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# Ideal gas thermodynamic properties of oxygen heterocyclic compounds.
# Part 2. Six-membered, seven-membered and eight-membered rings

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## Abstract

The available structural parameters, fundamental frequencies and enthalpies of formation for tetrahydro-2*H*-pyran, 3,4-dihydro-2*H*-pyran, 3,6-dihydro-2*H*-pyran, 1,3-dioxane, 1,4-dioxane, 3,6-dihydro-1,2-dioxin, 2,3-dihydro-1,4-dioxin, 1,4-dioxin, 1,3,5-trioxane, oxepane, oxepin, 1,3-dioxepane, 4,7-dihydro-1,3-dioxepin, oxocane, 1,3-dioxocane, 1,3,6-trioxocane and 1,3,5,7-tetraoxocane were critically evaluated and the recommended values were selected. Molecular constants and enthalpies of formation for some of the molecules were estimated, because experimental values for these compounds were not available. Using the rigid-rotor harmonic-oscillator approximation, this information was utilized to calculate the chemical thermodynamic functions $C^\circ_p$, $S^\circ$, $-(G^\circ - H^\circ_0)/T$ and $H^\circ - H^\circ_0$ and the properties of formation $\Delta_f H^\circ$, $\Delta_f G^\circ$ and $\log K^\circ_f$ to 1500 K in the ideal gas state at a pressure of 1 bar. The contributions to the thermodynamic properties of 1,4-dioxin undergoing inversion motion have been computed by employing a partition function formed by the summation of the inversional energy levels. These energy levels were calculated by solving the wave equation using a potential function of type $V(x) = ax^4 + bx^2$. The calculated values of the thermodynamic functions are compared with those reported in other work. Agreement with experimental data, where such are available, is satisfactory within the experimental uncertainties. Thermodynamic properties for 13 compounds are reported for the first time.

## INTRODUCTION

This report involves the calculation of the ideal gas thermodynamic properties of 17 monocyclic six-, seven- and eight-membered oxygen compounds. Only for four of these compounds have the thermodynamic properties been reported previously.

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Thermodynamic properties of 13 three-, four- and five-membered oxygen heterocycles were presented in Part I of this series [1].

A description of the methods used for calculation of the ideal gas thermodynamic properties and for evaluation of their uncertainties was presented in the Introduction of ref. 1.

In the present work, basic information about the molecular constants adopted and the calculated thermodynamic properties is given in the tables that follow; Tables 1 and 2 involve the selected molecular constants, the calculated thermodynamic properties are given in Tables 3–19 and uncertainties in the calculated thermodynamic properties and comparisons of the calculated and experimental entropy and heat capacity values are presented in Tables 20, 21 and 22, respectively.

## TETRAHYDRO-2*H*-PYRAN

The microwave spectrum of tetrahydro-2*H*-pyran shows the molecule to be in the chair form [2,3]. No rotational spectrum from the boat form nor any effect that could be definitely attributed to pseudorotation or to inversion of the chair form was found. The vibrational spectra have been assigned in terms of a chair form of $C_s$ symmetry [4,5] and the electron diffraction data have been found to be consistent with a chair form [6]. From conformational analysis, Pickett and Strauss [7] have shown that there are also two conformations, twist-boat and boat, with an energy above that of the chair form. The twist-boat and boat forms can interconvert by pseudorotation. Calculation suggests that the twist-boat forms are at the minima of the inversion path and that the boats are the transition states at the maxima. The twist-boat conformation is approximately 35 kJ mol$^{-1}$ higher in energy than the chair. Since the energy of the twist-boat conformation is rather high, we have not considered this form in our calculations. The product of the principal moments of inertia for the chair conformation of tetrahydro-2*H*-pyran (Table 1) was calculated using the rotational constants of Rao and Kewley [2].

Vibrational spectra of tetrahydro-2*H*-pyran in different phase states have been investigated by several authors [4,5,8] and the fundamentals have been assigned on the basis of force constant calculations [4,5]. The fundamental frequencies used in the present work (Table 2) were taken from the more reliable investigation of Vedal et al. [5]. These authors observed the vibrational frequencies from IR and Raman spectra for the vapour, liquid and solid states and carried out a normal coordinate analysis to confirm the vibrational assignment.

The enthalpy of formation for tetrahydro-2*H*-pyran (Table 3) was taken from the data of Pedley et al. [9].

Ideal gas thermodynamic properties for tetrahydro-2*H*-pyran are given in Table 3. The table of thermodynamic properties for this molecule is

TABLE 1

Symmetry groups and products of three principal moments of inertia for six-, seven- and eight-membered ring oxygen compounds in their ground electronic state [a]

| Molecule | | Point group | Symmetry number | Number of optical isomers | $I_AI_BI_c \times 10^{117}$ ($g^3$ $cm^6$) |
|---|---|---|---|---|---|
| $C_5H_{10}O$ | Tetrahydro-2*H*-pyran | $C_s$ | 1 | 1 | 10816 |
| $C_5H_8O$ | 3,4-dihydro-2*H*-pyran | $C_1$ | 1 | 2 | 8834 |
| | 3,6-Dihydro-2*H*-pyran | $C_1$ | 1 | 2 | 8836 |
| $C_4H_8O_2$ | 1,3-Dioxane | $C_s$ | 1 | 1 | 8918 |
| | 1,4-Dioxane | $C_{2h}$ | 2 | 1 | 8982 |
| $C_4H_6O_2$ | 3,6-Dihydro-1,2-dioxin | $C_2$ | 2 | 2 | 7654 |
| | 2,3-Dihydro-1,4-dioxin | $C_2$ | 2 | 2 | 7287 |
| $C_4H_4O_2$ | 1,4-Dioxin | $D_{2h}$ | 4 | 1 | 6356 |
| $C_3H_6O_3$ | 1,3,5-Trioxane | $C_{3v}$ | 3 | 1 | 7245 |
| $C_6H_{12}O$ | Oxepane [b] | $C_1$ | 1 | 2 | 30270 |
| $C_6H_6O$ | Oxepin | $C_s$ | 1 | 1 | 21700 |
| $C_5H_{10}O_2$ | 1,3-Dioxepane [b] | $C_2$ | 2 | 2 | 26350 |
| $C_5H_8O_2$ | 4,7-Dihydro-1,3-dioxepin | $C_2$ | 2 | 2 | 22400 |
| $C_7H_{14}O$ | Oxocane [c] | $C_1$ | 1 | 2 | 74300 |
| $C_6H_{12}O_2$ | 1,3-Dioxocane [d] | $C_1$ | 1 | 2 | 68500 |
| $C_5H_{10}O_3$ | 1,3,6-Trioxocane [e] | $C_1$ | 1 | 2 | 60100 |
| $C_4H_8O_4$ | 1,3,5,7-Tetraoxocane [f] | $C_s$ | 1 | 1 | 50150 |

[a] Ground state statistical weight is equal to 1. Other stable conformers were also taken into account for oxepane, 1,3-dioxepane, oxocane, 1,3-dioxocane, 1,3,6-trioxocane and 1,3,5,7-tetraoxocane (point group, symmetry number ($\sigma$), number of optical isomers ($n$) and relative energy ($T$) are listed below for each conformer).

[b] $C_1$, $\sigma = 1$, $n = 2$, $T = 0$ cm$^{-1}$.

[c] $C_s$, $\sigma = 1$, $n = 1$, $T = 150$ cm$^{-1}$; $C_1$, $\sigma = 1$, $n = 2$, $T = 500$ cm$^{-1}$; $C_1$, $\sigma = 1$, $n = 2$, $T = 1000$ cm$^{-1}$; $C_s$, $\sigma = 1$, $n = 1$, $T = 1000$ cm$^{-1}$; $C_{2v}$, $\sigma = 2$, $n = 1$, $T = 1000$ cm$^{-1}$; $C_s$, $\sigma = 1$, $n = 1$, $T = 1000$ cm$^{-1}$.

[d] $C_1$, $\sigma = 1$, $n = 2$, $T = 400$ cm$^{-1}$; $C_1$, $\sigma = 1$, $n = 2$, $T = 700$ cm$^{-1}$; $C_s$, $\sigma = 1$, $n = 1$, $T = 800$ cm$^{-1}$; $C_1$, $\sigma = 1$, $n = 2$, $T = 1000$ cm$^{-1}$.

[e] $C_s$, $\sigma = 1$, $n = 1$, $T = 700$ cm$^{-1}$; $C_1$, $\sigma = 1$, $n = 2$, $T = 800$ cm$^{-1}$; $C_1$, $\sigma = 1$, $n = 2$, $T = 1000$ cm$^{-1}$.

[f] $C_{4v}$, $\sigma = 4$, $n = 1$, $T = 275$ cm$^{-1}$.

reported for the first time and there are no experimental calorimetric data for comparison. Shaw et al. [10] have estimated the values of $S°(298.15$ K$)$ and $C°_p(300$ K$)$ by application of group additivity and structural considerations. The estimated $S°$ value is 4 J K$^{-1}$ mol$^{-1}$ higher than that given in Table 3, and the estimated $C°_p$ value is 9 J K$^{-1}$ mol$^{-1}$ lower than ours. Curl et al. [11] developed a technique for determination of the gas state free energy functions from absolute intensity measurements in microwave spectroscopy. The value of $-(G° - H°_0)/T$ at 298.15 K obtained by Curl et al. differs by $\approx 1$ J K$^{-1}$ mol$^{-1}$ from our calculation.

TABLE 2

Vibrational frequencies for the reference molecules

| Molecule | | Frequencies, cm$^{-1}$ |
|---|---|---|
| $C_5H_{10}O$ | Tetrahydro-2$H$-pyran | $A'$: 2958, 2942, 2933, 2860, 2849, 2842, 1468, 1454, 1434, 1384, 1297, 1254, 1170, 1155, 1030, 1009, 875, 856, 818, 565, 423, 400, 252; $A''$: 2958, 2924, 2860, 2849, 1441, 1420, 1360, 1347, 1338, 1271, 1242, 1195, 1090, 1046, 969, 880, 811, 458, 252 |
| $C_5H_8O$ | 3,4-Dihydro-2$H$-pyran | $A$: 3110, 3104, 2939, 2928, 2917, 2878, 2866, 2857, 1589, 1482, 1448, 1434, 1411, 1388, 1352, 1310, 1281, 1255, 1237, 1218, 1166, 1129, 1052, 1017, 957, 906, 891, 863, 835, 808, 765, 516, 489, 428, 280, 177 |
| | 3,6-Dihydro-2$H$-pyran | $A$: 3058, 3057, 2932, 2927, 2926, 2870, 2867, 2864, 1561, 1441, 1435, 1427, 1387, 1365, 1314, 1266, 1265, 1244, 1236, 1175, 1129, 1045, 1017, 976, 950, 897, 869, 855, 847, 783, 662, 516, 513, 393, 300, 178 |
| $C_4H_8O_2$ | 1,3-Dioxane | $A'$: 2974, 2968, 2929, 2862, 2861, 2856, 1488, 1480, 1446, 1378, 1297, 1200, 1167, 1097, 995, 906, 837, 651, 452, 435, 262; A″: 2968, 2861, 1465, 1435, 1408, 1380, 1339, 1291, 1233, 1121, 1058, 1018, 899, 488, 272 |
| | 1,4-Dioxane | $A_g$: 2968, 2856, 1444, 1397, 1305, 1128, 1015, 837, 435, 408; $A_u$: 2970, 2863, 1449, 1369, 1256, 1136, 1086, 881, 239; $B_g$: 2968, 2856, 1459, 1335, 1217, 1110, 853, 490; $B_u$: 2970, 2863, 1457, 1378, 1291, 1052, 889, 610, 279 |
| $C_4H_6O_2$ | 3,6-Dihydro 1,2-dioxin | $A$: 3059, 2941, 2877, 1600, 1492, 1375, 1339, 1193, 1103, 1048, 946, 860, 789, 541, 494, 357, $B$: 3057, 2940, 2877, 1491, 1389, 1329, 1257, 1152, 1010, 903, 835, 668, 534, 266 |
| | 2,3-Dihydro-1,4-dioxin | $A$: 3107, 2947, 2883, 1644, 1442, 1334, 1278, 1171, 1124, 1027, 1010, 950, 868, 537, 465, 297; $B$: 3115, 2945, 2881, 1466, 1384, 1345, 1321, 1233, 1029, 909, 830, 798, 501, 191 |
| $C_4H_4O_2$ | 1,4-Dioxin | $A_g$: 3121, 1686, 1211, 928, 542; $B_{1g}$: 748; $B_{2g}$: 857, 516; $B_{3g}$: 3121, 1312, 1078, 697; $A_u$: 830, 450; $B_{1u}$: 3060, 1395, 990, 901; $B_{2u}$: 3130, 1640, 1281, 1011; $B_{3u}$: 739, – [a] |
| $C_3H_6O_3$ | 1,3,5-Trioxane | $A_1$: 3025, 2850, 1495, 1235, 978, 752, 466; $A_2$: 1383, 1242, 1122; $E$: 3025, 2850, 1481, 1410, 1305, 1178, 1070, 945, 524, 296 |
| $C_6H_{12}O$ | Oxepane | $A$: 2960, 2960, 2930, 2930, 2910, 2910, 2865, 2865, 2865, 2863, 2860, 2860, 1470, 1455, 1450, 1443, 1432, 1420, 1379, 1368, 1323, 1308, 1286, 1262, 1257, 1250, 1234, 1220, 1205, 1188, 1148, 1111, 1035, 1020, 1000, 979, 935, 900, 887, 837, 819, 752, 752, 555, 509, 417, 357, 318, 285, 185, 135 |
| $C_6H_6O$ | Oxepin | $A'$: 3043, 3038, 3036, 1636, 1560, 1417, 1348, 1194, 1100, 1069, 1023, 908, 815, 714, 528, 441, 212; $A''$: 3042, 3038, 3034, 1606, 1413, 1396, 1303, 1238, 1145, 1062, 1002, 926, 818, 637, 562, 285 |

TABLE 2 (continued)

| Molecule | Frequencies, $cm^{-1}$ |
|---|---|
| $C_5H_{10}O_2$ 1,3-Dioxepane | *A*: 2925, 2920, 2877, 2865, 2850, 1465, 1432, 1427, 1410, 1345, 1320, 1254, 1220, 1136, 1047, 925, 830, 805, 760, 610, 437, 350, 215; *B*: 2975, 2965, 2955, 2866, 2860, 1447, 1445, 1385, 1375, 1295, 1257, 1238, 1175, 1118, 1075, 1005, 970, 845, 516, 377, 273, 175 |
| $C_5H_8O_2$ 4,7-Dihydro-1,3-dioxepin | *A*: 3045, 2925, 2869, 2868, 1621, 1458, 1445, 1393, 1345, 1298, 1149, 1078, 979, 898, 835, 680, 618, 373, 277, 114; *B*: 3042, 2929, 2924, 2868, 1459, 1447, 1401, 1304, 1286, 1186, 1046, 983, 915, 841, 694, 355, 272, 207, 118 |
| $C_7H_{14}O$ Oxocane | *A*: 2937, 2934, 2931, 2927, 2926, 2922, 2873, 2870, 2868, 2866, 2865, 2863, 2859, 1456, 1447, 1442, 1435, 1434, 1423, 1415, 1388, 1377, 1349, 1327, 1301, 1292, 1283, 1267, 1256, 1249, 1241, 1229, 1225, 1218, 1155, 1130, 1120, 1030, 989, 982, 942, 923, 886, 844, 831, 808, 797, 746, 711, 531, 507, 464, 410, 339, 325, 246, 206, 129, 94 |
| $C_6H_{12}O_2$ 1,3-Dioxocane | *A*: 2966, 2950, 2938, 2928, 2924, 2900, 2892, 2886, 2874, 2869, 2865, 2845, 1489, 1474, 1455, 1438, 1432, 1417, 1408, 1399, 1385, 1377, 1360, 1316, 1296, 1284, 1273, 1265, 1220, 1212, 1180, 1129, 1093, 1089, 1052, 1018, 976, 971, 895, 867, 859, 793, 754, 748, 639, 533, 501, 419, 374, 344, 305, 254, 220, 120 |
| $C_5H_{10}O_3$ 1,3,6-Trioxocane | *A*: 2979, 2960, 2955, 2953, 2932, 2899, 2892, 2885, 2871, 2865, 1480, 1474, 1456, 1436, 1417, 1415, 1409, 1399, 1379, 1358, 1336, 1297, 1281, 1263, 1255, 1191, 1151, 1126, 1100, 1066, 1023, 1018, 995, 917, 870, 857, 827, 804, 665, 542, 539, 440, 390, 337, 295, 256, 223, 122 |
| $C_4H_8O_4$ 1,3,5,7-Tetraoxocane | $A_1$: 2990, 2870, 1482, 1225, 918, 607, 484; $A_2$: 1388, 1209, 1180; $B_1$: 2960, 2908, 1465, 1107, 912, 354, 126; $B_2$: 1440, 1344, 1055, 415, 147; *E*: 2920, 2850, 1478, 1400, 1313, 1175, 1082, 921, 540, 415 |

[a] The ring-puckering frequency $\nu_{24} = 124$ $cm^{-1}$ is not given in the table because the contribution due to inversion of 1,4-dioxin was obtained by direct summation over the energy levels.

## 3,4-DIHYDRO-2*H*-PYRAN

Far-infrared [12] and Raman [13] spectra of 3,4-dihydro-2*H*-pyran have been analyzed with a two-dimensional potential energy surface for the ring-twisting and ring-bending vibrations. The twisted conformation was found to have the lowest energy. The bent form was calculated to have a second minimum on the potential surface only a few hundred $cm^{-1}$ higher in energy than the twist form. However, no direct evidence for the exis-

TABLE 3

Ideal gas thermodynamic properties for tetrahydro-2*H*-pyran

| $T$ (K) | $C^\circ_p$ (J $K^{-1}$ $mol^{-1}$) | $S^\circ$ (J $K^{-1}$ $mol^{-1}$) | $-(G^\circ - H^\circ_0)/T$ (J $K^{-1}$ $mol^{-1}$) | $H^\circ - H^\circ_0$ (kJ $mol^{-1}$) | $\Delta_f H^\circ$ (kJ $mol^{-1}$) | $\Delta_f G^\circ$ (kJ $mol^{-1}$) | log $K^\circ_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −188.366 | −188.366 | – |
| 100 | 41.621 | 240.133 | 204.873 | 3.526 | −201.595 | −166.107 | 86.764 |
| 200 | 66.278 | 276.136 | 231.836 | 8.860 | −212.823 | −126.209 | 32.962 |
| 298.15 | 99.139 | 308.453 | 251.732 | 16.911 | −223.400 | −81.416 | 14.264 |
| 300 | 99.823 | 309.069 | 252.084 | 17.095 | −223.593 | −80.541 | 14.023 |
| 400 | 137.092 | 342.909 | 270.539 | 28.948 | −232.941 | −31.390 | 4.099 |
| 500 | 171.015 | 377.238 | 288.447 | 44.395 | −240.298 | 19.881 | −2.077 |
| 600 | 199.699 | 411.031 | 306.075 | 62.974 | −245.740 | 72.467 | −6.309 |
| 700 | 223.664 | 443.669 | 323.416 | 84.178 | −249.599 | 125.822 | −9.389 |
| 800 | 243.798 | 474.888 | 340.414 | 107.579 | −252.141 | 179.643 | −11.729 |
| 900 | 260.833 | 504.614 | 357.021 | 132.834 | −253.604 | 233.713 | −13.564 |
| 1000 | 275.317 | 532.866 | 373.205 | 159.661 | −254.179 | 287.898 | −15.038 |
| 1100 | 287.677 | 559.701 | 388.950 | 187.827 | −254.018 | 342.103 | −16.245 |
| 1200 | 298.257 | 585.198 | 404.250 | 217.137 | −253.238 | 396.270 | −17.249 |
| 1300 | 307.339 | 609.439 | 419.110 | 247.428 | −251.959 | 450.340 | −18.095 |
| 1400 | 315.161 | 632.509 | 433.535 | 278.563 | −250.227 | 504.302 | −18.816 |
| 1500 | 321.922 | 654.489 | 447.539 | 310.425 | −248.142 | 558.126 | −19.435 |

tence of the metastable bent form has been found from IR, Raman or microwave spectra [12–16]. Dodziuk et al. [17] did not find a bent conformation from molecular mechanics calculations. Recently Tecklenburg and Laane [18] have reinvestigated the vibrational potential energy surface of 3,4-dihydro-2*H*-pyran and have determined that the molecule has an energy minimum corresponding to the twisted conformation and that the bent form is at a saddle point on the surface and is not energetically stable. Because of these new data, only one stable conformation, the twisted form ($C_1$ symmetry), of 3,4-dihydro-2*H*-pyran was taken into account in present work. The product of the principal moments of inertia for the twisted conformation of 3,4-dihydro-2*H*-pyran (Table 1) was calculated using the rotational constants determined from the microwave investigation [16].

Only the three lowest out-of-plane ring-deformation modes were assigned from the far-infrared spectra of 3,4-dihydro-2*H*-pyran [12,19] and these values are given in Table 2. The remaining fundamental frequencies (Table 2) were estimated by normal coordinate calculations in the present work. The force field with 26 parameters was constructed by transferring force constants from tetrahydro-2*H*-pyran, 1,4-dioxin and cyclohexene. Normal coordinate calculations were performed for the above three molecules using vibrational frequencies from Table 2 and ref. 20. Simple valence force fields for tetrahydro-2*H*-pyran, 1,4-dioxin and cyclohexene

TABLE 4

Ideal gas thermodynamic properties for 3,4-dihydro-2*H*-pyran

| $T$ (K) | $C^\circ_p$ (J K$^{-1}$ mol$^{-1}$) | $S^\circ$ (J K$^{-1}$ mol$^{-1}$) | $-(G^\circ - H^\circ_0)/T$ (J K$^{-1}$ mol$^{-1}$) | $H^\circ - H^\circ_0$ (kJ mol$^{-1}$) | $\Delta_f H^\circ$ (kJ mol$^{-1}$) | $\Delta_f G^\circ$ (kJ mol$^{-1}$) | $\log K^\circ_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −97.937 | −97.937 | ∞ |
| 100 | 42.077 | 245.716 | 209.851 | 3.587 | −108.106 | −83.249 | 43.484 |
| 200 | 62.902 | 280.778 | 236.965 | 8.762 | −116.798 | −54.994 | 14.363 |
| 298.15 | 92.157 | 311.113 | 256.393 | 16.315 | −125.100 | −22.871 | 4.007 |
| 300 | 92.761 | 311.685 | 256.732 | 16.486 | −125.252 | −22.242 | 3.873 |
| 400 | 125.367 | 342.866 | 274.359 | 27.403 | −132.631 | 13.252 | −1.730 |
| 500 | 154.639 | 374.072 | 291.188 | 41.442 | −138.472 | 50.423 | −5.268 |
| 600 | 179.152 | 404.503 | 307.553 | 58.170 | −142.836 | 88.643 | −7.717 |
| 700 | 199.472 | 433.694 | 323.504 | 77.133 | −145.998 | 127.483 | −9.513 |
| 800 | 216.439 | 461.470 | 339.029 | 97.953 | −148.169 | 166.712 | −10.885 |
| 900 | 230.734 | 487.812 | 354.110 | 120.332 | −149.534 | 206.161 | −11.965 |
| 1000 | 242.857 | 512.767 | 368.739 | 144.028 | −150.236 | 245.727 | −12.835 |
| 1100 | 253.187 | 536.411 | 382.917 | 168.844 | −150.386 | 285.334 | −13.549 |
| 1200 | 262.023 | 558.830 | 396.651 | 194.615 | −150.067 | 324.937 | −14.144 |
| 1300 | 269.608 | 580.110 | 409.951 | 221.206 | −149.367 | 364.489 | −14.645 |
| 1400 | 276.141 | 600.335 | 422.834 | 248.502 | −148.311 | 403.981 | −15.073 |
| 1500 | 281.791 | 619.585 | 435.314 | 276.405 | −146.975 | 443.384 | −15.440 |

(with 18, 18 and 14 parameters, respectively) obtained after refinements reproduce the experimental vibrational spectra of these molecules with an average error of 12, 26 and 14 cm$^{-1}$, respectively. The average uncertainty of the calculated vibrational frequencies of 3,4-dihydro-2*H*-pyran is believed to be about 50 cm$^{-1}$.

The enthalpy of formation of 3,4-dihydro-2*H*-pyran (Table 4) was taken from the data of Pedley et al. [9].

Ideal gas thermodynamic properties for 3,4-dihydro-2*H*-pyran are given in Table 4. No experimental or theoretical data are available for comparison.

## 3,6-DIHYDRO-2*H*-PYRAN

The microwave spectrum of 3,6-dihydro-2*H*-pyran has been studied by Wells and Malloy [21]. Based on the limited data available, the authors could not achieve a complete structural determination. Model calculations to reproduce the rotational constants indicated that the data are consistent with a twisted (half-chair) conformation. According to semiempirical calculations [22], 3,6-dihydro-2*H*-pyran can undergo interconversion, and the bent (boat) conformation was found to be 5 kJ mol$^{-1}$ less stable than the twisted form. The stable twisted ground-state configuration was established from the one-dimensional potential energy function for the twist vibration of 3,6-dihydro-2*H*-pyran, which was calculated by Dixon et al. [19] on the basis of far-infrared spectra. Tecklenburg and Laane [18] reanalyzed the far-infrared and Raman data for 3,6-dihydro-2*H*-pyran in terms of two-dimensional vibrational potential energy surfaces for the ring-bending and ring-twisting vibrations; they determined that the molecule has an energy minimum corresponding to the twisted conformation and that the bent form is at a saddle point on the surface and is not energetically stable. Because of these data, only one stable conformation, the twisted form ($C_1$ symmetry), of 3,6-dihydro-2*H*-pyran was taken into account in the present work. The product of the principal moments of inertia given in Table 1 was calculated using the rotational constants of Wells and Malloy [21].

Only the three lowest out-of-plane ring-deformation modes were assigned from the far-infrared spectra of 3,6-dihydro-2*H*-pyran [19] and these values are accepted in Table 2. The other fundamental frequencies (Table 2) were calculated in the present work using 22 force constants transferred from tetrahydro-2*H*-pyran, 1,4-dioxin and cyclohexane, as was done above for 3,4-dihydro-2*H*-pyran. The average uncertainty of calculated vibrational frequencies is believed to be about 50 $\text{cm}^{-1}$.

There are no experimental or theoretical data on the enthalpy of formation of 3,6-dihydro-2*H*-pyran. In Table 5 its value is assumed to be the same as for 3,4-dihydro-2*H*-pyran. Taking into account a close similarity between the $\Delta_f H°(298.15\ \text{K})$ values of 2,3- and 2,5-dihydrothiophene [9], the enthalpy of formation of 2,5-dihydrofuran was previously accepted as being nearly the same as for 2,3-dihydrofuran [1].

Ideal gas thermodynamic properties for 3,6-dihydro-2*H*-pyran are given in Table 5. No experimental or theoretical data are known for comparison.

## 1,3-DIOXANE

The microwave spectrum of 1,3-dioxane [23] showed that the observed conformer must be the chair form. The vibrational spectra have been assigned in terms of a chair form of $C_s$ symmetry [8]. Excellent agreement with the chair conformation was demonstrated by the electron diffraction data [24]. Conformational energy calculations [7,25–27] have shown that there are also two conformations, twist-boat and boat, with an energy above that of chair form. The twist-boat forms are at the minima of the inversion path and the boat forms are at the maxima. The twist-boat conformer ($C_2$ symmetry) is about 20 kJ $\text{mol}^{-1}$ higher in energy than the chair conformer and we have not considered this form in our calculations. The product of the principal moments of inertia for the chair conformer of 1,3-dioxane (Table 1) was calculated using the rotational constants determined from microwave data [3,23].

TABLE 5

Ideal gas thermodynamic properties for 3,6-dihydro-2*H*-pyran

| $T$ (K) | $C°_p$ (J $K^{-1}$ $mol^{-1}$) | $S°$ (J $K^{-1}$ $mol^{-1}$) | $-(G°-H°_0)/T$ (J $K^{-1}$ $mol^{-1}$) | $H°-H°_0$ (kJ $mol^{-1}$) | $\Delta_f H°$ (kJ $mol^{-1}$) | $\Delta_f G°$ (kJ $mol^{-1}$) | log $K°_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −98.035 | −98.035 | ∞ |
| 100 | 41.915 | 245.588 | 209.814 | 3.577 | −108.213 | −83.343 | 43.533 |
| 200 | 63.938 | 280.839 | 236.901 | 8.788 | −116.872 | −55.080 | 14.385 |
| 298.15 | 94.554 | 311.860 | 256.475 | 16.513 | −125.000 | −22.994 | 4.028 |
| 300 | 95.177 | 312.447 | 256.818 | 16.689 | −125.148 | −22.366 | 3.894 |
| 400 | 128.394 | 344.426 | 274.715 | 27.884 | −132.248 | 13.011 | −1.699 |
| 500 | 157.687 | 376.317 | 291.856 | 42.231 | −137.782 | 49.991 | −5.222 |
| 600 | 181.964 | 407.285 | 308.530 | 59.253 | −141.852 | 87.958 | −7.657 |
| 700 | 201.980 | 436.886 | 324.770 | 78.481 | −144.748 | 126.499 | −9.439 |
| 800 | 218.651 | 464.978 | 340.556 | 99.538 | −146.683 | 165.392 | −10.799 |
| 900 | 232.681 | 491.565 | 355.871 | 122.124 | −147.840 | 204.478 | −11.867 |
| 1000 | 244.576 | 516.712 | 370.710 | 146.003 | −148.359 | 243.658 | −12.727 |
| 1100 | 254.710 | 540.511 | 385.074 | 170.980 | −148.348 | 282.863 | −13.432 |
| 1200 | 263.378 | 563.055 | 398.975 | 196.896 | −147.885 | 322.050 | −14.018 |
| 1300 | 270.819 | 584.438 | 412.426 | 223.615 | −147.056 | 361.174 | −14.512 |
| 1400 | 277.229 | 604.748 | 425.444 | 251.025 | −145.886 | 400.228 | −14.933 |
| 1500 | 282.771 | 624.069 | 438.047 | 279.032 | −144.447 | 439.187 | −15.294 |

The vibrational frequencies of 1,3-dioxane used in our calculations (Table 2) were taken from the study of Pickett and Strauss [8]. These authors have examined the vapour and liquid-phase IR spectra and liquid-phase Raman spectrum, and have carried out a normal coordinate analysis to confirm their vibrational assignment.

The enthalpy of formation of 1,3-dioxane (Table 6) was taken from the data of Pedley et al. [9].

Ideal gas thermodynamic properties for 1,3-dioxane are given in Table 6. The calculated values of $S°$ (Table 21) and $C°_p$ (Table 22) are in good agreement with those presented in TRC tables [28]. The value of $-(G°-H°_0)/T$ at 298.15 K obtained by Curl et al. [11] from absolute intensity measurements in the microwave spectrum is 2 J $K^{-1}$ $mol^{-1}$ higher than that given in Table 6.

## 1,4-DIOXANE

It has been established from an electron diffraction study [29] and from conformational analysis [7,25,30], that the lowest energy form of 1,4-dioxane is the chair ($C_{2h}$ symmetry). On the energy profile during the chair–chair inversion process, the chair and twist-boat forms are located at the minima and the boat forms at the maxima. The twist-boat form is

TABLE 6

Ideal gas thermodynamic properties for 1,3-dioxane

| $T$ (K) | $C°_p$ (J $K^{-1}$ $mol^{-1}$) | $S°$ (J $K^{-1}$ $mol^{-1}$) | $-(G°-H°_0)/T$ (J $K^{-1}$ $mol^{-1}$) | $H°-H°_0$ (kJ $mol^{-1}$) | $\Delta_f H°$ (kJ $mol^{-1}$) | $\Delta_f G°$ (kJ $mol^{-1}$) | log $K°_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −311.470 | −311.470 | ∞ |
| 100 | 40.360 | 239.147 | 204.245 | 3.490 | −323.124 | −289.040 | 150.977 |
| 200 | 61.928 | 273.454 | 230.641 | 8.563 | −333.049 | −251.048 | 65.566 |
| 298.15 | 89.396 | 303.080 | 249.635 | 15.934 | −342.300 | −208.805 | 36.581 |
| 300 | 89.968 | 303.634 | 249.966 | 16.100 | −342.469 | −207.982 | 36.212 |
| 400 | 121.537 | 333.840 | 267.150 | 26.676 | −350.637 | −161.872 | 21.138 |
| 500 | 150.798 | 364.176 | 283.526 | 40.325 | −357.066 | −113.907 | 11.900 |
| 600 | 175.770 | 393.944 | 299.460 | 56.690 | −361.813 | −64.796 | 5.641 |
| 700 | 196.671 | 422.656 | 315.023 | 75.343 | −365.163 | −15.014 | 1.120 |
| 800 | 214.191 | 450.096 | 330.206 | 95.912 | −367.353 | 35.170 | −2.296 |
| 900 | 228.958 | 476.201 | 344.990 | 118.090 | −368.593 | 85.569 | −4.966 |
| 1000 | 241.463 | 500.989 | 359.361 | 141.628 | −369.053 | 136.063 | −7.107 |
| 1100 | 252.095 | 524.515 | 373.315 | 166.320 | −368.872 | 186.569 | −8.859 |
| 1200 | 261.166 | 546.849 | 386.853 | 191.995 | −368.151 | 237.039 | −10.318 |
| 1300 | 268.933 | 568.068 | 399.984 | 218.510 | −366.998 | 287.422 | −11.549 |
| 1400 | 275.608 | 588.249 | 412.717 | 245.745 | −365.453 | 337.708 | −12.600 |
| 1500 | 281.367 | 607.465 | 425.065 | 273.601 | −363.605 | 387.871 | −13.507 |

approximately 30 kJ $mol^{-1}$ higher in energy than the most stable chair conformation and this form was not taken into account in our calculations. The structural parameters derived by Davis and Hassel [29] from an electron diffraction study were employed for calculating the product of the principal moments of inertia of 1,4-dioxane (Table 1).

The vibrational spectra of 1,4-dioxane have been studied by several researchers [4,8,30–34]. The values of three out-of-plane ring modes (239, 279 and 408 $cm^{-1}$) given in Table 2 are those obtained from far-infrared study [30]. Other vibrational frequencies of 1,4-dioxane used in our calculations were taken from the study of Ellestad et al. [33]. These authors have investigated the IR spectra of 1,4-dioxane in the vapour phase and as a liquid and the Raman spectra of the liquid, and have carried out normal coordinate calculations to confirm their vibrational assignment.

The enthalpy of formation for 1,4-dioxane (Table 7) was taken from the data of Pedley et al. [9].

Ideal gas thermodynamic properties for 1,4-dioxane are given in Table 7. Agreement with other calculated data [28,33,35] (Tables 21 and 22) is satisfactory within the uncertainties of calculated values. No experimental data are available for comparison.

## 3,6-DIHYDRO-1,2-DIOXIN

Only microwave and photoelectron spectroscopic studies are known for 3,6-dihydro-1,2-dioxin [36,37]. According to microwave data [36], the molecule has a nonplanar half-chair conformation of $C_2$ symmetry. Using the bond lengths C=C, C–C, C–O and C–H and the bond angles C=C–C and H–C–H borrowed from analogous molecules, Kondo et al. [36] have estimated the remaining structural parameters. The value of the dihedral angle around the peroxide bond determined in this manner is close to that obtained from the photoelectron spectrum [37]. The product of the principal moments of inertia for 3,6-dihydro-1,2-dioxin (Table 1) was calculated using the rotational constants determined from microwave study [36].

The vibrational spectrum of 3,6-dihydro-1,2-dioxin was investigated neither experimentally nor theoretically. In this work vibrational frequencies of 3,6-dihydro-1,2-dioxin (Table 2) have been calculated using 21 force constants transferred from tetrahydro-2*H*-pyran, 1,3-dioxane, cyclohexene and 1,2,4-trioxolane. Simple valence force fields for these molecules (with 18, 20, 15 and 16 parameters, respectively) have been obtained using vibrational frequencies from Table 2 and refs. 1 and 20. The determined force fields reproduce the experimental vibrational spectra of the above four molecules with an average error of 12, 14, 14 and 17 cm$^{-1}$, respec-

TABLE 7

Ideal gas thermodynamic properties for 1,4-dioxane

| $T$ (K) | $C^\circ_p$ (J K$^{-1}$ mol$^{-1}$) | $S^\circ$ (J K$^{-1}$ mol$^{-1}$) | $-(G^\circ - H^\circ_0)/T$ (J K$^{-1}$ mol$^{-1}$) | $H^\circ - H^\circ_0$ (kJ mol$^{-1}$) | $\Delta_f H^\circ$ (kJ mol$^{-1}$) | $\Delta_f G^\circ$ (kJ mol$^{-1}$) | log $K^\circ_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −285.330 | −285.330 | ∞ |
| 100 | 41.056 | 233.706 | 198.584 | 3.512 | −296.962 | −262.334 | 137.027 |
| 200 | 63.625 | 268.795 | 225.280 | 8.703 | −306.768 | −223.836 | 58.459 |
| 298.15 | 92.123 | 299.299 | 244.648 | 16.294 | −315.800 | −181.178 | 31.741 |
| 300 | 92.711 | 299.871 | 244.987 | 16.465 | −315.964 | −180.348 | 31.401 |
| 400 | 124.760 | 330.947 | 262.586 | 27.345 | −323.828 | −133.906 | 17.486 |
| 500 | 153.969 | 362.004 | 279.370 | 41.317 | −329.934 | −85.689 | 8.952 |
| 600 | 178.637 | 392.325 | 295.684 | 57.985 | −334.379 | −36.390 | 3.168 |
| 700 | 199.165 | 421.452 | 311.586 | 76.906 | −337.460 | 13.532 | −1.010 |
| 800 | 216.329 | 449.200 | 327.068 | 97.706 | −339.419 | 63.820 | −4.167 |
| 900 | 230.782 | 475.539 | 342.114 | 120.082 | −340.461 | 114.296 | −6.633 |
| 1000 | 243.023 | 500.505 | 356.716 | 143.789 | −340.753 | 164.847 | −8.611 |
| 1100 | 253.435 | 524.169 | 370.873 | 168.625 | −340.427 | 215.395 | −10.228 |
| 1200 | 262.324 | 546.612 | 384.591 | 194.425 | −339.582 | 265.894 | −11.574 |
| 1300 | 269.941 | 567.918 | 397.881 | 221.048 | −338.320 | 316.296 | −12.709 |
| 1400 | 276.491 | 588.168 | 410.756 | 248.377 | −336.681 | 366.594 | −13.678 |
| 1500 | 282.146 | 607.441 | 423.231 | 276.316 | −334.749 | 416.762 | −14.513 |

TABLE 8

Ideal gas thermodynamic properties for 3,6-dihydro-1,2-dioxin

| $T$ (K) | $C^\circ_p$ (J $K^{-1}$ $mol^{-1}$) | $S^\circ$ (J $K^{-1}$ $mol^{-1}$) | $-(G^\circ - H^\circ_0)/T$ (J $K^{-1}$ $mol^{-1}$) | $H^\circ - H^\circ_0$ (kJ $mol^{-1}$) | $\Delta_f H^\circ$ (kJ $mol^{-1}$) | $\Delta_f G^\circ$ (kJ $mol^{-1}$) | log $K^\circ_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | 2.944 | 2.944 | ∞ |
| 100 | 38.198 | 237.501 | 203.170 | 3.433 | −5.768 | 18.409 | −9.616 |
| 200 | 59.186 | 269.793 | 228.735 | 8.212 | −13.292 | 45.559 | −11.899 |
| 298.15 | 86.938 | 298.476 | 246.982 | 15.353 | −20.000 | 75.905 | −13.298 |
| 300 | 87.484 | 299.015 | 247.301 | 15.514 | −20.120 | 76.496 | −13.319 |
| 400 | 116.063 | 328.159 | 263.876 | 25.713 | −25.758 | 109.593 | −14.311 |
| 500 | 140.785 | 356.799 | 279.611 | 38.594 | −30.033 | 143.948 | −15.038 |
| 600 | 161.069 | 384.323 | 294.787 | 53.721 | −33.090 | 179.055 | −15.588 |
| 700 | 177.650 | 410.439 | 309.461 | 70.684 | −35.191 | 214.588 | −16.013 |
| 800 | 191.352 | 435.083 | 323.639 | 89.156 | −36.525 | 250.370 | −16.347 |
| 900 | 202.804 | 458.302 | 337.324 | 108.880 | −37.245 | 286.281 | −16.615 |
| 1000 | 212.455 | 480.183 | 350.527 | 129.657 | −37.463 | 322.245 | −16.832 |
| 1100 | 220.640 | 500.827 | 363.261 | 151.322 | −37.270 | 358.209 | −17.010 |
| 1200 | 227.616 | 520.332 | 375.545 | 173.744 | −36.725 | 394.142 | −17.156 |
| 1300 | 233.586 | 538.793 | 387.399 | 196.812 | −35.896 | 430.011 | −17.278 |
| 1400 | 238.717 | 556.296 | 398.844 | 220.434 | −34.802 | 465.812 | −17.379 |
| 1500 | 243.146 | 572.921 | 409.899 | 244.532 | −33.502 | 501.526 | −17.464 |

tively. The average uncertainty of the calculated fundamentals of 3,6-dihydro-1,2-dioxin is believed to be about 50 $cm^{-1}$.

There are no experimental or theoretical data on the enthalpy of formation of 3,6-dihydro-1,2-dioxin, and its value was estimated in the present work (Table 8) by comparison with the enthalpies of formation for related six-membered rings (cyclohexane, cyclohexene, tetrahydro-2*H*-pyran) and aliphatic compounds, as was done previously for dioxirane [1].

The ideal gas thermodynamic properties for 3,6-dihydro-1,2-dioxin are given in Table 8. No experimental or theoretical data are available for comparison.

## 2,3-DIHYDRO-1,4-DIOXIN

The most stable form of 2,3-dihydro-1,4-dioxin has been determined by far-infrared [12,18,19], Raman [13] and microwave [38] spectroscopy to be the half-chair (twisted) configuration with $C_2$ symmetry. In all these works the potential energy surface for half-chair interconversion was also analyzed. From spectroscopic data [12,13,38] the bent structure ($C_s$ symmetry) was found to have a second minimum on the potential surface. However, using molecular mechanics calculations, Dodziuk et al. [17] did not find a bent structure. According to the improved potential energy surface of

Tecklenburg and Laane [18], 2,3-dihydro-1,4-dioxin has energy minima corresponding to the twisted conformations, whereas the bent conformations are at the saddle points on the surface and are not energetically stable. Since the energy of the bent conformation is rather high in all cases, this form was not considered in our calculations. The product of the principal moments of inertia for 2,3-dihydro-1,4-dioxin (Table 1) was calculated using the rotational constants determined from microwave study [38].

Only the three lowest out-of-plane ring-deformation modes were assigned from the far-infrared spectra of 2,3-dihydro-1,4-dioxin [19], and these values are accepted in Table 2. The other fundamental frequencies (Table 2) were calculated in the present work using 31 force constants transferred from 1,4-dioxane and 1,4-dioxin. Simple valence force fields for 1,4-dioxane and 1,4-dioxin with 17 and 15 parameters, respectively, were obtained using vibrational frequencies from Table 2. These force fields reproduce the experimental vibrational spectra of the above two molecules with an average error of 17 and 26 $\mathrm{cm}^{-1}$, respectively. The average uncertainty of the calculated fundamentals of 2,3-dihydro-1,4-dioxin is believed to be about 50 $\mathrm{cm}^{-1}$.

There are no experimental data on the enthalpy of formation of 2,3-dihydro-1,4-dioxin, but its value was calculated by a molecular mechanics method ($-151$ kJ $\mathrm{mol}^{-1}$) [17]. The enthalpy of formation of 2,3-dihydro-1,4-dioxin was estimated in the present work (Table 9) by comparison with known values of $\Delta_f H°(298.15\ \mathrm{K})$ for related compounds [9]. We considered the change in $\Delta_f H°(298.15\ \mathrm{K})$ values with the replacement of methylene groups by oxygen atoms in aliphatic and cyclic compounds, and we believed that in passing from cyclohexene or 3,4-dihydro-2*H*-pyran to 2,3-dihydro-1,4-dioxin the change in $\Delta_f H°(298.15\ \mathrm{K})$ values might be expected approximately the same as in passing from 1-pentene to ethoxyethene.

Ideal gas thermodynamic properties for 2,3-dihydro-1,4-dioxin are presented in Table 9. No experimental or calculated data are available for comparison.

## 1,4-DIOXIN

Interpretation of the far-infrared spectra [39–41], vibrational spectra [39,42,43], electron diffraction data [44] and theoretical calculations [45–48] indicates that the structure of 1,4-dioxin is planar ($D_{2h}$ symmetry) and corresponds to the parabolic potential energy function with large amplitude vibrations around the planar form. The structural parameters obtained from electron diffraction investigation [44] were used for calculation of the product of the principal moments of inertia given in Table 1.

Connett et al. [42] have studied the Raman spectrum of the liquid and IR spectra of the liquid and gas phases and have proposed a vibrational assignment for 1,4-dioxin. This assignment has been confirmed by normal

TABLE 9

Ideal gas thermodynamic properties for 2,3-dihydro-1,4-dioxin

| $T$ (K) | $C^\circ_p$ (J $K^{-1}$ $mol^{-1}$) | $S^\circ$ (J $K^{-1}$ $mol^{-1}$) | $-(G^\circ-H^\circ_0)/T$ (J $K^{-1}$ $mol^{-1}$) | $H^\circ-H^\circ_0$ (kJ $mol^{-1}$) | $\Delta_f H^\circ$ (kJ $mol^{-1}$) | $\Delta_f G^\circ$ (kJ $mol^{-1}$) | $\log K^\circ_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −217.396 | −217.396 | ∞ |
| 100 | 41.059 | 238.874 | 203.406 | 3.547 | −225.994 | −201.955 | 105.489 |
| 200 | 60.284 | 272.826 | 230.056 | 8.554 | −233.290 | −175.046 | 45.717 |
| 298.15 | 86.066 | 301.526 | 248.891 | 15.693 | −240.000 | −145.004 | 25.404 |
| 300 | 86.590 | 302.060 | 249.217 | 15.853 | −240.121 | −144.419 | 25.145 |
| 400 | 114.599 | 330.845 | 266.030 | 25.926 | −245.886 | −111.609 | 14.574 |
| 500 | 139.339 | 359.155 | 281.837 | 38.659 | −250.308 | −77.506 | 8.097 |
| 600 | 159.777 | 386.428 | 297.014 | 53.649 | −253.502 | −42.620 | 3.710 |
| 700 | 176.513 | 412.357 | 311.656 | 70.491 | −255.725 | −7.289 | 0.544 |
| 800 | 190.345 | 436.859 | 325.790 | 88.855 | −257.166 | 28.309 | −1.848 |
| 900 | 201.902 | 459.965 | 339.427 | 108.484 | −257.981 | 64.048 | −3.717 |
| 1000 | 211.641 | 481.756 | 352.581 | 129.175 | −258.285 | 99.851 | −5.216 |
| 1100 | 219.901 | 502.325 | 365.268 | 150.763 | −258.169 | 135.661 | −6.442 |
| 1200 | 226.942 | 521.769 | 377.507 | 173.114 | −257.695 | 171.448 | −7.463 |
| 1300 | 232.970 | 540.178 | 389.319 | 196.118 | −256.930 | 207.176 | −8.324 |
| 1400 | 238.153 | 557.638 | 400.723 | 219.680 | −255.896 | 242.841 | −9.060 |
| 1500 | 242.628 | 574.225 | 411.742 | 243.725 | −254.649 | 278.422 | −9.695 |

coordinate calculations [39,43]. Vibrational frequencies given in Table 2 are those of Connett et al. [42] except for $\nu_{13}(A_u) = 830$ cm$^{-1}$, the value for which is the mean between the results of two calculations [39,43].

The thermodynamic-property contributions due to ring-puckering motion of the 1,4-dioxin ring were obtained by direct summation over the energy levels calculated with the potential function. Three investigations of the ring-puckering potential function of 1,4-dioxin have been reported [39–41]. The potential function given by Strube and Laane [41] was used to calculate 60 energy levels (0 to 10500 cm$^{-1}$). The potential function for inversion is $V(x) = (2.861 \times 10^5\ x^4 + 3.382 \times 10^3\ x^2)$ cm$^{-1}$ (where $x$, in Å, is the ring-puckering coordinate) with a reduced mass of 99.75 a.u. The partition function for inversion is based on these 60 levels with the first 10 levels being the experimental levels from which the potential function was derived.

There are no experimental or theoretical data on the enthalpy of formation of 1,4-dioxin and its value was estimated in the present work (Table 10) by comparison with known values of $\Delta_f H^\circ$(298.15 K) for related compounds [9]. We considered the change in $\Delta_f H^\circ$ values with the exchange of a $-CH_2-$ unit for an –O– group in aliphatic and cyclic compounds, and we believe that in passing from 1,4-cyclohexadiene to 1,4-dioxin the change in $\Delta_f H^\circ$(298.15 K) values might be expected to be

TABLE 10

Ideal gas thermodynamic properties for 1,4-dioxin

| $T$ (K) | $C°_p$ (J $K^{-1}$ $mol^{-1}$) | $S°$ (J $K^{-1}$ $mol^{-1}$) | $-(G°-H°_0)/T$ (J $K^{-1}$ $mol^{-1}$) | $H°-H°_0$ (kJ $mol^{-1}$) | $\Delta_f H°$ (kJ $mol^{-1}$) | $\Delta_f G°$ (kJ $mol^{-1}$) | log $K°_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −125.363 | −125.363 | ∞ |
| 100 | 40.645 | 231.386 | 193.805 | 3.758 | −130.751 | −116.035 | 60.610 |
| 200 | 56.299 | 263.398 | 221.073 | 8.465 | −135.653 | −99.405 | 25.962 |
| 298.15 | 81.278 | 290.435 | 239.478 | 15.193 | −140.000 | −80.659 | 14.131 |
| 300 | 81.760 | 290.940 | 239.793 | 15.344 | −140.076 | −80.294 | 13.980 |
| 400 | 106.161 | 317.894 | 255.964 | 24.772 | −143.581 | −59.808 | 7.810 |
| 500 | 126.097 | 343.811 | 270.963 | 36.423 | −146.161 | −38.554 | 4.028 |
| 600 | 141.797 | 368.246 | 285.163 | 49.850 | −147.990 | −16.844 | 1.466 |
| 700 | 154.264 | 391.075 | 298.682 | 64.676 | −149.291 | 5.121 | −0.382 |
| 800 | 164.365 | 412.357 | 311.577 | 80.623 | −150.196 | 27.244 | −1.779 |
| 900 | 172.705 | 432.213 | 323.890 | 97.490 | −150.799 | 49.463 | −2.871 |
| 1000 | 179.687 | 450.781 | 335.662 | 115.120 | −151.160 | 72.738 | −3.747 |
| 1100 | 185.590 | 468.191 | 346.926 | 133.392 | −151.321 | 94.037 | −4.465 |
| 1200 | 190.615 | 484.561 | 357.721 | 152.208 | −151.305 | 116.343 | −5.064 |
| 1300 | 194.916 | 499.992 | 368.077 | 171.490 | −151.140 | 138.638 | −5.570 |
| 1400 | 198.617 | 514.576 | 378.025 | 191.172 | −150.823 | 160.919 | −6.004 |
| 1500 | 201.811 | 528.391 | 387.593 | 211.197 | −150.387 | 183.171 | −6.378 |

approximately twice as great as in passing from 1,4-pentadiene to divinyl ether. On the other hand, in passing from 1,4-dioxane to 1,4-dioxin, the change in $\Delta_f H°$(298.15 K) values may be expected to be nearly the same as in passing from tetrahydrofuran to furan. The adopted value of enthalpy of formation of 1,4-dioxin is the average of these two estimates.

Ideal gas thermodynamic properties for 1,4-dioxin are given in Table 10. No experimental or calculated data are available for comparison.

## 1,3,5-TRIOXANE

Electron diffraction studies [49,50], analysis of microwave [51–53] and vibrational [8,50,54–57] spectra and molecular mechanics calculations [7,27] indicate that the chair conformation ($C_{3v}$ symmetry) is the most stable form of 1,3,5-trioxane. Calculation suggests that the twist-boat forms are at the minima of the pseudorotation path and are about 30 kJ $mol^{-1}$ less stable than the chair forms [7]. The product of the principal moments of inertia for the chair conformation of 1,3,5-trioxane (Table 1) was calculated using the rotational constants determined from microwave data [52].

Vibrational frequencies, listed in Table 2, were obtained by Pickett and Strauss [8] from the IR spectrum in the gas phase. This assignment was confirmed by normal coordinate calculations [8,50].

TABLE 11

Ideal gas thermodynamic properties for 1,3,5-trioxane

| $T$ (K) | $C^\circ_p$ (J K$^{-1}$ mol$^{-1}$) | $S^\circ$ (J K$^{-1}$ mol$^{-1}$) | $-(G^\circ - H^\circ_0)/T$ (J K$^{-1}$ mol$^{-1}$) | $H^\circ - H^\circ_0$ (kJ mol$^{-1}$) | $\Delta_f H^\circ$ (kJ mol$^{-1}$) | $\Delta_f G^\circ$ (kJ mol$^{-1}$) | log $K^\circ_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −439.335 | −439.335 | ∞ |
| 100 | 38.633 | 228.792 | 194.381 | 3.441 | −449.428 | −415.810 | 217.194 |
| 200 | 57.688 | 261.114 | 220.049 | 8.213 | −458.087 | −378.768 | 98.923 |
| 298.15 | 81.883 | 288.478 | 238.106 | 15.018 | −465.900 | −338.143 | 59.240 |
| 300 | 82.383 | 288.986 | 238.418 | 15.170 | −466.041 | −337.354 | 58.738 |
| 400 | 109.751 | 316.442 | 254.492 | 24.780 | −472.716 | −293.406 | 38.314 |
| 500 | 134.796 | 343.692 | 269.615 | 37.038 | −477.812 | −247.961 | 25.904 |
| 600 | 155.899 | 370.193 | 284.183 | 51.606 | −481.448 | −201.622 | 17.553 |
| 700 | 173.340 | 395.578 | 298.298 | 68.096 | −483.902 | −154.779 | 11.550 |
| 800 | 187.796 | 419.697 | 311.979 | 86.175 | −485.395 | −107.648 | 7.029 |
| 900 | 199.868 | 442.535 | 325.228 | 105.576 | −486.112 | −60.380 | 3.504 |
| 1000 | 210.018 | 464.133 | 338.049 | 126.084 | −486.199 | −13.065 | 0.682 |
| 1100 | 218.600 | 484.564 | 350.448 | 147.527 | −485.773 | 34.230 | −1.625 |
| 1200 | 225.892 | 503.906 | 362.438 | 169.761 | −484.917 | 81.471 | −3.546 |
| 1300 | 232.116 | 522.239 | 374.031 | 192.670 | −483.718 | 128.619 | −5.168 |
| 1400 | 237.452 | 539.641 | 385.244 | 216.155 | −482.212 | 175.668 | −6.554 |
| 1500 | 242.048 | 556.184 | 396.093 | 240.136 | −480.496 | 222.601 | −7.752 |

The enthalpy of formation for 1,3,5-trioxane (Table 11) was taken from the data of Pedley et al. [9].

Ideal gas thermodynamic properties for 1,3,5-trioxane are given in Table 11. No experimental or theoretical data are available for comparison.

## OXEPANE

Vibrational spectra of oxepane have been interpreted on the basis of a mixture of two asymmetric ($C_1$ symmetry) rigid twist-chair conformations of approximately equal energy [58]. The electron diffraction data for gaseous oxepane [59] have also been explained in terms of an approximately equimolar mixture of two twist-chair conformers. According to conformational calculation [60], other minimum-energy conformations (twist-chair and twist-boat) lie about 10 kJ mol$^{-1}$ above the most stable twist-chair conformations. The mixture of two twist-chair conformations of equal energy was taken into account in the present work. The electron diffraction structural data of Dillen and Geise [59] for the twist-chair form ($^3TC_4$, see notation in ref. 59) were used to calculate the product of the principal moments of inertia of oxepane (Table 1).

The vibrational frequencies of oxepane used in our calculations (Table 2) were taken from the study of Bocian and Strauss [58]. These authors

TABLE 12

Ideal gas thermodynamic properties for oxepane

| $T$ (K) | $C^\circ_p$ (J $K^{-1}$ $mol^{-1}$) | $S^\circ$ (J $K^{-1}$ $mol^{-1}$) | $-(G^\circ - H^\circ_0)/T$ (J $K^{-1}$ $mol^{-1}$) | $H^\circ - H^\circ_0$ (kJ $mol^{-1}$) | $\Delta_f H^\circ$ (kJ $mol^{-1}$) | $\Delta_f G^\circ$ (kJ $mol^{-1}$) | $\log K^\circ_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −178.971 | −178.971 | ∞ |
| 100 | 50.960 | 263.282 | 224.245 | 3.904 | −194.882 | −151.542 | 79.156 |
| 200 | 82.109 | 307.862 | 255.304 | 10.512 | −207.858 | −103.091 | 26.924 |
| 298.15 | 121.657 | 347.714 | 279.168 | 20.437 | −220.000 | −49.049 | 8.593 |
| 300 | 122.474 | 348.469 | 279.593 | 20.663 | −220.222 | −47.995 | 8.357 |
| 400 | 166.789 | 389.803 | 301.906 | 35.137 | −230.891 | 11.090 | −1.448 |
| 500 | 206.908 | 431.444 | 323.698 | 53.873 | −239.215 | 72.587 | −7.583 |
| 600 | 240.758 | 472.252 | 345.074 | 76.307 | −245.288 | 135.564 | −11.802 |
| 700 | 269.030 | 511.553 | 366.070 | 101.838 | −249.507 | 199.390 | −14.878 |
| 800 | 292.797 | 549.073 | 386.619 | 129.963 | −252.181 | 263.720 | −17.219 |
| 900 | 312.926 | 584.754 | 406.669 | 160.276 | −253.588 | 328.303 | −19.054 |
| 1000 | 330.058 | 618.634 | 426.186 | 192.448 | −253.952 | 392.986 | −20.527 |
| 1100 | 344.692 | 650.797 | 445.156 | 226.205 | −253.451 | 457.662 | −21.732 |
| 1200 | 357.227 | 681.340 | 463.576 | 261.317 | −252.220 | 522.264 | −22.733 |
| 1300 | 367.996 | 710.370 | 481.453 | 297.592 | −250.402 | 586.725 | −23.575 |
| 1400 | 377.276 | 737.989 | 498.799 | 334.866 | −248.048 | 651.037 | −24.290 |
| 1500 | 385.301 | 764.299 | 515.629 | 373.005 | −245.277 | 715.163 | −24.904 |

investigated the vapour-phase IR and liquid-phase Raman spectra; special attention was paid to the low-frequency region. In order to confirm the vibrational assignments, the normal coordinate calculations have been carried out.

No experimental or theoretical data on the enthalpy of formation of oxepane are available. The value presented in Table 12 was estimated in the present work by assuming that in passing from cycloheptane to oxepane the change in the $\Delta_f H^\circ$(298.15 K) values will be approximately the same as in passing from cyclohexane to tetrahydro-2*H*-pyran. It should be noted that the slight change in $\Delta_f H^\circ$(298.15 K) values takes place with the exchange of a $-CH_2-$ unit for an –O– group in three-, four- and five-membered rings and in aliphatic compounds.

Ideal gas thermodynamic properties for oxepane are given in Table 12. No experimental or theoretical data are available for comparison.

## OXEPIN

For oxepin no experimental structural information is available so far. According to ab initio and semiempirical calculations [61,62], oxepin possesses a nonplanar boat conformation ($C_s$ symmetry). The product of the principal moments of inertia, given in Table 1, was calculated using the estimated structural parameters $r(\text{C–O}) = 1.40 \pm 0.02$ Å, $r(\text{C=C}) = 1.35 \pm 0.02$ Å, $r(\text{C–C}) = 1.45 \pm 0.02$ Å, $r(\text{C–H}) = 1.08 \pm 0.01$ Å, $\angle$ C–O–C = 116 ± 2°, $\angle$ C=C–C = 126 ± 2°, $\angle$ C–C–H = 120°. These values are based on comparison with parent compounds and on the results of ab initio calculation by Cremer et al. [61].

No vibrational spectral studies are known for oxepin. The fundamental frequencies presented in Table 2 were estimated in this work by normal coordinate calculations using force constants transferred from related molecules (1,3,5-cycloheptatriene, 1,3-cycloheptadiene, oxepane, 1,4-dioxin etc.) for which simple valence force fields were initially determined using vibrational frequencies from ref. 20 and Table 2. The average uncertainty of calculated vibrational frequencies of oxepin is believed to be about 50 $\text{cm}^{-1}$.

No experimental data on the enthalpy of formation of oxepin are available. The value of $\Delta_f H°(298.15\ \text{K}) = -8\ \text{kJ mol}^{-1}$ was calculated by the semiempirical MINDO/3 method [62]. From a comparison of MINDO/3 and experimental $\Delta_f H°(298.15\ \text{K})$ values for 1,3,5-cycloheptatriene, one can suggest that this value is underestimated. In the present work the $\Delta_f H°(298.15\ \text{K})$ value of oxepin was estimated by comparison with known values of $\Delta_f H°(298.15\ \text{K})$ for related compounds [9]. We considered the change in $\Delta_f H°$ values with the exchange of a $-\text{CH}_2-$ unit for an –O– group in aliphatic and cyclic compounds, and we believe that in passing from oxepane to oxepin the change in $\Delta_f H°(298.15\ \text{K})$ values might be expected to be nearly the same as in passing from cycloheptane to 1,3,5-cycloheptatriene. On the other hand, in passing from 1,3,5-cycloheptatriene to oxepin, the change in $\Delta_f H°(298.15\ \text{K})$ values may be expected to be approximately the same as in passing from 1,4-pentadiene to divinyl ether. The accepted value of $\Delta_f H°(298.15\ \text{K})$ for oxepin (Table 13) is the average of these two estimates.

Ideal gas thermodynamic properties for oxepin are presented in Table 13. No experimental or theoretical data are available for comparison.

## 1,3-DIOXEPANE

The conformational properties of 1,3-dioxepane have been studied by vibrational spectroscopy [58] and by theoretical calculations [27,60,63–65]. Vibrational spectra [57] were interpreted in terms of a $C_2$ symmetric twist-chair form as the most stable conformation. All of the conformational calculations have also indicated that the lowest energy form of 1,3-dioxepane is the twist-chair form ($C_2$ symmetry), but conflicting results concerning the other stable conformations have been reported. Three twist-chair and one twist-boat forms of $C_1$ symmetry with an energy of about 10 $\text{kJ mol}^{-1}$ above that of the most stable twist-chair form of $C_2$ symmetry were obtained by Bocian and Strauss [60] from conformational

TABLE 13

Ideal gas thermodynamic properties for oxepin

| $T$ (K) | $C^\circ_p$ ($\mathrm{J\ K^{-1}\ mol^{-1}}$) | $S^\circ$ ($\mathrm{J\ K^{-1}\ mol^{-1}}$) | $-(G^\circ - H^\circ_0)/T$ ($\mathrm{J\ K^{-1}\ mol^{-1}}$) | $H^\circ - H^\circ_0$ ($\mathrm{kJ\ mol^{-1}}$) | $\Delta_f H^\circ$ ($\mathrm{kJ\ mol^{-1}}$) | $\Delta_f G^\circ$ ($\mathrm{kJ\ mol^{-1}}$) | $\log K^\circ_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | 79.868 | 79.868 | $\infty$ |
| 100 | 40.816 | 244.182 | 208.931 | 3.525 | 72.575 | 87.608 | −45.761 |
| 200 | 62.756 | 278.614 | 235.529 | 8.617 | 66.165 | 105.136 | −27.458 |
| 298.15 | 92.543 | 309.054 | 254.729 | 16.197 | 60.000 | 125.592 | −22.003 |
| 300 | 93.139 | 309.628 | 255.066 | 16.368 | 59.886 | 125.995 | −21.937 |
| 400 | 124.641 | 340.793 | 272.600 | 27.277 | 54.367 | 148.896 | −19.444 |
| 500 | 152.141 | 371.653 | 289.337 | 41.158 | 49.960 | 173.055 | −18.079 |
| 600 | 174.708 | 401.458 | 305.558 | 57.540 | 46.617 | 198.012 | −17.238 |
| 700 | 193.075 | 429.816 | 321.302 | 75.960 | 44.102 | 223.449 | −16.674 |
| 800 | 208.167 | 456.615 | 336.557 | 96.046 | 42.248 | 249.205 | −16.271 |
| 900 | 220.717 | 481.880 | 351.315 | 117.509 | 40.912 | 275.158 | −15.970 |
| 1000 | 231.254 | 505.696 | 365.574 | 140.122 | 40.002 | 301.240 | −15.735 |
| 1100 | 240.167 | 528.166 | 379.343 | 163.706 | 39.447 | 327.393 | −15.546 |
| 1200 | 247.751 | 549.397 | 392.638 | 188.112 | 39.203 | 353.585 | −15.391 |
| 1300 | 254.235 | 569.491 | 405.476 | 213.219 | 39.220 | 379.778 | −15.259 |
| 1400 | 259.806 | 588.541 | 417.878 | 238.928 | 39.496 | 405.968 | −15.147 |
| 1500 | 264.614 | 606.633 | 429.864 | 265.155 | 39.983 | 432.128 | −15.048 |

energy surface calculation. According to the conformational calculations of Sauriol-Lord and Grindley [63], three unsymmetrical twist-chair forms are less stable than the twist-chair ($C_2$) form by only 4–7 kJ $\mathrm{mol^{-1}}$. Molecular mechanics calculation [27] has predicted the energy of the twist-boat form ($C_1$ symmetry) to be nearly the same as for the twist-chair form of $C_2$ symmetry. From the conformational energy calculations of Kamalov et al. [64,65], 1,3-dioxepane exists predominantly as the twist-chair ($C_2$ symmetry) form. In the present work we have performed calculations of the standard entropy of gaseous 1,3-dioxepane for models of different conformational composition. A good agreement between experimental [66] and calculated entropy values was achieved by assuming that 1,3-dioxepane exists as an equimolar mixture of twist-chair ($C_2$ symmetry) and twist-boat ($C_1$ symmetry) forms. Thus the low-energy conformations obtained from molecular mechanics calculation [27] were taken into account in the present work (Table 1). The product of the principal moments of inertia for the twist-chair conformation of $C_2$ symmetry given in Table 1 was calculated using the estimated structural parameters $r(\mathrm{C{-}O}) = 1.42 \pm 0.02$ Å, $r(\mathrm{C{-}C}) = 1.53 \pm 0.02$ Å, $r(\mathrm{C{-}H}) = 1.11 \pm 0.02$ Å, $\angle\ \mathrm{O_1{-}C_2{-}O_3} = 111.6 \pm 2^\circ$, $\angle\ \mathrm{C_2{-}O_3{-}C_4} = 113.8 \pm 2^\circ$, $\angle\ \mathrm{C_3{-}C_4{-}C_5} = 108.7 \pm 2^\circ$, $\angle\ \mathrm{C_4{-}C_5{-}C_6} = 114.0 \pm 2^\circ$, $\angle\ \mathrm{C{-}C{-}H} = 109 \pm 2^\circ$, $\angle\ \mathrm{O{-}C{-}H} = 109 \pm 2^\circ$, $\tau(\mathrm{C_2{-}O_3}) = 46.9 \pm 2^\circ$, $\tau(\mathrm{O_3{-}C_4}) = 97.7 \pm 2^\circ$, $\tau(\mathrm{C_4{-}C_5}) = 68.2 \pm 2^\circ$, $\tau(\mathrm{C_5{-}C_6}) = 45.8 \pm 2^\circ$.

TABLE 14

Ideal gas thermodynamic properties for 1,3-dioxepane

| $T$ (K) | $C°_p$ (J $K^{-1}$ $mol^{-1}$) | $S°$ (J $K^{-1}$ $mol^{-1}$) | $-(G°-H°_0)/T$ (J $K^{-1}$ $mol^{-1}$) | $H°-H°_0$ (kJ $mol^{-1}$) | $\Delta_f H°$ (kJ $mol^{-1}$) | $\Delta_f G°$ (kJ $mol^{-1}$) | log $K°_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −309.746 | −309.746 | ∞ |
| 100 | 48.384 | 258.285 | 220.691 | 3.759 | −324.191 | −281.853 | 147.223 |
| 200 | 78.271 | 300.854 | 250.500 | 10.071 | −335.898 | −234.879 | 61.343 |
| 298.15 | 113.614 | 338.463 | 273.292 | 19.431 | −346.600 | −182.981 | 32.057 |
| 300 | 114.336 | 339.168 | 273.696 | 19.642 | −346.794 | −181.972 | 31.684 |
| 400 | 153.459 | 377.445 | 294.843 | 33.041 | −356.081 | −125.570 | 16.398 |
| 500 | 188.952 | 415.600 | 315.188 | 50.206 | −363.250 | −67.077 | 7.007 |
| 600 | 218.917 | 452.781 | 335.040 | 70.645 | −368.411 | −7.318 | 0.637 |
| 700 | 243.890 | 488.461 | 354.428 | 93.823 | −371.923 | 53.158 | −3.967 |
| 800 | 264.811 | 522.434 | 373.324 | 119.288 | −374.071 | 114.046 | −7.446 |
| 900 | 282.461 | 554.672 | 391.699 | 146.676 | −375.104 | 175.133 | −10.164 |
| 1000 | 297.433 | 585.228 | 409.538 | 175.691 | −375.222 | 236.285 | −12.342 |
| 1100 | 310.184 | 614.191 | 426.838 | 206.089 | −374.585 | 297.409 | −14.123 |
| 1200 | 321.080 | 641.660 | 443.605 | 237.666 | −373.313 | 358.452 | −15.603 |
| 1300 | 330.424 | 667.738 | 459.852 | 270.253 | −371.531 | 419.356 | −16.850 |
| 1400 | 338.463 | 692.527 | 475.593 | 303.707 | −369.287 | 480.115 | −17.913 |
| 1500 | 345.406 | 716.121 | 490.848 | 337.909 | −366.683 | 540.697 | −18.829 |

These values are based on comparison with related compounds and on results of theoretical calculations [60].

The vibrational frequencies of 1,3-dioxepane used in our calculations (Table 2) were taken from the study of Bocian and Strauss [58]. These authors investigated the vapour-phase IR and liquid-phase Raman spectra. In order to confirm the vibrational assignments, the normal coordinate calculations have been carried out.

The enthalpy of formation for 1,3-dioxepane (Table 14) was taken from the data of Pedley et al. [9].

Ideal gas thermodynamic properties for 1,3-dioxepane are presented in Table 14. No other statistical calculations are available for comparison. The calculated value of $S°$(298.15 K), as shown in Table 21, coincides with the calorimetric entropy [66] within the experimental uncertainty.

## 4,7-DIHYDRO-1,3-DIOXEPIN

The investigations of nuclear magnetic resonance, dipole moments, photoelectronic spectra and intensities of infrared spectra [67–70], as well as a molecular mechanics calculation [70], predict that the preferred conformation of 4,7-dihydro-1,3-dioxepin is the twist-boat form of $C_2$ symmetry. The product of the principal moments of inertia for this confor-

TABLE 15

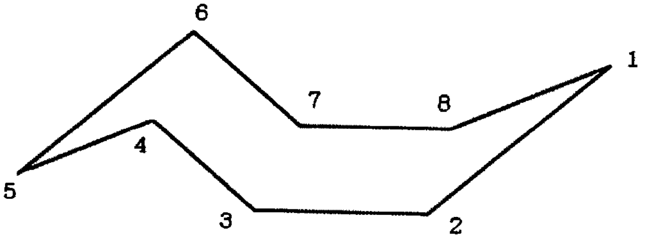
Ideal gas thermodynamic properties for 4,7-dihydro-1,3-dioxepin

| $T$ (K) | $C°_p$ (J $K^{-1}$ $mol^{-1}$) | $S°$ (J $K^{-1}$ $mol^{-1}$) | $-(G°-H°_0)/T$ (J $K^{-1}$ $mol^{-1}$) | $H°-H°_0$ (kJ $mol^{-1}$) | $\Delta_f H°$ (kJ $mol^{-1}$) | $\Delta_f G°$ (kJ $mol^{-1}$) | log $K°_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −213.771 | −213.771 | ∞ |
| 100 | 58.525 | 256.402 | 213.593 | 4.281 | −224.696 | −192.242 | 100.416 |
| 200 | 86.999 | 305.876 | 247.977 | 11.580 | −232.721 | −156.589 | 40.896 |
| 298.15 | 117.682 | 346.188 | 273.777 | 21.589 | −240.000 | −117.647 | 20.611 |
| 300 | 118.292 | 346.918 | 274.226 | 21.808 | −240.133 | −116.893 | 20.353 |
| 400 | 150.848 | 385.450 | 297.251 | 35.280 | −246.441 | −74.818 | 9.770 |
| 500 | 179.873 | 422.315 | 318.606 | 51.855 | −251.277 | −31.329 | 3.273 |
| 600 | 204.226 | 457.331 | 338.836 | 71.097 | −254.706 | 13.012 | −1.133 |
| 700 | 224.477 | 490.380 | 358.148 | 92.563 | −256.992 | 57.823 | −4.315 |
| 800 | 241.430 | 521.495 | 376.641 | 115.883 | −258.333 | 102.899 | −6.719 |
| 900 | 255.735 | 550.780 | 394.379 | 140.761 | −258.901 | 148.094 | −8.595 |
| 1000 | 267.876 | 578.370 | 411.412 | 166.958 | −258.833 | 193.318 | −10.098 |
| 1100 | 278.223 | 604.400 | 427.785 | 194.276 | −258.237 | 238.508 | −11.326 |
| 1200 | 287.072 | 628.998 | 443.537 | 222.552 | −257.189 | 283.627 | −12.346 |
| 1300 | 294.666 | 652.283 | 458.707 | 251.649 | −255.775 | 328.633 | −13.204 |
| 1400 | 301.205 | 674.365 | 473.329 | 281.450 | −254.021 | 373.526 | −13.936 |
| 1500 | 306.857 | 695.344 | 487.437 | 311.860 | −252.000 | 418.281 | −14.566 |

mation given in Table 1 was calculated using the estimated structural parameters $r(\text{C–O}) = 1.42 \pm 0.02$ Å, $r(\text{C–C}) = 1.51 \pm 0.02$ Å, $r(\text{C=C}) = 1.35 \pm 0.02$ Å, $r(\text{=C–H}) = 1.08 \pm 0.02$ Å, $r(\text{–C–H}) = 1.10 \pm 0.02$ Å, $\angle\ O_1–C_2–O_3 = 110.7 \pm 2°$, $\angle\ C_2–O_3–C_4 = 114.1 \pm 2°$, $\angle\ O_3–C_4–C_5 = 112 \pm 2°$, $\angle\ C_4–C_5–C_6 = 123 \pm 2°$, $\angle\ \text{C=C–H} = 119 \pm 2°$, $\angle\ \text{H–C–H} = 106 \pm 3°$, $\tau(C_2–O_3) = 47.8 \pm 3°$, $\tau(O_3–C_4) = 89.2 \pm 3°$, $\tau(C_4–C_5) = 39 \pm 3°$, $\tau(C_5–C_6) = 6 \pm 3°$. These values are based on comparison with related compounds and on results of molecular mechanics calculation [70].

No vibrational spectra studies are known for 4,7-dihydro-1,3-dioxepin. Fundamental frequencies presented in Table 2 were estimated in this work by normal coordinate calculations using 17 force constants transferred from cycloheptene and 1,3-dioxepane for which simple valence force fields were initially determined using vibrational frequencies from ref. 20 and Table 2. The average uncertainty of the calculated vibrational frequencies of 4,7-dihydro-1,3-dioxepin is believed to be about 50 $cm^{-1}$.

No experimental or theoretical data on the enthalpy of formation of 4,7-dihydro-1,3-dioxepin are available. The $\Delta_f H°$(298.15 K) value given in Table 15 was estimated in the present work by assuming that in passing from 1,3-dioxepane to 4,7-dihydro-1,3-dioxepin the change in the $\Delta_f H°$(298.15 K) values will be approximately the same as in passing from cycloheptane to cycloheptene.



Boat–chair.

Scheme 1.

Ideal gas thermodynamic properties for 4,7-dihydro-1,3-dioxepin are given in Table 15. No experimental or calculated data are available for comparison.

## OXOCANE

The boat–chair conformations were preferred for oxocane from nuclear magnetic resonance spectra [71] and molecular mechanics calculations [72], but although the experimental data supported the boat–chair-1 most stable conformation (i.e. oxygen at the (1) position), the calculation favoured the boat–chair-3 form. Burket [72] has calculated the relative energies of eight stable conformations of oxocane. Seven of these conformations were taken into account in the present work (Table 1): the most stable boat–chair-3 form ($C_1$ symmetry) as well as the boat–chair-1 ($C_s$), boat–chair-4 ($C_1$), boat–chair-2 ($C_1$), boat–chair-5 ($C_s$), crown ($C_{2v}$) and boat–boat-1 ($C_s$) forms with energies higher than the boat–chair-3 by 150 $cm^{-1}$ (boat–chair-1), 500 $cm^{-1}$ (boat–chair-4) and 1000 $cm^{-1}$ (the rest of the conformations). The product of the principal moments of inertia for the boat–chair-3 conformation of oxocane given in Table 1 was calculated using the estimated structural parameters $r(C{-}O) = 1.42 \pm 0.02$ Å, $r(C{-}C) = 1.53 \pm 0.02$ Å, $r(C{-}H) = 1.10 \pm 0.02$ Å, $\angle\ C_8{-}C_1{-}C_2 = 113 \pm 3°$, $\angle\ C_1{-}C_2{-}O_3 = 113 \pm 3°$, $\angle\ C_2{-}O_3{-}C_4 = 114 \pm 3°$, $\angle\ O_3{-}C_4{-}C_5 = 111 \pm 3°$, $\angle\ C_4{-}C_5{-}C_6 = 116.8 \pm 3°$, $\angle\ C_5{-}C_6{-}C_7 = 115.7 \pm 3°$, $\angle\ C_6{-}C_7{-}C_8 = 115 \pm 3°$, $\angle\ C_7{-}C_8{-}C_1 = 114 \pm 3°$, $\angle$ H–C–C $= 109 \pm 3°$, $\angle$ H–C–O $= 109 \pm 3°$, $\tau(C_1{-}C_2) = 65 \pm 4°$, $\tau(C_2{-}O_3) = 56 \pm 4°$, $\tau(O_3{-}C_4) = 113 \pm 4°$, $\tau(C_4{-}C_5) = 62.2 \pm 4°$, $\tau(C_5{-}C_6) = 61.9 \pm 4°$, $\tau(C_6{-}C_7) = 99.7 \pm 4°$, $\tau(C_7{-}C_8) = 41.1 \pm 4°$ $\tau(C_8{-}C_1) = 68 \pm 4°$. These values are based on comparison with structural parameters of cycloheptane, cyclooctane and their oxygen derivatives.

No vibrational spectral studies are known for oxocane. Fundamental frequencies listed in Table 2 were estimated in this work by normal coordinate calculations using 18 force constants transferred from oxepane, for which the simple valence force field was initially determined using vibrational frequencies from Table 2. The obtained force field reproduces

TABLE 16

Ideal gas thermodynamic properties for oxocane

| $T$ (K) | $C°_p$ (J $K^{-1}$ $mol^{-1}$) | $S°$ (J $K^{-1}$ $mol^{-1}$) | $-(G°-H°_0)/T$ (J $K^{-1}$ $mol^{-1}$) | $H°-H°_0$ (kJ $mol^{-1}$) | $\Delta_f H°$ (kJ $mol^{-1}$) | $\Delta_f G°$ (kJ $mol^{-1}$) | log $K°_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −178.580 | −178.580 | ∞ |
| 100 | 61.552 | 271.146 | 226.902 | 4.424 | −197.032 | −144.310 | 75.379 |
| 200 | 100.262 | 325.293 | 263.014 | 12.456 | −211.606 | −85.825 | 22.415 |
| 298.15 | 148.019 | 373.929 | 291.531 | 24.567 | −225.000 | −21.191 | 3.713 |
| 300 | 148.987 | 374.847 | 292.042 | 24.842 | −225.243 | −19.935 | 3.471 |
| 400 | 200.745 | 424.862 | 318.983 | 42.351 | −236.819 | 50.326 | −6.572 |
| 500 | 246.788 | 474.744 | 345.161 | 64.791 | −245.694 | 123.183 | −12.869 |
| 600 | 285.298 | 523.251 | 370.826 | 91.455 | −252.026 | 197.605 | −17.203 |
| 700 | 317.351 | 569.711 | 395.946 | 121.636 | −256.282 | 272.899 | −20.364 |
| 800 | 344.284 | 613.896 | 420.452 | 154.755 | −258.817 | 348.690 | −22.767 |
| 900 | 367.115 | 655.801 | 444.295 | 190.356 | −259.940 | 424.709 | −24.649 |
| 1000 | 386.576 | 695.515 | 467.449 | 228.066 | −259.899 | 500.788 | −26.158 |
| 1100 | 403.223 | 733.161 | 489.908 | 267.578 | −258.893 | 576.815 | −27.390 |
| 1200 | 417.502 | 768.874 | 511.680 | 308.632 | −257.071 | 652.720 | −28.412 |
| 1300 | 429.784 | 802.789 | 532.780 | 351.011 | −254.592 | 728.429 | −29.268 |
| 1400 | 440.379 | 835.037 | 553.228 | 394.532 | −251.511 | 803.937 | −29.995 |
| 1500 | 449.549 | 865.740 | 573.047 | 439.040 | −247.963 | 879.204 | −30.616 |

the experimental vibrational frequencies of oxepane [58] with an average error of 13 $cm^{-1}$. The average uncertainty of the calculated vibrational frequencies of oxocane is believed to be about 50 $cm^{-1}$.

There are no experimental or theoretical data on the enthalpy of formation of oxocane. The value of $\Delta_f H°$(298.15 K) given in Table 16 was estimated in the present work by assuming that in passing from cyclooctane to oxocane the change in the $\Delta_f H°$(298.15 K) values will be approximately the same as in passing from cyclohexane to tetrahydro-2*H*-pyran.

Ideal gas thermodynamic properties for oxocane are given in Table 16. No experimental or theoretical data are available for comparison.

## 1,3-DIOXOCANE

Nuclear magnetic resonance experiments [71,73,74] established the boat–chair-1,3 form (i.e oxygen atoms at the (1) and (3) positions; see the illustration in the Oxocane section) for 1,3-dioxocane. The vibrational frequencies calculated from the potential function were consistent only with the boat–chair-1,3 structure [75]. From the conformational calculations [72,75] it was concluded that the 1,3-dioxocane conformation of lowest energy is the boat–chair-1,3, with other minimum-energy forms 400–3000 $cm^{-1}$ higher in energy. On the basis of these calculations, five

TABLE 17

Ideal gas thermodynamic properties for 1,3-dioxocane

| $T$ (K) | $C^\circ_p$ (J $K^{-1}$ $mol^{-1}$) | $S^\circ$ (J $K^{-1}$ $mol^{-1}$) | $-(G^\circ - H^\circ_0)/T$ (J $K^{-1}$ $mol^{-1}$) | $H^\circ - H^\circ_0$ (kJ $mol^{-1}$) | $\Delta_f H^\circ$ (kJ $mol^{-1}$) | $\Delta_f G^\circ$ (kJ $mol^{-1}$) | $\log K^\circ_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −293.792 | −293.792 | ∞ |
| 100 | 53.594 | 263.652 | 223.998 | 3.965 | −311.092 | −259.124 | 135.351 |
| 200 | 94.575 | 313.134 | 256.441 | 11.338 | −324.759 | −201.697 | 52.677 |
| 298.15 | 139.655 | 359.154 | 282.689 | 22.798 | −336.800 | −138.677 | 24.295 |
| 300 | 140.535 | 360.021 | 283.163 | 23.057 | −337.016 | −137.455 | 23.933 |
| 400 | 186.960 | 406.889 | 308.238 | 39.460 | −347.242 | −69.321 | 9.052 |
| 500 | 227.979 | 453.138 | 332.612 | 60.263 | −355.028 | 1.100 | −0.115 |
| 600 | 262.385 | 497.840 | 356.451 | 84.834 | −360.546 | 72.890 | −6.346 |
| 700 | 291.090 | 540.508 | 379.723 | 112.550 | −364.206 | 145.436 | −10.852 |
| 800 | 315.223 | 580.999 | 402.374 | 142.900 | −366.325 | 218.405 | −14.260 |
| 900 | 335.663 | 619.340 | 424.371 | 175.472 | −367.177 | 291.559 | −16.921 |
| 1000 | 353.062 | 655.630 | 445.699 | 209.931 | −366.984 | 364.751 | −19.052 |
| 1100 | 367.922 | 689.996 | 466.360 | 245.999 | −365.927 | 437.879 | −20.793 |
| 1200 | 380.651 | 722.569 | 486.365 | 283.444 | −364.138 | 510.883 | −22.238 |
| 1300 | 391.585 | 753.480 | 505.734 | 322.070 | −361.761 | 583.700 | −23.453 |
| 1400 | 401.007 | 782.853 | 524.488 | 361.711 | −358.849 | 656.324 | −24.487 |
| 1500 | 409.155 | 810.804 | 542.652 | 402.229 | −355.520 | 728.723 | −25.376 |

conformations of 1,3-dioxocane were considered in the present work (Table 1): the most stable boat–chair-1,3 form ($C_1$ symmetry) as well as the boat–boat ($C_1$), twist-boat–chair ($C_1$), boat–chair-4,6 ($C_s$) and boat–chair-3,5 ($C_1$) forms with energies higher than the boat–chair-1,3 by 400, 700, 800 and 1000 $cm^{-1}$, respectively. The product of the principal moments of inertia for the boat–chair-1,3 conformation of 1,3-dioxocane, presented in Table 1, was obtained using the structural parameters calculated by Pakes et al. [75].

The vibrational frequencies of 1,3-dioxocane used in our calculations (Table 2) were taken from the study of Pakes et al. [76]. These authors have investigated the IR, far-infrared and Raman spectra, giving special attention to the low-frequency region. In order to confirm the vibrational assignments, the normal coordinate calculations have been carried out.

The enthalpy of formation for 1,3-dioxocane (Table 17) was taken from the data of Pedley et al. [9].

Ideal gas thermodynamic properties for 1,3-dioxocane are given in Table 17. No experimental or calculated data are available for comparison.

## 1,3,6-TRIOXOCANE

Nuclear magnetic resonance data [71,73] have indicated that, together with the boat–chair form, in a solution of 1,3,6-trioxocane there is an appreciable amount of another conformer with about the same energy. This conformer was thought to be a member of the crown family. The boat–chair-1,3,6 form (i.e. oxygen atoms at the (1), (3) and (6) positions; see the illustration in Oxocane section) was found to be the most stable conformation for 1,3,6-trioxocane from conformational calculations [72,75]. The other minimum-energy conformations have been estimated to be higher in energy than the boat–chair-1,3,6 by 400–3000 $cm^{-1}$. On the basis of these calculations, four low-energy conformations of 1,3,6-trioxocane were accepted in the present work (Table 1): the most stable boat–chair-1,3,6 form ($C_1$ symmetry) as well as the boat–chair-1,4,6 ($C_s$), boat–chair-2,4,7 ($C_1$) and boat–boat ($C_1$) forms with energies higher than the boat–chair-1,3,6 form by 700, 800 and 1000 $cm^{-1}$, respectively. The product of the principal moments of inertia for the boat–chair-1,3,6 form given in Table 1 was obtained using the structural parameters calculated by Pakes et al. [75].

The vibrational frequencies of 1,3,6-trioxocane listed in Table 2 were taken from a study by Pakes et al. [76]. These authors investigated the IR, far-infrared and Raman spectra, giving special attention to the low-frequency region. The proposed vibrational assignment was supported by a normal coordinate analysis based on a valence force field.

The enthalpy of formation for 1,3,6-trioxocane (Table 18) was taken from the data of Pedley et al. [9].

Ideal gas thermodynamic properties for 1,3,6-trioxocane are given in Table 18. No experimental or theoretical data are available for comparison.

## 1,3,5,7-TETRAOXOCANE

From nuclear magnetic resonance [71,73,77,78] and IR and Raman [56,79–81] spectroscopy, as well as from an X-ray investigation [82] of 1,3,5,7-tetraoxocane, it was established that only the crown conformer exists in the solid state, although two conformers, crown and boat–chair, are presented in solution, with predominance of the crown form. However, in the gas phase, the boat–chair form was found to be predominant by electron diffraction study [83] and molecular mechanics calculations [26,72]. Two conformations of 1,3,5,7-tetraoxocane were considered in the present work (Table 1): the most stable boat–chair form ($C_s$ symmetry) and the crown form ($C_{4v}$ symmetry) with energy higher than that of the boat–chair by 275 $cm^{-1}$. The adopted relative energy of the crown form was estimated on the basis of electron diffraction data [83] from which the equilibrium mixture of 68% boat–chair and 32% crown was found for 1,3,5,7-tetraoxocane in the gas phase. The product of the principal moments of inertia for the boat–chair conformation presented in Table 1 was calculated using the structural parameters determined by electron diffraction [83].

TABLE 18

Ideal gas thermodynamic properties for 1,3,6-trioxocane

| $T$ (K) | $C°_p$ (J $K^{-1}$ $mol^{-1}$) | $S°$ (J $K^{-1}$ $mol^{-1}$) | $-(G°-H°_0)/T$ (J $K^{-1}$ $mol^{-1}$) | $H°-H°_0$ (kJ $mol^{-1}$) | $\Delta_f H°$ (kJ $mol^{-1}$) | $\Delta_f G°$ (kJ $mol^{-1}$) | log $K°_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −428.050 | −428.050 | ∞ |
| 100 | 52.339 | 262.954 | 223.571 | 3.938 | −443.767 | −393.231 | 205.400 |
| 200 | 88.108 | 309.923 | 255.333 | 10.918 | −456.261 | −337.707 | 88.199 |
| 298.15 | 130.005 | 352.720 | 280.357 | 21.575 | −467.100 | −277.150 | 48.555 |
| 300 | 130.833 | 353.527 | 280.806 | 21.816 | −467.291 | −275.978 | 48.051 |
| 400 | 174.325 | 397.213 | 304.447 | 37.106 | −476.173 | −210.795 | 27.527 |
| 500 | 211.927 | 440.283 | 327.327 | 56.478 | −482.665 | −143.660 | 15.008 |
| 600 | 242.765 | 481.742 | 349.635 | 79.264 | −487.058 | −75.406 | 6.565 |
| 700 | 268.069 | 521.127 | 371.346 | 104.846 | −489.794 | −6.565 | 0.490 |
| 800 | 289.105 | 558.337 | 392.417 | 132.736 | −491.186 | 62.578 | −4.086 |
| 900 | 306.795 | 593.440 | 412.822 | 162.556 | −491.490 | 131.827 | −7.651 |
| 1000 | 321.784 | 626.561 | 432.556 | 194.005 | −490.905 | 201.061 | −10.502 |
| 1100 | 334.550 | 657.845 | 451.628 | 226.839 | −489.588 | 270.198 | −12.830 |
| 1200 | 345.465 | 687.435 | 470.057 | 260.854 | −487.653 | 339.193 | −14.764 |
| 1300 | 354.830 | 715.466 | 487.866 | 295.880 | −485.224 | 407.994 | −16.393 |
| 1400 | 362.893 | 742.064 | 505.081 | 331.776 | −482.346 | 476.600 | −17.782 |
| 1500 | 369.863 | 767.345 | 521.730 | 368.423 | −479.119 | 544.986 | −18.978 |

TABLE 19

Ideal gas thermodynamic properties for 1,3,5,7-tetraoxocane

| $T$ (K) | $C°_p$ (J $K^{-1}$ $mol^{-1}$) | $S°$ (J $K^{-1}$ $mol^{-1}$) | $-(G°-H°_0)/T$ (J $K^{-1}$ $mol^{-1}$) | $H°-H°_0$ (kJ $mol^{-1}$) | $\Delta_f H°$ (kJ $mol^{-1}$) | $\Delta_f G°$ (kJ $mol^{-1}$) | log $K°_f$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.000 | 0.000 | 0.000 | 0.000 | −584.954 | −584.954 | ∞ |
| 100 | 50.586 | 257.141 | 217.611 | 3.953 | −599.046 | −549.431 | 286.989 |
| 200 | 81.620 | 301.439 | 248.829 | 10.522 | −610.385 | −495.284 | 129.353 |
| 298.15 | 116.255 | 340.343 | 272.598 | 20.198 | −620.200 | −436.651 | 76.498 |
| 300 | 116.943 | 341.065 | 273.018 | 20.414 | −620.374 | −435.518 | 75.829 |
| 400 | 153.870 | 379.800 | 294.882 | 33.967 | −628.535 | −372.605 | 48.657 |
| 500 | 187.139 | 417.805 | 315.683 | 51.061 | −634.580 | −307.887 | 32.164 |
| 600 | 215.068 | 454.473 | 335.781 | 71.215 | −638.697 | −242.125 | 21.079 |
| 700 | 238.147 | 489.415 | 355.255 | 93.912 | −641.258 | −175.812 | 13.119 |
| 800 | 257.285 | 522.504 | 374.112 | 118.713 | −642.553 | −109.217 | 7.131 |
| 900 | 273.270 | 553.758 | 392.353 | 145.264 | −642.826 | −42.524 | 2.468 |
| 1000 | 286.708 | 583.266 | 409.983 | 173.282 | −642.270 | 24.154 | −1.262 |
| 1100 | 298.065 | 611.139 | 427.015 | 202.537 | −641.038 | 90.740 | −4.309 |
| 1200 | 307.710 | 637.499 | 443.467 | 232.838 | −639.240 | 157.194 | −6.842 |
| 1300 | 315.936 | 662.463 | 459.362 | 264.031 | −636.993 | 223.469 | −8.979 |
| 1400 | 322.984 | 686.141 | 474.722 | 295.986 | −634.344 | 289.563 | −10.804 |
| 1500 | 329.050 | 708.636 | 489.573 | 328.596 | −631.385 | 355.456 | −12.378 |

TABLE 20

Uncertainties of the calculated thermodynamic functions (J $K^{-1}$ $mol^{-1}$) and adopted enthalpies of formation (kJ $mol^{-1}$)

| Molecule | | Uncertainties in $-(G^\circ - H^\circ_0)/T$ | | Uncertainties in $C^\circ_p$ | | Uncertainties in $\Delta_f H^\circ$ (298.15 K) |
|---|---|---|---|---|---|---|
| | | 298.15 K | 1000 K | 298.15 K | 1000 K | |
| $C_5H_{10}O$ | Tetrahydro-2*H*-pyran | 2.0 | 5.0 | 3.5 | 12.0 | 1.0 |
| $C_5H_8O$ | 3,4-Dihydro-2*H*-pyran | 2.0 | 5.5 | 4.0 | 11.0 | 1.5 |
| | 3,6-Dihydro-2*H*-pyran | 2.0 | 5.5 | 4.5 | 11.0 | 20.0 |
| $C_4H_8O_2$ | 1,3-Dioxane | 2.5 | 5.5 | 3.5 | 11.0 | 4.3 |
| | 1,4-Dioxane | 2.0 | 4.5 | 3.0 | 10.5 | 0.8 |
| $C_4H_6O_2$ | 3,6-Dihydro-1,2-dioxin | 2.5 | 5.5 | 4.0 | 9.5 | 50.0 |
| | 2,3-Dihydro-1,4-dioxin | 2.0 | 5.0 | 4.0 | 9.5 | 50.0 |
| $C_4H_4O_2$ | 1,4-Dioxin | 2.0 | 5.0 | 4.0 | 9.5 | 50.0 |
| $C_3H_6O_3$ | 1,3,5-Trioxane | 2.0 | 4.0 | 3.0 | 9.0 | 0.5 |
| $C_6H_{12}O$ | Oxepane | 2.5 | 7.0 | 5.0 | 15.0 | 10.0 |
| $C_6H_6O$ | Oxepin | 3.0 | 7.0 | 4.5 | 10.5 | 50.0 |
| $C_5H_{10}O_2$ | 1,3-Dioxepane | 2.5 | 6.0 | 4.5 | 13.5 | 1.5 |
| $C_5H_8O_2$ | 4,7-Dihydro-1,3-dioxepin | 4.0 | 10.0 | 5.5 | 12.5 | 30.0 |
| $C_7H_{14}O$ | Oxocane | 4.0 | 11.0 | 8.0 | 18.5 | 10.0 |
| $C_6H_{12}O_2$ | 1,3-Dioxocane | 3.0 | 8.5 | 8.0 | 17.0 | 1.8 |
| $C_5H_{10}O_3$ | 1,3,6-Trioxocane | 3.5 | 8.5 | 6.0 | 16.0 | 1.0 |
| $C_4H_8O_4$ | 1,3,5,7-Tetraoxocane | 3.5 | 7.5 | 5.0 | 13.0 | 0.6 |

The vibrational frequencies listed in Table 2 are based on the results of the investigations of IR and Raman spectra of 1,3,5,7-tetraoxocane in the solid state and in solution [56,79–81]. Vibrational assignments proposed in these works for the crown conformer were supported by normal coordinate calculations.

TABLE 21

Comparison of experimental [a] entropies $S^\circ(T)$ (J $K^{-1}$ $mol^{-1}$) with calculated values

| Molecule | 298.15 K | 500 K | 1000 K | 1500 K | Reference |
|---|---|---|---|---|---|
| $C_4H_8O_2$ 1,3-Dioxane | 303.2 | 364.5 | 501.3 | 607.8 | 28 |
| | 303.1 | 364.2 | 501.0 | 607.5 | This work |
| $C_4H_8O_2$ 1,4-Dioxane | 299.9 | 363.7 | 503.7 | | 35 |
| | | 360.5 | | | 33 |
| | 299.7 | 362.4 | 500.9 | 607.8 | 28 |
| | 299.3 | 362.0 | 500.5 | 607.4 | This work |
| $C_5H_{10}O_2$ 1,3-Dioxepane | *338.7 ± 4.8* | | | | 66 |
| | 338.5 | 415.6 | 585.2 | 716.1 | This work |
| $C_4H_8O_4$ 1,3,5,7-Tetraoxocane | *345.7 ± 4.6* | | | | 84 |
| | 340.3 | 417.8 | 583.3 | 708.6 | This work |

[a] Experimental values of $S^\circ$(298.15 K) are italic.

TABLE 22

Comparison of heat capacity values $C^\circ_p(T)$ (J $K^{-1}$ $mol^{-1}$) calculated in different works

| $T$ (K) | $C_4H_8O_2$ 1,3-Dioxane | | $C_4H_8O_2$ 1,4-Dioxane | | | |
|---|---|---|---|---|---|---|
| | Ref. 28 | This work | Ref. 35 | Ref. 33 | Ref. 28 | This work |
| 298.15 | 89.4 | 89.4 | 94.1 | | 92.1 | 92.1 |
| 500 | 150.7 | 150.8 | 156.9 | 153.8 | 153.9 | 154.0 |
| 1000 | 241.4 | 241.5 | 242.9 | | 242.9 | 243.0 |
| 1500 | 281.3 | 281.4 | | | 281.9 | 282.1 |

The enthalpy of formation for 1,3,5,7-tetraoxocane (Table 19) was taken from the data of Pedley et al. [9].

Ideal gas thermodynamic properties for 1,3,5,7-tetraoxocane are given in Table 19. The calculated value of $S^\circ$(298.15 K) is about 5 J $K^{-1}$ $mol^{-1}$ lower than that obtained from calorimetric measurements [84] (Table 21). This discrepancy is essentially within the uncertainties of the experimental and calculated values. No other statistical calculations are available for comparison.

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