\ominus}$, entropy, $\Delta S_x^{\ominus}$, and heat capacity at constant pressure, $\Delta C_{p,x}^{\ominus}$) for processes (1)–(3). The index x assumes the values of 1 or 2 for the partial terms (formation of HF · HCl or HCl · HF, respectively), and for the overall terms it symbolises T (formation according to the total process (3)). Here the correspondence between the HT and IR approaches is not as close as that shown in Table 3. With increasing temperature, the values resulting from the two approaches exhibit significant differences. From this standpoint, the parallel evaluation by both treatments enables a better estimation of the possible interval of values (especially so with regard to the fact that the IR values represent a limiting situation for all internal rotations differing by various heights of potential barriers). At

TABLE 4

Partial and overall standard[a] enthalpies[b] $\Delta H_x^\ominus$, entropies[b] $\Delta S_x^\ominus$ and heat capacities at constant pressure[b] $\Delta C_{p,x}^\ominus$ of HF(g) and HCl(g) associations

T (K)	HT[c]			IR[c]		
	$\Delta H_x^\ominus$ (kJ mol^{-1})	$\Delta S_x^\ominus$ (J K^{-1} mol^{-1})	$\Delta C_{p,x}^\ominus$ (J K^{-1} mol^{-1})	$\Delta H_x^\ominus$ (kJ mol^{-1})	$\Delta S_x^\ominus$ J K^{-1} mol^{-1})	$\Delta C_{p,x}^\ominus$ (J K^{-1} mol^{-1})
HF(g) + HCl(g) = HF · HCl(g)						
20	−6.51	−44.1	−24.4	−6.98	−44.3	−25.4
50	−7.11	−63.0	−15.7	−7.69	−66.2	−21.2
100	−7.62	−70.4	−5.35	−8.53	−78.2	−12.5
200	−7.63	−70.8	3.33	−9.09	−82.6	−0.19
298.15	−7.15	−69.0	5.87	−8.85	−81.6	4.02
500	−5.78	−65.5	7.41	−7.98	−79.4	4.15
1000	−1.84	−60.0	8.13	−6.00	−76.7	3.99
HF(g) + HCl(g) = HCl · HF(g)						
20	−5.32	−40.6	−24.6	−5.80	−40.7	−25.4
50	−5.93	−59.9	−16.6	−6.52	−62.9	−22.1
100	−6.54	−68.6	−8.32	−7.46	−76.2	−15.8
200	−6.85	−71.1	0.82	−8.55	−84.1	−7.13
298.15	−6.57	−70.0	4.38	−9.02	−86.1	−2.58
500	−5.39	−67.1	6.79	−8.85	−85.8	3.58
1000	−1.61	−61.9	7.98	−6.21	−82.2	5.24
HF(g) + HCl(g) = HF · HCl(g)						
20	−6.51	−44.1	−23.9	−6.98	−44.3	−24.9
50	−7.02	−60.5	−10.9	−7.59	−63.6	−16.3
100	−7.34	−65.3	−3.47	−8.25	−72.9	−10.7
200	−7.33	−65.4	2.81	−8.89	−77.7	−2.58
298.15	−6.91	−63.8	5.37	−8.92	−77.8	1.49
500	−5.61	−60.5	7.16	−8.29	−76.3	4.03
1000	−1.74	−55.1	8.06	−6.07	−73.2	4.42

[a] The standard state is an ideal gas at 1 atm = 101 325 Pa pressure.

[b] The parameter x denotes either 1, 2 (i.e. the partial processes) or T (the overall process).

[c] See Tables 1 and 3.

low temperatures, however, the values derived from both the approaches converge (with a certain exception for the $\Delta H_x^{\ominus}$ terms, cf. Table 1). This convergence is due, in fact, to the direct summation technique [34,35] applied in the IR approach. If the conventional formula for the partition function of free internal rotation were used, the values derived from the two approaches would be quite different or even divergent [29–35], including in the low-temperature region.

Table 4, of course, not only offers a comparison of the results from the HT and IR treatments of the torsional motion in the complexes, but also visualises the process of weighting of contributions from both isomers, i.e. a transition from partial to overall values of standard thermodynamic terms. Only the latter terms mentioned should be relevant in relation to the (isomeric structures non-distinguishing) types of observation at thermodynamic equilibrium. At higher temperatures, there are significant differences between an overall quantity and any one of the related partial ones, the difference being quite large with the entropy and heat capacity terms.

It has become customary to express the differences between the overall value of the quantity X and its partial value corresponding to the more (the most) stable structure (labelled with the subscript 1) within an isomeric set, in terms of the isomerism contributions to the thermodynamics related to the particular structure [15–17,40]

$$\delta X_l^{(\mathrm{iso})} = \Delta X_{\mathrm{T}}^{\ominus} - \Delta X_l^{\ominus} \qquad (4)$$

with particular attention being paid to the case where $X = C_p$, when it is quite usual that the isomerism contribution to the heat capacity, $\delta C_{p,1}^{(\mathrm{iso})}$, often exhibits a course with a pronounced maximum which sometimes also occurs in the temperature course of the overall term, $\Delta C_{p,\mathrm{T}}^{\ominus}$. Whereas the $\Delta C_{p,\mathrm{T}}^{\ominus}$ values presented in Table 4 exhibit only a regular increase with temperature, for the $\delta C_{p,1}^{(\mathrm{iso})}$ values the course with a maximum is quite clear. This is documented in Table 5 where the temperature maximum is characterised. In accordance with the previous reasoning concerning the converging phenomena at low temperatures, there are no substantial differences between the coordinates of these maxima in the HT and IR treatments. However, it can be seen that these maxima are relatively rather small [16,40].

TABLE 5

Positions of the maximum in the isomerism contribution [a] $\delta C_{p,1}^{(\mathrm{iso})}$ to the overall heat capacity of HF–HCl

Treatment [b]	T (K)	$\delta C_{p,1}^{(\mathrm{iso})}$ (J K^{-1} mol^{-1})
HT	52.9	4.81
IR	52.7	4.89

[a] Related to the HF·HCl isomer as the reference structure.

[b] See Tables 1 and 3.

The RRHO approximation for the evaluation of partial terms for processes (1) and (2), and the subsequent weighting treatment for estimation of overall characteristics of the total process (3), represent the only applicable computational approach at present. So far it is only possible to speculate [40] on the advanced procedures in terms of the whole hypersurface of potential energy and, hence, about a unification of the HF–HCl system. Of course, it is clear that the barrier between the two isomers will be relatively very low, e.g. it was evaluated [19] as about 2 kJ mol^{-1}, so it will be possible for the individual potential wells to accommodate quite a few vibrational levels. The rest will lie in the common area above the barrier top. This alone, however, does not contradict the application of the weighting treatment, because (as already discussed [23,24]) the amplification of the number of energy levels compared with the situation without isomerism is qualitatively reflected in the weighting treatment. In addition, another supporting argument is supplied by the studies on the principal differences between the phenomena of tunnelling and localisation in symmetric and asymmetric double-minimum potential profiles [41–47]. This, of course, does not negate the necessity of the comparison, at least in terms of a one-dimensional model, of the results from the RRHO weighting treatment with direct summation over the energy levels determined within this simple potential modelling of an isomeric system.

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