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MOLECULAR THERMODYNAMICS OF FREE INTERNAL ROTATION VERSUS HARMONIC TORSIONAL VIBRATION: FORMATION OF THE COMPLEX Cl_2–HF(g) *

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ABSTRACT

The thermodynamics of gas-phase association of Cl_2 and HF have been studied, taking into account two isomeric structures for the resulting associate, viz. $HF \cdot Cl_2$ and $Cl_2 \cdot HF$, and also the equilibrium mixture of both these structures. The molecular parameters necessary for constructing the RRHO partition functions are taken from recent MO calculations. Two limiting kinds of description are considered for the motion of both sub-systems around the complex axis — either a harmonic torsional vibration or a simple internal rotation. These two approaches lead to relatively large differences in the calculated values of thermodynamic quantities. Nevertheless, as regards characterization of the contributions of both isomers, the two limiting approaches are in good agreement, which strenghtens confidence in the results. This applies to the temperature of equimolarity of the two isomers as well as to the temperature of the maximum isomerism contribution to the heat capacity.

INTRODUCTION

In the context of studies of molecular clusters [2] considerable attention is paid at present to the thermodynamics of formation of molecular complexes, see e.g. refs. [3–14]. As observations usually do not provide sufficient information for characterization of these molecular complexes, quantum-chemical calculations are used as an alternative source of information. Nevertheless, the extent of such information about molecular parameters is so limited that it is necessary to adopt the approximations of partition functions of rigid rotors and harmonic oscillators. A frequent and thermodynamically interesting complication of such molecular complexes consists in

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their isomerism [15–24] which can lead to a number of distinct manifestations. Studies of such manifestations are important for planning experiments designed to prove the presence of this isomerism [25].

A complete description of the thermodynamics of a gaseous system requires consideration and characterization of a number of associate types. The full information necessary for such a complete approach, however, is not available. Hence at present it is usual to study only a single selected type of molecular complex and to hope that concentrated efforts will create favourable conditions for a complete description of the real gas phase, involving the selected complex as one of several components, in the future. Thus it is possible at present to start a study of the HF–Cl_2(g) hetero-complex from its recently published quantum-chemical characteristics [26]. This hetero-complex exists, together with both homo-dimers as well as higher aggregates, in a mixture of HF(g) and Cl_2(g). The present communication deals with the calculation of thermodynamics of this particular hetero-cluster, with due attention being paid to its theoretically proven [26] isomerism.

DESCRIPTION OF SYSTEM AND CALCULATIONS

It was shown [26] that there are two local energy minima on the potential hypersurface of the Cl_2–HF system, viz. a deeper well representing the non-hydrogen-bonded structure HF · Cl_2 and the other one due to the hydrogen-bonded structure Cl_2 · HF. Two approximations were used to evaluate the potential energy, namely the simple SCF approach and also evaluation of the electron correlation effects by the CPF method (Table 1). In these approximations, besides the energetics, the structural parameters were determined and the harmonic vibrational analysis of both the dimers and corresponding monomers carried out. Also, after the transition from potential energy terms to the ground-state energy terms (i.e. after correction

TABLE 1

Survey of energetics of formation of the Cl_2–HF(g) system: potential energy changes ΔE_i and ground state energy [a] changes $\Delta H^0_{0,i}$ upon association of Cl_2(g) and HF(g)

Association process	SCF [b] (kJ mol^{-1})			CPF [b] (kJ mol^{-1})		
	ΔE_i	$\Delta H^0_{0,i}$		ΔE_i	$\Delta H^0_{0,i}$	
		IR	HT		IR	HT
$Cl_2(g)+HF(g) = HF \cdot Cl_2(g)$	−3.18	−1.71	−1.35	−3.47	−1.93	−1.62
$Cl_2(g)+HF(g) = Cl_2 \cdot HF(g)$	−2.01	−0.12	0.44	−2.55	−0.58	−0.06

[a] The standard enthalpy changes at absolute zero temperature.

[b] According to ref. 26.

for the zero-point vibrations) the non-hydrogen-bonded structure exhibits a lower value for the energy term.

For thermodynamical purposes it is useful to consider two reactions leading to the individual structures of the hetero-dimer

$$Cl_2(g) + HF(g) = HF \cdot Cl_2(g) \tag{1}$$

$$Cl_2(g) + HF(g) = Cl_2 \cdot HF(g) \tag{2}$$

as well as the overall process leading to the equilibrium mixture of both these isomeric structures

$$Cl_2(g) + HF(g) = Cl_2\text{–}HF(g) \tag{3}$$

The evaluations of thermodynamic characteristics of the reactions (1) and (2) were carried out in terms of the RRHO partition functions as specified in the report of the computer program [27], the values of universal physical constants being taken from ref. 28 and the atomic masses from ref. 29.

Molecular complexes usually exhibit the presence of a motion close to free internal rotation [30,31]. In terms of harmonic vibrational analysis, this motion is described as a torsional vibration of very low frequency. In addition, this frequency is usually determined from quantum-chemical calculations [30,31] with relatively low accuracy (because of limitations of the numerical method typically used to evaluate the second derivatives of energy). Therefore, two approaches were considered in treating this particular motion: (i) a description as a harmonic vibrational torsion motion (HT), and (ii) a description as free internal rotation (IR) (although the barrier heights for internal rotation cannot be evaluated in the complexes considered, it is possible — from analogy with other cases [30,31] — reasonably to presume that they are very low). The reduced moments of inertia for use in the treatment (ii) were determined in the usual way [32]. The partition function of free internal rotation was constructed by direct summation [33].

In the study of the thermodynamics of the equilibrium isomeric mixture of both hetero-dimers, we made use of the earlier approach [34–36] of isomerism contributions to values of thermodynamic functions. The mole fractions w_1 and w_2 of both the structures 1 and 2 in their equilibrium mixture are evaluated. These mutual relative populations of both isomers are applicable to any mixture fulfilling the condition of inter-isomer equilibrium between structures 1 and 2, irrespective of the presence of other components in the mixture (presuming ideal behaviour of this mixture). Thereafter, the isomeric contributions to values of thermodynamic functions $\delta X_1^{(\mathrm{iso})}$ are determined relative to isomer 1 as the reference structure. These contributions are introduced as differences between the overall values ΔX_T^0 corresponding to the equilibrium mixture of isomers (i.e. the values corresponding to reaction (3) in our case) and the partial value ΔX_1^0 corresponding to isomer 1 (i.e. to reaction (1) in our case)

$$\delta X_1^{(\mathrm{iso})} = \Delta X_T^0 - \Delta X_1^0 \tag{4}$$

The calculations were carried out for the enthalpy, entropy, and heat capacity at constant pressure ($X = H$, S, or C_p). For these isomerism contributions we can derive expressions which involve only the mole fractions w_1 and w_2 and the partial terms corresponding to both isomers, i.e. ΔX_1^0 and ΔX_2^0; e.g. for $X = C_p$ it is [37]

$$\delta C_{p,1}^{(\mathrm{iso})} = w_2\left(\Delta C_{p,2}^0 - \Delta C_{p,1}^0\right) + w_1 w_2 \frac{\left(\Delta H_1^0 - \Delta H_2^0\right)^2}{RT^2} \tag{5}$$

RESULTS AND DISCUSSION

Figure 1 presents the temperature dependences of the mole fractions w_i of both isomers of the hetero-complex evaluated in terms of both the approximations of potential energy and in terms of the IR and HT approaches to the description of internal rotation. The results appear to be qualitatively identical in all four situations. Structure 1 ($HF \cdot Cl_2$) exhibits an abrupt decrease in its stability relative to that of structure 2 with temperature, and finally a temperature is reached at which the populations of the isomers are just equimolar. Within the terms of the SCF approximation of potential energy, this happens at 110.9 and 118.6 K for the HT and IR partition functions, respectively. In the CPF approximation these temperatures of inversion of relative stabilities are 96.6 and 113.0 K for the HT and IR procedures, respectively. Hence the equimolarity temperatures are quite close in the two approaches to internal rotation.

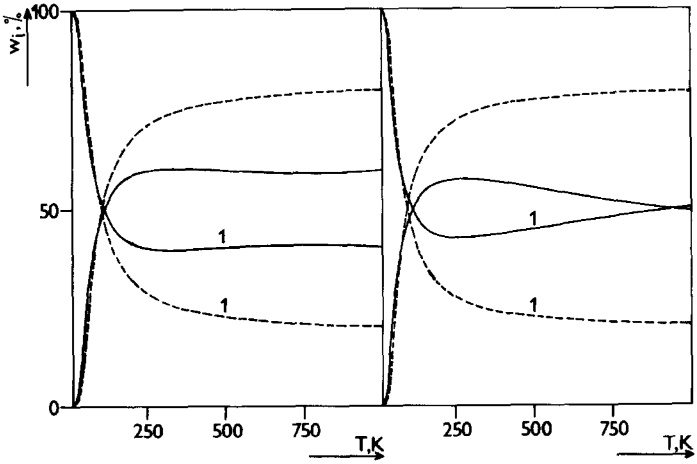

Fig. 1. Temperature dependences of the mole fractions w_i for the equilibrium mixture of $HF \cdot Cl_2(g)$ (1) and $Cl_2 \cdot HF(g)$. The results based on the SCF and CPF approaches [26] are given in the left and right part, respectively; the solid and dashed lines represent the IR and HT results, respectively.

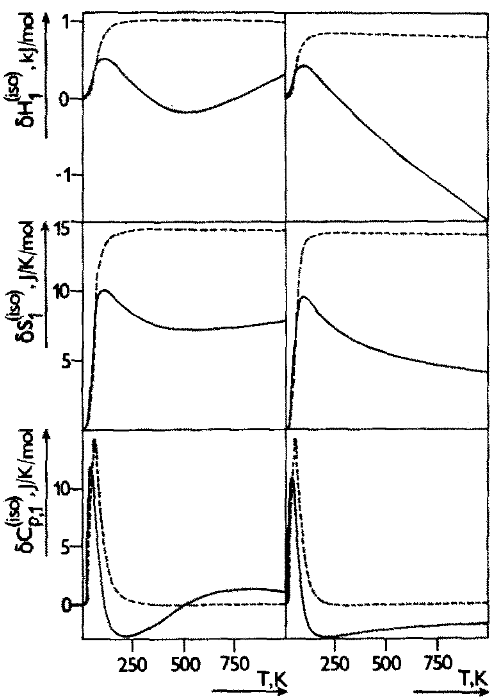

Fig. 2. Temperature dependences of the isomerism contributions to enthalpy, $\delta H_1^{(iso)}$, entropy, $\delta S_1^{(iso)}$, and heat capacity at constant pressure, $\delta C_{p,1}^{(iso)}$, in the Cl_2–HF(g) equilibrium system (the isomerism contribution terms are related to $HF \cdot Cl_2$ isomer as the reference structure). The results based on the SCF and CPF approaches [26] are given in the left and right part, respectively; the solid and dashed lines represent the IR and HT results, respectively.

Figure 2 presents the temperature dependences of $\delta X_1^{(iso)}$ terms ($X = H, S, C_p$) again for both the approaches to energetics and for both the limiting descriptions of internal rotation. Here we must state that, at least at some temperatures, relatively distinct differences exist between the results of the IR and HT approximations. Figure 2 clearly shows the variability of terms of isomerism contributions, depending on both the input data and the approximations used. Nevertheless, again one qualitative feature is maintained in all four situations — the variation of the $\delta C_{p,1}^{(iso)}$ term with a local maximum, the temperature of this maximum being not much different in the IR and HT approximations. In terms of the SCF energetics, this maximum lies at 59.2 K (the height of this maximum is 14.2 J K^{-1} mol^{-1}) and 49.0 K (when the height is 11.9 J K^{-1} mol^{-1}) for the HT and IR approximations, respectively. In the case of CPF energetics, the respective values are 51.7 K (14.3 J K^{-1} mol^{-1}) and 42.9 K (10.8 J K^{-1} mol^{-1}).

Table 2 presents the temperature evolution of the standard terms of enthalpy, entropy, and heat capacity at constant pressure for reactions (1)–(3) in terms of the SCF and CPF approximations of potential energy

TABLE 2

Temperature dependences of partial and overall standard enthalpies ΔH_x^0, entropies ΔS_x^0, and heat capacities at constant pressure $\Delta C_{p,x}^0$ for associations of Cl_2(g) and HF(g) evaluated within the IR and HT treatments [a,b]

T (K)	SCF						CPF					
	ΔH_x^0 (kJ mol^{-1})		ΔS_x^0 (J K^{-1} mol^{-1})		$\Delta C_{p,x}^0$ (J K^{-1} mol^{-1})		ΔH_x^0 (kJ mol^{-1})		ΔS_x^0 (J K^{-1} mol^{-1})		$\Delta C_{p,x}^0$ (J K^{-1} mol^{-1})	
	IR	HT	IR	HT	IR	HT	IR	HT	IR	HT	IR	HT
$Cl_2(g) + HF(g) = HF \cdot Cl_2(g)$												
20	−2.07	−1.70	−61.3	−61.0	−17.4	−16.8	−2.27	−1.97	−58.8	−60.0	−13.8	−16.3
50	−2.31	−1.95	−69.7	−69.5	−2.43	−2.27	−2.51	−2.22	−66.8	−68.5	−4.77	−2.55
100	−2.32	−1.85	−70.0	−68.4	1.19	4.60	−2.59	−2.13	−68.1	−67.5	0.68	4.45
200	−2.08	−1.22	−68.4	−64.1	3.25	7.28	−2.36	−1.51	−66.6	−63.3	3.17	7.23
298.15	−1.73	−0.47	−66.9	−61.1	3.74	7.84	−2.01	−0.76	−65.2	−60.3	3.70	7.82
500	−0.94	1.15	−64.9	−57.0	4.01	8.14	−1.23	0.86	−63.2	−56.1	3.99	8.14
1000	1.10	5.26	−62.1	−51.3	4.12	8.27	0.81	4.97	−60.4	−50.4	4.12	8.27
$Cl_2(g) + HF(g) = Cl_2 \cdot HF(g)$												
20	−0.44	0.12	−43.1	−43.1	−16.2	−15.8	−0.89	−0.36	−41.5	−41.4	−16.7	−16.1
50	−0.81	−0.17	−54.9	−52.7	−9.97	−5.24	−1.29	−0.67	−54.4	−51.9	−11.0	−6.00
100	−1.18	−0.23	−60.3	−53.8	−5.45	1.73	−1.70	−0.76	−60.2	−53.3	−5.79	1.50
200	−1.51	0.21	−62.7	−50.9	−1.84	6.13	−2.04	−0.32	−62.7	−50.5	−1.97	6.07
298.15	−1.61	0.88	−63.1	−48.2	−0.22	7.27	−2.18	0.34	−63.3	−47.8	−0.95	7.24
500	−1.25	2.43	−62.3	−44.2	3.75	7.93	−2.29	1.89	−63.6	−43.8	−0.35	7.92
1000	1.60	6.49	−58.4	−38.6	5.92	8.22	−2.38	5.94	−63.7	−38.2	−0.09	8.21
$Cl_2(g) + HF(g) = Cl_2\text{–}HF(g)$												
20	−2.07	−1.70	−61.3	−61.0	−17.0	−16.6	−2.26	−1.97	−58.7	−59.9	−12.7	−15.9
50	−2.11	−1.78	−64.4	−65.3	9.43	10.5	−2.27	−1.98	−60.3	−62.4	5.10	11.7
100	−1.81	−1.12	−59.9	−56.1	2.07	11.1	−2.17	−1.42	−58.6	−54.5	−0.01	8.59
200	−1.74	−0.25	−59.4	−50.0	0.51	7.85	−2.18	−0.68	−58.7	−49.3	0.32	7.31
298.15	−1.66	0.52	−59.1	−46.8	1.36	7.90	−2.11	0.06	−58.4	−46.3	1.04	7.70
500	−1.13	2.14	−57.8	−42.7	3.86	8.12	−1.82	1.65	−57.7	−42.2	1.73	8.06
1000	1.40	6.24	−54.3	−37.0	5.20	8.26	−0.77	5.74	−56.3	−36.5	2.34	8.24

[a] The parameter x denotes either the partial association to $HF \cdot Cl_2$(g) and to $Cl_2 \cdot HF$(g), or the overall association to the equilibrium mixture of both isomers, Cl_2–HF(g).

[b] The standard state is an ideal gas at 1 atm (101 325 Pa) pressure.

and the IR and HT approximations of internal-rotational motion. Thus, the thermodynamics of the system are described. For practical purposes it is preferable to use the CPF data rather than the less sophisticated SCF approximation. On the other hand, it is impossible to decide which of the two limiting approaches (IR and HT) should be preferred. In principle the IR values should be, but further studies on the nature of this motion in the complexes considered will be necessary. Finally, note that not only the $\delta C_{p,1}^{(\mathrm{iso})}$ terms in Fig. 2, but also the overall terms of the standard changes of heat capacity at constant pressure in Table 2 exhibit courses with local maxima. At the same time the corresponding partial terms exhibit only a monotonic increase with temperature. This difference suggests that the presence of such local maxima in the temperature dependences of the heat capacity term could be used to prove of the existence of isomerism in the system studied.

In spite of a number of differences between the values from the IR and HT approximations, the approaches agree in two respects. The first consists in the finding that mutual relative stabilities of the isomers $HF \cdot Cl_2$ and $Cl_2 \cdot HF$ are changed at relatively low temperature. In addition, this feature is reproduced in both approaches to the potential energy (SCF and CPF). Similarly, a local maximum is always present in the temperature course of the $\delta C_{p,1}^{(\mathrm{iso})}$ term, its exact position being only a little different in the IR and HT treatments. These fairly concordant findings in terms of various approximations strenghten the reliability of the data.

In analogy with the ratio of the mole fractions w_1 and w_2, the isomerism contributions $\delta X_1^{(\mathrm{iso})}$ are also transferable for the Cl_2–HF(g) species into all ideal systems in which the condition is fulfilled (cf. also ref. 38) concerning the establishment of inter-isomer equilibrium between both the structures representing this species (hence de facto pseudo-species). In particular, the problem in question will be the concern of a study of a system containing both the homo-dimers as soon as the molecular thermodynamic data are available to the same extent as provided for the hetero-dimer by the present communication.

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