

ClHCl⁻(g): A model for evaluation of thermodynamics of systems with strong-hydrogen-bond isomerism

Zdeněk Slanina ^{a,1} and Shigeru Ikuta ^b

^a *Max-Planck-Institut für Chemie (Otto-Hahn-Institut), W-6500 Mainz (Germany)*

^b *Computer Center, Tokyo Metropolitan University, Hachioji-shi, Tokyo 192-03 (Japan)*

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Abstract

A computational evaluation of relative stabilities and thermodynamics of two ClHCl⁻ isomers in ideal gas phase has been carried out on the basis of recent quantum-chemical data (five different approximations of potential energy). In four of the approximations a relative stability interchange takes place at quite a low temperature. The relative stability interplay is reflected in the isomerism contributions to heat capacity in the form of a pronounced temperature maximum. It causes an enhancement of the standard overall heat capacity at constant pressure by more than 15% and interesting irregularities in the temperature course of the latter term. The system is considered as a simple but useful model of thermodynamic consequences of isomerism originating in a strong hydrogen bond.

INTRODUCTION

Representation of potential-energy hypersurfaces by their sole stationary (critical) points has become a prevailing approach in computational treatments of organic (and also inorganic) species (see, for example, refs. 1–3). Quite frequently, several relevant stationary points were located, all of them representing a particular chemical system. This isomerism has recently been examined more closely [4–6] and considerable thermodynamic consequences have been proved. Quite recently, an interesting system, namely ClHCl⁻, was comprehensively described [7]; it is being considered in this study as a convenient model for treating thermodynamics of isomerism originating in a strong hydrogen bond.

COMPUTATIONAL TREATMENT

Let us consider a set of n isomers characterized by the values of the mole fractions w_i of the individual isomers. In a first approximation, the

¹ Permanent and reprint-order address: The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, CS-18223 Prague 8-Kobylišy (Czech and Slovak Federal Republic).

isomers can be described by their potential energy terms ΔE_i (related to the global minimum). However, if their rotational–vibrational motions are also considered then relevant quantities are standard enthalpy changes at the absolute zero $\Delta H_{0,i}^\circ$ and the isomeric partition functions q_i . Under conditions of inter-isomeric thermodynamic equilibrium the mole fractions are given [2,4–6] as

$$w_i = \frac{q_i \exp[-\Delta H_{0,i}^\circ/(RT)]}{\sum_{j=1}^n q_j \exp[-\Delta H_{0,j}^\circ/(RT)]} \quad (1)$$

where R denotes the gas constant and T the temperature. It is useful to mention a critical difference from rather frequent treatments based on so called simple Boltzmann, configurational or steric factors [8–12]

$$w_i' = \frac{\exp[-\Delta E_i/(RT)]}{\sum_{j=1}^n \exp[-\Delta E_j/(RT)]} \quad (2)$$

In the latter case no reference to the rotational–vibrational motions is made.

In terms of partition functions and energetics the whole system thermodynamics can of course be described. For isomeric systems it has become customary to distinguish [2,4–6] two categories of quantities. One of the categories refers to standard partial terms ΔX_i° belonging to the individual isomers. The other deals with the standard overall terms ΔX_T° , into which all the isomers contribute accordingly, i.e. according to their mole fractions w_i . In other words, for the overall terms the equilibrium isomeric mixture operates as one pseudospecies. Finally, in addition to the partial and overall terms a third quantity has been introduced, namely the so called isomerism contributions to thermodynamic terms δX_1 defined as

$$\delta X_1 = \Delta X_T^\circ - \Delta X_1^\circ \quad (3)$$

The values of δX_1 however generally depend on the choice of the reference isomer labelled by $i = 1$. It is convenient that the most stable species (in the low temperature region) be chosen as the reference structure (mostly, but not necessarily [2], the global minimum; the zero-point vibrational energy contribution in principle can change the energy ordering of structures). In our connections X denotes one of the three key standard thermodynamic terms: enthalpy $X = H$, entropy $X = S$, or heat capacity at constant pressure $X = C_p$. It holds for $X = C_p$ that

$$\delta C_{p,1} = \delta C_{p,w,1} + \frac{1}{RT^2} \left[\sum_{i=1}^n w_i (\Delta H_i^\circ - \Delta H_1^\circ)^2 - (\delta H_1)^2 \right] \quad (4)$$

where $\delta C_{p,w,1}$ denotes the so called isofractional isomerism contribution to heat capacity

$$\delta C_{p,w,1} = \sum_{i=1}^n w_i (\Delta C_{p,i}^{\circ} - \Delta C_{p,1}^{\circ}) \quad (5)$$

and the isomerism contribution to enthalpy is given by

$$\delta H_1 = \sum_{i=1}^n w_i (\Delta H_i^{\circ} - \Delta H_1^{\circ}) \quad (6)$$

Accordingly the $\delta C_{p,1}$ term in eqn. (4) considers the effects of changes in composition upon a temperature change (being called the relaxation isomerism contribution to heat capacity). The relaxation term is reduced to the isofractional contribution if w_i values are considered to be temperature independent (this situation is practically reached in both high- and low-temperature limits).

DESCRIPTION OF THE ClHCl⁻ SYSTEM

The ClHCl⁻ anion has received considerable interest [13–16] as a convenient model of a strongly hydrogen-bonded system. For our model purposes we shall employ just one of its features, possible isomerism. The anion can assume two different structures, non-centro-symmetric $C_{\infty v}$ and centro-symmetric $D_{\infty h}$. Structure, energetics and vibrational frequencies of the system have been comprehensively studied [7], the energetics evaluated in five different potential-energy approximations being surveyed in Table 1 (of course the potential-energy terms presented there are to be corrected for vibrational zero-point energy contributions prior to their application as the ground-state energies in eqn. (1)). For our methodical purposes (i.e. in order to ascertain the sensitivity of thermodynamic isomeric effects to energetics) it is convenient to consider all the energy approximations (though they exhibit different degrees of reliability [7]). For present pur-

TABLE 1

Survey of the ClHCl⁻ relative energetics^a

Approximation [7]	Acronym ^b	ΔE^a (kJ mol ⁻¹)
MP2	2	6.95
MP3	4	3.68
MP4SDQ	43	2.64
MP4SDTQ	44	4.10
CISD(Q)	CI	3.01

^a Potential-energy changes ΔE for the isomerization ClHCl⁻(g; $C_{\infty v}$) = ClHCl⁻(g; $D_{\infty h}$).

^b Used in Table 2 and in the figures.

poses SCF geometry evaluated in a large basis set [7] is considered for the $C_{\infty v}$ species while in the $D_{\infty h}$ case MP2 geometry [7] is employed. Finally, the $C_{\infty v}$ SCF harmonic vibrational frequencies are used for the partition function construction. With the $D_{\infty h}$ structure, vibrational frequencies were evaluated [7] at several different methodical levels and here just two of them are considered; namely, MP2 (harmonic in their nature) and MP4SDTQ (reflecting potential anharmonicity) terms. Again, this diversity of vibrational frequency set enables one to study sensitivity of thermodynamic isomeric effects to the molecular parameters. Combining the five energy-difference estimations (Table 1) and the two evaluations of the $D_{\infty h}$ vibrations results altogether in ten different situations.

RESULTS AND DISCUSSION

Figure 1 presents temperature evolutions of the weight factors w_i and simple Boltzmann factors w'_i . With an exception of the MP2 energetics the

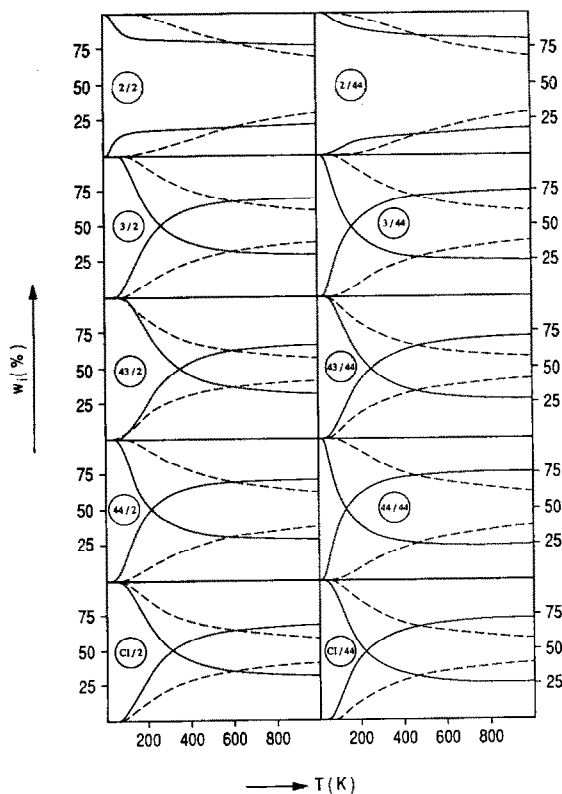


Fig. 1. Temperature dependences of the weight factors w_i and simple Boltzmann factors w'_i (broken curves) for the ClHCl^- isomeric system. For an explanation of the X/Y labels, see Tables 1 and 2.

TABLE 2

Characterization of some distinguished points of the ClHCl^- isomeric interplay

Approximation ^a [7]	Type ^b	T (K)	w_1 ^c (%)	$\delta C_{p,1}$ ^d (J K^{-1} mol^{-1})	C_p° (J K^{-1} mol^{-1})	$\delta C_{p,1}/C_p^\circ$ (%)
2/2	M: $\delta C_{p,1}$	37	96.1	1.7	31.6	5.4
	M: $\delta C_{p,1}$	708	79.5	0.9	54.6	1.7
2/44	M: $\delta C_{p,1}$	75	97.5	1.3	34.8	3.8
	M: $\delta C_{p,1}$	756	82.9	0.7	55.0	1.3
3/2	Cross	255	50.0	4.4	46.4	9.6
	M: $\delta C_{p,1}$	145	25.7	7.0	43.7	16.0
3/44	Cross	169	50.0	2.6	40.3	6.3
	M: $\delta C_{p,1}$	71	15.7	5.1	38.2	13.3
43/2	Cross	344	50.0	5.1	50.7	10.1
	M: $\delta C_{p,1}$	189	23.9	8.9	47.6	18.6
43/44	Cross	257	50.0	4.0	46.0	8.7
	M: $\delta C_{p,1}$	139	23.3	6.8	43.2	15.6
44/2	Cross	219	50.0	4.0	44.2	9.0
	M: $\delta C_{p,1}$	124	25.8	6.0	41.9	14.4
44/44	Cross	131	50.0	1.7	37.9	4.5
	M: $\delta C_{p,1}$	44	10.7	5.8	36.4	15.9
CI/2	Cross	311	50.0	4.9	49.3	10.0
	M: $\delta C_{p,1}$	174	24.6	8.3	46.3	17.9
CI/44	Cross	226	50.0	3.5	44.1	8.0
	M: $\delta C_{p,1}$	120	23.1	6.1	41.8	14.6

^a The notation X/Y is used where X stands for the potential-energy approximation and Y denotes the origin of vibrations of the ClHCl^- (g; D_{oh}) species (see Table 1).

^b Point of two-isomer equimolarity (Cross), or maximum in the isomerism contribution to heat capacity $\delta C_{p,1}$ (M: $\delta C_{p,1}$).

^c Mole fraction of the ClHCl^- (g; C_{ov}) species in the equilibrium isomeric mixture with ClHCl^- (g; D_{oh}).

^d Isomerism contribution to heat capacity related to the species more stable in the very low temperature region, i.e. to the ClHCl^- (g; C_{ov}) species.

behaviour of the w_i terms is quite similar. They approach one another rather fast and finally they cross. This means a relative stability interchange is present. The exceptional behaviour of the MP2 energetics can be well rationalized. The MP2 ΔE term [7] is in fact overestimated owing to a large electron correlation contribution of the D_{oh} structure. Table 2 gives a more detailed specification of the crossing points. The crossing point is located below or in the vicinity of room temperature so that it could certainly be of experimental importance. Thus, we can arrive at the conclusion that in a hydrogen-bonded system consisting of two isomeric configurations the potential-energy difference cannot itself be considered as decisive. A compensation of the latter term by temperature excitations of the rotational–vibrational motions could take place resulting in the reported stability interchange. Incidentally, it is interesting to note that the

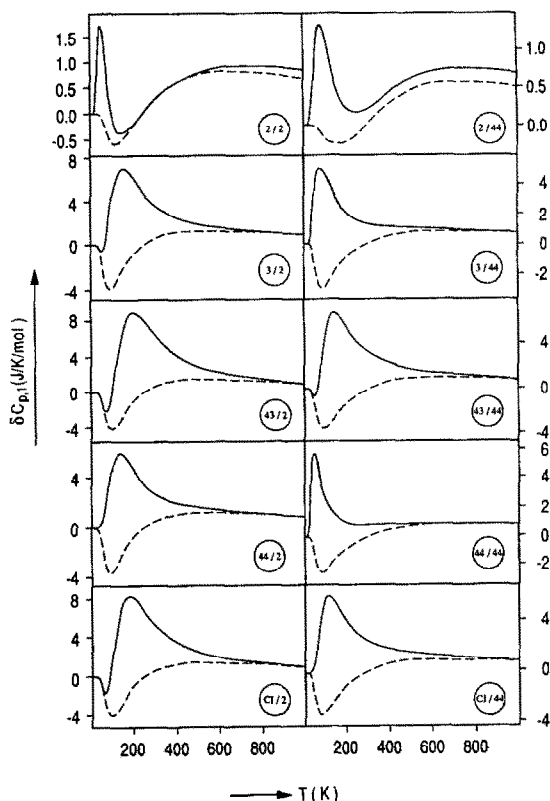


Fig. 2. Temperature dependences of the isomerism contribution to heat capacity at constant pressure $\delta C_{p,1}$ (relaxation term related to the $\text{ClHCl}^- (\text{g}; C_{\infty})$ species) or $\delta C_{p,w,1}$ (isofractional term, dashed curves) for the ClHCl^- isomeric system. For an explanation of the X/Y labels, see Tables 1 and 2.

simple Boltzmann factors generally are not a good representation of the rigorous weight factors (eqn. (1)). In particular, the Boltzmann factors are unable to produce any relative stability crossing (i.e. if $\Delta E_i > \Delta E_j$, then always $w'_i < w'_j$). In other words this finding states that the rotational-vibrational (and the vibrational in particular) motions are indeed important in the system behaviour.

Figure 2 deals with temperature dependences of the isomerism contribution to heat capacity at constant pressure, $\delta C_{p,1}$ and $\delta C_{p,w,1}$. The striking temperature maximum in the $\delta C_{p,1}$ term, present in any of the approximations considered, is of particular interest. It is essentially a consequence of the relative-stability temperature approach observed with Fig. 1. The pronounced maximum is always located below room temperature and if there is a crossing point, below this crossing point. Moreover, in the crossing-free MP2 treatment there is also a rather flat second maximum. Table 2 again presents a more detailed specification of all the temperature

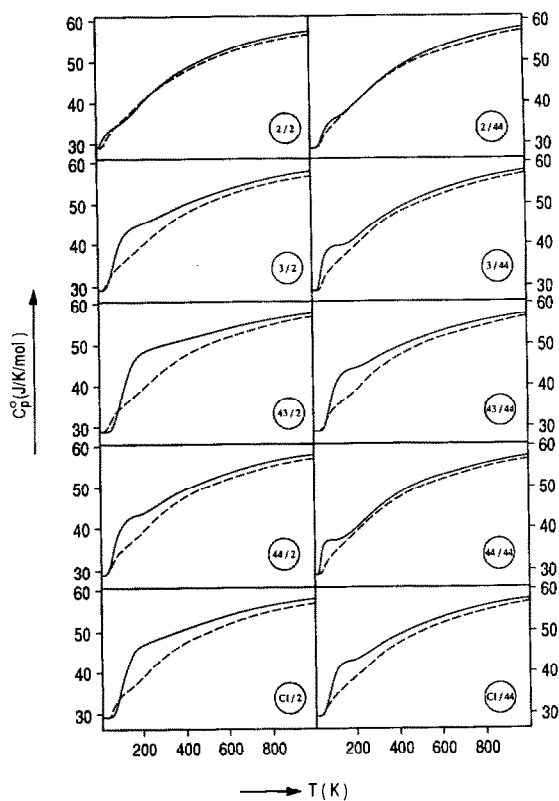


Fig. 3. Temperature dependences of the standard molar heat capacity at constant pressure for the equilibrium mixture of the ClHCl^- isomers (C_p°) and for the sole ClHCl^- (g; C_{ov}°) structure ($C_{p,1}^\circ$, dashed curve). For an explanation of the X/Y labels, see Tables 1 and 2.

maxima. Finally, Fig. 2 demonstrates a clear difference between the full relaxation term and its isofractional component.

The isomerism contributions to thermodynamics are useful; however they are still auxiliary terms and they cannot be directly observed. Therefore, Fig. 3 compares the standard overall molar heat capacity at constant pressure for the equilibrium mixture of the ClHCl^- isomers taken as one pseudospecies (C_p° term) and for the sole ClHCl^- (g; C_{ov}°) structure ($C_{p,1}^\circ$). Although the temperature maxima from Fig. 2 are not conserved as such, they are still felt in the apparent irregularities of the overall C_p° term compared with the $C_{p,1}^\circ$ partial one. Such irregularities could be recorded experimentally and thus, they could serve as experimental evidence for the presence of isomerism. The enhancement of the heat capacity term by the isomeric interplay at the temperature of the $\delta C_{p,1}$ maximum can be higher than 15%, this being of clear importance from the point of view of thermodynamic quantities evaluation.

There is one gas-phase ClHCl^- vibrational observation; Kawaguchi [17] detected one band of the D_{oh} species. The species was produced in a

discharge of a CHCl_3 , H_2 , and He mixture. The observation was carried out using a cell cooled to -30°C . Relating the fact to the computational results one should first investigate the question of thermodynamic equilibrium. It is however difficult to decide whether the equilibrium was reached under the observation conditions. It could be speculated that just the $D_{\infty\text{h}}$ species was selectively generated in the particular arrangement. In fact, there are eight points of equimolarity in Table 2, of which six are below room temperature. Thus, the calculations tend to suggest that close to room temperature the $D_{\infty\text{h}}$ species represents a more stable component of the equilibrium mixture, i.e. it is more easily observable.

Our study considers the ClHCl^- system as a model. The results are primarily important for qualitative conclusions (rather than for a precise description of the particular system). The computed characteristics of the ClHCl^- species can still be the subject of a substantial future improvement (particularly regarding the energy difference and probably the vibrational frequencies). From that point of view, of the two vibrational frequency sets considered in our study with the $D_{\infty\text{h}}$ structure the MP4SDTQ frequencies should clearly be given preference as they respect the potential anharmonicity. Moreover, some improvements can be expected from a direct inclusion of vibrational-anharmonicity corrections into the partition functions in eqn. (1). Nevertheless, such improvements should not change the qualitative conclusions of this paper, supposing that the finding itself of the two-fold isomerism is conserved. In other words, in spite of the considerable diversity of the considered energy (and to some extent also vibrational) terms they produce qualitatively the same kind of thermodynamic isomeric effects. Nevertheless, a further study with similar model systems [18] can bring a deeper understanding of some aspects.

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