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TEMPERATURE INTERPLAY OF ISOMERIC STRUCTURES OC · HF(g) AND CO · HF(g) *

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ABSTRACT

The recent finding of two local energy minima at the ab initio hypersurfaces of CO–HF system has been studied in more detail in terms of the temperature-dependent weight factors of both the isomeric structures OC·HF(g) and CO·HF(g) constructed on the basis of theoretically derived molecular data. Relative stability of the two isomers has been shown to be reversed at temperatures just above 400 K. At moderate and higher temperatures this isomerism contributes substantially to overall values of thermodynamic terms of the association of CO(g) and HF(g), the contributions of the isomerism being the most distinct with the heat capacity at constant pressure. The importance of pressure for observations at higher temperatures is also shown.

INTRODUCTION

A vigorous development has been observed recently in both theoretical and experimental studies of the isomerism of molecular complexes in the gas phase (e.g., [2–4]). Among these isomeric complexes quite often encountered [5–8] are the associations involving HF. Recently, another such system was studied in more detail [9–13], viz. CO–HF. The ab initio calculations [12,13] involving the electron correlation proved the existence of two isomeric structures: OC · HF and CO · HF. A study by Curtiss et al. [13] gave a basic set of molecular parameters of this isomeric pair enabling a more detailed study of its thermodynamics.

Generally, a description in terms of mere depths ΔE_i of the local energy minima of the potential hypersurface (i.e., in terms of simple configurational factors $\exp(-\Delta E_i/RT)$) is not sufficient for a study of relative stabilities of several (m) isomeric structures representing the molecular complex considered. If the individual isomeric structures are taken as independent species,

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* Part XXVIII in the series; for part XXVII see ref. 1.

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the molar fractions w_i of the individual isomers in the equilibrium mixture are given by eqn. (1)

$$w_i = \frac{q_i \exp\left(-\Delta H_{0,i}^0/RT\right)}{\sum_{j=1}^{m} q_j \exp\left(-\Delta H_{0,j}^0/RT\right)} \tag{1}$$

where $\Delta H_{0,i}^0$ denotes the change in the ground-state energy during the formation of the ith isomer from the associated units, and q_i denotes its partition function with respect to this level as the energy zero.

The information set [13] enables a construction of $w_{\mathrm{OC \cdot HF}}$ and $w_{\mathrm{CO \cdot HF}}$ using the usual rigid rotor and harmonic oscillator approximation for the evaluation of q_i. Figure 1 presents the temperature dependences of these weights based on the 4-31G equilibrium geometries and harmonic vibration frequences and the most sophisticated energetics reported in ref. 13. The effects of rotational and, in particular, vibrational motions are noteworthy. Although (in terms of the potential energy) the OC · HF structure is more stable by more than 6 kJ mol^{-1}, the mutual convergency of relative stabilities of the two structures is such that the two structures are equimolar

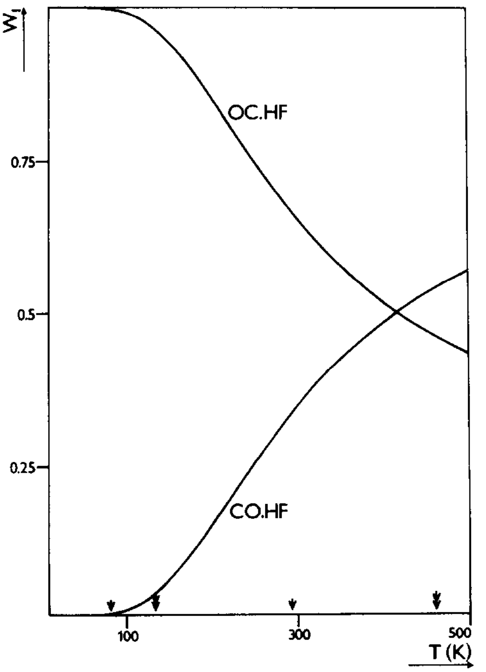

Fig. 1. Temperature dependences of the weight factors w_i of the OC·HF(g) and CO·HF(g) forms of CO–HF associates. The arrow and double arrow indicates the CO or HF normal boiling point and critical temperature, respectively (the value for CO is lower than that corresponding to HF in both cases).

TABLE 1

Various approximations of the weight $w_{OC \cdot HF}$ of OC·HF in the gas-phase equilibrium mixture [a] with CO·HF

T (K)	Simple configurational factor	$w_{OC \cdot HF}$	
		4-31G [b]	6-31G* [b]
100	0.999	0.992	0.992
298.15	0.927	0.655	0.646
406.3	0.866	0.510	0.500 [c]
416.0	0.861	0.500 [c]	0.490
500	0.820	0.431	0.422

[a] Corresponding weight $w_{CO \cdot HF}$ of the other isomer is given as: $w_{CO \cdot HF} = 1 - w_{OC \cdot HF}$.

[b] Basis set used in geometry optimization [13].

[c] Equimolar point of the gas-phase equilibrium isomeric mixture.

at about 416 K, and above this temperature the more shallow energy minimum, CO · HF, becomes the relatively more abundant component of the equilibrium isomeric mixture. Table 1 demonstrates the inapplicability of simple configurational factors to the estimation of mixture composition at moderate and higher temperatures. Reference 13 also gave an evaluation of the geometry parameters in the 6-31G* basis set; Table 1 shows that the differences in the weight factor values only are indistinct with these two sources of structural data. It should be mentioned also that the arguments already given [14] show that a transition to more sophisticated approximations [15] of q_i should not affect markedly the w_i values reported.

As far as the isomerism of the associate resulting from the process is concerned

$$\mathrm{CO(g) + HF(g) \rightleftharpoons CO{-}HF(g)} \qquad (2)$$

two types of thermodynamic characteristics of the equilibrium (2) can be differentiated [16,17]: the partial values connected with the processes (2) involving either the OC · HF or the CO · HF isomer on the right-hand side, and the overall values for the process (2) with equilibrium mixture of the two isomers on the right-hand side. The standard thermodynamic terms ΔH_T^0, ΔS_T^0, and $\Delta C_{p,T}^0$ were determined (for the same type of approximation of q_i and molecular parameters as those used for the determination of w_i in Fig. 1) for both the formation of individual isomers and the overall association process (Fig. 2) using [16,17] the earlier-constructed weights w_i. For all the situations included in Fig. 2 it is generally true that the overall thermodynamic terms can be approximated reasonably well with the partial values from the OC · HF isomer at the lower temperatures of the range studied, but —at higher temperatures—the isomerism contribution to the overall values becomes more and more significant. An interesting situation is encountered with the heat capacity at constant pressure, where it is possible to differentiate [16,17] between two types of the overall term—the relaxation value fully

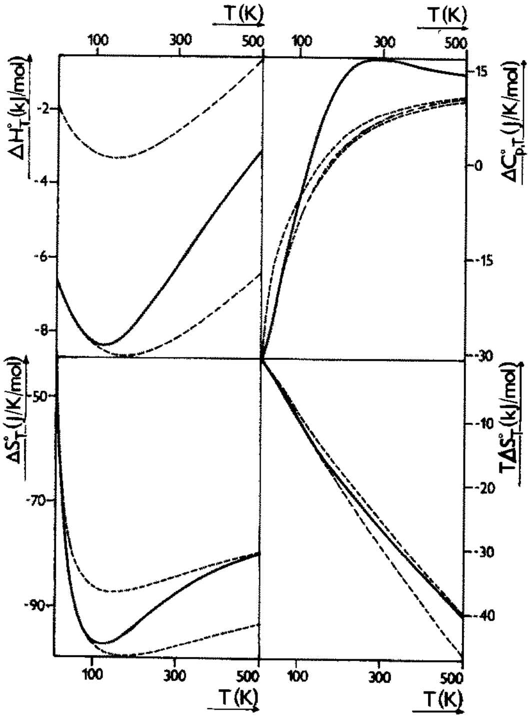

Fig. 2. Temperature dependence of the standard enthalpy ΔH_T^0, heat capacity at constant pressure $\Delta C_{p,T}^0$, and entropy ΔS_T^0 and $T\Delta S_T^0$ terms for the partial associations (OC·HF(g) or CO·HF(g); in all cases the OC·HF isomer formation is given by the lower dashed line) and overall associations (the solid lines; with heat capacity the solid line indicates the relaxation term while the dashed-dotted line the isofractional term) of CO(g) and HF(g). The standard state is an ideal gas at 1 atm pressure (1 atm = 101 325 Pa).

respecting the temperature changes in w_i and the isofractional value involving the presumption that there is not enough time (during experimental observation) for w_i to change with the changing temperature, so that the fractions of isomers are maintained. With weak isomeric molecular complexes, of course, the observations will usually provide the relaxation term. The value of $\Delta C_{p,T}^0$ can be distinctly affected by the isomerism: e.g., at room temperature the overall relaxation term is almost 2.5 times higher than the value corresponding to the formation of the OC · HF isomer. At the same temperature the isomerism contribution [16] to ΔH_T^0 and ΔS_T^0 terms makes about 31 and 11% of the values of corresponding overall terms, respectively. Thus it can be concluded by stating that at moderate and higher temperatures it is unjustifiable to approximate the thermodynamics of formation of the CO–HF system by the partial values corresponding to the more stable isomer—e.g., at the potential energy scale (i.e., OC · HF), and it is necessary to use the values following from the weighting of the contributions of the two isomers to the thermodynamics of the overall association process (2).

Finally, let us note that observation of the CO–HF system is not necessarily meaningful at low temperatures only [9] (i.e., when, according to the w_i values, the OC · HF isomer represents the dominant form of the associate). The equilibrium constant of the association (2), decreasing with temperature, can be compensated for (especially in the region above the critical temperature of HF) by application of higher pressures of the gaseous mixture. So, for example, at a temperature of 500 K the overall content [18] of the associate in the mixture (CO to HF ratio 1 : 1) gives 0.004, 3.4 and 59.7 molar % at pressures of 1, 10^3 and 10^5 atm, respectively (the degree of association was evaluated with the presumption that no other associates were present besides the hetero-dimers).

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