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A computational evaluation of the thermodynamics of HCP(g) dimerization [a]

Zdeněk Slanina

Max-Planck-Institut für Chemie, Otto-Hahn-Institut, Mainz (Germany)

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Abstract

Dimerization of HCP(g) is treated as a convolution of two partial processes recognized in recent computational treatments, namely, dimerizations to the T-shaped or linear structure. The overall thermodynamics is influenced substantially by the presence of the two species, this being particularly true for the term for the heat capacity at constant pressure. Up to one third of the standard molar heat capacity at constant pressure of the $(HCP)_2$ equilibrium isomeric mixture can originate in the isomeric interplay. Characteristic heat-capacity–temperature maxima are described.

INTRODUCTION

Isomerism of molecular complexes represents their essential feature [1–6], though being of considerable diversity (for a new type, van der Waals isomers of chemically bonded molecules, see ref. 7). $(HCP)_2$ serves as an interesting illustration. The system has so far been studied rarely [8–12]; however the most recent report [12] supplied a complete description which can support further derived studies (the species is a phosphorous analogue of the more frequently treated HCN associating system [13–17]). The present study deals with computational evaluation of the HCP gas-phase dimerization, due attention being paid to the computationally predicted [12] isomerism in the dimer.

THE $(HCP)_2$ ISOMERS

Two different minimum-energy structures for $(HCP)_2$ have been found [12]: T-shaped and linear species. Two energy approximations were used

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Correspondence to: Z. Slanina, The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, CS-18223 Prague 8-Kobylisy, Czech and Slovak Federal Republic.

[a] Part LXVIII in the series Multi-Molecular Clusters and Their Isomerism; for Part LXVII, see ref. 1.

TABLE 1

Survey of the dimerization energetics [12] (in kJ mol^{-1}) for the T-shaped and linear $(\mathrm{HCP})_2$

Association	RHF		MP2	
	ΔE_i [a]	$\Delta H^{\ominus}_{0,i}$ [b]	ΔE_i [a]	$\Delta H^{\ominus}_{0,i}$ [b]
2HCP = T-shaped $(\mathrm{HCP})_2$	−1.39	−0.39	−5.48	−4.48
2HCP = linear $(\mathrm{HCP})_2$	−0.15	0.25	−2.76	−2.36

[a] Potential-energy change.

[b] Ground-state energy change, i.e. the standard enthalpy change at absolute zero temperature.

[12] for geometry optimizations (restricted Hartree–Fock (RHF) and second-order perturbation (MP2) treatments, both in an STO/6-31G** basis set); however, only the MP2 geometry is employed in our study (also for the monomer). The T-shaped isomer lies lower in both potential-energy approximations (Table 1). Investigation of the stationary points in terms of the force-constant matrix revealed that only in the RHF approximation are both structures local energy minima; in the MP2 vibrational treatment the linear species exhibited a (degenerate) imaginary frequency. Hence, the RHF harmonic vibrational frequencies served in our approach for construction of the vibrational partition function.

COMPUTATIONS

We shall describe an equilibrium (n membered) isomeric mixture by the values of the mole fractions w_i of the individual isomers. The isomeric mole fractions do not depend on the total pressure but on the temperature T only. The isomers are, in a first approximation, described by their potential energy terms ΔE_i. However, if their rotational-vibrational motions are to be considered, then relevant quantities are the standard enthalpy changes at absolute zero $\Delta H^{\ominus}_{0,i}$ and the isomeric partition functions q_i. Under the conditions of inter-isomer thermodynamic equilibrium, the mole fractions are given [2,3] by

$$w_i = \frac{q_i \exp\left[-\Delta H^{\ominus}_{0,i}/(RT)\right]}{\sum_{j=1}^{n} q_j \exp\left[-\Delta H^{\ominus}_{0,j}/(RT)\right]} \tag{1}$$

where R denotes the gas constant.

The whole system thermodynamics can be described in terms of partition functions and energetics. For isomeric systems two categories of quantities are to be considered [2,3]: partial and overall. The standard partial terms $\Delta X_i^{\ominus}$ belong to the processes dealing with the individual isomers. The standard overall terms $\Delta X_T^{\ominus}$ correspond to a total process involving a pseudo-species formed by the equilibrium isomeric mixture. Finally, in addition to the partial and overall terms, a third quantity has been introduced [2,3], namely, the so-called isomerism contributions to thermodynamic terms δX_1

$$\delta X_1 = \Delta X_T^{\ominus} - \Delta X_1^{\ominus} \tag{2}$$

It is convenient that the most stable species (in the low-temperature region) be chosen as the reference structure, labelled $n = 1$. The relationships for isomerism contributions to enthalpy $X = H$, entropy $X = S$, or heat capacity at constant pressure $X = C_p$ are given elsewhere [2,3]. It should, however, be mentioned that two kinds of terms are considered in the case of the heat capacity: relaxation $\delta C_{p,1}$ and isofractional $\delta C_{p,w,1}$. The latter represents an approximation of the former for temperature-independent w_i weights (the two types of terms coincide in the high- and low-temperature limits).

RESULTS AND DISCUSSION

Two energy sets are employed in our study, either RHF or MP2 energetics. Although there is a significant difference between both energetics (Table 1) (moreover, the RHF $\Delta H_{0,i}^{\ominus}$ term for the the linear isomer is positive), the temperature evolution of the relative stabilities (Fig. 1) is quite similar in both cases. In fact, only the ground-state energy separation between both isomers is important for the relative-stability reasoning. In

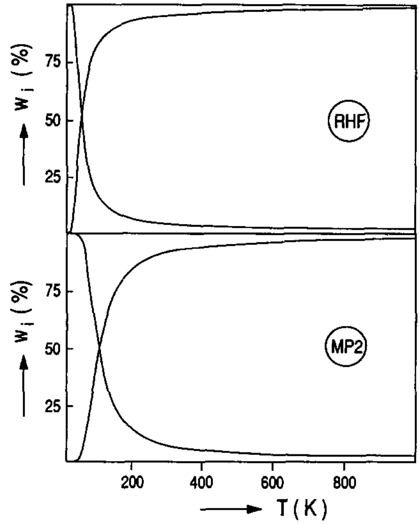

Fig. 1. Temperature dependences of the weight factors w_i for the T-shaped (decreasing curves) and linear $(HCP)_2$ isomers evaluated for the RHF and MP2 approach.

TABLE 2

Characterization of some distinguished [a] points in temperature interplay of the T-shaped and linear dimers $(HCP)_2$

Approach	Type [a]	T (K)	w_1 [b] (%)	w_2 [b] (%)	$\delta C_{p,1}$ [c] (J K^{-1} mol^{-1})	$C_p^{\ominus}$ (J K^{-1} mol^{-1})	$\delta C_{p,1}/C_p^{\ominus}$ (%)
RHF	Cross	48.8	50.0	50.0	21.0	83.7	25.0
	M:$\delta C_{p,1}$	38.7	67.3	32.7	23.8	84.8	28.0
	M:$C_p^{\ominus}$	41.4	62.2	37.8	23.5	85.1	27.6
	M:%	37.7	69.3	30.7	23.7	84.5	28.1
MP2	Cross	105	50.0	50.0	26.9	92.5	29.0
	M:$\delta C_{p,1}$	84.5	69.0	31.0	31.5	96.6	32.6
	M:$C_p^{\ominus}$	85.4	68.0	32.0	31.4	96.6	32.5
	M:%	84.0	69.4	30.6	31.4	96.6	32.6

[a] The equimolarity point (cross), the maximum in the isomerism contribution to heat capacity $\delta C_{p,1}$ (M:$\delta C_{p,1}$), the maximum in the standard overall heat capacity at constant pressure $C_p^{\ominus}$ (M:$C_p^{\ominus}$) and the maximum of the relative enhancement $\delta C_{p,1}/C_p^{\ominus}$ of the $C_p^{\ominus}$ term by isomeric interplay (M:%).

[b] w_1 and w_2 denote the equilibrium mole fraction of the T-shaped and the linear isomer, respectively, in their equilibrium mixture ($w_1 + w_2 = 100\%$).

[c] Isomerism contribution to heat capacity related to the species more stable in the low-temperature region, i.e. to the T-shaped isomer (see Table 1).

any case, at the lowest temperatures the ground-state structure is essentially prevailing. With a further temperature increase, Fig. 1 shows a fairly rapid relative-stability approaching. Finally, a point of equimolarity is reached— the linear isomer becomes progressively more stable compared to the T-shaped isomer. Table 2 gives a precise specification of the equimolarity point in both approaches to energy. The low-temperature position of the equimolarity points imply that in a real experimental situation we should either deal with an isomeric coexistence or even with a prevailing linear species.

Figure 2 illustrates the isomerism contributions to enthalpy, entropy and heat capacity. Again, the results from both approaches to the energetics are quite close. For each of the thermodynamic terms there is a temperature interval in which the term becomes clearly significant. Especially interesting is the pronounced temperature maximum present with the relaxation isomerism contribution to heat capacity. It is interesting to note that the isofractional part represents a quite negligible term in the temperature region of the maximum. Again, Table 2 reports a detailed description of the $\delta C_{p,1}$ maximum.

The isomerism contributions to thermodynamics cannot be measured directly. Therefore, Figs. 3–5 show the standard enthalpy, entropy, and heat capacity at constant pressure changes for the dimerization

$$2HCP(g) = (HCP)_2(g) \qquad (3)$$

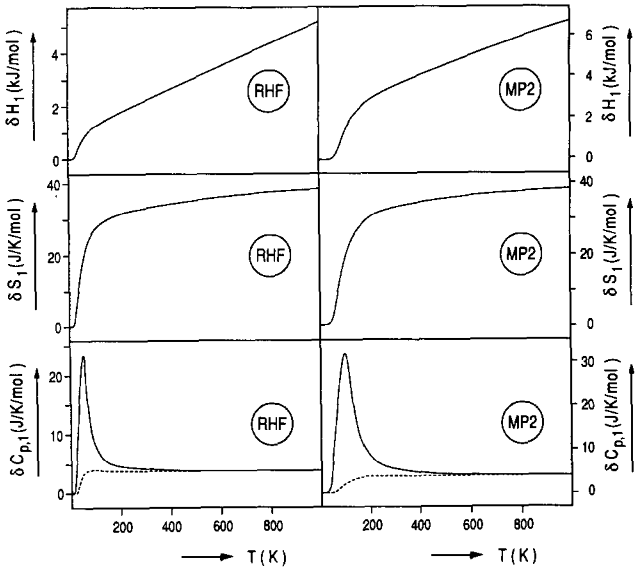

Fig. 2. Temperature dependences of the isomerism contributions to enthalpy δH_1, entropy δS_1, and heat capacity at constant pressure $\delta C_{p,1}$ (relaxation term) or $\delta C_{p,w,1}$ (isofractional term, dashed curve) for the system of the T-shaped and linear $(HCP)_2$ isomers evaluated for the RHF and MP2 approach; the contributions are related to the T-shaped isomer.

Actually, eqn. (3) represents three chemical processes: dimerization to either the T-shaped $(HCP)_2$ or the linear $(HCP)_2$, and the overall dimerization to the pseudo-species formed by the equilibrium mixture of both

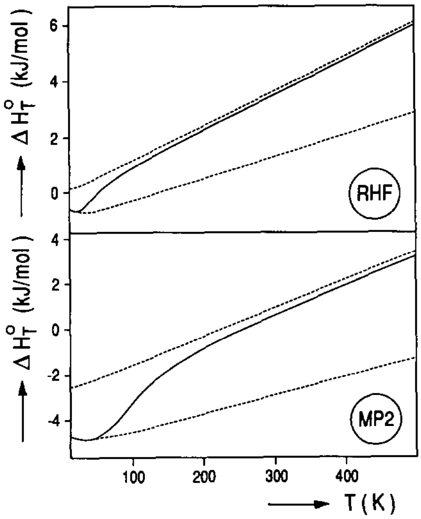

Fig. 3. Temperature dependences of the partial (T-shaped or linear $(HCP)_2$, dashed curves) and overall standard enthalpy terms $\Delta H_T^{\ominus}$ for the HCP(g) dimerizations evaluated for the RHF and MP2 approach.

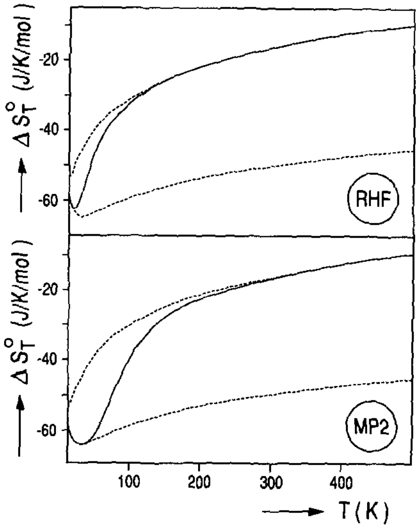

Fig. 4. Temperature dependences of the partial (T-shaped or linear $(HCP)_2$, dashed curves) and overall standard entropy terms $\Delta S_T^{\ominus}$ for the HCP(g) dimerizations evaluated for the RHF and MP2 approach.

isomers. Hence, there are three different terms—two partial and one overall. Figures 3–5 show interrelations of the three terms (in the heat capacity case, a fourth term is also included—the isofractional part of the overall $\Delta C_{p,T}^{\ominus}$ term). It is evident that the temperature maximum observed

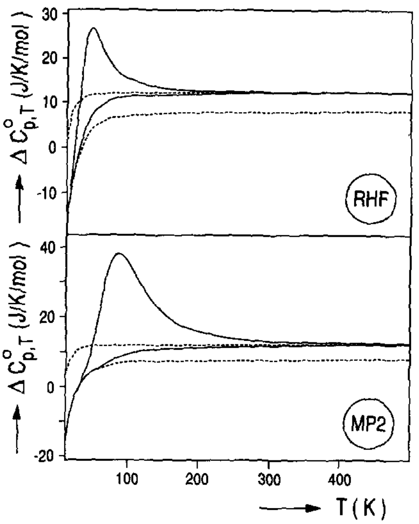

Fig. 5. Temperature dependences of the partial (T-shaped or linear $(HCP)_2$, dashed curves) and overall standard heat capacity at constant pressure terms $\Delta C_{p,T}^{\ominus}$ for the HCP(g) dimerizations evaluated for the RHF and MP2 approach (the solid curve without maximum: isofractional term).

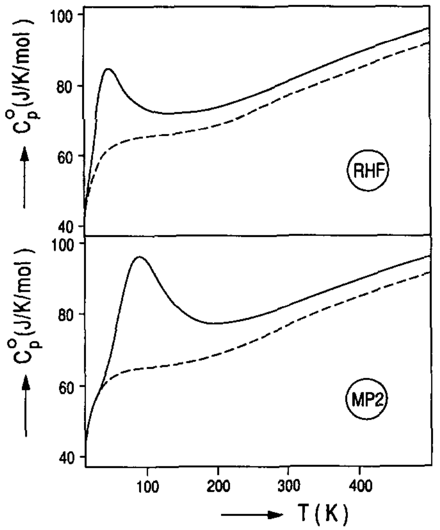

Fig. 6. Temperature dependences of the standard molar heat capacity at constant pressure for the pure T-shaped $(HCP)_2$ isomer (the partial $C^{\ominus}_{p,1}$ term, dashed curve) and for the equilibrium mixture of the two $(HCP)_2$ isomers (the overall $C^{\ominus}_p$ term) evaluated for the RHF and MP2 approach.

in Fig. 2 with the $\delta C_{p,1}$ isomerism contribution is conserved in the $\Delta C^{\ominus}_{p,T}$ behaviour.

Figure 6 considers the standard molar heat capacity at constant pressure for the dimer, presenting temperature dependences for the pure T-shaped $(HCP)_2$ isomer (the partial $C^{\ominus}_{p,1}$) and for the equilibrium mixture of the two $(HCP)_2$ isomers (the overall $C^{\ominus}_p$ term). The temperature maximum is also present with the latter term. (It can be noticed 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 an effect [18] of the conventional translational and rotational partition functions with wrong limiting behaviour.) Table 2 shows that the isomerism contribution can form up to nearly one third of the overall $C^{\ominus}_p$ term. The temperature maxima in heat capacity reported in this study could serve as a device for proving the molecular-complex isomerism predicted in computations.

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REFERENCES

1 Z. Slanina, Thermochim. Acta, 198 (1992), 53.
2 Z. Slanina, Contemporary Theory of Chemical Isomerism, Academia and Reidel, Prague and Dordrecht, 1986.
3 Z. Slanina, Int. Rev. Phys. Chem., 6 (1987) 409.
4 M.R. Hoare, Adv. Chem. Phys., 40 (1979) 49.
5 Z. Slanina, Adv. Quantum Chem., 13 (1981) 89.
6 T.P. Martin, Phys. Rep., 95 (1983) 167.
7 C.R. Bieler, K.E. Spence and K.C. Janda, J. Phys. Chem., 95 (1991) 5058.
8 C. Thomson, Theor. Chim. Acta, 35 (1974) 237.
9 P.A. Kollman, J. McKelvey, A. Johnson and S. Rothenberg, J. Am. Chem. Soc., 97 (1975) 955.
10 K.D. Dobbs, J.E. Boggs and A.H. Cowley, Chem. Phys. Lett., 141 (1987) 372.
11 K.A. Peterson and R.C. Woods, J. Chem. Phys., 90 (1989) 7239.
12 J.S. Craw and W.B. De Almeida, Chem. Phys. Lett., 177 (1991) 517.
13 M. Kofranek, A. Karpfen and H. Lischka, Chem. Phys., 113 (1987) 53.
14 M. Kofranek, H. Lischka and A. Karpfen, Mol. Phys., 61 (1987) 1519.
15 W.B. De Almeida and A. Hinchliffe, J. Mol. Struct., 198 (1989) 17.
16 W.B. De Almeida and A. Hinchliffe, J. Mol. Struct. (Theochem), 204 (1990) 171.
17 I.J. Kurnig, H. Lischka and A. Karpfen, J. Chem. Phys., 92 (1990) 2469.
18 Z. Slanina, D.Sc. Thesis, Czechoslovak Academy of Sciences, Prague, 1985.