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Computed gas-phase thermodynamics of the N_2–O_2 complexes [1]

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Abstract

The thermodynamics of the gas-phase dimerizations of N_2 and O_2 has been evaluated in terms of partition functions, constructed using quantum chemical ab initio computations. Two different evaluations of the dimerization energetics have been employed and two minimum-energy structures of the dimer (a linear structure and a T shape) have been considered. In both sets, the structures co-exist, although at temperatures relevant for atmospheric conditions the T-shaped species is more populated. The isomeric interplay is reflected in an enhancement of heat capacity, especially at very low temperatures. For the dimerization equilibrium constant, an interval in which the true value should be applicable is suggested.

INTRODUCTION

Weak molecular complexes have been of interest in atmospheric studies [2–8], primarily in view of their role in atmospheric spectroscopy. The dimers have been recognized not only in the earth's atmosphere but also in other planetary [6] or even cometary [7] atmospheres.

The hetero-dimer [9] N_2–O_2 represents a natural subject of interest in relation to the earth's atmosphere. In contrast to the parent homo-dimers [10–24], $(N_2)_2$ and $(O_2)_2$, it has been paid rather limited attention. This computational study continues the previous quantum-chemical treatment [9] and aims at an evaluation of the hetero-dimer thermodynamics.

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COMPUTATIONS

The key term to be computed in this study is the dimerization equilibrium constant K_p expressed in terms of the partial monomeric and dimeric pressures p_i

$$K_p = \frac{p_{N_2-O_2}}{p_{N_2}p_{O_2}} \tag{1}$$

for the dimerization process

$$N_2(g) + O_2(g) = N_2–O_2(g) \tag{2}$$

The K_p term is evaluated by means of partition functions supplied partly with parameters from ab initio computations [9] and partly with data reported in this paper. For the computed information available, the partition functions are of the usual rigid-rotor and harmonic-oscillator (RRHO) quality [25].

The molecular orbital calculations were carried out [26] in the standard 6-31 + G* basis set with the second- and fourth-order Møller–Plesset (MP2 and MP4) perturbation treatment. In particular, the energetics of the system was computed for the optimal MP2/6-31 + G* geometry [9] by means of the fourth-order treatment (MP4/6-31 + G*). The basis set superposition error (BSSE) was estimated by the counterpoise method [27, 28], which leads to two sets of energetics, **A** and **B** (Table 1).

In fact, MP2/6-31 + G* geometry optimization [9] recognized three different stationary points: linear ($C_{\infty v}$), T-shaped (C_{2v}), and parallel (C_{2v}) (Fig. 1), all of them being in triplet electronic states. Basically, one can even think of two different T-shaped structures, differing in the species coinciding with the two-fold symmetry axis. However, the geometry optimization at the MP2/6-31 + G* level could only be finished for the structure with the N_2 molecule placed in the axis. When the O_2 molecule is located in the axis, the optimization does not converge (this being in

TABLE 1

Changes in potential ΔE and ground-state $\Delta H_0^{\ominus}$ energy connected with the dimerizations of N_2 and O_2

Method [a]		Dimer [b]	ΔE/kJ mol^{-1}	$\Delta H_0^{\ominus}$/kJ mol^{-1}
MP4/6-31 + G*	**A**	$C_{\infty v}$	−4.16	−2.10
		C_{2v}	−3.30	−2.13
MP4/6-31 + G* and BSSE	**B**	$C_{\infty v}$	−0.51	1.55
		C_{2v}	−0.26	0.93

[a] See ref. 9 for details. [b] See Fig. 1; C_{2v} refers to the T-shaped structure with the N_2 molecule in the two-fold symmetry axis.

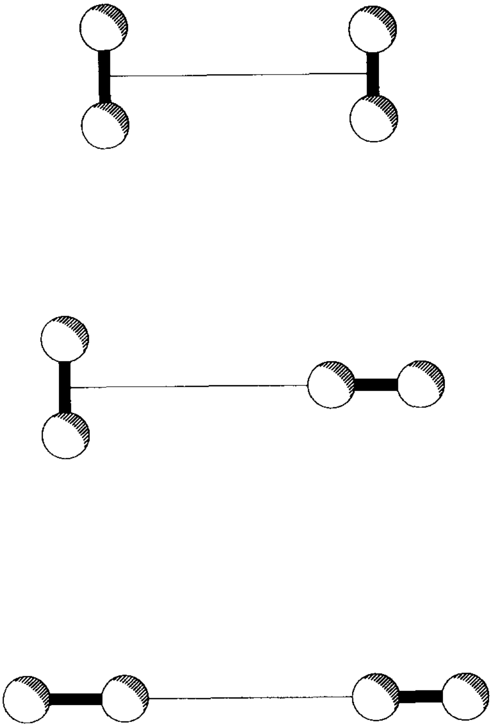

Fig. 1. Schemes of the N_2–O_2 stationary points found: (top) C_{2v} parallel; (middle) C_{2v} T shaped (the N_2 molecule in the symmetry axis); and (bottom) $C_{\infty v}$ linear.

conjunction with a poor SCF convergency). Further differentiation of the three stationary points is possible after harmonic vibrational analysis, presented in Table 2. In fact, the parallel structure exhibits two imaginary frequencies so that it is not relevant for thermodynamic equilibrium.

TABLE 2

The MP2/6-31 + G* harmonic vibrational frequencies ω_i in the stationary points found

Species [a]	ω_i in cm^{-1} [b]		
C_{2v} parallel	24.1i	23.4i	34.1
	49.5	1409.5	2174.9
C_{2v} T-shaped	34.4	42.8	53.0
	65.3	1413.0	2183.0
$C_{\infty v}$	48.6	53.0	53.4
	97.3	97.6	1408.4
	2178.3		
N_2	2178.0		
O_2	1413.4		

[a] See Table 1 and Fig. 1. [b] Imaginary frequencies presented using the imaginary unit $i = \sqrt{-1}$.

Hence, we shall consider two isomers only, the linear and the T-shaped with the nitrogen molecule in the symmetry axis. Table 2 completes the study [9], including also the MP2/6-31 + G* harmonic vibrational frequences of the related monomers.

Primarily, the partial dimerization constants can be computed for each of the isomers, $N_2 \cdot O_2$: $K_p = p_{N_2 \cdot O_2}/(p_{N_2} p_{O_2})$. However, their sum, i.e. the total equilibrium constant $K_p = p_{N_2 - O_2}/(p_{N_2} p_{O_2})$, is more important for an observation. As can be seen in Table 1, in the **B** case both ground-state energy changes $\Delta H_0^{\ominus}$ are positive; it is not excluded, although, it could create (in our combination with the RRHO partition functions) a wrong temperature dependence of the computed K_p terms. Hence, we neglected the harmonic vibrational contributions in the **B** case, i.e. we dealt with the potential energy ΔE terms, and the translational and rotational partition functions only.

RESULTS AND DISCUSSION

The stability of weak dimers is determined by their dimerization energetics and rotational-vibrational motions. Neither of these is sufficiently clear in the present case. Although it is expected that the true dimerization energy should lie between the **A** and **B** values, we cannot come down in favor of either of them. Therefore, the K_p terms are evaluated for both energy estimates (Table 3), with the above-mentioned difference in the partition functions. There is, however, a considerable difference in the values of the dimerization equilibrium constants computed in the **A** and **B** approaches. It is believed that the true K_p values fall somewhere between these limits, although we cannot be too specific about a more precise location.

The results from the two treatments are, however, more consistent as far as the relative stabilities of both isomers are concerned. Table 4 presents the mole fractions of the isomers in their equilibrium mixture. The T-shaped species has a slightly lower ground-state energy in the **A** approach. Thus, it has to prevail at very low temperatures, where, although the mole fraction of the species decreases with temperature, the highest degree of co-existence with the linear form is reached at about 8 K, and then the relative population of the C_{2v} state changes rather slowly. In the **B** treatment, the linear form possesses lower potential energy. However, the T-shaped structure soon (at about 29 K) reaches equimolarity with the linear isomer. The high-temperature relative stabilities are considerably similar in the **A** and **B** treatments.

It is known [25] that temperature variability in the relative stabilities of isomers is manifested in their heat capacities. As can be seen in Table 4,

TABLE 3

Temperature dependence of the calculated dimerization equilibrium constants[a] $K_p/\text{atm}^{-1} = p_{N_2 \cdot O_2}/(p_{N_2}p_{O_2})$

T/K	Term[b]	**A**	**B**
50.0	$C_{\infty v}$	7.62×10^{-2}	6.85×10^{-4}
	C_{2v}	4.14×10^{-1}	1.36×10^{-3}
	Total	4.90×10^{-1}	2.04×10^{-3}
100.0	$C_{\infty v}$	2.74×10^{-3}	3.32×10^{-5}
	C_{2v}	2.04×10^{-2}	1.26×10^{-4}
	Total	2.32×10^{-2}	1.59×10^{-4}
150.0	$C_{\infty v}$	1.07×10^{-3}	6.58×10^{-6}
	C_{2v}	8.59×10^{-3}	3.37×10^{-5}
	Total	9.66×10^{-3}	4.03×10^{-5}
200.0	$C_{\infty v}$	7.45×10^{-4}	2.18×10^{-6}
	C_{2v}	6.03×10^{-3}	1.35×10^{-5}
	Total	6.77×10^{-3}	1.57×10^{-5}
250.0	$C_{\infty v}$	6.43×10^{-4}	9.39×10^{-7}
	C_{2v}	5.11×10^{-3}	6.72×10^{-6}
	Total	5.75×10^{-3}	7.66×10^{-6}
298.15	$C_{\infty v}$	6.12×10^{-4}	4.88×10^{-7}
	C_{2v}	4.74×10^{-3}	3.88×10^{-6}
	Total	5.35×10^{-3}	4.37×10^{-6}
300.0	$C_{\infty v}$	6.12×10^{-4}	4.77×10^{-7}
	C_{2v}	4.73×10^{-3}	3.81×10^{-6}
	Total	5.34×10^{-3}	4.29×10^{-6}

[a] The standard state is an ideal gas at 1 atm = 101 325 Pa pressure. [b] C_{2v} refers to the T-shaped structure with the N_2 molecule in the two-fold symmetry axis.

there are maxima in isomerism contributions to the heat capacity, however, at very low temperatures. At higher temperatures, the isomeric enhancement of heat capacity is rather modest though not negligible.

The RRHO approximation applied is rough but only possible with respect to the amount of computed information available. It is clear that a more advanced approach should deal with a direct summation of levels from vibrational problems in a realistic, at least four-dimensional, anharmonic potential. Moreover, the quantum-chemical part of the computations should also be carried out at a still higher level, concerning both the basis set and correlation energy. Nevertheless, even this first non-empirical estimation of the stability of the N_2–O_2 system brings new, applicable information for observations.

TABLE 4

Temperature dependence of the equilibrium mole fractions w_i in % of the $N_2 \cdot O_2$ isomers [a]

T/K	$C_{\infty v}$	C_{2v}	$\delta C_{p,1}$/J K^{-1} mol^{-1} [b]
***A** energetics*			
1.3 [c]	5.8	94.3	3.43
8.2 [d]	28.9	71.1	−1.44
50.0	15.6	84.4	0.01
100.0	11.8	88.2	0.30
150.0	11.1	88.9	0.35
200.0	11.0	89.0	0.39
250.0	11.2	88.8	0.43
298.15	11.4	88.6	0.47
300.0	11.5	88.5	0.47
***B** energetics*			
15.2 [c]	78.2	21.8	9.51
29.4 [e]	50.0	50.0	6.86
50.0	33.5	66.5	4.99
100.0	20.9	79.1	4.16
150.0	16.3	83.7	4.03
200.0	13.9	86.1	4.00
250.0	12.3	87.7	3.99
298.15	11.2	88.8	3.99
300.0	11.1	88.9	3.99

[a] See Table 3. [b] Isomerism contribution to heat capacity related to the structure that is more stable in the low-temperature region (**A**, C_{2v}; **B**, $C_{\infty v}$). [c] Maximum in the $\delta C_{p,1}$ term. [d] Point of the highest two-structure co-existence. [e] Point of two-structure equimolarity.

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