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THERMODYNAMIC PROPERTIES OF NORMAL AND DEUTERATED CYCLOPROPENES

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ABSTRACT

The specific heat, entropy, enthalpy, and Gibbs free energy of cyclopropene-d_0, cyclopropene-1-d_1, cyclopropene-3-d_1, cyclopropene-1,2-d_2, cyclopropene-3,3-d_2, cyclopropene-1,3,3-d_3, and cyclopropene-d_4 have been calculated for the temperature range 100–1500 K using the rigid-rotor and harmonic oscillator model. The standard enthalpy and Gibbs free energy of formation of cyclopropene-d_0 have also been evaluated for the same temperature range using the experimental standard enthalpy of formation at 298.15 K.

INTRODUCTION

The physical and chemical properties of cyclopropene and its derivatives have been of considerable interest to chemists since the small bonding angles in three-membered rings represent the extremes in chemical bonding. This highly strained ring system has been subject to theoretical calculations by several workers[1–3]. Extensive SCF-MO calculations of strain energies have been presented by Baird and Dewar[3]. Also, experimental values for the strain energy and heat of formation of cyclopropene have been reported by Wiberg et al.[4]. However, only brief references to the ideal gas state thermodynamic properties of normal cyclopropene for a limited temperature range have appeared in the literature[5, 6].

It is the purpose of this paper to report the statistical thermodynamic properties of normal and deuterated cyclopropenes over a wide temperature range using the most recent spectroscopic data available.

STRUCTURAL AND VIBRATIONAL DATA

The molecular structure of cyclopropene has been investigated with electron diffraction[7] and microwave spectroscopic[8, 9] techniques. The most accurate results are those of Stigliani et al.[9], whose principal moments of inertia for cyclopropene-d_0

TABLE 1

STRUCTURAL AND VIBRATIONAL DATA OF NORMAL AND DEUTERATED CYCLOPROPENES

	$-d_0$	$-1-d_1$	$-3-d_1$	$-1,2-d_2$	$-3,3-d_2$	$-1,3,3-d_3$	$-d_4$
MW (g mole^{-1})	40.0646	41.0708	41.0708	42.0770	42.0770	43.0832	44.0894
Symmetry number	2	1	1	2	2	1	2
Moments of inertia[a] (amu Å^2)							
I_a	16.8117[b]	18.9214	17.6424	21.7685	18.4628	18.0046	23.5995
I_b	23.1549[b]	24.8182	26.1273	25.0244	28.8724	30.6679	31.2928
I_c	36.6325[b]	40.3614	38.6595	43.4147	40.5844	41.9215	47.8520
Fundamentals[c] (cm^{-1})	3138	3124	3139	2995	3138	3119	2452
	3109	2994	3109	2904	3109	2394	2309
	2995	2905	2963	2450	2260	2261	2262
	2909	2391	2203	2309	2144	2144	2142
	1653	1607	1649	1572	1648	1593	1548
	1483	1480	1354	1460	1154	1148	1147
	1106	1106	1030	1080	1014	966	1027
	1088	1087	1010	1061	1000	916	885
	1047	1044	1009	1042	890	862	863
	1040	1040	927	1040	863	862	863
	1011	974	899	880	863	822	822
	905	801	880	683	822	770	640
	816	760	815	680	816	725	639
	769	678	718	669	710	674	637
	569	479	565	431	562	471	424

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[a] Calculated, this work, unless otherwise indicated.

[b] Taken from ref. 9.

[c] Taken from ref. 13.

have been adopted in this work. In addition, the molecular dimensions[9] [r(C–C) = 1.509 ± 0.001 Å, r(C=C) = 1.2959 ± 0.0004 Å, r(C–H ethylenic) = 1.072 ± 0.001 Å, r(C–H methylenic) = 1.088 ± 0.002 Å, $\angle$(C–C=C) = 50.84 ± 0.05°, $\angle$(C=C–H) = 149.85 ± 0.08°, and $\angle$(H–C–H) = 114.57 ± 0.19°] have been used to calculate the principal moments of inertia of the other deuterated cyclopropenes.

Cyclopropene-d_0, cyclopropene-1,2-d_2, cyclopropene-3,3-d_2, and cyclopropene-d_4 possess C_{2v} symmetry and have fifteen normal modes which are divided into six A_1, two A_2, four B_1, and three B_2 vibrations. The symmetry number is $\sigma = 2$. With the exception of the A_2 block, whose transitions are not allowed in the infrared, all fundamental vibrations are infrared and Raman active.

Cyclopropene-1-d_1, cyclopropene-1,3,3-d_3, and cyclopropene-3-d_1 belong to the point group C_s. The fifteen normal modes of the first two molecules are divided into ten A′ and five A″ vibrations, while those of cyclopropene-3-d_1 are divided into nine A′ and six A″ vibrations. All fundamentals are infrared and Raman active in both cases. The symmetry number is $\sigma = 1$.

TABLE 2

THERMODYNAMIC PROPERTIES OF NORMAL AND DEUTERATED CYCLOPROPENES

Temperature (K)	$C_p°$ [*cal (deg mole)$^{-1}$*]	$S°$ [*cal (deg mole)$^{-1}$*]	$-(G° - H_0°)/T$ [*cal (deg mole)$^{-1}$*]	$H° - H_0°$ (*kcal mole^{-1}*)
Cyclopropene-d_0				
100.0	7.99	48.03	40.07	0.795
200.0	9.38	53.86	45.64	1.644
273.15	11.69	57.11	48.28	2.411
298.15	12.59	58.17	49.05	2.714
300.0	12.65	58.25	49.12	2.737
400.0	16.17	62.38	51.92	4.182
500.0	19.18	66.32	54.41	5.955
600.0	21.62	70.04	56.71	7.998
700.0	23.62	73.53	58.86	10.263
800.0	25.30	76.79	60.90	12.711
900.0	26.73	79.86	62.84	15.314
1000.0	27.96	82.74	64.79	18.050
1100.0	29.03	85.46	66.46	20.901
1200.0	29.95	88.02	68.15	23.852
1300.0	30.76	90.45	69.77	26.888
1400.0	31.46	92.76	71.33	30.000
1500.0	32.06	94.95	72.83	33.176
Cyclopropene-1-d_1				
100.0	8.06	49.79	41.82	0.796
200.0	9.89	55.80	47.43	1.674
273.15	12.35	59.23	50.14	2.485
298.15	13.26	60.36	50.95	2.805
300.0	13.33	60.44	51.00	2.830
400.0	16.82	64.76	53.91	4.340
500.0	19.78	68.84	56.49	6.175
600.0	22.19	72.67	58.87	8.278

TABLE 2 *(continued)*

Temperature (K)	$C_p°$ [*cal (deg mole)$^{-1}$*]	$S°$ [*cal (deg mole)$^{-1}$*]	$-(G° - H_0°)/T$ [*cal (deg mole)$^{-1}$*]	$H° - H_0°$ (*kcal mole^{-1}*)
700.0	24.19	76.24	61.10	10.600
800.0	25.87	79.59	63.20	13.105
900.0	27.30	82.72	65.20	15.766
1000.0	28.52	85.66	67.10	18.558
1100.0	29.56	88.43	68.92	21.463
1200.0	30.46	91.04	70.65	24.466
1300.0	31.24	93.51	72.32	27.551
1400.0	31.91	95.85	73.91	30.709
1500.0	32.48	98.07	75.45	33.929
Cyclopropene-3-d_1				
100.0	8.00	49.71	41.76	0.796
200.0	9.64	55.60	47.33	1.654
273.15	12.25	58.98	50.00	2.451
298.15	13.22	60.09	50.80	2.770
300.0	13.30	60.18	50.86	2.794
400.0	16.99	64.52	53.74	4.313
500.0	20.04	68.65	56.31	6.170
600.0	22.48	72.53	58.69	8.301
700.0	24.47	76.15	60.93	10.652
800.0	26.12	79.53	63.05	13.183
900.0	27.52	82.68	65.06	15.867
1000.0	28.70	85.65	66.97	18.680
1100.0	29.72	88.43	68.79	21.602
1200.0	30.60	91.06	70.54	24.619
1300.0	31.35	93.54	72.22	27.717
1400.0	32.00	95.88	73.82	30.886
1500.0	32.57	98.11	75.37	34.114
Cyclopropene-1,2-d_2				
100.0	8.14	48.72	40.74	0.798
200.0	10.38	54.91	46.39	1.703
273.15	13.00	58.52	49.16	2.556
298.15	13.93	59.70	49.99	2.893
300.0	14.00	59.78	50.05	2.919
400.0	17.49	64.31	53.06	4.497
500.0	20.41	68.53	55.73	6.397
600.0	22.81	72.47	58.20	8.562
700.0	24.81	76.14	60.50	10.946
800.0	26.49	79.56	62.67	13.514
900.0	27.90	82.77	64.73	16.235
1000.0	29.10	85.77	66.69	19.087
1100.0	30.12	88.60	68.55	22.049
1200.0	30.99	91.26	70.33	25.106
1300.0	31.74	93.77	72.04	28.244
1400.0	32.38	96.14	73.68	31.450
1500.0	32.92	98.40	75.25	34.716
Cyclopropene-3,3-d_2				
100.0	8.04	48.60	40.65	0.796
200.0	9.87	54.54	46.23	1.663
273.15	12.72	58.03	48.93	2.486

TABLE 2 *(continued)*

Temperature (K)	C_p° [cal (deg mole)$^{-1}$]	S° [cal (deg mole)$^{-1}$]	$-(G^\circ - H_0^\circ)/T$ [cal (deg mole)$^{-1}$]	$H^\circ - H_0^\circ$ (kcal mole^{-1})
298.15	13.76	59.18	49.74	2.817
300.0	13.84	59.27	49.80	2.842
400.0	17.68	63.79	52.73	4.424
500.0	20.78	68.08	55.38	6.352
600.0	23.24	72.10	57.84	8.558
700.0	25.22	75.84	60.14	10.984
800.0	26.86	79.31	62.32	13.592
900.0	28.32	82.56	64.39	16.348
1000.0	29.39	85.60	66.36	19.231
1100.0	39.36	88.44	68.24	22.220
1200.0	31.20	91.12	70.04	25.300
1300.0	31.91	93.65	71.76	28.455
1400.0	32.52	96.04	73.41	31.678
1500.0	33.05	98.30	74.99	34.957
Cyclopropene-1,3,3-d_3				
100.0	8.08	50.13	42.16	0.797
200.0	10.48	56.29	47.79	1.698
273.15	13.54	59.99	50.57	2.575
298.15	14.61	61.23	51.41	2.926
300.0	14.68	61.32	51.47	2.954
400.0	18.50	66.08	54.54	4.620
500.0	21.54	70.55	57.30	6.628
600.0	23.95	74.70	59.86	8.906
700.0	25.91	78.54	62.26	11.402
800.0	27.53	82.11	64.52	14.077
900.0	28.88	85.44	66.66	16.900
1000.0	30.00	88.54	68.69	19.845
1100.0	30.95	91.44	70.63	22.894
1200.0	31.75	94.17	72.48	26.031
1300.0	32.43	96.74	74.25	29.241
1400.0	33.01	99.17	75.94	32.513
1500.0	33.50	101.46	77.57	35.839
Cyclopropene-d_4				
100.0	8.17	49.26	41.28	0.798
200.0	10.96	55.60	46.96	1.729
273.15	14.08	59.48	49.80	2.644
298.15	15.13	60.75	50.66	3.009
300.0	15.21	60.85	50.72	3.037
400.0	18.96	65.76	53.88	4.752
500.0	21.96	70.32	56.71	6.803
600.0	24.38	74.54	59.34	9.124
700.0	26.36	78.46	61.79	11.664
800.0	28.00	82.09	64.11	14.385
900.0	29.36	85.47	66.29	17.255
1000.0	30.49	88.62	68.37	20.250
1100.0	31.42	91.57	70.35	23.346
1200.0	32.21	94.34	72.23	26.529
1300.0	32.86	96.94	74.03	29.783
1400.0	33.42	99.40	75.76	33.098
1500.0	33.89	101.72	77.41	36.464

Several infrared and Raman spectroscopic studies have been performed for the normal and deuterated cyclopropenes[10-13]. We have adopted the vibrational assignments given by Yum[13], whose results are vastly superior to those previously reported[10-12].

The values of the principal moments of inertia and the vibrational fundamentals used in this work are summarized in Table 1.

RESULTS

The thermodynamic functions C_p^0, S^0, $-(G^0 - H_0^0)/T$, and $H^0 - H_0^0$ have been evaluated for the temperature range 100–1500 K. An ideal gas, rigid-rotor, harmonic oscillator at 1 atm pressure has been used as the model for these calculations. The contribution due to nuclear spin has been neglected. The atomic masses[14] C = 12.011, H = 1.0079, and D = 2.0141, and the most recent fundamental constants[15] have been employed throughout this work. The standard enthalpy of formation[4] $\Delta H_{298.15}^0 = 66.6 \pm 0.6$ kcal mole^{-1}, which is available only for cyclopropene-d_0, and the functions[16] $H^0 - H_0^0$ and $-(G^0 - H_0^0)/T$ of C and H_2 were used to calculate the enthalpy (ΔH_f^0), the Gibbs free energy (ΔG_f^0) and logarithmic equilibrium constant ($\ln K_f$) of formation for this molecule. The results are given in Tables 2 and 3.

In order to assess the uncertainties in these calculated thermodynamic properties, we observed the effects of varying the structural and vibrational data by amounts corresponding to their estimated uncertainties. The results are summarized in Table 4.

TABLE 3

ENTHALPY, GIBBS FREE ENERGY, AND LOGARITHMIC EQUILIBRIUM CONSTANT OF FORMATION OF CYCLOPROPENE-d_0

Temperature (K)	*$\Delta H_f°$ (kcal mole^{-1})*	*$\Delta G_f°$ (kcal mole^{-1})*	*ln K_f*
100.0	67.92	68.06	−342.5
200.0	67.33	68.41	−172.1
273.15	66.78	68.88	−126.9
298.15	66.60	69.09	−116.6
300.0	66.59	69.11	−115.9
400.0	65.90	70.05	− 88.1
500.0	65.32	71.16	− 71.6
600.0	64.83	72.37	− 60.7
700.0	64.42	73.66	− 53.0
800.0	64.08	75.01	− 47.2
900.0	63.80	76.39	− 42.7
1000.0	63.58	77.82	− 39.2
1100.0	63.42	79.21	− 36.2
1200.0	62.99	80.68	− 33.8
1300.0	63.18	82.13	− 31.8
1400.0	63.10	83.63	− 30.1
1500.0	63.04	85.08	− 28.6

TABLE 4

ESTIMATED UNCERTAINTIES IN THE THERMODYNAMIC PROPERTIES OF NORMAL AND DEUTERATED CYCLOPROPENES[a, b]

Temperature (K)	$C_p°$	$S°$	$-(G° - H_0°)/T$	$H° - H_0°$
Cyclopropene-d_0				
100.0	0.002	0.01	0.02	0.003
298.15	0.10	0.06	0.03	0.01
500.0	0.12	0.12	0.06	0.03
1000.0	0.06	0.18	0.10	0.07
1500.0	0.03	0.19	0.13	0.10
Cyclopropene-1,2-d_2				
100.0	0.02	0.02	0.01	0.002
298.15	0.11	0.08	0.04	0.01
500.0	0.10	0.14	0.07	0.04
1000.0	0.06	0.20	0.12	0.08
1500.0	0.03	0.22	0.15	0.10
Cyclopropene-3,3-d_2				
100.0	0.003	0.02	0.01	0.003
298.15	0.11	0.07	0.03	0.01
500.0	0.12	0.14	0.06	0.04
1000.0	0.06	0.20	0.12	0.08
1500.0	0.04	0.21	0.15	0.10

[a] The units are the same as in Table 2.

[b] The estimated uncertainties of the other deuterated cyclopropenes are essentially the same as those shown here.

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