

## THERMODYNAMICS OF EQUILIBRIUM ISOMERIC MIXTURES: THE DIDEUTERIOCYCLOBUTADIENES

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### ABSTRACT

Thermodynamics of equilibrium mixtures of three possible positional isomers of the rectangular dideuteriocyclobutadiene were studied based on recent 4-31G and 6-31G\*/MP2 evaluations of molecular parameters of the species. Relative stabilities of isomers were evaluated with due respect paid to the rotational–vibrational motions involved. Significant values of isomerism contributions to overall values of thermodynamic functions were found. The results represent the first example of a consistent treatment of overall thermodynamics of equilibrium mixtures of isomeric isotopomers available.

### INTRODUCTION

In recent years an increasing interest has been paid to properties of isomeric mixtures. This type of study has been aided considerably by applying various theoretical approaches [1,2], particularly quantum-chemical and molecular-mechanical methods. In this connection, the problem of observational distinguishability has been analyzed [3] and convolutional, overall nature of some measured terms have been pointed out [4]. When two or more isomeric structures of comparable stability coexist then it is useful, or even necessary, for any structure-dependent observed parameter to consider its average value resulting from contributions of all the isomers. This type of reasoning has, *inter alia*, been developed for standard thermodynamic terms [5] and, moreover, a profound temperature dependence of the isomeric interplay has been observed with some systems.

The problem of the cyclobutadiene structure [6,7], and in particular its manifestation in vibrational spectra [8], has been studied vigorously both experimentally [6] and theoretically [7] and it supplies an interesting example

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of a special isomeric set. It has been concluded [6b,7] that the cyclobutadiene skeleton is rectangular (and not square). Consequently, three different isomers are to be considered with dideuteriocyclobutadiene (cyclobutadiene-1,2-d<sub>2</sub> (2) and -1,4-d<sub>2</sub> (4) with two deuterium atoms attached to the shorter and longer C–C bond, respectively, and -1, 3-d<sub>2</sub> (3)). The present article deals with thermodynamic consequences of the isomerism.

#### DATA AND PROCEDURES USED

Molecular geometry and harmonic vibrational frequencies of (2), (3), and (4) are taken from ab initio SCF calculation [7c] using the 4-31G basis set (4-31G), and from the calculation [7d] of the 6-31G \* basis set including evaluation of electronic correlation according to Møller–Plesset [9] at the second order level (6-31G \*/MP2). Within the Born–Oppenheimer approximation the potential energy of (2), (3), and (4) is essentially the same; (small) differences [10] between the isomeric isotopomers, however, appear at the level of zero-point vibrational energies (or in other words, ground state energies, or enthalpies at absolute zero,  $H_{0,i}^0$ ).

Relative stabilities within an *n*-membered isomeric set can be evaluated approximately through the simple factors:

$$w'_i = \frac{\exp(-H_{0,i}^0/R/T)}{\sum_{j=1}^n \exp(-H_{0,j}^0/R/T)} \quad (1)$$

resembling the usual Boltzmann factors in terms of the potential energy (*R* denotes the gas constant, and *T* the absolute temperature). In a more rigorous way, the mole fraction or weight factor characterizing the relative content of the *i*th isomer in the ideal gas-phase equilibrium mixture can be considered [10]:

$$w_i = \frac{q_i \exp(-H_{0,i}^0/R/T)}{\sum_{j=1}^n q_j \exp(-H_{0,j}^0/R/T)} \quad (2)$$

where  $q_i$  denotes the partition function of the *i*th isomer (first of all covering rotational–vibrational motions). In the present study the partition functions were evaluated in the rigid rotor and harmonic oscillator approximation [11].

Overall thermodynamics of an equilibrium isomeric mixture described by  $w_i$  weight factors can be obtained from the thermodynamic terms belonging to the most stable isomer (arbitrarily labelled as 1) through isomerism contributions  $\delta_n X_1^{(iso)}$ , i.e. the terms which must be added to the (partial)

terms of isomer 1 in order to obtain the overall terms to which all the isomers contribute. In the present study three types of quantities are considered: standard enthalpy, entropy, and heat capacity at constant pressure ( $X = H, S, \text{ or } C_p$ ).

## RESULTS AND DISCUSSION

Figure 1 presents temperature dependences of  $w_i$  (eqn. (2)) factors evaluated in the 4-31G and 6-31G \*/MP2 approaches for the equilibrium isomeric mixture of (2), (3), and (4). In both approaches to the hypersurface of cyclobutadiene the structure lowest in the ground-state energy (i.e., (3) and (4) in the 4-31G and 6-31G \*/MP2 method, respectively) is also the most stable isomer in the whole temperature interval studied. At moderate and higher temperatures the picture is the same in both potential energy approximations. The weights  $w_i$  of all the isomers approach the value of 1/3. However, at low temperatures there are significant differences between

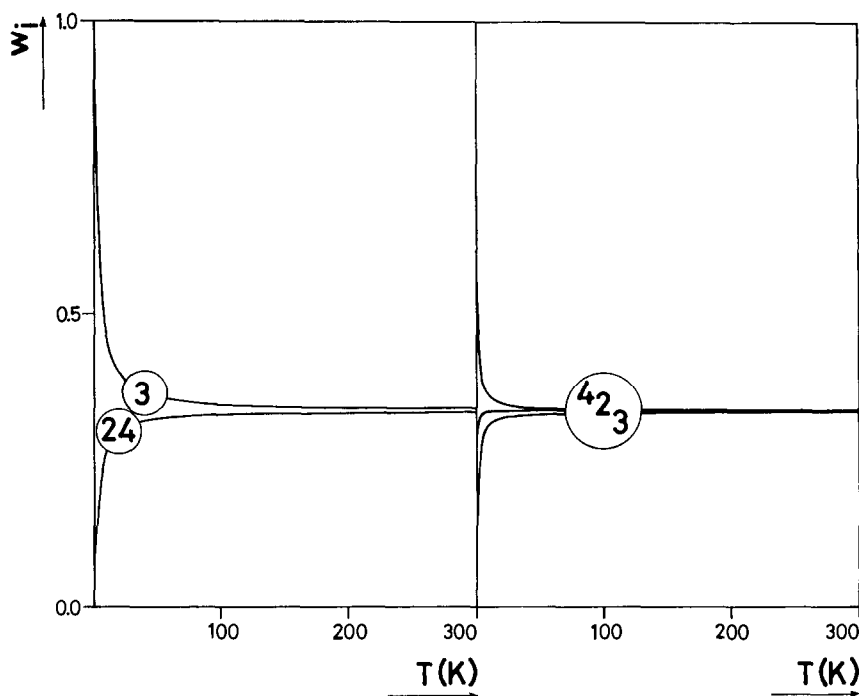


Fig. 1. Temperature dependence of weight factors (mole fractions)  $w_i$  of cyclobutadiene-1, 2- $d_2$ (g) (2), -1, 3- $d_2$ (g) (3), and -1, 4- $d_2$ (g) (4) in their equilibrium mixture; the 4-31G and 6-31G \*/MP2 values are given to the left and right part of the figure, respectively. (The curves for (2) and (4) cannot be distinguished in the figure in the 4-31G approach.)

TABLE 1

Examples of changes in the relative stability <sup>a</sup> between cyclobutadiene-1, 2-d<sub>2</sub>(g) (2), -1, 3-d<sub>2</sub>(g) (3), and -1, 4-d<sub>2</sub>(g) (4) with temperature

<i>T</i> (K)	<i>w</i> <sub>(4)</sub>	<i>w</i> <sub>(2)</sub>	<i>w</i> <sub>(3)</sub>
5	0.194 (0.194)	0.194 <sup>b</sup> (0.194)	<u>0.612</u> (0.613)
	<u>0.383</u> (0.382)	0.331 (0.331)	0.286 (0.287)
10	0.265 (0.265)	0.265 <sup>b</sup> (0.265)	<u>0.470</u> (0.471)
	<u>0.358</u> (0.358)	0.333 (0.333)	0.309 (0.310)
298.15	0.332 (0.331)	0.331 (0.331)	<u>0.337</u> (0.338)
	<u>0.334</u> (0.334)	0.333 (0.333)	0.332 (0.333)

<sup>a</sup> Treated in the terms of weights *w<sub>i</sub>* from eqn. (2); the 4-31G and 6-31G \*/MP2 values are given in the upper and lower line, respectively. The weight of the most stable isomer in each line is underlined. Simple factors of the Boltzmann type according to eqn. (1) are given in parentheses.

<sup>b</sup> (2) is slightly more stable than (4) (however, within the 4-31G vibrational frequencies [7c] the *H*<sub>0, i</sub><sup>0</sup> terms, and thus also the factors *w<sub>i</sub>*, are incidentally the same for (2) and (4) structures).

both approximations. With the 4-31G approach, (3) is predominant at low temperatures and, moreover, stability order between (2) and (4) is interchanged in this region (so that (2) is slightly more stable than (4) while at moderate and higher temperatures the stability order is reversed—cf. Fig. 1 and Table 1). In the more sophisticated 6-31G \*/MP2 approximation, (4) would be the most abundant component of the equilibrium ideal gas-phase mixture at low temperatures, but its increase in stability with decreasing temperature is slower than is the case of (3) in the 4-31G approximation. At any temperature studied, (2) is slightly more stable than (3) in the 6-31G \*/MP2 approximation, and the convergence of their relative stability with increasing temperature is slower than the convergence of (2) and (4) in the 4-31G case. Clearly enough, the isomeric interplay is extremely sensitive to even a small change in energetics in the very low temperature region. However, in both approximations to molecular energy considered all three isomeric structures—(2), (3), and (4)—are significantly populated even at very low temperatures so that it is expected that their concentration will be of the same order of magnitude under the conditions of the full gas-phase thermodynamic equilibrium. The simple *w<sub>i</sub>* factors (eqn. (1)) are presented in Table 1 for comparison. It is apparent that in the particular case studied the latter represent (in contrast with other recently studied isomeric systems [5]) a good approximation to the “rigorous” *w<sub>i</sub>* values (eqn. (2)). Let us mention for the completeness that the genuine Boltzmann factors (i.e., given by eqn. (1) but employing the potential energy terms instead of *H*<sub>0, i</sub><sup>0</sup>) would all be exactly the same at any temperature (i.e., 1/3).

TABLE 2

Temperature dependence of isomerism contributions <sup>a</sup>  $\delta_n X_1^{(\text{iso})}$  to the standard molar enthalpy ( $X = H$ ), entropy ( $X = S$ ), and heat capacity ( $X = C_p$ ) of two and three isomer equilibrium mixtures <sup>b</sup> of dideuteriocyclobutadienes <sup>c</sup>

$T$ (K)	$\delta_n H_1^{(\text{iso})}$		$\delta_n S_1^{(\text{iso})}$		$\delta_n C_{p1}^{(\text{iso})} \times 10^3$	
	$n = 2$	$n = 3$	$n = 2$	$n = 3$	$n = 2$	$n = 3$
50	22.6	30.7	5.76	9.14	27.4	25.2
	2.97	5.92	5.76	9.12	1.01	1.73
100	23.1	31.0	5.77	9.15	-2.06	-8.03
	3.01	6.14	5.76	9.13	-6.42	4.11
200	22.4	29.2	5.77	9.13	-8.43	-20.4
	1.79	6.31	5.76	9.13	1.10	8.39
298.15	21.0	26.9	5.76	9.13	-20.3	-28.7
	2.89	7.52	5.76	9.13	14.4	12.0
500	16.3	20.6	5.75	9.11	-22.4	-29.5
	4.58	8.63	5.76	9.14	3.03	0.65
1000	9.12	11.1	5.74	9.10	-8.37	-11.1
	4.29	7.50	5.76	9.13	-1.73	-3.11

<sup>a</sup> Related to isomer (3) <sup>c</sup> and (4) <sup>c</sup> for the 4-31G and 6-31G \*/MP2 approaches, respectively; the 4-31G and 6-31G \*/MP2 values are given in the upper and lower line, respectively, in  $\text{J mol}^{-1}$  or  $\text{J K}^{-1} \text{mol}^{-1}$ .

<sup>b</sup> Two ( $n = 2$ ) and three ( $n = 3$ ) isomer mixtures are formed by (3, 4) <sup>c</sup> ((2, 4) <sup>c</sup> for the 6-31G \*/MP2 approach) and (2, 3, 4) <sup>c</sup> isomeric sets, respectively.

<sup>c</sup> Cyclobutadiene-1, 2-d<sub>2</sub> (g) (2), -1, 3-d<sub>2</sub> (g) (3), -1, 4-d<sub>2</sub> (g) (4).

Having the weights  $w_i$  available we can evaluate the overall thermodynamics of equilibrium isomeric mixtures of dideuteriocyclobutadienes. The most stable (i.e., reference) isomeric structures are different in both energy approximations studied, viz. (3) and (4) are used for evaluation of the isomerism contributions with, the 4-31G and 6-31G \*/MP2 approaches, respectively (Table 2). In addition to the full, three-membered isomeric set, a two-membered set was also considered, viz. that formed by either (3) and (4), or by (2) and (4). The highest values of the isomerism contributions are met with the entropy term, this being in accord with its physical significance. The isomerism contribution to entropy is at any temperature considered in Table 2 quite close to its upper limit <sup>1</sup> within a three-membered isomeric set, viz.  $R \ln 3$ . Enthalpy contents of the isomeric isotopomers are essentially very close and the isomerism contribution to enthalpy cannot,

<sup>1</sup> More specifically, it appears that [12]:  $S_{\text{min}}^0 - S_1^0 < \delta_n S_1^{(\text{iso})} < S_{\text{max}}^0 - S_1^0 + R \ln n$ , where  $S_{\text{min}}^0$  and  $S_{\text{max}}^0$  denote the minimum and maximum in the set of partial standard entropies, and  $S_1^0$  is the partial entropy of the reference isomer 1.

TABLE 3

Standard <sup>a</sup> entropy terms,  $S_T^0$ , of cyclobutadiene-1, 2-d<sub>2</sub>(g) (2), -1, 3-d<sub>2</sub>(g) (3), and -1, 4-d<sub>2</sub>(g) (4) and of various equilibrium mixtures of the isomers <sup>b</sup>

$T$ (K)	$S_T^0$ (J K <sup>-1</sup> mol <sup>-1</sup> )					
	(2); (3); (4) <sup>b</sup>		(2, 3); (2, 4); (3, 4) <sup>b</sup>		(2, 3, 4) <sup>b</sup>	
	4-31G	6-31G */MP2	4-31G	6-31G */MP2	4-31G	6-31G */MP2
50	190	190	196	196	199	200
100	213	214	219	219	223	223
200	239	241	245	246	248	250
298.15	259	263	265	269	269	272
500	299	306	305	312	309	315
1000	381	390	386	396	390	400

<sup>a</sup> Standard state—an ideal gas at 1 atm pressure (1 atm = 101 325 Pa).

<sup>b</sup> The isomers composing a particular equilibrium mixture are given in parentheses; in the three-digit representation of data used, no difference can be seen in the entropy term at a given temperature between the three individual isomers as well as between the three two-component mixtures composed of them.

therefore, be too large. The same holds for the isomerism contribution to heat capacity as a temperature derivative of enthalpy. Although the values of isomerism contribution to heat capacity are small their oscillating behaviour is noteworthy. The differences between the two- and three-membered isomeric sets are noticeable, too. The isomerism contributions to entropy within the two-membered sets considered in Table 2, i.e. (3, 4) and (2, 4) for the 4-31G and 6-31G \*/MP2 approximations, respectively, approaches closely the upper limit <sup>1</sup>, viz.  $R \ln 2$ , again so in the whole temperature region presented therein. Finally, while the isomerism contributions to entropy are practically the same in both approaches, the remaining two terms in Table 2 are quite different in the 4-31G and 6-31G \*/MP2 approximations.

Table 3 surveys the standard entropy terms both of individual isomers and of all possible two- and three-membered equilibrium mixtures of them. The differences in entropy terms of individual isotopomers are quite small being in any case substantially lower than 1 JK<sup>-1</sup> mol<sup>-1</sup>; the same is true of entropy terms of the three possible two-isomer equilibrium mixtures. However, at higher temperatures there are no negligible differences in the standard entropy terms originated from the 4-31G and 6-31G \*/MP2 approaches. To apply the data to a particular experimental situation, a supposed type of equilibrium (i.e., two- or three-interisomer equilibrium) has to be reached in the observation. The establishing of inter-isomer equilibria must be discussed in every particular case in terms of relevant kinetic factors involved, including the history of mixture preparation.

## CONCLUSIONS

In this paper the first study of overall thermodynamics of isomeric isotopomers has been carried out. Equilibrium thermodynamic interplay of three isomers of dideuteriocyclobutadiene (*g*) has been treated as an example of an isomeric set composed of highly similar, energetically close members. To estimate a possible range of effects, two essentially different *ab initio* evaluations of molecular parameters were employed.

It has been shown that even in such a case significant differences in relative stability proportions can exist between low and moderate temperatures including a relative-stability interchange between two structures. High-temperature limit leads to equal populations of all isomers. There is a disagreement between both energy approximations used in the stability ordering of isomers; in the more sophisticated approximation (4) has been found to be the most stable structure. Simple factors of the Boltzmann type, however, based on the ground state energy (instead of the conventional potential energy) terms represent a good approximation to the "rigorous" values of weight factors of the isomeric isotopomers.

Simultaneous presence of different isomers in their equilibrium mixture raises the question on changes in thermodynamic properties of the mixture compared to the individual terms belonging to the most stable structure, the question being studied comprehensively. It has been shown that the isomerism contributions to thermodynamic functions are generally not negligible in the case of isomeric isotopomers, being the largest with the entropy term. With the exception of the lowest temperatures, the isomerism contribution to entropy is quite close to that of an equimolar mixture of (two or three) optical isomers. However, there are significant differences in the overall values of standard entropy of the equilibrium mixture of isotopomers in both approaches to potential energy considered. The isomerism contributions can be comparable or even higher than the most frequently mentioned corrections to tabulated computational thermodynamic data [13], viz. the corrections with respect to vibrational anharmonicity and rotational non-rigidity.

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