Thermochimica Acta, 173 (1990) 171–176
Elsevier Science Publishers B.V., Amsterdam

O_6(g): THE PRESENT STATE IN COMPUTATIONAL EVALUATION OF ITS THERMODYNAMICS *

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(Received 9 May 1990)

ABSTRACT

The thermodynamics of formation of O_6(g) have been studied on the basis of recent ab initio data. Particular attention has been paid to the interesting temperature-dependent interconversion of the two isomers forming this system. The trimer appears to be practically undetectable under the conditions of temperature equilibrium with O_2(g).

INTRODUCTION

Oligomerism of sulphur atoms is well known and has also been much studied theoretically (see, for example, refs. 1–3). Analogous oligomeric configurations of oxygen greater than O_3 have so far been studied only sporadically, the van der Waals dimer $(O_2)_2$ being the subject of investigation [4]. Quite recently, however, Blahous and Schaefer [5] have presented an ab initio self-consistent field (SCF) study of the O_6 system. In terms of three different basis sets (STO-3G, double zeta (DZ), and double zeta plus polarization, (DZP)) they showed that there are two local energy minima on the hypersurface of O_6, namely the chair (D_{3d}) and twist (D_2) forms. Starting from the computational data of ref. 5, the present study carries out an evaluation of the thermodynamics of formation of O_6 with particular reference to the interconversion of the two isomers.

TEMPERATURE DEPENDENCE OF THE INTERCONVERSION OF THE TWO ISOMERS OF O_6(g)

For the DZ and DZP approximations, ref. 5 gives structural and energetic data and harmonic vibrational frequencies for both isomers. This enables

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[*] Part XLVI in the series Multi-molecular clusters and their isomerism; for Part XLV, see ref. 14.

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0040-6031/90/$03.50

TABLE 1

Temperature dependence of the weight factor [a] w_1 of the chair (D_{3d}) structure of O_6(g)

T(K)	w_1 (%) [b]	
	DZ [c]	DZP [c]
100	100.0 (100.0)	100.0 (100.0)
298.15	100.0 (100.0)	100.0 (100.0)
500	100.0 (100.0)	100.0 (100.0)
1000	98.6 (99.8)	99.8 (100.0)
1500	90.7 (98.2)	97.4 (99.5)
2000	78.3 (95.3)	90.9 (98.2)
3000	57.0 (88.1)	72.6 (93.5)
3493 [d]	50.0 (84.8)	–
4729 [d]	–	50.0 (84.4)

[a] In addition to the RRHO values, the simple Boltzmann factors are given in parentheses.
[b] The mole fraction of the chair isomer in its equilibrium mixture with the twist isomer.
[c] See ref. 5 for a description of the computational approximation.
[d] Temperature of equimolarity in the w_i terms ($w_1 = w_2 = 50.0\%$).

evaluation of the relative stabilities of the species in terms of the usual approximation of rigid rotor and harmonic oscillator (RRHO) to the partition function [6].

A fairly considerable separation exists between the two isomers in terms of their potential energies: about 50 and 67 kJ mol^{-1} in the DZ and DZP approaches, respectively. It is useful to follow the mutual populations of both isomers in the equilibrium mixture in terms of their mole fractions (weight factors) w_i, whose relation to partition functions is well known [7–9]. Table 1 presents the temperature dependence of the weight factor of the chair structure in both approximation schemes considered. At low and medium temperatures the chair form predominates, but at higher temperatures the population of the twist form cannot be neglected. If we accept the applicability of the RRHO approximation at high temperatures, we can show that there exists a temperature at which the relative populations of both isomers is equal (i.e., $w_1 = w_2 = 50\%$). The twist isomer is the more stable form above this equimolarity point.

If all the differences in rotational–vibrational partition functions between the two isomers, as well as those in the contribution of vibrations to zero-point energy, were omitted, the weight factors w_i would be reduced to simple Boltzmann factors based on the potential energy differences alone [7–9]. Table 1 shows that these simple Boltzmann factors are inadequate approximations of the weight factors w_i, and hence the differences in rotational–vibrational motions between the two isomers are also significant in thermodynamical respects.

In a number of other contexts it was shown [10–12] that thermodynamic functions of an equilibrium mixture of isomers generally differ from those corresponding to any individual isomer. Consequently, it is necessary to consider, besides the partial terms resulting from the individual structures, the overall terms corresponding to the equilibrium mixture of these isomers taken as a single pseudospecies. It has been shown to be useful to introduce the so-called isomerism contributions to thermodynamic functions, defined as correction terms which when added to the value of thermodynamic functions of a chosen isomer give the overall terms corresponding to the equilibrium mixture of isomers. (Thus, generally, these isomerism contributions depend on the reference isomer chosen—conventionally the most stable structure at low temperatures.)

Table 2 illustrates the temperature dependences of the isomerism contributions $\delta X_1^{(\mathrm{iso})}$, related to the chair structure as the reference isomer (which is conventionally assigned the index 1 [10–12]), for three fundamental thermodynamic functions: enthalpy ($X = H$), entropy ($X = S$), and heat capacity at constant pressure ($X = C_p$). Obviously, these correction factors are significant for any of the thermodynamic terms when considered at higher temperatures in both of the methodologies used (DZ and DZP).

Whereas the isomerism contributions to enthalpy and entropy increase monotonically with temperature, the correction $\delta C_{p,1}^{(\mathrm{iso})}$ for heat capacity exhibits a distinct temperature maximum. In the DZ and DZP approximations this maximum lies at 1882 K and 2519 K, and attains the magnitude of 12.8 J K^{-1} mol^{-1} and 12.6 J K^{-1} mol^{-1}, respectively. The shape of this

TABLE 2

Temperature dependencies of isomerism contributions [a] to enthalpy, $\delta H_1^{(\mathrm{iso})}$, entropy $\delta S_1^{(\mathrm{iso})}$, and heat capacity at constant pressure, $\delta C_{p,1}^{(\mathrm{iso})}$, of $O_6(g)$

T (K)	DZ [b]			DZP [b]		
	$\delta H_1^{(\mathrm{iso})}$	$\delta S_1^{(\mathrm{iso})}$	$\delta C_{p,1}^{(\mathrm{iso})}$	$\delta H_1^{(\mathrm{iso})}$	$\delta S_1^{(\mathrm{iso})}$	$\delta C_{p,1}^{(\mathrm{iso})}$
100	8×10^{-24}	8×10^{-23}	5×10^{-21}	4×10^{-32}	4×10^{-31}	3×10^{-29}
298.15	6×10^{-7}	2×10^{-6}	4×10^{-5}	1×10^{-9}	4×10^{-9}	9×10^{-8}
500	2×10^{-3}	4×10^{-3}	4×10^{-2}	4×10^{-5}	9×10^{-5}	1×10^{-3}
1000	0.68	0.80	4.02	0.12	0.14	0.98
1500	4.62	3.89	11.2	1.71	1.36	5.90
2000	10.8	7.45	12.7	6.02	3.80	10.9
3000	21.4	11.8	8.16	18.2	8.73	11.7

[a] Related to the chair (D_{3d}) structure as the reference isomer 1; $\delta H_1^{(\mathrm{iso})}$ in kJ mol^{-1}, $\delta S_1^{(\mathrm{iso})}$ and $\delta C_{p,1}^{(\mathrm{iso})}$ in J K^{-1} mol^{-1}.

[b] See ref. 5 for a description of the computational approximation.

curve is in accordance with earlier findings concerning other isomeric systems [10–12].

THERMODYNAMICS OF O_6(g) FORMATION

From a chemical standpoint, of course, it is interesting to evaluate the stability of O_6 with regard to O_2, i.e. in two partial equilibria:

$$3O_2(g) = O_6(D_{3d};\ g) \qquad (1)$$

$$3O_2(g) = O_6(D_2;\ g) \qquad (2)$$

and one overall equilibrium:

$$3O_2(g) = O_6(g) \qquad (3)$$

Here the crucial term is the enthalpy of these processes at absolute zero temperature (i.e. the heat of formation of the individual forms of O_6 at absolute zero). For determination of this term Blahous and Schaefer [5] adopted two thermodynamic cycles, homodesmotic (H) and hyperhomodesmotic (HH). The purpose of these cycles was to compensate for errors in the correlation energy in the SCF calculations used (which, of course, do not take this effect into account). It was shown, however, that there exist considerable differences between the heats of formation obtained by the H and HH approaches.

Table 3 presents a survey of the standard thermodynamic functions for reactions (1)–(3) in terms of the DZP approximation for the H and HH evaluations of the heat of formation. The thermodynamic characteristics of O_2(g) were taken from ref. 13. The values of the overall equilibrium constant for the formation of O_6(g) appear to be much too low in both the H and HH approaches. Although it is true that the population of O_6 at a chosen temperature must also be followed as a function of the total pressure of the gaseous mixture, it is nevertheless obvious that the degree of association at the temperatures considered in Table 3 is too low, and experimental detection of this species cannot reasonably be expected. (This remains true even when possible dissociation of O_2 at high temperatures is taken into account through balance considerations.)

CONCLUSION

Exclusively on the basis of calculated characteristics [5] of the two isomers of O_6(g), the possibility of a temperature interchange of their stability has been shown. Values of thermodynamic functions of their equilibrium mixture (at least at some temperatures) can be non-negligibly affected by the interplay of the two isomers. Available energy data indicate very low

TABLE 3

Survey of standard [a] thermodynamic terms for partial [b] and overall processes $3O_2(g) = O_6(g)$ evaluated within the DZP approach [c] [5]

T (K)	Chair (D_{3d})			Twist (D_2)			Overall		
	$\Delta H_T^\ominus$	$\Delta S_T^\ominus$	log K_p	$\Delta H_T^\ominus$	$\Delta S_T^\ominus$	log K_p	$\Delta H_T^\ominus$	$\Delta S_T^\ominus$	log K_p
100	533.5	−299.0	−294.3	597.8	−292.6	−327.5	533.5	−299.0	−294.3
	306.3		−175.6	370.6		−208.9	306.3		−175.6
200	528.8	−332.5	−155.5	593.6	−322.3	−171.9	528.8	−332.5	−155.5
	301.6		−96.13	366.4		−112.5	301.6		−96.13
298.15	525.6	−345.6	−110.1	590.8	−333.7	−120.9	525.6	−345.6	−110.1
	298.4		−70.33	363.6		−81.14	298.4		−70.33
300	525.5	−345.8	−109.6	590.8	−333.8	−120.3	525.5	−345.8	−109.6
	298.4		−70.01	363.6		−80.74	298.4		−70.01
400	523.9	−350.7	−86.73	589.4	−337.8	−94.62	523.9	−350.7	−86.73
	296.7		−57.06	362.2		−64.95	296.7		−57.06
500	523.4	−351.8	−73.05	589.1	−338.5	−79.23	523.4	−351.8	−73.05
	296.2		−49.32	361.9		−55.49	296.2		−49.32
600	523.7	−351.3	−63.94	589.6	−337.8	−68.97	523.7	−351.3	−63.94
	296.5		−44.16	362.4		−49.19	296.5		−44.16
700	524.5	−350.1	−57.42	590.4	−336.4	−61.63	524.5	−350.1	−57.42
	297.3		−40.47	363.2		−44.68	297.3		−40.47
800	525.6	−348.6	−52.52	591.6	−334.8	−56.12	525.6	−348.6	−52.52
	298.4		−37.69	364.4		−41.28	298.4		−37.69
900	526.9	−347.0	−48.71	593.0	−333.2	−51.82	526.9	−347.0	−48.71
	299.7		−35.52	365.8		−38.64	299.7		−35.52
1000	528.4	−345.5	−45.65	594.5	−331.6	−48.38	528.5	−345.4	−45.64
	301.2		−33.78	367.3		−36.51	301.3		−33.78

[a] Standard enthalpy change $\Delta H_T^\ominus$ in kJ mol^{-1}, standard entropy change $\Delta S_T^\ominus$ in J K^{-1} mol^{-1}, equilibrium constant K_p in atm^{-2}; the standard state is an ideal gas phase at 1 atm pressure (1 atm = 101 325 Pa).

[b] Associations yielding either the chair (D_{3d}) or the twist (D_2) isomer of O_6.

[c] $\Delta H_T^\ominus$ and K_p values in the upper and lower lines refer to the heat of formation derived [5] from the homodesmotic and hyperhomodesmotic schemes, respectively.

thermodynamic stability of $O_6(g)$, but nevertheless, a final judgement on this necessitates the evaluation of correlation contributions to energy terms [5]. The present study is only concerned with the conditions of gas-phase thermodynamic equilibrium, and hence its conclusions cannot be applied directly to other conditions, e.g. observation of the O_6 species isolated on solid matrices.

ACKNOWLEDGEMENTS

Support from the Alexander von Humboldt-Stiftung is gratefully acknowledged as are valuable discussions with Professor Karl Heinzinger, to whom I am grateful for his kind hospitality. Finally, a valuable information exchange with Professor Henry F. Schaefer III is highly appreciated.

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