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Gas-phase association of O_2: a computational thermodynamic study [1]

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Abstract

The thermodynamics of the gas-phase O_2 dimerization have been computed in terms of partition functions, supplied with parameters from quantum-chemical ab initio computations. Two different evaluations of the dimerization energetics have been employed and three different isomers of the dimer considered. In both sets the non-linear structures co-exist at temperatures relevant for atmospheric conditions. Enhancement of heat capacity through this isomeric interplay is quite large at very low temperatures. For the total dimerization equilibrium constant an interval, in which the true value should be present, is suggested.

INTRODUCTION

Recently, we reported [1,2] computations of the formation thermodynamics for the $(N_2)_2$ and N_2–O_2 complexes; now we finalize the series with a similar treatment of the $(O_2)_2$ complexes. Although the complexes have been studied by both experimental and theoretical approaches [3–17], not too much is known about their thermodynamic stabilities. Moreover, there has been a growing interest in molecular complexes present in the atmosphere [18–22] so that an estimation of the populations of such species has become quite useful. Under atmospheric conditions such complexes are primarily important in atmospheric spectroscopy but they can also play a role in atmospheric chemistry processes. In fact, the complexes are important not only in the Earth's atmosphere but also in some planetary atmospheres.

This study aims at evaluation of the O_2 dimerization equilibrium

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constant purely from quantum-chemical calculations, i.e. without any input information originated from observation (with the exception of the universal constants and atomic masses).

COMPUTATIONS

The target of this study is the O_2 dimerization equilibrium constant K_p in terms of the partial monomeric and dimeric pressures p_i

$$K_p = \frac{p_{(O_2)_2}}{p^2_{O_2}} \tag{1}$$

for the gas-phase dimerization process

$$2O_2(g) = (O_2)_2(g) \tag{2}$$

The K_p term is evaluated by means of partition functions supplied with parameters from ab initio computations [23]. With respect to the amount of the computed information available, the partition functions are of the usual rigid-rotor and harmonic-oscillator (RRHO) quality.

The molecular orbital calculations were carried out [23] using the GAUSSIAN 90 program package [24]. Structure and vibrations were computed at the Hartree–Fock (HF) level in the standard 6-31+G* basis set. The dimers were treated in the quintet electronic states and the monomer in the triplet state. The dimerization energetics was further refined by means of the fourth order Møller–Plesset (MP4) perturbation treatment. The basis set superposition error (BSSE) was estimated by the counterpoise method [25]. It creates two sets of energetics, **A** and **B** (Table 1).

In fact, the HF/6-31+G* geometry optimization [23] revealed three different energy-minimum structures: linear $D_{\infty h}$, T-shape C_{2v}, and rhomboid C_{2h}. Although a partial dimerization constant can be computed for each of the isomers, their sum, i.e. the total equilibrium constant, is primarily important for the atmospheric application. However, in the **B** case two

TABLE 1

Changes in potential ΔE and ground-state $\Delta H_0^{\ominus}$ energy for O_2 dimerization

Method [a]	Acronym	Dimer	ΔE/kJ mol^{-1}	$\Delta H_0^{\ominus}$/kJ mol^{-1}
MP4/6-31 + G*	**A**	$D_{\infty h}$	−4.75	−2.65
		C_{2v}	−2.92	−2.43
		C_{2h}	−2.41	−2.04
MP4/6-31 + G* and BSSE	**B**	$D_{\infty h}$	−0.59	1.51
		C_{2v}	−0.47	0.02
		C_{2h}	−0.47	−0.10

[a] See ref. 23 for computational details.

ground-state energy changes $\Delta H_0^\ominus$ are positive. Although it might be a real fact, however, it could create (in combination with the RRHO partition functions) a wrong temperature dependency of the computed K_p terms. Therefore, we neglected the harmonic vibrational contributions in the **B** case, i.e. we dealt with the ΔE terms and translational and rotational partition functions only.

RESULTS AND DISCUSSION

The dimeric stabilities are primarily determined by the dimerization energetics and rotational–vibrational motions. Although the precise dimerization energetics is virtually unknown, it can be expected between the **A** and **B** values. Therefore the K_p terms are evaluated for both estimations of the energetics (Table 2). There is, however, a considerable difference between both series of the computed dimerization equilibrium constants. One can, at least, expect the true K_p value somewhere between both bounds, and this result itself can be useful in the applications. Temperature dependency of the total K_p term is more pronounced in the **B** treatment. Clearly enough, a further computational effort is needed in order to obtain still more reliable values of the dimerization energies. The BSSE treatment is [26, 27] after all only an approximation, and thus further computations will employ still larger basis sets.

Table 2 reports the dimerization equilibrium constant evaluated in the **A** and **B** approaches. The equilibrium constants are presented for partial and the total dimerization processes. However, in an application, most probably one shall deal with the total dimerization [28–30]. Owing to the differences between the **A** and **B** techniques, the values of the equilibrium constants differ substantially; however, we can understand the values as upper and lower bounds.

Table 2 in fact also allows for a relative stability reasoning; however the inter-isomeric stabilities are treated in Table 3 in more detail. In fact, there is an interesting common feature. In both cases, the linear species is important only at very low temperatures, while at higher temperatures the C_{2v} and C_{2h} species coexist and dominate. This is particularly true with the temperature region relevant for atmospheric conditions. Table 3 points out several points of relative-stability interchange in the low temperature region. In both **A** and **B** treatments the C_{2h} isomer becomes the most populated species in the high temperature limit.

Such variability in relative stabilities has to be seen in the overall heat capacity term. Indeed, there is a maximum in isomerism contributions to the heat capacity at very low temperature (Table 3); this maximum is especially pronounced in the **A** case. A similar maximum is also exhibited by the total molar heat capacity $C_p^\ominus$ term for O_4 at slightly higher temperature. For example, in the **A** case the maximum $C_p^\ominus$ value

TABLE 2

Temperature dependence of the calculated dimerization equilibrium constant[a] $K_p = p_{(O_2)_2}/p^2_{O_2}$

T/K	$K_p = (p_{(O_2)_2}/p^2_{O_2})/\mathrm{atm}^{-1}$		
	Term	**A**	**B**
50.0	$D_{\infty h}$	9.35×10^{-2}	2.21×10^{-4}
	C_{2v}	5.19×10^{0}	1.24×10^{-3}
	C_{2h}	5.81×10^{0}	1.41×10^{-3}
	Total	1.11×10^{1}	2.87×10^{-3}
100.0	$D_{\infty h}$	1.81×10^{-3}	9.70×10^{-6}
	C_{2v}	3.33×10^{-1}	8.90×10^{-5}
	C_{2h}	6.68×10^{-1}	1.01×10^{-4}
	Total	1.00×10^{0}	2.00×10^{-4}
150.0	$D_{\infty h}$	5.70×10^{-4}	1.86×10^{-6}
	C_{2v}	1.57×10^{-1}	2.19×10^{-5}
	C_{2h}	3.85×10^{-1}	2.50×10^{-5}
	Total	5.43×10^{-1}	4.87×10^{-5}
200.0	$D_{\infty h}$	3.57×10^{-4}	6.04×10^{-7}
	C_{2v}	1.18×10^{-1}	8.43×10^{-6}
	C_{2h}	3.18×10^{-1}	9.60×10^{-6}
	Total	4.36×10^{-1}	1.86×10^{-5}
250.0	$D_{\infty h}$	2.88×10^{-4}	2.58×10^{-7}
	C_{2v}	1.04×10^{-1}	4.09×10^{-6}
	C_{2h}	2.99×10^{-1}	4.65×10^{-6}
	Total	4.03×10^{-1}	8.99×10^{-6}
298.15	$D_{\infty h}$	2.63×10^{-4}	1.33×10^{-7}
	C_{2v}	9.90×10^{-2}	2.32×10^{-6}
	C_{2h}	2.96×10^{-1}	2.65×10^{-6}
	Total	3.95×10^{-1}	5.10×10^{-6}
300.0	$D_{\infty h}$	2.62×10^{-4}	1.30×10^{-7}
	C_{2v}	9.89×10^{-2}	2.28×10^{-6}
	C_{2h}	2.96×10^{-1}	2.59×10^{-6}
	Total	3.95×10^{-1}	5.00×10^{-6}

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

(82.0 J K^{-1} mol^{-1}) is formed by the isomeric enhancement to the extent of some 54%.

The finding of isomeric co-existence has a value for understanding the observations; it indicates a still more complex structure of molecular spectra. The finding of isomeric co-existence should not be changed by computing at a higher methodological level. Nevertheless, in spite of the relatively low temperatues considered, there is still a problem with the quality of the partition functions applied. Although their approximation is quite simple, it is the only possibility applicable with respect to the amount of the computed information available. It is however clear that a more

TABLE 3

Temperature dependence of the equilibrium mole fractions w_i of the $(O_2)_2$ isomers [a]

T/K	w_i/%			$\delta C_{p,1}$ [a]/J K^{-1} mol^{-1}
	$D_{\infty h}$	C_{2v}	C_{2h}	
Case **A**				
13.0 [c]	48.8	48.8	2.4	44.0
14.8 [b]	36.8	58.5	4.8	45.4
20.3 [c]	15.2	69.6	15.2	39.2
45.6 [c]	1.1	49.5	49.5	12.6
50.0	0.8	46.8	52.4	10.4
100.0	0.2	33.2	66.6	0.2
150.0	0.1	29.0	70.9	−2.1
200.0	0.08	27.0	72.9	−3.0
250.0	0.07	25.8	74.1	−3.4
298.15	0.07	25.1	74.9	−3.6
300.0	0.07	25.1	74.9	−3.6
Case **B**				
5.4 [b]	74.0	11.9	14.1	17.6
10.6 [c]	35.0	30.1	35.0	9.4
11.5 [c]	31.7	31.7	36.7	8.5
50.0	7.7	43.1	49.2	4.2
100.0	4.9	44.5	50.7	4.1
150.0	3.8	45.0	51.2	4.1
200.0	3.2	45.2	51.5	4.1
250.0	2.9	45.4	51.7	4.1
298.15	2.6	45.6	51.8	4.1
300.0	2.6	45.6	51.8	4.1

[a] Isomerism contribution to heat capacity related to the structure most stable in low temperature region, i.e. to the linear isomer. [b] Maximum in the $\delta C_{p,1}$ term. [c] Point of two-structure equimolarity.

advanced approach at a later stage should deal with a direct summation of levels from vibrational problems in a realistic, at least four-dimensional, anharmonic potential. This should be connected with a further improvement of the quantum-chemical part of the computations, concerning both the basis set and correlation part.

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REFERENCES

1 F. Uhlík, Z. Slanina and A. Hinchliffe, Thermochim. Acta, 223 (1993) 1.
2 F. Uhlík, Z. Slanina, W.B. De Almeida and A. Hinchliffe, Thermochim. Acta, 225 (1993) 1.
3 G.N. Lewis, J. Am. Chem. Soc., 46 (1924) 2027.
4 A.R.W. McKellar, N.H. Rich and H.L. Welsh, Can. J. Phys., 50 (1972) 1.
5 C.A. Long and G. Henderson, Chem. Phys., 2 (1973) 485.
6 A. Horowitz, G. von Helden, W. Schneider, F.G. Simon, P.J. Crutzen and G.K. Moortgat, J. Phys. Chem., 92 (1988) 4956.
7 A. Horowitz, W. Schneider and G.K. Moortgat, J. Phys. Chem., 93 (1989) 7859.
8 A. Horowitz, W. Schneider and G.K. Moortgat, J. Phys. Chem., 94 (1990) 2904.
9 R.M. Berns and A. van der Avoird, J. Chem. Phys., 72 (1980) 6107.
10 B. Jönsson, G. Karlström and S. Romano, J. Chem. Phys., 74 (1981) 2896.
11 J. Tennyson and A. van der Avoird, J. Chem. Phys., 77 (1982) 5664; 80 (1984) 2986.
12 M.S.H. Ling and M. Rigby, Mol. Phys., 51 (1984) 855.
13 P.J. Hay, R.T. Pack and R.L. Martin, J. Chem. Phys., 81 (1984) 1360.
14 G. Brocks and A. van der Avoird, Mol. Phys., 55 (1985) 11.
15 H.-J. Böhm and R. Ahlrichs, Mol. Phys., 55 (1985) 1159.
16 R. Hashemi, T. Jaffke, L.G. Christophorou and E. Illenberger, J. Phys. Chem., 96 (1992) 10605.
17 T. Jaffke, R. Hashemi, L.G. Christophorou and E. Illenberger, Z. Phys. D, 25 (1992) 77.
18 J.M. Calo and R.S. Narcisi, Geophys. Res. Lett., 7 (1980) 289.
19 Z. Slanina, J. Atmos. Chem., 6 (1988) 185.
20 A.R.W. McKellar, Astrophys. J., 326 (1988) L75.
21 K. Fox and S.J. Kim, J. Quant. Spectrosc. Radiat. Transfer, 40 (1988) 177.
22 J.F. Crifo, Icarus, 84 (1990) 414.
23 F. Uhlík, Z. Slanina and A. Hinchliffe, J. Mol. Struct. (Theochem), 285 (1993) 273.
24 M.J. Frisch, M. Head-Gordon, G.W. Trucks, J.B. Foresman, H.B. Schlegel, K. Raghavachari, M. Robb, J.S. Binkley, C. Gonzalez, D.J. Defrees, D.J. Fox, R.A. Whiteside, R. Seeger, C.F. Melius, J. Baker, R.L. Martin, L.R. Kahn, J.J.P. Stewart, S. Topiol and J.A. Pople, GAUSSIAN 90, Revision I, Gaussian Inc., Pittsburgh, 1990.
25 S.F. Boys and F. Bernardi, Mol. Phys., 19 (1970) 553.
26 D.W. Schwenke and D.G. Truhlar, J. Chem. Phys., 82 (1985) 2418.
27 I. Mayer and A. Vibok, Chem. Phys. Lett., 140 (1987) 558.
28 C.A. Long and G.E. Ewing, Chem. Phys. Lett., 9 (1971) 225.
29 C.A. Long and G.E. Ewing, J. Chem. Phys., 58 (1973) 4824.
30 J.J. Orlando, G.S. Tyndall, K.E. Nickerson and J.G. Calvert, J. Geophys. Res., 96 (1991) 20755.