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Computed gas-phase thermodynamics of N_2 association [1]

Filip Uhlík [2], Zdeněk Slanina *[,3] and Alan Hinchliffe
Department of Chemistry, UMIST, P.O. Box 88, Manchester M60 1QD (UK)

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Abstract

The thermodynamics of the gas-phase N_2 dimerization has been computed in terms of partition functions constructed on the basis of ab initio quantum-chemical computations. Two different evaluations of the dimerization energetics have been employed, indicating four and three $(N_2)_2$ minimum energy structures. In both sets, two particular structures co-exist at temperatures relevant for atmospheric conditions. Enhancement of heat capacity through this isomerism is felt at very low temperatures only. For the dimerization equilibrium constant, an interval in which the true value should be present is suggested.

INTRODUCTION

It has been recognized that molecular complexes, especially dimers, can play an important role in atmospheric spectroscopy [1–5]. Some dimers can even be observed more readily under atmospheric than under laboratory conditions [6]. The dimers are relevant not only to the Earth's atmosphere but also to cometary [5] and planetary [4] atmospheres. In the latter case they could even contribute to the energy budget.

Although the presence of the dimers has been sufficiently demonstrated, their equilibrium concentrations are not well established. At present, computations of the dimer populations seem to be more straightforward than direct measurements. The key term, the dimerization equilibrium constant, can be estimated from quantum-chemical calculations alone, i.e. without any input information originating from observation (with the exception of the universal constants and atomic masses).

For the Earth's atmosphere, three complexes are of particular interest: $(N_2)_2$, $(O_2)_2$, and N_2–O_2; this report is devoted to the stability of the first

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* Corresponding author: Max-Planck-Institut für Chemie (Otto-Hahn-Institut), D-W-65 Mainz, Germany.

[1] Part IX in the series Computational Studies of Atmospheric Chemistry Species; for Part VIII, see ref. 23.

[2] Permanent address: Faculty of Science, Charles University, Prague 2, Czech Republic.

[3] On a leave of absence from the Czechoslovak Academy of Sciences, Prague, Czech Republic.

species based on recent quantum-chemical computations [7]. Although the N_2–N_2 interactions have been studied [8–19], no systematic stability evaluation of $(N_2)_2$ is available. This study aims to fill the gap.

COMPUTATIONS

We shall deal with the dimerization equilibrium constant K_p in terms of the partial monomeric and dimeric pressures p_i

$$K_p = \frac{p_{(N_2)_2}}{p^2_{N_2}} \tag{1}$$

for the dimerization process

$$2N_2(g) = (N_2)_2(g) \tag{2}$$

The K_p term is evaluated here from partition functions supplied with parameters from ab initio computations [7]. With respect to the computed information available, the partition functions are of the usual rigid-rotor and harmonic-oscillator (RRHO) quality [20].

The molecular orbital calculations were carried out [7] 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 by means of the fourth-order treatment (MP4/6-31 + G*). The basis set superposition error (BSSE) was estimated by the counterpoise method [21]. It creates two sets of energetics, ***A*** and ***B*** (Table 1).

In fact, MP2/6-31 + G* geometry optimization [7] recognized four different energy-minimum structures. 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 an observation. There is a

TABLE 1

Changes in potential energy ΔE and ground-state energy $\Delta H_0^\ominus$ connected with N_2 dimerization

Method[a]	Acronym	Dimer	ΔE/kJ mol^{-1}	$\Delta H_0^\ominus$/kJ mol^{-1}
MP4/6-31 + G*	***A***	$D_{\infty h}$	−2.52	−0.38
		D_{2d}	−2.89	−2.34
		C_{2h}	−2.88	−2.17
		C_{2v}	−3.45	−2.26
MP4/6-31 + G* and BSSE	***B***	$D_{\infty h}$	−0.10	2.05
		D_{2d}	0.33	0.88
		C_{2h}	−0.40	0.30
		C_{2v}	−0.42	0.78

[a] See ref. 7 for details.

particular problem for one of the species D_{2d}, in that its dimerization energy ΔE becomes positive when the BSSE estimation is considered. This may well be an artifact of the procedure [21, 22] and for our practical purposes we decided to remove the D_{2d} structure from the **B** set. Moreover, in the **B** case, all the ground-state energy changes $\Delta H_0^\ominus$ are positive. Though this may be real, it could create (in conjunction with the RRHO partition functions) a clearly wrong temperature dependency for the computed K_p terms. Hence, we neglected the harmonic vibrational contributions in the **B** case, i.e. we considered the ΔE terms and the translational and rotational partition functions only.

RESULTS AND DISCUSSION

The dimerization energetics and rotational-vibrational motions are particularly important in the stability evaluations. It is expected that the true dimerization energy should lie between the **A** and **B** values. Therefore, the K_p terms are evaluated for both situations (Table 2). There is, however,

TABLE 2

Temperature dependence of the calculated dimerization equilibrium constant[a] $K_p = p_{(N_2)_2}/p^2_{N_2}$

T/K	K_p/atm^{-1}			T/K	K_p/atm^{-1}		
	Term	**A**	**B**		Term	**A**	**B**
50.0	$D_{\infty h}$	1.25×10^{-3}	2.16×10^{-4}	250.0	$D_{\infty h}$	2.85×10^{-4}	6.59×10^{-7}
	D_{2d}	4.61×10^{0}	–		D_{2d}	9.67×10^{-2}	–
	C_{2h}	3.53×10^{0}	2.47×10^{-3}		C_{2h}	8.18×10^{-2}	9.39×10^{-6}
	C_{2v}	6.73×10^{-1}	2.51×10^{-3}		C_{2v}	6.27×10^{-3}	9.27×10^{-6}
	Total	8.81×10^{0}	5.20×10^{-3}		Total	1.85×10^{-1}	1.93×10^{-5}
100.0	$D_{\infty h}$	3.58×10^{-4}	1.73×10^{-5}	298.15	$D_{\infty h}$	3.09×10^{-4}	3.53×10^{-7}
	D_{2d}	3.06×10^{-1}	–		D_{2d}	9.21×10^{-2}	–
	C_{2h}	2.52×10^{-1}	1.94×10^{-4}		C_{2h}	7.82×10^{-2}	5.37×10^{-6}
	C_{2v}	2.79×10^{-2}	1.94×10^{-4}		C_{2v}	5.75×10^{-3}	5.30×10^{-6}
	Total	5.86×10^{-1}	4.05×10^{-4}		Total	1.76×10^{-1}	1.10×10^{-5}
150.0	$D_{\infty h}$	2.76×10^{-4}	4.04×10^{-6}	300.0	$D_{\infty h}$	3.10×10^{-4}	3.46×10^{-7}
	D_{2d}	1.46×10^{-1}	–		D_{2d}	9.20×10^{-2}	–
	C_{2h}	1.22×10^{-1}	4.92×10^{-5}		C_{2h}	7.81×10^{-2}	5.27×10^{-6}
	C_{2v}	1.11×10^{-2}	4.88×10^{-5}		C_{2v}	5.73×10^{-3}	5.20×10^{-6}
	Total	2.79×10^{-1}	1.02×10^{-4}		Total	1.76×10^{-1}	1.08×10^{-5}
200.0	$D_{\infty h}$	2.70×10^{-4}	1.45×10^{-6}				
	D_{2d}	1.09×10^{-1}	–				
	C_{2h}	9.22×10^{-2}	1.92×10^{-5}				
	C_{2v}	7.53×10^{-3}	1.90×10^{-5}				
	Total	2.09×10^{-1}	3.97×10^{-5}				

[a] The standard state, i.e. an ideal gas at 1 atm = 101325 Pa pressure.

a considerable difference between the computed dimerization equilibrium constants. Still, at this stage of research one can expect that the true K_p value falls somewhere between these limits. The temperature dependence of the total K_p term is more pronounced in the ***B*** treatment. Although one can expect that the true K_p value lies between the ***A*** and ***B*** values, at this level of computations we still cannot specify a more precise location; further computational effort is thus needed in the respect.

Table 3 deals with relative stabilities of the individual $(N_2)_2$ isomers. However, the data are, of course, influenced by the fact the D_{2d} species was removed from the ***B*** set. Nevertheless, there is an interesting common feature. In both cases, two species prevail and co-exist throughout a temperature region relevant for atmospheric conditions. These are the D_{2d} and C_{2h}, and C_{2h} and C_{2v} pairs in the ***A*** and ***B*** cases, respectively. Table 3 indicates one relative-stability interchange in the low temperature region for each energetics. In the ***A*** case, the interchange concerns the C_{2h} and C_{2v}

TABLE 3

Temperature dependence of the equilibrium mole fractions w_i of the $(N_2)_2$ isomers[a]

T/K	w_i in %				$\delta C_{p,1}$[a]/J K^{-1} mol^{-1}
	$D_{\infty h}$	D_{2d}	C_{2h}	C_{2v}	
A energetics set					
3.9[b]	4×10^{-25}	87.8	0.9	11.3	6.86
14.4[c]	1×10^{-6}	55.0	22.5	22.5	−1.76
50.0	0.01	52.3	40.0	7.6	−0.06
100.0	0.06	52.2	42.9	4.8	-7×10^{-3}
150.0	0.1	52.2	43.7	4.0	1×10^{-3}
200.0	0.1	52.2	44.0	3.6	6×10^{-3}
250.0	0.2	52.2	44.2	3.4	9×10^{-3}
298.15	0.2	52.2	44.3	3.3	0.01
300.0	0.2	52.2	44.3	3.3	0.01
B energetics set					
0.8[b]	2×10^{-19}	–	8.4	91.6	3.71
50.0	4.1	–	47.5	48.4	−0.15
94.0[c]	4.3	–	47.9	47.9	−0.17
100.0	4.3	–	47.9	47.8	−0.17
150.0	4.0	–	48.2	47.8	−0.14
200.0	3.7	–	48.4	47.9	−0.12
250.0	3.4	–	48.6	48.0	−0.11
298.15	3.2	–	48.7	48.1	−0.10
300.0	3.2	–	48.7	48.1	−0.10

[a] Isomerism contribution to the heat capacity related to the structure most stable in the low temperature region (***A***, D_{2d}; ***B***, C_{2v}). [b] Maximum in the $\delta C_{p,1}$ term. [c] Point of two-structure equimolarity.

isomers, while the ground-state structure D_{2d} possesses the highest stability over the whole temperature interval considered. In the ***B*** case, the deepest minimum considered, C_{2v}, is the most populated only upto about 94 K, when it is replaced by the C_{2h} species. Such variability in relative stabilities has to be manifested in the overall heat capacity term [20]. Indeed, there are maxima in the isomerism contributions to the heat capacity at very low temperatures (Table 3). The demonstration of isomeric co-existence clearly indicates an even more complex structure of molecular spectra.

Although the temperatures considered are relatively low, there is still a problem of the quality of the partition functions applied. Their approximation is rough but only possible with respect to the amount of the computed information available. It is, however, clear that a more advanced approach would have to deal with a direct summation of levels from a vibrational problem in a realistic, at least four-dimensional, anharmonic potential. Moreover, we are also dealing here with some basic (but insufficiently defined at the molecular level) concepts, such as the dimer versus monomer or the activity versus pressure terms. Finally, the quantum-chemical part of the computations should also be carried out at a still higher level with respect to both the basis set and the correlation part.

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