Thermochimica Acta, 127 (1988) 237–246
Elsevier Science Publishers B V , Amsterdam – Printed in The Netherlands

ISOMERISM OF C_6(g) CLUSTER AND ITS MANIFESTATIONS IN THE SYSTEM THERMODYNAMICS *,**

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(Received 28 July 1987)

ABSTRACT

In contrast to earlier conclusions based on simple models, the newest calculations showed that the C_6(g) cluster isomer of the lowest potential energy is a cyclic structure of D_{3h} symmetry The evaluation given in the present study, however, shows that increasing temperature increases the importance of the energetically higher linear structure which becomes the dominant component of the equilibrium gaseous mixture of isomers in the end Therefore, the D_{3h} structure alone cannot be used in simulating the C_6(g) system thermodynamics, and it is necessary to apply the overall terms including the contributions of all the isomers The effects of isomerism are especially noticeable with the heat capacity term whose temperature dependence shows a markedly extremal course This study fundamentally changes both the values of the quantities used so far and the approaches to the thermodynamics of this system

INTRODUCTION

The most recent study by Raghavachari et al [1] represents a substantial development to the solution of the structural problem of the C_6(g) system, this problem being still best attacked by theoretical means (see, e g., refs 2 and 3), which is connected with the rather extreme conditions during observation of this system (the temperature of 2500 K in ref 4) The study of carbon clusters is undertaken (see, e g , refs 5–8) because of their technological applications (for references see, e g , ref 3) and, more recently, of their presumed presence and significant role in the chemism of interstellar space [9–15] The description of the thermodynamics and composition of the equilibrium gas phase above graphite at higher temperatures represents an important item of information for a series of application treatments, and

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* Dedicated to Academician Antonín A Vlček on the occasion of his 60th birthday

** Part XXXII in the series Multimolecular Clusters and Their Isomerism, Part XXXI, see Ref 25

0040-6031/88/$03 50

therefore it is desirable that the values of these data be known with the highest possible accuracy The data predominantly used at present [16] are based on the assumption of linearity and very approximate values of molecular parameters, in particular they do not take into account the isomerism of these clusters The present paper is intended to fill this gap, starting from ref 1 as the source of molecular information about the $C_6(g)$ isomers

DESCRIPTION OF THE SYSTEM

The C_6 system was studied [1] in two different atomic orbital basis sets, 3-21G and 6-31G*, both of them giving the potential hypersurfaces with six stationary points four of these structures are local energy minima, which was shown by means of the harmonic vibrational analysis in the 3-21G basis Table 1 presents a survey of these four isomers, and the description of their energetics adopts two higher approximations which go beyond the level of the approximations used for evaluation of molecular geometry [1] In particular, this means involvement of correlation effects at the level of the Møller–Plesset theory [17] within the complete fourth-order treatment (MP4) and possibly also with the estimate of higher, finer effects ("Best") In both these energy series, however, the order of isomers is the same, no difference being observed between application of the potential energy scale and the scale of potential energy with inclusion of the zero-point vibrational motions Reference 1 denotes these four isomers with the identifying numbers 1, 2, 4 and 6 which are also included in Table 1

In all the approaches considered, the cyclic structure, lowest in energy, with the D_{3h} point group of symmetry and the ${}^1A_1'$ symmetry of electronic wavefunction is conventionally denoted as 4 Then there follows the linear $D_{\infty h}$ structure with the ${}^3\Sigma_g^-$ triplet electronic state denoted as 1 The third structure is again linear $D_{\infty h}$, but its electronic state symmetry is ${}^3\Sigma_u^+$ it is

TABLE 1

Survey of relative energies [a] of $C_6(g)$ isomers

Identifying number	Point group	Electronic state	6-31G*/MP4		"Best"	
			$\Delta E_{i\,4}$	$\Delta H^{\ominus}_{0\,i\,4}$	$\Delta E_{i\,4}$	$\Delta H^{\ominus}_{0\,i\,4}$
1	$D_{\infty h}$	${}^3\Sigma_g^-$	85 34	80 75	46 43	41 84
2	$D_{\infty h}$	${}^3\Sigma_u^+$	231 1	220 1	157 5	146 4
4	D_{3h}	${}^1A_1'$	0 0	0 0	0 0	0 0
6	D_{6h}	${}^1A_1'$	335 4	328 0	335 4	328 0

[a] Reference 1, $\Delta E_{i\,4}$ and $\Delta H^{\ominus}_{0\,i\,4}$ denote potential energy and ground-state energy, respectively, relative to the global minimum (4), in kJ mol^{-1}

denoted as 2 Finally, the highest in energy is the cyclic structure of D_{6h} symmetry and $^1A_1'$ electronic state it is denoted as 6

The molecular parameters of these isomers from ref 1 serve in the present paper for construction of their partition functions in the usual approximation of rigid rotator and harmonic oscillator [18] The rotational partition function is constructed on the basis of the 3-21G molecular geometries, although the molecular geometry of the 6-31G* quality is also used for comparison in some cases The calculations of thermodynamic quantities are carried out side by side for both the energetics series of Table 1, i e 6-31G*/MP4 and "Best" Finally, the thermodynamic functions of graphite are taken from ref 16

THE ISOMERISM CONTRIBUTION TO THERMODYNAMICS

In terms of the potential energy with inclusion of zero-point vibrations for the i-th isomer with respect to the structure 4, $\Delta H^{\ominus}_{0,i,4}$, and the partition function q_i of the i-th isomer, the mole fractions or weight factors w_i of these isomers are given, in our case, as follows [19,20]

$$w_i = \frac{q_i \exp\left(-\Delta H^{\ominus}_{0,i,4}/RT\right)}{\sum\limits_{j}^{4} q_j \exp\left(-\Delta H^{\ominus}_{0,j,4}/RT\right)} \tag{1}$$

Sometimes, in the literature the simple Boltzmann factors w_i' are given instead of these more rigorous w_i values

$$w_i' = \frac{\exp(-\Delta E_{i,4}/RT)}{\sum\limits_{j}^{4} \exp(-\Delta E_{j,4}/RT)} \tag{2}$$

They are constructed only on the basis of the relative potential energy terms $\Delta E_{i,4}$

The existence of four different isomers justifies four different partial equilibrium processes to be considered

$$6\mathrm{C(s)} = \mathrm{C_6(g,}\ i) \tag{3}$$

which are characterized by their standard molar enthalpy changes $\Delta H^{\ominus}_{T,i}$, entropy changes $\Delta S^{\ominus}_{T,i}$, and heat capacity changes at constant pressure $\Delta C^{\ominus}_{pT,i}$ The technique of observation used for the study of C_6 (viz mass spectroscopy [4]) of course allows no differentiation between the individual isomers and takes them as a whole group Hence it is necessary to introduce the thermodynamic terms $\Delta H^{\ominus}_T$, $\Delta S^{\ominus}_T$, $\Delta C^{\ominus}_{pT}$ which are called overall terms

[19,20], all the isomers contribute to these values according to their weights w_i

$$\Delta H_T^{\ominus} = \sum_i^4 w_i \Delta H_{T,i}^{\ominus} \tag{4}$$

$$\Delta S_T^{\ominus} = \sum_i^4 w_i \left(\Delta S_i^{\ominus} - R \ln w_i \right) \tag{5}$$

$$\Delta C_{\mathrm{p},T}^{\ominus} = \sum_i^4 w_i \Delta C_{\mathrm{p}\,T,i}^{\ominus} + \frac{1}{RT^2} \left[\sum_i^4 w_i \left(\Delta H_{T,i}^{\ominus} \right)^2 - \left(\Delta H_T^{\ominus} \right)^2 \right] \tag{6}$$

Whereas the overall terms (4)–(6) are related to a certain chemical reaction (i e (3)), it is also possible to introduce the isomerism contributions related to a reference structure, usually the most stable isomer In our case the contributions are related to the structure 4 and are defined as correction terms which must be added to the partial value of thermodynamic function of the isomer 4 to obtain the respective overall term

$$\delta_4 H_4^{(\mathrm{iso})} = \Delta H_T^{\ominus} - \Delta H_{T\,4}^{\ominus} \tag{7}$$

$$\delta_4 S_4^{(\mathrm{iso})} = \Delta S_T^{\ominus} - \Delta S_{T\,4}^{\ominus} \tag{8}$$

$$\delta_4 C_{\mathrm{p},4}^{(\mathrm{iso})} = \Delta C_{\mathrm{p},T}^{\ominus} - \Delta C_{\mathrm{p},T,4}^{\ominus} \tag{9}$$

These isomerism contributions are independent of the particular stoichiometry and represent thus more general, transferable terms

In the case of the heat capacity term a notice must be added In eqn (6) the temperature dependence of w_i is taken into account If the observation were specially arranged to have fixed w_i values even at changing temperatures, the term (6) and (9), called the relaxation term, would be reduced to the special case of the so-called isofractional term [19,20]

$$\Delta C_{\mathrm{p}\,T,w}^{\ominus} = \sum_i^4 w_i \Delta C_{\mathrm{p},T,i}^{\ominus} \tag{10}$$

$$\delta_4 C_{\mathrm{p},w\,4}^{(\mathrm{iso})} = \Delta C_{\mathrm{p}\,T,w}^{\ominus} - \Delta C_{\mathrm{p}\,T\,4}^{\ominus} \tag{11}$$

For methodical reasons, both isofractional and relaxation types of quantities will be considered

RESULTS AND DISCUSSION

The behaviour of the $C_6(g)$ system is obviously determined by the interplay of the isomers 4 and 1 (Table 2) Whereas relative stability of the D_{3h} isomer decreases with temperature, that of the linear structure 1 increases until a temperature at which the stability order is interchanged

TABLE 2

Temperature dependences of weight factors [a] w_i and simple Boltzmann factors [b] w_i' of C_6(g) isomers in their equilibrium mixture

T (K)	w_i (w_i')							
	6-31G*/MP4				"Best"			
	4	1	2	6	4	1	2	6
500	100 0	1×10^{-5}	3×10^{-20}	3×10^{-33}	99 89	0 11	2×10^{-12}	3×10^{-33}
	(100 0)	(1×10^{-7})	(7×10^{-23})	(9×10^{-34})	(100 0)	(1×10^{-3})	(4×10^{-15})	(9×10^{-34})
1000	99 51	0 50	4×10^{-8}	6×10^{-16}	65 09	34 91	2×10^{-4}	4×10^{-16}
	(100 0)	(3×10^{-3})	(8×10^{-11})	(3×10^{-16})	(99 63)	(0 37)	(6×10^{-7})	(3×10^{-16})
1500	82 96	17 04	4×10^{-4}	3×10^{-10}	17 69	82 28	0 03	6×10^{-11}
	(99 89)	(0 11)	(9×10^{-7})	(2×10^{-10})	(97 64)	(2 36)	(3×10^{-4})	(2×10^{-10})
2000	42 25	57 73	0 03	1×10^{-7}	6 56	93 09	0 35	2×10^{-8}
	(99 41)	(0 59)	(9×10^{-5})	(2×10^{-7})	(94 22)	(5 78)	(7×10^{-3})	(2×10^{-7})
2500	18 65	81 13	0 21	3×10^{-6}	3 37	95 30	1 33	5×10^{-7}
	(98 38)	(1 62)	(1×10^{-3})	(1×10^{-5})	(90 28)	(9 67)	(0 05)	(9×10^{-6})
3000	9 41	89 84	0 75	2×10^{-5}	2 08	94 73	3 19	5×10^{-6}
	(96 83)	(3 16)	(9×10^{-3})	(1×10^{-4})	(86 41)	(13 43)	(0 16)	(1×10^{-4})

[a] Mole fractions in isomeric equilibrium mixture, in %, $i = 4$, 1, 2, or 6 (for identifying numbers, see Table 1)

[b] In parentheses

This temperature is about 1900 and 1100 K in the cases of the isomer energetics from the approximations 6-31G*/MP4 and "Best", respectively Above these stability interchange temperatures the ratio of structure 1 continues to increase until this structure becomes dominant The molar fraction of structure 2 also increases with temperature, but it does not exceed 10% even at the highest temperatures studied The molar fraction of the last isomer, cyclic D_{6h} structure, is negligible at all the temperatures investigated In particular it can be stated that at the temperature of observation [4] the most significant component of the equilibrium gas phase is the linear structure 1 (and not the structure 4, which could be deduced from a straightforward consideration of the stability order at absolute zero)

Table 2 also shows that, except for low temperatures, the simple Boltzmann factors w_i' cannot be used instead of the rigorous w_i values Specially, these w_i' factors do not allow the interchange of relative isomer stabilities In other words this means that the rotational–vibrational motions of the individual isomers are essential for evaluation of their populations in the equilibrium mixture

Table 3 gives a survey of temperature course of the isomerism contributions The isomerism contribution to the enthalpy term $\delta_4 H_4^{(iso)}$ related to the structure 4 increases with increasing temperature and reaches tens of kJ mol^{-1} at higher temperatures Still more distinct values are observed with the isomerism contribution to the entropy term $\delta_4 S_4^{(iso)}$ In the TS scale it makes about 150 kJ mol^{-1} at 3000 K From this it is clear that a simulation of the C_6(g) thermodynamics by means of the partial terms belonging to the ground state structure (i e 4) would lead to tremendous errors

Whereas the isofractional contribution of isomerism to heat capacity $\delta_4 C_{p,w\,4}^{(iso)}$ increases with increasing temperature, the relaxational contribution exhibits a marked maximum In the isomer energetics approximated by 6-31G*/MP4 this maximum appears at 1750 K and attains the value of 84 J K^{-1} mol^{-1}, whereas in the approximation denoted as "Best" the respective maximum comes sooner, at about 1000 K, and is about 79 J K^{-1} mol^{-1} These maxima are due to the temperature dependence of w_i and are so distinct that they could serve as experimental means for revealing the isomerism of a reaction component

Table 3 also enables evaluation of the effect of interchange of molecular geometry of isomers, i e on going from 3-21G to 6-31G* structures All the four quantities studied are less sensitive to this interchange, the changes being below 1 kJ mol^{-1} or 1 J K^{-1} mol^{-1}

Beside the full four-membered set we can also consider sets with a smaller number of members, e g , the triad 4,1,2 or the pair 4,1 Thereby we admit a variable dimension of the isomeric set n, and thus we work with the isomerism contributions $\delta_n X_4^{(iso)}$ instead of the $\delta_4 X_4^{(iso)}$ terms considered so far Thus it is possible to study the convergency properties of the $\delta_n X_4^{(iso)}$ quantities as functions of the number n of the set members (Table 4) In

TABLE 3

Temperature dependences of isomerism contributions [a] to standard molar enthalpy $\delta_4 H_4^{(\mathrm{iso})}$, entropy $\delta_4 S_4^{(\mathrm{iso})}$, and heat capacity [b] at constant pressure $\delta_4 C_{\mathrm{p}\,w\,4}^{(\mathrm{iso})}$ and $\delta_4 C_{\mathrm{p}\,4}^{(\mathrm{iso})}$ in four-membered isomeric [c] set $C_6(g)$

T (K)	6-31G*/MP4				"Best"			
	$\delta_4 H_4^{(\mathrm{iso})}$	$\delta_4 S_4^{(\mathrm{iso})}$	$\delta_4 C_{\mathrm{p},w\,4}^{(\mathrm{iso})}$	$\delta_4 C_{\mathrm{p}\,4}^{(\mathrm{iso})}$	$\delta_4 H_4^{(\mathrm{iso})}$	$\delta_4 S_4^{(\mathrm{iso})}$	$\delta_4 C_{\mathrm{p},w,4}^{(\mathrm{iso})}$	$\delta_4 C_{\mathrm{p}\,4}^{(\mathrm{iso})}$
500	8×10^{-6}	2×10^{-5}	1×10^{-6}	4×10^{-4}	0 06	0 12	0 01	1 34
	(9×10^{-6})	(2×10^{-5})	(1×10^{-6})	(4×10^{-4})	(0 06)	(0 12)	(0 01)	(1 39)
1000	0 46	0 50	0 02	5 04	18 54	22 11	1 39	78 46
	(0 47)	(0 52)	(0 02)	(5 24)	(19 02)	(22 70)	(1 43)	(79 39)
1500	15 98	12 21	0 57	67 02	45 20	44 53	2 74	26 42
	(16 51)	(12 62)	(0 59)	(68 77)	(45 50)	(45 01)	(2 76)	(25 84)
2000	55 17	34 75	2 01	69 12	53 22	49 26	3 26	10 48
	(56 08)	(35 40)	(2 04)	(68 73)	(53 35)	(49 63)	(3 26)	(10 29)
2500	79 41	45 73	2 97	31 65	57 82	51 32	3 54	8 81
	(79 99)	(46 22)	(2 99)	(30 99)	(57 90)	(51 66)	(3 54)	(8 73)
3000	90 87	49 94	3 42	16 96	62 43	53 00	3 71	9 78
	(91 20)	(50 35)	(3 44)	(16 61)	(62 48)	(53 33)	(3 71)	(9 74)

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[a] Related to the global minimum, 4, see Table 1, H terms in kJ mol^{-1}, S and C_{p} in J K^{-1} mol^{-1} In the upper and lower (i e in parentheses) lines, data are given based on 3-21G and 6-31G* structural parameters [1], respectively

[b] Isofractional $\delta_4 C_{\mathrm{p}\,w\,4}^{(\mathrm{iso})}$, and relaxation $\delta_4 C_{\mathrm{p}\,4}^{(\mathrm{iso})}$ terms

[c] See Table 1

TABLE 4

Convergency properties of isomerism contributions [a] $\delta_n H_4^{(\mathrm{iso})}$, $\delta_n S_4^{(\mathrm{iso})}$, and $\delta_n C_{\mathrm{p}\,4}^{(\mathrm{iso})}$ with increasing number n of isomeric set members [b]

T (K)	n	6-31G*/MP4			"Best"		
		$\delta_n H_4^{(\mathrm{iso})}$	$\delta_n S_4^{(\mathrm{iso})}$	$\delta_n C_{\mathrm{p}\,4}^{(\mathrm{iso})}$	$\delta_n H_4^{(\mathrm{iso})}$	$\delta_n S_4^{(\mathrm{iso})}$	$\delta_n C_{\mathrm{p}\,4}^{(\mathrm{iso})}$
1000	2	0 46	0 50	5 04	18 54	22 11	78 46
	3, 4	0 46	0 50	5 04	18 54	22 11	78 46
2000	2	55 12	34 72	68 87	52 82	49 03	9 17
	3, 4	55 17	34 75	69 12	53 22	49 26	10 48
3000	2	89 71	49 50	14 68	58 90	51 55	4 71
	3, 4	90 87	49 94	16 96	62 43	53 00	9 78

[a] See Table 3 for a specification

[b] Isomeric sets $n = 2$ 4, 1, $n = 3$ 4, 1, 2, $n = 4$ 4, 1, 2, 6 (for identifying numbers 4, 1, 2, 6, see Table 1)

accordance with negligible populations of the structure 6, the differences between $n = 3$ and $n = 4$ are also negligible However, the role of the linear structure 2 is already perceptible, the greatest differences being observed in

TABLE 5

Standard molar terms [a] for partial and overall [b] reactions 6C(s) = C_6(g)

T (K)	Process [c]	6-31G*/MP4			"Best"		
		$\Delta H^{\ominus}_{T,i}$	$\Delta S^{\ominus}_{T,i}$	$\Delta C^{\ominus}_{\mathrm{p},T,i}$	$\Delta H^{\ominus}_{T,i}$	$\Delta S^{\ominus}_{T,i}$	$\Delta C^{\ominus}_{\mathrm{p}\,T,i}$
1000	6C(s) = C_6(g, 1)	1270 43	269 39	−10 62	1231 52	269 39	−10 62
	6C(s) = C_6(g, 2)	1412 62	276 31	−7 97	1338 98	276 31	−7 97
	6C(s) = C_6(g, 4)	1178 41	221 46	−14 60	1178 41	221 46	−14 60
	6C(s) = C_6(g, 6)	1509 52	222 66	−11 37	1509 52	222 66	−11 37
	6C(s) = C_6(g, overall)	1178 87	221 96	−9 56	1196 95	243 57	63 86 [d]
2000	6C(s) = C_6(g, 1)	1255 95	259 54	−16 00	1217 04	259 54	−16 00
	6C(s) = C_6(g, 2)	1399 73	267 64	−15 09	1326 09	267 64	−15 09
	6C(s) = C_6(g, 4)	1160 49	209 21	−19 48	1160 49	209 21	−19 48
	6C(s) = C_6(g, 6)	1493 51	211 82	−18 40	1493 51	211 82	−18 40
	6C(s) = C_6(g, overall)	1215 66	243 96	49 64	1213 71	258 47	−9 00
3000	6C(s) = C_6(g, 1)	1239 18	252 76	−17 66	1200 27	252 76	−17 66
	6C(s) = C_6(g, 2)	1383 59	261 12	−17 23	1309 95	261 12	−17 23
	6C(s) = C_6(g, 4)	1140 08	200 97	−21 44	1140 08	200 97	−21 44
	6C(s) = C_6(g, 6)	1473 85	203 89	−20 92	1473 85	203 89	−20 92
	6C(s) = C_6(g, overall)	1230 94	250 91	−4 48	1202 51	253 96	−11 66

[a] Standard states ideal gas and solid at 1 atm = 101325 Pa pressure, H terms in kJ mol^{-1}, S and C_{p} in J K^{-1} mol^{-1} Derived for the best estimation [1] of the heat of formation at 0 K of the structure 4^c $\Delta H^{\ominus}_{0\,4} = 1177$ 14 kJ mol^{-1}

[b] The relaxation term is given with the overall $\Delta C^{\ominus}_{\mathrm{p}\,T}$

[c] For identifying numbers 1, 2, 4, 6, see Table 1

[d] For the sake of extremal behaviour visualization, cf $\Delta C^{\ominus}_{\mathrm{p}\,500} = -1$ 46 J K^{-1} mol^{-1}

the relaxational contribution to heat capacity This is especially distinct in the "Best" approximation, because at the end of the interval studied the structure 2 becomes even more significant than the structure 4 (cf Table 2)

Of course, the terms from Tables 2–4 are applicable to any reaction with participation of $C_6(g)$ Nevertheless, especially important are the equilibria over graphite (3), Table 5 gives a survey of their partial and overall standard molar changes of enthalpy, entropy, and heat capacity at constant pressure It is noteworthy that the extremal temperature course of the $\delta_4 C_{p4}^{(iso)}$ term is retained also with the overall relaxational reaction terms $\Delta C_{pT}^{\ominus}$ of the reactions (3)

CONCLUDING REMARKS

It has been shown that, although the cyclic D_{3h} isomer represents the ground state structure in the $C_6(g)$ system, the linear structure with triplet electronic state becomes the most populated or even predominant isomer at the temperatures relevant for observation This interplay of isomeric structures markedly affects the values of overall thermodynamic terms and necessitates a careful regard for the isomerism contributions These conclusions obviously will not be restricted only to the particular $C_6(g)$ system, but the isomerism will apparently play a substantial part also in the case of other carbon clusters (and not necessarily only the higher ones) These qualitative conclusions will most probably not depend on the use of the rigid rotator and harmonic oscillator approximation to partition functions So far C_3 is the largest carbon aggregate for which a more sophisticated description of thermodynamics is available [21,22], while for higher clusters one could guess their deviations from the simple model from spectral data on polyacetylenes and cyanopolyyenes [23,24]

ACKNOWLEDGEMENTS

The study was finalized during a stay supported by the University of Ulm Valuable discussions with and the kind hospitality of Professor Wolfgang Witschel are gratefully acknowledged as well as the support

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