Thermochimica Acta, 182 (1991) 67–75
Elsevier Science Publishers B.V., Amsterdam

HF–ClF(g) molecular complex: two limiting approaches to its thermodynamics *

Zdeněk Slanina **
Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Mainz (Germany)
(Received 26 September 1990)

Abstract

An evaluation has been carried out of the thermodynamics of the gas-phase association of HF and ClF which gives two isomeric complexes, HF·ClF and ClF·HF. The evaluation has been carried out in terms of the RRHO partition functions and the energetics supplied with molecular data from recent quantum-chemical calculations. Special attention has been paid to the internal rotational motion in these complexes which, as well as being described as a harmonical torsion, has also been treated by another limiting approach, namely the free internal rotation. To describe the thermodynamics of the latter motion, the technique of direct summation, recently introduced for these purposes, was used. Under certain conditions both limiting approaches to this motion can lead to relatively great differences in the values of the thermodynamic terms. Special attention has been paid to the interplay of both isomeric structures within their equilibrium mixture which is characterized in detail. In particular it has been shown that the order of the relative stabilities of both isomers can be interchanged with temperature.

INTRODUCTION

In the current intensive studies of multiparticle clusters (see, for example, ref. 2), gradually increasing attention has been paid to the temperature term as one of the determining and limiting factors. At the same time, however, there is a difference in the nature of the temperature phenomena obtained from experiment and treatable by current computational theory. The problem lies in the fact that cluster experiments often deal with thermodynamically non-equilibrium situations, whereas theory works in terms of the equilibrium thermodynamical concepts. Of course, this does not mean that equilibrium situations cannot be observed, but merely that non-equilibrium

---

* Part XLVII in the series Multimolecular Clusters and Their Isomerism; for Part XLVI, see ref. 1.

** Permanent and reprint request address: The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, CS-18223 Prague 8, Czechoslovakia.

0040-6031/91/$03.50

conditions can be useful for some observations. For computational theory, interest is frequently focused on the evaluation of the standard thermodynamic characteristics of cluster formation [3–14], namely on the basis of partition functions, the parameters required to characterize the individual quantum models being taken from the computations within the methods of quantum chemistry or molecular mechanics. With respect to the computational demands, these partition functions are typically constructed in terms of the usual rigid rotor and harmonic oscillator (RRHO) approach, treatments beyond this approach, though undoubtedly necessary, being nevertheless exceptional at present [5].

Recently, theory has indicated the possibility of isomerism in these clusters, which would, of course, have its thermodynamical consequences [15–19]. These cases of cluster isomerism fall within a more general region of reaction-component isomerism and its impact on equilibrium behaviour [20–27]. Nevertheless, in the case of cluster isomerism, the problems [23] of attaining thermodynamic equilibrium, of deviations from the RRHO model, of distinguishing the individual isomeric structures etc. become particularly important. These studies are also directly connected with the organization of observation: they can suggest estimated optimum conditions leading to the experimental appearance of this isomerism.

The present work deals with this set of problems using a particular system —the gas-phase heterosystem HF–ClF.

CHARACTERIZATION AND TREATMENT OF THE HF–ClF(g) COMPLEX

The system studied is interesting both theoretically [28,29] and experimentally [30]. So far, the most detailed quantum-chemical description of this system has been presented by Rendell et al. [29]. Their computations adopt two approaches: one in terms of a mere SCF treatment, and the other, on a more sophisticated level uses the coupled-pair functional (CPF) formalism. When optimizing the structure of the complex in terms of minimization of the potential energy, they found two local minima in each of the two approaches: the energetically lower-lying structure bonded via the F atom of the HF monomer (HF · ClF) and the H-bonded structure (ClF · HF). Harmonic vibrational analysis was carried out in these local minima which led to the frequencies of the intermolecular vibrational modes. The respective constituent monomer units were similarly described. Hence it was possible to determine both the potential energy changes, ΔE_i, and the ground state energy changes, $\Delta H^{\ominus}_{0,i}$ for the reactions

$$\mathrm{HF(g) + ClF(g) \rightarrow HF \cdot ClF(g)} \tag{1}$$

$$\mathrm{HF(g) + ClF(g) \rightarrow ClF \cdot HF(g)} \tag{2}$$

as shown in Table 1. The F-bonded structure lies lower on both these energy scales and in both approaches to the potential energy (SCF, CPF).

TABLE 1

Energetics [a] of the gas-phase associations of HF and ClF

Association process	SCF [b] (kJ mol^{-1})			CPF [b] (kJ mol^{-1})		
	ΔE_t	$\Delta H^{\ominus}_{0,t}$		ΔE_t	$\Delta H^{\ominus}_{0,t}$	
		IR	HT		IR	HT
$HF(g) + ClF(g) \rightarrow HF \cdot ClF(g)$	−8.41	−6.12	−5.55	−8.70	−6.37	−5.96
$HF(g) + ClF(g) \rightarrow ClF \cdot HF(g)$	−7.95	−4.87	−3.00	−8.37	−4.96	−3.45

[a] Potential energy changes, ΔE_t, and ground state energy changes, $\Delta H^{\ominus}_{0,t}$, (i.e. the standard enthalpy changes at absolute zero).

[b] According to ref. 29.

The thermodynamics of reactions (1) and (2) were described in terms of the RRHO approximation to the partition functions using the calculated structural, vibrational and energy parameters [29]. Beyond the usual RRHO approach, attention was paid to the approaches that describe the harmonic vibrational torsion in these complexes. This harmonic torsion follows from the harmonic vibrational analysis as an equivalent corresponding to the internal rotation. Although there is not enough information available so far, it is presumed that in the complexes of the type considered this internal rotation is close [31,32] to the free internal rotation. Free internal rotation represents a limiting case of hindered internal rotation [33] which maximizes the contributions of this type of motion to the values of the equilibrium constants. Therefore two limiting approaches were considered in the present work when evaluating the thermodynamics: (i) the description of internal rotation in the complexes as the harmonic torsion (HT) and (ii) its description as the free internal rotation (IR). The reduced moments of inertia, I_r, necessary for approach (ii) were calculated by a known procedure [33].

The partition function of the internal free rotation was used in the standard way in a simple form:

$$q_0 = (\pi/\sigma)^{1/2} \tag{3}$$

where σ is a quantity inversely proportional to the product of I_r and the temperature T. However, function (3) fails in the region of large σ values (which are significant for molecular complexes); this is dramatically manifested in the limiting case of $\sigma \rightarrow \infty$ where eqn. (3) gives an entropy contribution value of $-\infty$ instead of the expected [34,35] value of zero. Therefore approximations were suggested which exhibit the correct limiting behaviour [34–38]:

$$q_1 = q_0 + 1 \tag{4}$$

$$q_2 = (\pi/\sigma)^{1/2} + 1 + \exp(-\sigma) - (\pi/\sigma)^{1/2}\Phi(\sigma^{1/2}) \tag{5}$$

where Φ is the error function. However, even the relatively most sophisticated formula, eqn. (5), does not exhibit quite satisfactory behaviour [39] in the region of $\sigma \approx 1$. Therefore it was finally recommended that the modified technique of direct summation [40] be used. This technique is also used exclusively in approach (ii) in the present work. Nevertheless, it should be noted that quite recently a closed-form formula has been suggested which is even more sophisticated than eqn. (5), namely that derived by Pan [41] starting from the Korsch semiclassical approximation [42,43]

$$q_3 = q_0 + 2q_0 \exp(-\pi q_0^2) + 2q_0 \exp(-4\pi q_0^2) \tag{6}$$

This three-term formula suggested by Pan exhibits excellent behaviour around the point $\sigma = 1$, and from this standpoint it is clearly superior to eqn. (5). Moreover, by its precision in this region it is quite comparable with the results obtained from the direct summation, being of course more appropriate for practical calculations. Nevertheless, for large σ values (i.e. for $q_0 \to 0$), q_3 is reduced to $5q_0$ and hence has the same limiting features as given above for q_0. Therefore in the present context it seemed more appropriate to retain the technique of direct summation [40].

From the thermodynamics of the partial equilibria in which the individual isomeric structures take part (eqns. (1) and (2)), it is also possible to describe the thermodynamics of the overall association process

$$\mathrm{HF(g) + ClF(g) \rightarrow HF\text{–}ClF(g)} \tag{7}$$

leading to an equilibrium mixture of both structures. For this purpose, a method developed for describing the thermodynamics of equilibrium isomeric mixtures [44–47] was used. The proportions of the relative populations of both isomers were expressed by their mole fractions, w_i. For evaluation of the effects of isomerism for the overall thermodynamics (eqn. (7)) we used the isomerism contributions to the values of the thermodynamic function $\Delta X^{\ominus}$ related to isomer 1:

$$\delta X_1^{(\mathrm{iso})} = \Delta X^{\ominus} - \Delta X_1^{\ominus} \tag{8}$$

defined as the difference between the overall standard term of this quantity, $\Delta X^{\ominus}$ (i.e. in our case the value corresponding to reaction (7)), and the partial term $\Delta X_1^{\ominus}$ corresponding to the structure which is more stable at low temperatures, labelled 1 (i.e. in our case the value corresponding to reaction (1)).

RESULTS AND DISCUSSION

Figure 1 represents the temperature courses of the mole fractions, w_i, of both isomers in their equilibrium mixture for both approximations of potential energy [29] and both approaches to the description of internal rotation (IR and HT). In all four cases thus considered it is observed that the F-bonded structure is predominant at the lowest temperatures, but with

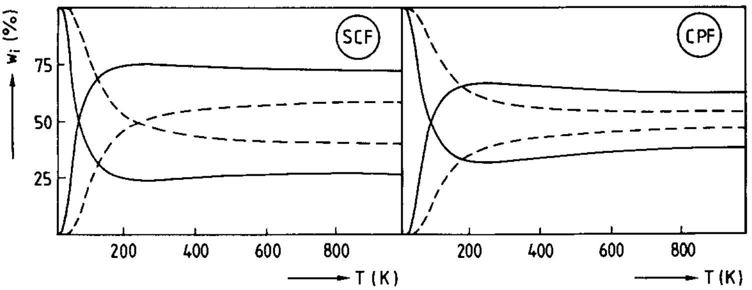

Fig. 1. Temperature dependences of the mole fractions w_i for the gas-phase equilibrium mixture of HF·ClF and ClF·HF. The results based on the SCF and CPF approaches [29] are given in the left-hand part and right-hand part respectively; the solid and broken lines represent the IR and HT results respectively.

increasing temperature the relative stabilities of the two structures approach each other. In three out of the four situations considered in Fig. 1, the relative stabilities are even interchanged; hence the H-bonded structure becomes relatively more abundant above a certain temperature. Within the SCF approach these temperatures of interchange are 75.5 K and 248.8 K in the IR and HT approximations respectively. In the CPF description of potential energy this crossing is only observed with the IR approximation where the temperature of equimolarity is 93.4 K. Thus it can be concluded that all four combinations of the methodical approaches considered show that, except for the lowest temperatures, it is necessary to presume the considerable coexistence of both isomers. The fact that only the F-bonded structure was observed experimentally [30] seems to indicate that a very low effective temperature [34] was used in this observation.

Figure 2 represents the temperature dependences of the isomerism contributions related to HF · ClF as the reference structure for three thermodynamic quantities: enthalpy ($X = H$), entropy ($X = S$) and heat capacity at constant pressure ($X = C_p$). An especially interesting course is that of the $\delta C_{p,I}^{(iso)}$ term because of the presence of a relatively high local maximum. Within the SCF approximation this maximum appears at 46.4 K (the maximum height is 16.6 J K^{-1} mol^{-1}) and 79.0 K (the maximum height 9.9 J K^{-1} mol^{-1}) for the IR and HT approaches respectively. Similarly, in the CPF method the local maxima appear at 50.7 K (maximum height 14.3 J K^{-1} mol^{-1}) and 76.2 K (maximum height 6.7 J K^{-1} mol^{-1}) for the IR and HT partition functions respectively. Although these maxima are one order lower than the highest maximum of this type reported so far [47], nevertheless they are sufficiently distinct and represent another interesting illustration of the possibility of enhancement of heat capacity by isomeric interplay [44–47].

Table 2 lists the values of standard changes of enthalpy, entropy and heat capacity at constant pressure for the partial reactions (1) and (2), and for the

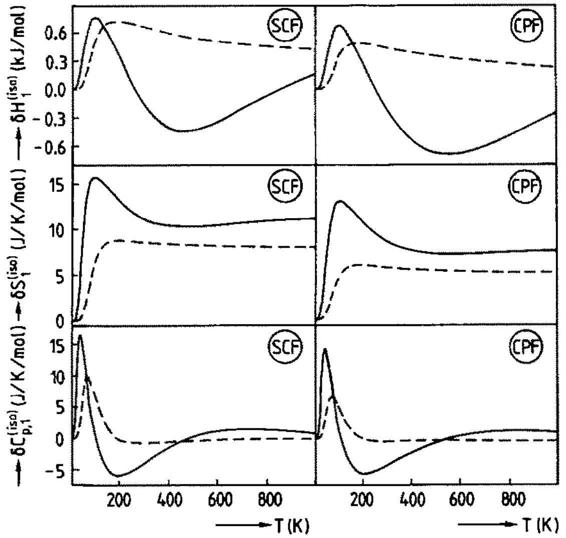

Fig. 2. Temperature dependences of the isomerism contributions to enthalpy, $\delta H_1^{(iso)}$, entropy, $\delta S_1^{(iso)}$, and heat capacity at constant pressure, $\delta C_{p,1}^{(iso)}$, in the HF–ClF gas-phase equilibrium system (the isomerism contribution terms are related to the HF·ClF isomer as the reference structure). The results based on the SCF and CPF approaches [29] are given in the left-hand part and right-hand part respectively; the solid and broken lines represent the IR and HT results respectively.

overall association, eqn. (7). The data are evaluated again for both quantum-chemical methods considered, SCF and CPF, and also for both approaches to the description of internal rotation in the complexes, IR and HT. These data make it possible to determine the limits within which we can expect the values of the standard thermodynamic characteristics of the reactions studied to fall. In the particular case of standard changes of heat capacity, $\Delta C_{p,x}^{\ominus}$, it can be seen that the partial terms increase steadily with temperature, but the overall term (as already found with the isomerism contribution, $\delta C_{p,1}^{(iso)}$) exhibits a local maximum. This qualitative difference in behaviour between the partial and overall standard changes could serve as a diagnostic tool to prove the presence of isomers in this system, if it were possible in the observation to ensure the fulfilment of conditions of equilibrium and the recording of the overall term of standard change of heat capacity.

In spite of the quantitative differences between the individual approximations (at least at some temperatures), it can be stressed, in conclusion, that two qualitative features of the system were found in all four methodical combinations considered: the coexistence of both structures within a substantial part of the relevant temperature interval, and the existence of local temperature maxima with the terms of heat capacity, indicating isomerism. The study describes, to a sufficient extent from the standpoint of possible

TABLE 2

Temperature dependences of partial [a] and overall [a] standard [b] enthalpies, $\Delta H_x^\ominus$, entropies, $\Delta S_x^\ominus$, and heat capacities at constant pressure, $\Delta C_{p,x}^\ominus$, for gas-phase associations of HF and ClF evaluated within the IR and HT treatments [c]

T	SCF						CPF					
(K)	$\Delta H_x^\ominus$ (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})	
	IR	HT	IR	HT	IR	HT	IR	HT	IR	HT	IR	HT
$HF(g) + ClF(g) = HF \cdot ClF(g)$												
20	−6.52	−5.95	−68.7	−68.6	−24.0	−23.6	−6.77	−6.36	−69.5	−69.1	−23.8	−22.3
50	−7.08	−6.43	−86.6	−84.4	−14.0	−9.46	−7.34	−6.80	−87.5	−83.5	−14.4	−8.29
100	−7.52	−6.60	−93.0	−87.1	−4.18	0.882	−7.79	−6.93	−94.1	−85.7	−4.33	1.24
200	−7.38	−6.18	−92.4	−84.4	4.40	6.04	−7.66	−6.50	−93.6	−82.9	4.34	6.13
298.15	−6.92	−5.52	−90.6	−81.8	4.59	7.25	−7.21	−5.83	−91.7	−80.2	4.54	7.29
500	−6.08	−3.97	−88.4	−77.8	3.95	7.93	−6.37	−4.27	−89.6	−76.2	3.93	7.94
1000	−4.08	0.091	−85.6	−72.2	4.07	8.22	−4.37	−0.210	−86.8	−70.6	4.07	8.22
$HF(g) + ClF(g) = ClF \cdot HF(g)$												
20	−5.24	−3.37	−53.0	−53.0	−20.4	−20.4	−5.34	−3.83	−54.6	−54.6	−20.7	−20.7
50	−5.74	−3.87	−68.8	−68.8	−13.9	−13.9	−5.88	−4.36	−71.4	−71.3	−15.8	−15.5
100	−6.30	−4.39	−76.7	−76.2	−9.00	−7.07	−6.52	−4.93	−80.5	−79.5	−10.3	−7.27
200	−6.91	−4.60	−81.1	−78.0	−3.81	1.58	−7.21	−5.12	−85.6	−81.2	−4.45	1.88
298.15	−7.12	−4.26	−82.1	−76.7	−0.67	4.84	−7.51	−4.75	−86.8	−79.7	−1.78	5.04
500	−6.69	−3.02	−81.1	−73.5	4.45	6.98	−7.40	−3.48	−86.6	−76.5	2.78	7.06
1000	−3.88	0.800	−77.2	−68.3	5.27	7.97	−4.75	0.355	−83.1	−71.2	5.92	7.99
$HF(g) + ClF(g) = HF{-}ClF(g)$												
20	−6.51	−5.95	−68.5	−68.6	−22.5	−23.6	−6.77	−6.36	−69.4	−69.1	−23.2	−22.3
50	−6.74	−6.40	−77.3	−83.6	2.30	−5.24	−7.09	−6.77	−80.9	−82.8	−0.06	−4.93
100	−6.76	−6.14	−77.4	−80.6	−2.99	8.87	−7.12	−6.61	−81.2	−81.1	−2.69	6.37
200	−7.03	−5.46	−79.3	−75.8	−1.59	5.87	−7.36	−6.01	−82.9	−76.9	−1.39	5.94
298.15	−7.07	−4.86	−79.5	−73.3	0.65	6.51	−7.41	−5.39	−83.2	−74.4	0.32	6.75
500	−6.53	−3.43	−78.2	−69.7	4.35	7.49	−7.04	−3.92	−82.3	−70.7	3.31	7.62
1000	−3.94	0.513	−74.6	−64.3	4.95	8.08	−4.61	0.052	−79.0	−65.2	5.22	8.12

[a] The index x denotes either the partial association to $HF \cdot ClF$ and to $ClF \cdot HF$, or the overall association to the equilibrium mixture of both isomers, $HF{-}ClF$.

[b] The standard state is an ideal gas at 1 atm = 101325 Pa pressure.

[c] IR and HT denotes the free internal rotation and harmonical torsion approaches respectively to the internal rotation in the complexes.

applications, the thermodynamics of formation of the HF–ClF(g) associates. Nevertheless, a complete description of the behaviour of the associating mixture of HF(g) and ClF(g) represents a more general problem whose solution will also require the analogous description of the thermodynamics of formation of the corresponding homodimers.

ACKNOWLEDGEMENTS

Support from the Alexander von Humboldt-Stiftung is appreciated as well as the valuable discussions and kind hospitality of Professor Karl Heinzinger.

REFERENCE

1 Z. Slanina, Thermochim. Acta, 173 (1990) 171.
2 P. Jena, B.K. Rao and S.N. Khanna (Eds.), Physics and Chemistry of Small Clusters, Plenum, New York, 1987.
3 M.R. Hoare, Adv. Chem. Phys., 40 (1979) 49.
4 Z. Slanina, Adv. Quantum Chem., 13 (1981) 89.
5 L.S. Bernstein and J. Wormhoudt, J. Chem. Phys., 80 (1984) 4630.
6 S. Yamabe, T. Minato and K. Hirao, J. Chem. Phys., 80 (1984) 1576.
7 S. Yamabe, T. Minato, M. Sakamoto and K. Hirao, Can. J. Chem., 63 (1985) 2571.
8 A. Pullman, P. Claverie and M.-C. Cluzan, Chem. Phys. Lett., 117 (1985) 419.
9 M.T. Nguyen, Chem. Phys. Lett., 117 (1985) 571.
10 S. Yamabe, Y. Furumiya, K. Hiraoka and K. Morise, Chem. Phys. Lett., 131 (1986) 261.
11 K. Hiraoka, T. Shoda, K. Morise, S. Yamabe, E. Kawai and K. Hirao, J. Chem. Phys., 84 (1986) 2091.
12 K. Hiraoka, H. Takimoto and S. Yamabe, J. Phys. Chem., 90 (1986) 5910.
13 P. Pal and M.R. Hoare, J. Phys. Chem., 91 (1987) 2474.
14 M.T. Nguyen, A.F. Hegarty and T.-K. Ha, J. Mol. Struct. (Theochem), 150 (1987) 319.
15 D.J. McGinty, Chem. Phys. Lett., 13 (1972) 525.
16 J.J. Burton, Chem. Phys. Lett., 17 (1972) 199.
17 Z. Slanina, Collect. Czech. Chem. Commun., 40 (1975) 1997.
18 Z. Slanina, Adv. Mol. Relax. Interact. Proc., 14 (1979) 133.
19 Z. Slanina, J. Phys. Chem., 90 (1986) 5908.
20 R.A. Alberty, Ind. Eng. Chem. Fundam., 22 (1983) 318.
21 R.A. Alberty, J. Phys. Chem., 87 (1983) 4999.
22 R.A. Alberty, J. Phys. Chem., 89 (1985) 880.
23 Z. Slanina, Contemporary Theory of Chemical Isomerism, Academia and Reidel, Prague and Dordrecht, 1986.
24 G.Ya. Kabo, G.N. Roganov and M.L. Frenkel′, Thermodynamics and Equilibria of Isomers, IU, Minsk, 1986, (in Russian).
25 L.T. Wille, Mol. Phys., 61 (1987) 409.
26 B.I. Dunlap, Int. J. Quantum Chem., Quantum Chem. Symp., 22 (1988) 257.
27 M.L. Frenkel′, G. Ya. Kabo and G.N. Roganov, Thermodynamical Characteristics of Isomerization Reactions, IU, Minsk, 1988, (in Russian).
28 H. Umeyama, K. Morokuma and S. Yamabe, J. Am. Chem. Soc., 99 (1977) 330.
29 A.P.L. Rendell, G.B. Bacskay and N.S. Hush, J. Chem. Phys., 87 (1987) 535.
30 S.E. Novick, K.C. Janda and W. Klemperer, J. Chem. Phys., 65 (1976) 5115.

31 Z. Slanina, Collect. Czech. Chem. Commun., 47 (1982) 3206.
32 A.A. Vigasin, Zh. Strukt. Khim., 28 (1987) 120.
33 K.S. Pitzer, J. Chem. Phys., 14 (1946) 239.
34 Z. Slanina, J. Phys. Chem., 86 (1982) 4782.
35 Z. Slanina, Ber. Bunsenges. Phys. Chem., 87 (1983) 28.
36 Z. Slanina, Int. J. Quantum Chem., 27 (1985) 691.
37 Z. Slanina, Theor. Chim. Acta, 69 (1986) 135.
38 Z. Slanina, Z. Phys. Chem. (Leipzig), 267 (1986) 737.
39 Z. Slanina, J. Phys. Chem., 90 (1986) 2957.
40 Z. Slanina, Comput. Chem., 11 (1987) 231.
41 H.-Y. Pan, Chem. Phys. Lett., 151 (1988) 35.
42 H.J. Korsch, J. Phys. A, 12 (1979) 1521.
43 H.-Y. Pan, J. Chem. Phys., 87 (1987) 4846.
44 Z. Slanina, Chem. Phys. Lett., 131 (1986) 420.
45 Z. Slanina, Int. Rev. Phys. Chem., 6 (1987) 251.
46 Z. Slanina, Thermochim. Acta, 128 (1988) 157.
47 Z. Slanina, J. Phys. Chem., 92 (1988) 5836.