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A computational evaluation of relative stabilities of the open C_{2v} and cyclic D_{3h} forms of ozone [α,β]

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Abstract

In addition to the open (C_{2v}) form, the ozone molecule can also exist in the higher-lying cyclic (D_{3h}) form. In the present study four different computational evaluations of the relative energy difference between the two forms (12, 19, 50 and 122 kJ mol^{-1}) were employed to study the influence of temperature on the two conformers. It is shown that the results obtained strongly depend on the energy difference used. The threshold temperature at which the cyclic D_{3h} structure reaches the 1% mole fraction level in the equilibrium mixture with the C_{2v} form varies from about 350 to about 3800 K. Similarly, although the highest value of the contribution of isomerism to the heat capacity $\delta C_{p,1}$ for the equilibrium mixture is always about 1.8 J K^{-1} mol^{-1}, the temperature at which the maximum is reached varies from about 650 to about 6600 K. The possible role of the cyclic isomer is discussed, including its relation to the dissociation limit of ozone.

INTRODUCTION

The properties of ozone have been studied extensively (for a review see ref. 1) because of the critically important role of this molecule in the Earth's atmosphere and the phenomenon of ozone depletion [2–4]. Computational tools have been used [5–22] in order to enhance and complete observations. The normal (ground-state) open form of ozone which has C_{2v} symmetry with a bond angle of 116.8° [23] has been known for many years.

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[β] Part LXX in the series Multi-molecular Clusters and their Isomerism. For part LXIX, see ref. 29.

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The discovery [5–7] of a bound cyclic isomer of ozone represents probably the most important theoretical contribution made to the study of ozone.

The existence of the higher-lying cyclic D_{3h} isomer (bond angle 60 °) has only been proved computationally and there is still no generally accepted value of the potential energy difference (ΔE) between the two forms. For example, Burton [11] has reported quite low values for ΔE of 12 and 19 kJ mol^{-1}, whilst the value determined by Jones [14] (135 kJ mol^{-1}) is one order of magnitude higher. However, the fact that isomerism exists can be taken for granted, and thus it makes a sense to study the thermodynamic consequences of this isomerism using the methods developed recently [24–26].

COMPUTATIONS

Let us consider an equilibrium isomeric mixture and describe it using the values of the mole fractions w_i of the individual isomers. The isomeric mole fractions do not depend on the total pressure imposed on the system but on the temperature T only. The isomers are, to a first approximation, described by their potential energy terms ΔE_i. However, if the rotational–vibrational motions are to be considered then the relevant quantities are the standard enthalpy changes at absolute zero $\Delta H_{0,i}^{\ominus}$ and the isomeric partition functions q_i. Under the conditions of inter-isomer thermodynamic equilibrium the mole fractions are given [24] by

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

where n is the number of isomers (in the present case $n = 2$) and R is the gas constant.

The thermodynamics of the whole system can be described in terms of the partition functions and energies. For isomeric systems it has become customary [24–26] to consider two categories of quantities. One of the categories comprises the standard partial terms $\Delta X_i^{\ominus}$ belonging to the individual isomers. The other category, required in some practical applications, are the standard overall terms $\Delta X_T^{\ominus}$, to which all the isomers contribute according to their mole fractions or weighting factors w_i. Finally, in addition to the partial and overall terms a third quantity has been introduced, i.e. the so-called isomerism contribution to the thermodynamic terms δX_1 which is defined as

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

The values of δX_1 generally depend on the choice of the reference isomer which is here labelled as $i = 1$. It is convenient to choose the most stable species (in low temperature region) as the reference structure. In the present paper X denotes a standard thermodynamic term (enthalpy H, entropy S, or heat capacity at constant pressure C_p). However, in principle, the treatment could be used for any structure-dependent quantity. For $X = C_p$ it holds that

$$\delta C_{p,1} = \delta C_{p,w,1} + \frac{1}{RT^2}\left(\sum_{i=1}^{n} w_i\left(\Delta H_i^{\ominus} - \Delta H_1^{\ominus}\right)^2 - \left(\delta H_1\right)^2\right) \tag{3}$$

where $\delta C_{p,w,1}$ is given by

$$\delta C_{p,w,1} = \sum_{i=1}^{n} w_i\left(\Delta C_{p,i}^{\ominus} - \Delta C_{p,1}^{\ominus}\right) \tag{4}$$

and for the isomerism contribution to enthalpy

$$\delta H_1 = \sum_{i=1}^{n} w_i\left(\Delta H_i^{\ominus} - \Delta H_1^{\ominus}\right) \tag{5}$$

The $\delta C_{p,1}$ term in eqn. (3) includes the effects of changes in composition that occur on a change in temperature and this term is therefore called the relaxation isomerism contribution to the heat capacity. The latter term is reduced to the so-called isofractional isomerism contribution to the heat capacity $\delta C_{p,w,1}$ (eqn. (4)) if the w_i terms are considered to be temperature independent (this situation is practically reached at both the high- and the low-temperature limits). In fact, eqn. (3) follows from eqn. (5) by temperature differentiation with a due respect paid to the fact all terms involved are temperature dependent.

The above described treatment was applied to the ozone isomer system. For the potential energy change ΔE upon isomerization of the open C_{2v} to the cyclic D_{3h} form four different values were selected (Table 1). Partition functions were constructed in the usual approximation of the rigid rotor and harmonic oscillator (RRHO) [24]. The molecular parameters of the

TABLE 1

The considered calculated isomerization energies of ozone used in the present study

ΔE [a] (kJ mol^{-1})	Label [b]	Ref.
12.1	12	11
19.2	19	11
50.0	50	13
121.8	122	19

[a] The change in potential energy for isomerization of the open C_{2v} form to the cyclic D_{3h} form.

[b] Used in the figures.

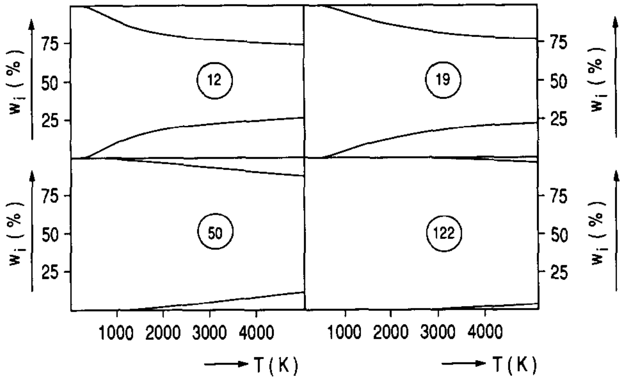

Fig. 1. The temperature dependence of the weight factors w_i for the two ozone isomers as evaluated at the four energies given in Table 1.

open form were taken from calculations made at the CCSD(T) level with a 5s,4p,3d,2f basis set [17]. The cyclic form was described using data derived within the same approximation [19].

RESULTS AND DISCUSSION

In view of the existing disagreement between estimations of the potential energy difference between the cyclic and open forms of ozone, we allowed for a wide variability of the ΔE term. The temperature dependence of the mole fractions w_i of the equilibrium isomeric mixture is shown in Fig. 1. The behaviour is not particularly surprising, even at very high temperatures the open form is the main component. However, the increase in the population of the cyclic isomer is quite interesting: there is a threshold temperature at which the relative population of the cyclic D_{3h} structure reaches a mole fraction of 1%. The values of the threshold temperatures for the four energy values considered are given in Table 2. While for the lowest ΔE value the temperature threshold is about 350 K, for the highest it increases by one order of magnitude to about 3800 K.

The potential energy difference ΔE should not be considered independently of the dissociation limit of the open form (to triplet atomic and molecular oxygen). The experimentally determined value of the dissociation limit is 109.2 kJ mol^{-1} [27]. The position of the cyclic form with respect to the dissociation limit is particularly important [19] photochemically (although the electronic configuration of the cyclic form does not correlate directly [28] with the ground-state dissociation products). However, the approach used in the present work is purely thermodynamic and thus the mechanistic and kinetic aspects are out of the scope of this study. Moreover, three of the considered ΔE values (Table 1) are lower than the dissociation limit. Incidentally, in constructing a realistic potential energy

TABLE 2

Characteristics of the C_{2v}/D_{3h} isomeric interconversion of ozone

ΔE (kJ mol^{-1})	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})	$\delta C_{p,1}/C_p^{\ominus}$ (%)
12	1%	357	99.0	1.0	1.1	42.7	2.6
	M:$\delta C_{p,1}$	649	94.9	5.1	1.8	52.1	3.4
19	1%	590	99.0	1.0	1.2	50.3	2.3
	M:$\delta C_{p,1}$	1041	95.1	4.9	1.8	56.5	3.2
50	1%	1570	99.0	1.0	1.2	57.7	2.1
	M:$\delta C_{p,1}$	2719	95.2	4.8	1.8	59.5	3.1
122	1%	3837	99.0	1.0	1.2	59.1	2.0
	M:$\delta C_{p,1}$	6622	95.2	4.8	1.8	60.0	3.1

[a] The threshold temperature at which the cyclic D_{3h} structure reaches the 1% mole fraction population (1%), and the maximum isomerism contribution to the heat capacity $\delta C_{p,1}$ (M:$\delta C_{p,1}$).

[b] The mole fraction of the species in the equilibrium isomeric mixture; inferior 1 and 2 denote the C_{2v} and D_{3h} isomers, respectively.

[c] The isomerism contribution to the heat capacity related to the more stable species, i.e. to the C_{2v} isomer.

surface for ozone Varandas and Pais [15] selected and adopted the 50 kJ mol^{-1} estimate [13] as the surface feature.

There has recently been particular interest in the contribution of isomerism to the heat capacity $\delta C_{p,1}$ [25,26] because the contribution frequently exhibits a change with temperature with a maximum. It can be seen from Fig. 2 that this is also the case for the ozone isomer system. A more

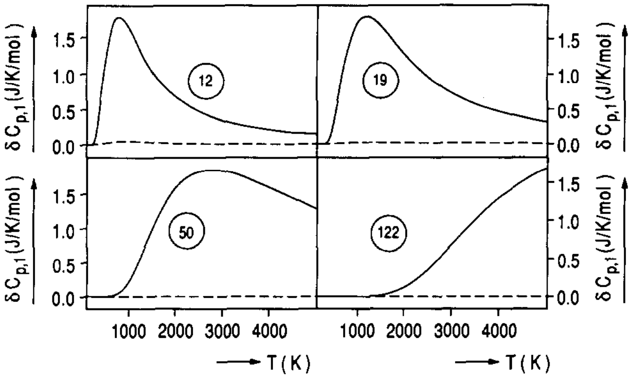

Fig. 2. The temperature dependence of the isomerism contribution to the heat capacity at constant pressure $\delta C_{p,1}$ (relaxation term) or $\delta C_{p,w,1}$ (isofractional term, broken curve) for the two ozone isomers as evaluated at the four energies given in Table 1. The contributions are related to the open C_{2v} isomer.

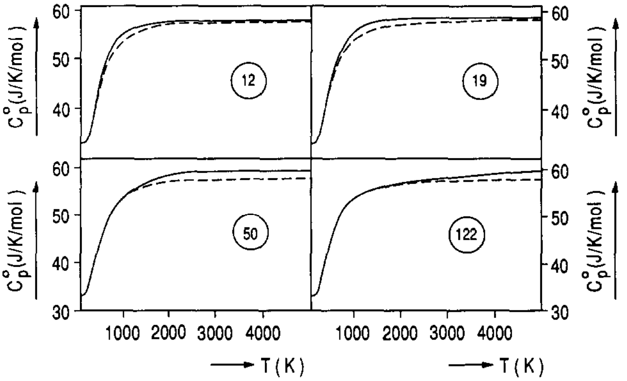

Fig. 3. The temperature dependence of the standard molar heat capacity at constant pressure for the pure open C_{2v} isomer (the partial $C_{p,1}^{\ominus}$ term, broken curve) and for the equilibrium mixture of the two isomers of ozone (the overall $C_p^{\ominus}$ term) evaluated at the four energies given in Table 1.

detailed characterization of the maxima for the four energy values considered is given in Table 2. While the height of the maximum is almost constant, its temperature position depends strongly on ΔE. For the lowest ΔE value considered here the maximum appears at about 650 K while with the highest ΔE term it is shifted to about 6600 K (so that it cannot be seen in Fig. 2). It should be noted that the isofractional term $\delta C_{p,w,1}$ is an almost negligible component of the total, relaxational term.

The isomerism contribution terms cannot be observed directly and, therefore, in Fig. 3 the partial (belonging to the pure open isomer) and overall (belonging to the equilibrium isomeric mixture) molar heat capacities at constant pressure $C_{p,1}^{\ominus}$ and $C_p^{\ominus}$ are used. The isomeric enhancement of the heat capacity is, at the temperature of the $\delta C_{p,1}$ maximum, slightly above 3%, which is significant for precise thermodynamic considerations. However, such contributions can be lower than those expected for deviations from the RRHO model.

This first treatment of the thermodynamic effects of ozone isomerism provides another illustration of the general problem of the consequences of isomerism on evaluating thermodynamic functions. Furthermore, this study has shown that the phenomenon occurs in even very simple species and emphasizes the possible importance of this factor in some complex systems.

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