Thermochimica Acta, 181 (1991) 119–125
Elsevier Science Publishers B.V., Amsterdam

CONFORMERS OF 1,2-DIFLUOROETHANE: THEIR THERMODYNAMIC INTERPLAY AND THE EXTREMUM TEMPERATURE COURSE OF SOME TERMS *

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(Received 4 September 1990)

ABSTRACT

The temperature behaviour of various thermodynamic characteristics of the ideal gas-phase equilibrium mixture of *gauche*- and *trans*-1,2-difluoroethane has been studied on the basis of recently calculated molecular data. An interesting extremum temperature behaviour has been shown in a number of terms characterizing this isomeric interplay: among them, the isomerism contribution to heat capacity, whose maximum value is 3.39 J K^{-1} mol^{-1}, is particularily distinctive.

INTRODUCTION

The recent increasing interest in the thermodynamics of gas-phase isomeric mixtures is obviously connected with studies of complex reaction systems [1–5]. Isomeric mixtures differ from mixtures of non-reacting components in that their populations are not arbitrary but are governed by the conditions for reaching inter-isomer equilibrium; this is interesting from the point of view of thermodynamics methodology. At the same time, these problems are also of practical interest, because the isomerism effects were recently found to provide a substantial correction term to the conventional tabulated single-species thermodynamic data in the cases of non-separable or even non-distinguishable isomers. The present communication deals with the thermodynamics of conformers of 1,2-difluoroethane.

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* Dedicated to Professor Kenneth B. Wiberg on the occasion of his 65th birthday.

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0040-6031/91/$03.50

ISOMERIC SYSTEM

The explanation of the gauche preference in the rotational isomerism of simple species represents an object of lively interest in theoretical chemistry (see, for example refs. 3,6–14). A particularly simple system of this type is represented by 1,2-difluoroethane [15–26] whose most recent study [26] of the ab initio type with perturbation evaluation of the electron-correlation contribution provides a complete set of information for investigation of the thermodynamics of its gauche and trans conformers in the ideal gas phase in the rigid-rotator and harmonic-oscillator approach (RRHO) to the partition functions [27].

The geometrical parameters of the gauche (C_2 point group of symmetry) and trans (C_{2h} point group of symmetry) rotamers of 1,2-difluoroethane were taken from the ab initio calculations [26] in the 6-31G** basis set. In this basis set the harmonic vibrational frequencies of both species were also determined [26]; this present study makes use of the frequencies based on 0.01 a.u. (about 0.0053 Å) coordinate shifts. Finally, the potential energy difference between the gauche and trans isomers was taken [26] from the 6-31G** ab initio calculation with the MP2 perturbation evaluation of the correlation effects in the 6-31G** equilibrium geometry; this energy term is -1.088 kJ mol^{-1} (i.e. the gauche structure is below the trans isomer on the potential energy scale).

TREATMENT OF ISOMERIC THERMODYNAMICS

For a description of the thermodynamics of the two conformers, the system introduced recently to describe a general isomeric system [3,5,28–30] may be applied. Using the RRHO partition functions calculated from the molecular parameters and energy differences between the two isomers, it is possible to express their mole fractions (weight factors), w_i, in their gaseous equilibrium mixture.For the sake of comparison it is also useful to calculate the simple Boltzmann factors, w_i', based on the potential energy difference term alone. For the present purposes, the following indexing of isomers is adopted: 1 denotes the gauche isomer (lower in energy) and 2 denotes the trans isomer (higher in energy). Obviously, $w_1 + w_2 = 1$ and $w_1' + w_2' = 1$. The next step is to evaluate the so-called isomerism contributions to the values of thermodynamic functions: $\delta X_1^{(\mathrm{iso})}$ for isomer 1 where $X = H$, S, or C_p for the enthalpy, entropy or heat capacity at constant pressure. These values enable [28–30] a condensed treatment of the isomerism effects and transitions between the partial terms of isomer 1 and the overall terms of the equilibrium mixture of both isomers treated as a single pseudo-species (super-species). For the isomerism contribution to heat capacity, $\delta C_{\mathrm{p},1}^{(\mathrm{iso})}$, it is also useful to consider its so-called isofractional component, $\delta C_{\mathrm{p},w,1}^{(\mathrm{iso})}$, corresponding to the situation of fixed populations, w_i, during a temperature change. The $\delta C_{p,1}^{(iso)}$ term, which takes into account the temperature changes of w_i, is also denoted as relaxation [28–30].

As well as these isomerism contributions to the values of the thermodynamic functions, the temperature courses of the standard changes of enthalpy, entropy and heat capacity, $(H_2^{\ominus} - H_1^{\ominus})$, $(S_2^{\ominus} - S_1^{\ominus})$ and $(C_{p,2}^{\ominus} - C_{p,1}^{\ominus})$, where also studied for the reaction

gauche-1,2-difluoroethane → *trans*-1,2-difluoroethane (1)

with special attention being paid to their extremum behaviour. Here it can be seen that, in the sense of basic thermodynamic relations, if one of the functions $(H_2^{\ominus} - H_1^{\ominus})$ or $(S_2^{\ominus} - S_1^{\ominus})$ assumes the extremum, then the extremum must also occur for the other function, both extrema being at precisely the same temperature (cf. ref. 31). This follows from the requirement that the first derivatives of both functions with respect to temperature vanish at the extremum point:

$$\frac{d(H_2^{\ominus} - H_1^{\ominus})}{dT} = C_{p,2}^{\ominus} - C_{p,1}^{\ominus} = 0 \tag{2}$$

$$\frac{d(S_2^{\ominus} - S_1^{\ominus})}{dT} = \frac{C_{p,2}^{\ominus} - C_{p,1}^{\ominus}}{T} = 0 \tag{3}$$

However, a similar rule also applies [31] to the case of the extremum with the functions $\delta H_1^{(iso)}$ and $\delta S_1^{(iso)}$ which attain the extremum (if any) simultaneously at a common temperature point.

RESULTS AND DISCUSSION

The partition functions of both isomers were constructed in the RRHO approach on the basis of the molecular parameters from ref. 26 (a few geometrical parameters not tabulated in ref. 26 were taken from ref. 21; the perfect agreement between the standard entropy values at room temperature obtained by this calculation and those presented in ref. 26 showed that this procedure is acceptable). With the use of these partition functions and on the basis of the energetics [26], the weight factors w_i and w_i' were generated along with the isomerism contributions to enthalpy, $\delta H_1^{(iso)}$, entropy, $\delta S_1^{(iso)}$, and heat capacity, $\delta C_{p,1}^{(iso)}$ and $\delta C_{p,w,1}^{(iso)}$, related to the gauche rotamer as the reference structure. Table 1 presents the courses of these quantities over a wide temperature interval. Although the gauche rotamer predominates at the lowest temperatures, the relative stabilities of the two structures approach each other quite rapidly with increasing temperature; hence, near room temperature the less stable trans isomer is present as almost 40% of the equilibrium mixture of the two structures. At the high temperature limit, the populations of the isomers asymptotically approach the equimolar values,

TABLE 1

Temperature dependence of the weight factor [a], w_1, the simple Boltzmann factor [a], w_1', the isomerism contributions [a] to enthalpy, $\delta H_1^{(\mathrm{iso})}$, entropy, $\delta S_1^{(\mathrm{iso})}$, and heat capacity, $\delta C_{\mathrm{p},w,1}^{(\mathrm{iso})}$ (isofractional) and $\delta C_{\mathrm{p},1}^{(\mathrm{iso})}$ (relaxation), for the equilibrium ideal gas-phase mixture of *gauche*- and *trans*-1,2-difluoroethane

T (K)	w_1 (%)	w_1' (%)	$\delta H_1^{(\mathrm{iso})}$ (kJ mol^{-1})	$\delta S_1^{(\mathrm{iso})}$ (J K^{-1} mol^{-1})	$\delta C_{\mathrm{p},w,1}^{(\mathrm{iso})}$ (J K^{-1} mol^{-1})	$\delta C_{\mathrm{p},1}^{(\mathrm{iso})}$ (J K^{-1} mol^{-1})
50	95.7	93.2	0.054	1.448	−0.008	3.104
100	83.1	78.7	0.214	3.677	0.111	2.807
200	69.3	65.8	0.415	5.128	0.246	1.412
298.15	63.2	60.8	0.517	5.551	0.105	0.725
300	63.1	60.7	0.518	5.555	0.103	0.716
400	59.7	58.1	0.569	5.705	−0.011	0.351
500	57.7	56.5	0.594	5.761	−0.063	0.169
600	56.3	55.4	0.606	5.783	−0.082	0.077
700	55.3	54.7	0.611	5.791	−0.085	0.029
800	54.6	54.1	0.612	5.793	−0.082	0.003
900	54.1	53.6	0.612	5.792	−0.076	−0.011
1000	53.6	53.3	0.610	5.791	−0.070	−0.018
1100	53.3	53.0	0.608	5.789	−0.064	−0.022
1200	53.0	52.7	0.606	5.787	−0.058	−0.024
1300	52.7	52.5	0.604	5.785	−0.053	−0.024
1400	52.5	52.3	0.601	5.783	−0.048	−0.023
1500	52.3	52.2	0.599	5.782	−0.044	−0.023

[a] Gauche rotamer is labelled 1.

i.e. 50% each. The simple Boltzmann factors, w_i', seem to be acceptable enough approximations to the precise w_i values in this particular case.

The isomerism contribution to enthalpy, $\delta H_1^{(\mathrm{iso})}$, follows a course with a maximum, the same being true of the entropy term, $\delta S_1^{(\mathrm{iso})}$ (see also Fig. 1), the temperature position of both the maxima being, of course, precisely the same (Table 2). The influence of isomerism on the entropy term is more clear: the maximum value of 4.73 kJ mol^{-1} on the $T\delta S_1^{(\mathrm{iso})}$ scale substantially exceeds the maximum $\delta H_1^{(\mathrm{iso})}$ value (0.612 kJ mol^{-1}). This indicates that the thermodynamic characteristics of an equilibrium mixture of two rotamers, despite their considerable similarity, cannot be simulated by the partial quantities corresponding to one of them in a more precise treatment.

Still more interesting is the temperature course of the isomerism contributions to heat capacity, $\delta C_{\mathrm{p},1}^{(\mathrm{iso})}$ and $\delta C_{\mathrm{p},w,1}^{(\mathrm{iso})}$, which exhibit not only a maximum but also a minimum. Of course, the position of the maximum in $\delta C_{\mathrm{p},1}^{(\mathrm{iso})}$ differs very much from that of the isomerism contributions to enthalpy and entropy; the isomerism contribution to heat capacity must vanish in the latter maxima (Fig. 1).

Maxima are also exhibited by the standard changes in enthalpy, entropy and heat capacity of reaction (1), the first two terms, of course, reaching the

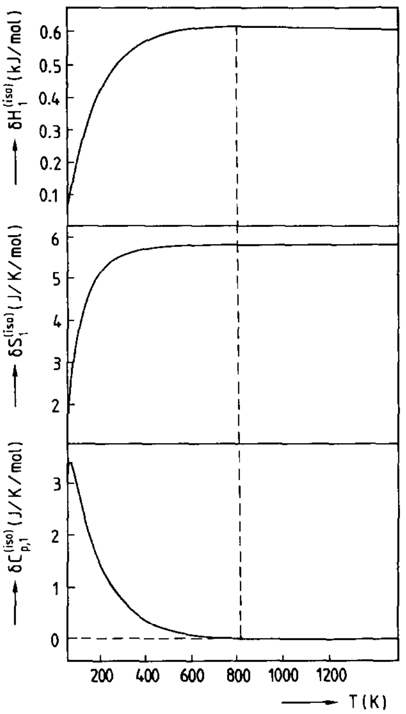

Fig. 1. Temperature dependences of the isomerism contributions to enthalpy, $\delta H_1^{(iso)}$, (top) and entropy, $\delta S_1^{(iso)}$, (middle) and to heat capacity, $\delta C_{p,1}^{(iso)}$, (bottom) for the equilibrium mixture of both rotamers of 1,2-difluoroethane related to the gauche rotamer.

TABLE 2

Coordinates of the extremum points of temperature dependence for various thermodynamic terms [a] related to the equilibrium ideal gas-phase mixture of *gauche* [b]- and *trans* [b]-1,2-difluoroethane

Term [a,b]	Extremum temperature position (K)	Extremum type [c]	Extremum value
$\delta H_1^{(iso)}$	815.8	max	0.612 kJ mol^{-1}
$\delta S_1^{(iso)}$	815.8	max	5.793 J K^{-1} mol^{-1}
$(H_2^{\ominus} - H_1^{\ominus})$	387.2	max	1.414 kJ mol^{-1}
$(S_2^{\ominus} - S_1^{\ominus})$	387.2	max	0.251 J K^{-1} mol^{-1}
$T(S_2^{\ominus} - S_1^{\ominus})$	627.8	max	0.119 kJ mol^{-1}
$\delta C_{p,1}^{(iso)}$	64.2	max	3.386 J K^{-1} mol^{-1}
$\delta C_{p,1}^{(iso)}$	1280	min	-0.024 J K^{-1} mol^{-1}
$\delta C_{p,w,1}^{(iso)}$	176.5	max	0.256 J K^{-1} mol^{-1}
$\delta C_{p,w,1}^{(iso)}$	689.0	min	-0.085 J K^{-1} mol^{-1}
$(C_{p,2}^{\ominus} - C_{p,1}^{\ominus})$	151.0	max	0.944 J K^{-1} mol^{-1}

[a] The standard-state specification, due to the form of the terms, is not relevant.
[b] Gauche and trans rotamers are labelled 1 and 2, respectively.
[c] Local maxima and minima are denoted max and min, respectively.

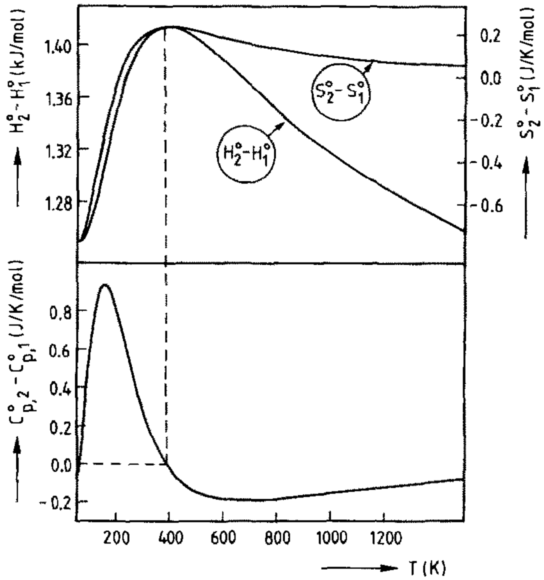

Fig. 2. Temperature dependences of the differences between trans (2) and gauche (1) rotamers of 1,2-difluoroethane for standard enthalpy, $(H_2^\ominus - H_1^\ominus)$, and entropy, $(S_2^\ominus - S_1^\ominus)$, (top) and heat capacity, $(C_{p,2}^\ominus - C_{p,1}^\ominus)$, (bottom).

maximum at the same temperature point (Fig. 2). The temperature at which these two extrema occur is rather different from that at which the isomerism contributions to enthalpy and entropy culminated (Table 2). Finally it is also noteworthy that the $T(S_2^\ominus - S_1^\ominus)$ term also exhibits a course with a maximum, though at a different temperature from that of the maximum of the $(S_2^\ominus - S_1^\ominus)$ term alone.

CONCLUSION

The investigation of the system of gauche and trans rotamers of 1,2-difluoroethane showed relatively varied changes with changing temperature over a wide temperature interval. It was shown that the relative positions of the extrema of the individual terms can be used to test the consistency of data, e.g. from various sources. The report also stresses the necessity of generalising the conventional format [32] used for tabulating thermochemical data: for species exhibiting isomerism, not only the partial terms corresponding to the individual isomers but also the isomerism contributions enabling an easy transition to thermodynamic characteristics of equilibrium mixtures of the isomers should be tabulated.

ACKNOWLEDGEMENT

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

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