Thermochimica Acta, 232 (1994) 1-6
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01380-L

A computational evaluation of the ozone dimer altitude profile [1]

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(Received 16 April 1993; accepted 24 May 1993)

Abstract

The mole fraction x_2 of the ozone dimer in its equilibrium mixture with the monomer is evaluated on a base of recent ab initio correlated quantum-chemical computations. The dimerization equilibrium constant is evaluated in terms of partition functions. The pressure and temperature profiles are taken from observations in Antarctic conditions. The resulting x_2 altitude profiles exhibit dependencies with maxima and minima. The seasonal dependency follows that known for the ozone partial pressure. Depending on the computational treatment applied, the highest x_2 values found are of the order of 10^{-8}% or 10^{-10}%.

INTRODUCTION

Most diverse properties of the ozone molecule have been studied (for a review, see Steinfeld et al. [1]) in relation to its important role in the Earth's atmosphere and the phenomenon of ozone depletion [2–4]. Quantum-chemical computations have also been applied in the research [5–9].

Although various species are primarily present in the atmosphere in monomeric forms, molecular complexes can become important in some situations. This is especially the case with atmospheric spectroscopy [10–14]. Hence, populations of various dimers under atmospheric conditions have been computed [15–17] and very recently, investigation of ozone containing dimers has also started [18–20]. The present study evaluates the

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population of the ozone dimer in equilibrium with the monomer under atmospheric conditions.

COMPUTATIONS

The results of ab initio computations of the ozone dimer [20] represent our starting point. The computations were performed in the diffuse-orbital augmented polarization 6-31 + G* basis set with an inclusion of the electron correlation through the second order Møller–Plesset perturbation treatment (MP2). The full geometry optimization followed by harmonic vibrational analysis was carried out in the MP2/6-31 + G* approach. The interaction energy in the energy minimum was corrected for the basis set superposition error (BSSE). Table 1 surveys the MP2/6-31 + G* changes in potential energy ΔE and ground-state energy $\Delta H_0^\ominus$ for the ozone dimerization.

The computed structural, vibrational and energy data serve for construction of partition functions in the approximation of the rigid rotator and harmonic oscillator (see, for example, ref. 21). In particular, the dimerization equilibrium constant K_p in terms of the partial monomeric and dimeric pressures p_i

$$K_p = \frac{p_{(O_3)_2}}{p^2_{O_3}} \tag{1}$$

for the dimerization process

$$2O_3(g) = (O_3)_2(g) \tag{2}$$

has been calculated for the relevant temperature region.

Although the atmosphere represents a complex mixture, components other than O_3 and $(O_3)_2$ can be disregarded for our purpose. Hence, only a partial thermodynamic equilibrium between the monomer and dimer is considered. It is supposed that the equilibrium constant K_p has the same value in the presence or absence of the other atmospheric components. Then, the particular equilibrium condition (1) is the same in the absence or

TABLE 1

Changes in potential ΔE and ground-state $\Delta H_0^\ominus$ energy connected with ozone dimerization

Method [a]	Acronym	ΔE in kJ mol^{-1}	$\Delta H_0^\ominus$ in kJ mol^{-1}
MP2/6-31 + G*	**A**	−12.83	−10.14
MP2/6-31 + G* & BSSE	**B**	−3.25	−0.57

[a] See ref. 20 for details.

presence of the other components, supposing the governing total ozone pressure P is the same (of course, the P term is just the partial pressure of ozone in the complete atmosphere context). There may be a question as to the exact meaning of the quantity P which depends on the particular way in which P is extracted from measurements. Here, we simply suppose that

$$P = p_{O_3} + p_{(O_3)_2} \qquad (3)$$

(In fact, P is practically given by the term p_{O_3}.) Composition of the partial equilibrium monomer–dimer mixture is described by the mole fractions x_1 and x_2 ($x_1 + x_2 = 100\%$). It holds for the dimer mole fraction that

$$x_2 = \frac{2PK_p + 1 - (4PK_p + 1)^{1/2}}{2PK_p} \qquad (4)$$

An Antarctic ozone pressure profile was taken from observations of Hoffmann et al. [22]. In fact, two profiles are treated, from August and October, for a region of heights Z between 5 and 30 km. As related temperature profile is not given in ref. 22 we adopted a representative dependency taken from ref. 4.

RESULTS AND DISCUSSION

The dimerization potential energy ΔE represents a key term in the K_p evaluations. The term is considerably sensitive to the BSSE correction inclusion. However, the BSSE correction itself is evaluated by an approximate technique. Hence, neither the MP2/6-31 + G* (approach **A**) nor the BSSE corrected MP2/6-31 + G* value (approach **B**) represents an exact term. Most probably, the true ΔE value is located between these two boundaries. Hence, also the computed dimeric mole fractions x_2 are to be expected somewhere between the **A** and **B** values.

Table 2 presents temperature dependences of the dimerization equilibrium constant K_p calculated in the **A** and **B** approaches. There are considerable differences between both treatments for low temperatures. One can notice a minor temperature increase in the K_p values for the **B** treatment at higher temperatures. This is likely to be a computational artifact. If the ΔE term is very small, its contribution vanishes at higher temperatures and cannot compensate some features of the approximate partition functions. It is clear that the employed partition-function approximation becomes less reliable with increasing temperature. However, the highest temperature actually used in the reported x_2 evaluations is 230 K (the lowest 183 K). Hence, the partition-function approximation should not be a critical factor.

Figures 1 and 2 represent the primary output of this study. They report altitude profiles of the ozone-dimer mole fraction in its equilibrium with the monomer calculated in the approaches **A** (Fig. 1) and **B** (Fig. 2). Pressures

TABLE 2

Temperature evolution of the ozone-dimerization equilibrium[a] constant K_p

T in K	K_p in atm^{-1}	
	A	**B**
100	1.2	1.2×10^{-5}
150	1.9×10^{-2}	8.7×10^{-6}
200	2.7×10^{-3}	8.6×10^{-6}
250	9.5×10^{-4}	9.5×10^{-6}
298.15	5.1×10^{-4}	1.1×10^{-5}
300	5.0×10^{-4}	1.1×10^{-5}

[a] The standard state — an ideal gas at 1 atm = 101 325 Pa pressure.

and temperatures for selected values of the altitude Z were extrapolated from measured values so that the input information does not exhibit a smooth course but contains an error drift. This is reflected in the computed x_2 dependences.

The input pressure and temperature profiles exhibit courses with extrema. Both a pressure increase and a temperature decrease stabilize the dimer. Cooperation or competition of these two effects creates the final x_2 dependency. Qualitatively, the dependencies are quite similar in the **A** and

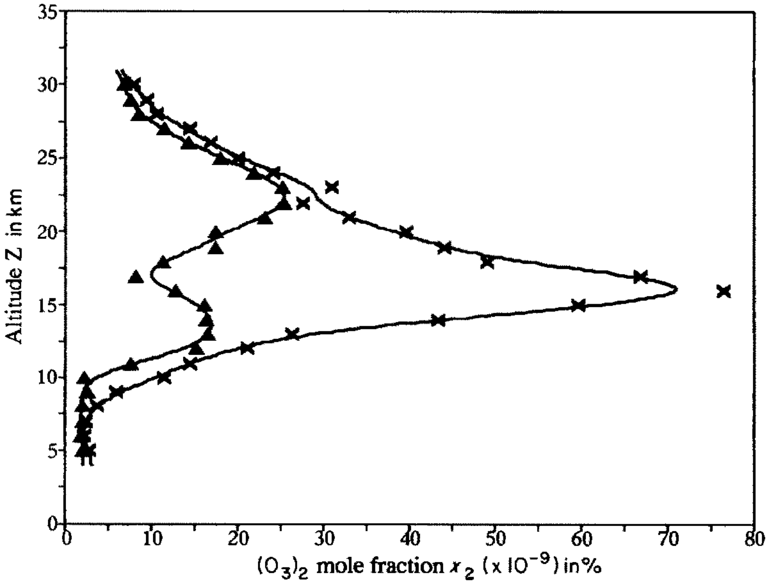

Fig. 1. Altitude Z profile of the ozone dimer mole fraction x_2 in the equilibrium mixture with ozone evaluated in the approach **A** for August (×) and October (▲) conditions.

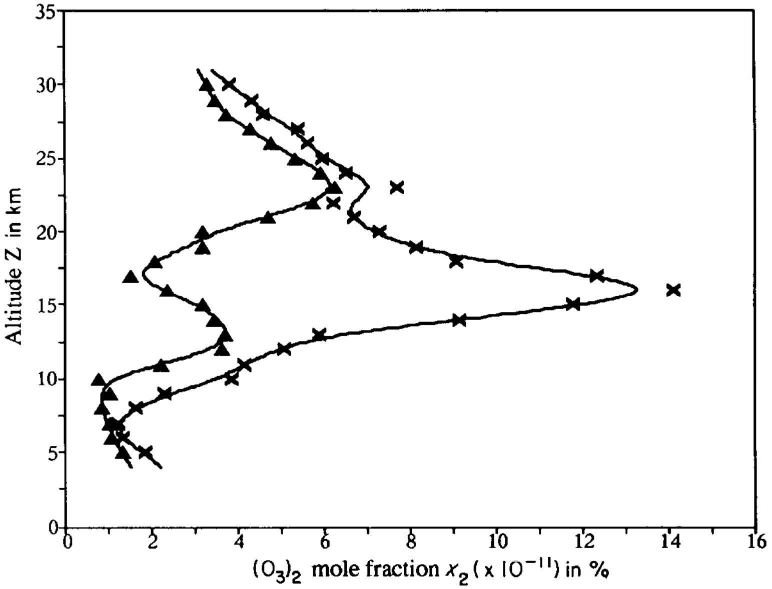

Fig. 2. Altitude Z profile of the ozone dimer mole fraction x_2 in the equilibrium mixture with ozone evaluated in the approach **B** for August (×) and October (▲) conditions.

B approaches. However, there is a difference of two orders of magnitude between them. The seasonal variation between August and October follows the changes in the ozone pressure P.

The computed values of the x_2 term are quite small, the highest values found being of the order of 10^{-8}% and 10^{-10}% in the **A** and **B** approaches. This is a considerably smaller degree of dimerization than reported for saturated steam at similar temperatures [23].

To the authors' knowledge this is the first evaluation of the degree of ozone dimerization. A still higher level of methodical sophistication can be applied with further computational progress. This involves a larger basis set and higher order contributions to the correlation energy and also an inclusion of anharmonicity and non-rigidity effects into partition functions. Nevertheless, it should not dramatically change the interval of the expected x_2 values set by our **A** and **B** approaches.

ACKNOWLEDGEMENTS

F.U. appreciates a research fellowship from the European Environmental Research Organization. The study was initiated during a research stay of Z.S. at the Max-Planck-Institut für Chemie (Otto-Hahn-Institut) partially supported by the Alexander von Humboldt-Stiftung and the Institut. Valuable discussions and suggestions of Professor Paul J. Crutzen are gratefully acknowledged.

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