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Thermodynamic Parameters and Group Additivity Ring Corrections for Three- to Six-Membered Oxygen Heterocyclic Hydrocarbons

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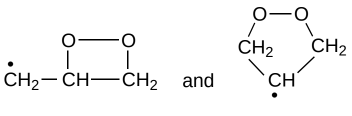
Ideal gas thermodynamic properties ($\Delta H_f°_{298}$, $S°_{298}$, and $C_p(T)$, $300 \leq T/\mathrm{K} \leq 1500$) for 34 cyclic oxygenated hydrocarbons are calculated using the PM3 method, including 12 species on which data are not previously reported. Enthalpies of formation obtained using PM3 are further corrected by $-1.642 + 0.882\Delta H_f°_{298,\mathrm{PM3}}$, which is obtained by comparison to experimentally-determined $\Delta H_f°_{298}$ of 10 cyclic oxygenated hydrocarbon molecules. Enthalpies of formation ($\Delta H_f°_{298}$, in kcal mol^{-1}) and entropy ($S°_{298}$, in cal mol^{-1} K^{-1}) for 12 species are calculated as follows: −57.24 and 64.10 for 1,3-dioxetane, 25.08 and 61.36 for dioxirene, −4.62 and 68.16 for 1,2-dioxolene, −49.03 and 66.11 for 1,3-dioxolene, 16.72 and 68.21 for 1,2,3-trioxolene, −32.96 and 73.79 for 1,2-dioxane, −11.45 and 75.07 for 3,4-dihydro-1,2-dioxin, −57.44 and 72.62 for 2,4-dihydro-1,3-dioxin, −59.82 and 73.30 for 1,2,4-trioxane, −13.05 and 74.80 for 1,2,3-trioxane, −38.08 and 74.68 for 1,2,4-trioxene, and 9.14 and 74.68 for 1,2,3-trioxane, respectively. $\Delta H_f°_{298}$ of seven molecules is different from previously estimated values by more than 4 kcal mol^{-1}. Our recommended $\Delta H_f°_{298}$ values (in kcal mol^{-1}) are: dioxirane (−2.47), 1,2-dioxetane (−6.38), 2,3-dihydrofuran (−23.52), 2,5-dihydrofuran (−20.90), 1,2-dioxolane (−27.42), 1,2,4-trioxolane (−59.12), and 3,6-dihydro-1,2-dioxin (−9.80). The standard deviations of $\Delta H_f°_{298}$ and $S°_{298}$ values determined in the present study are evaluated as 2.89 kcal/mol and 1.15 cal mol^{-1} K^{-1}. Group Additivity ring corrections for corresponding heterocyclics are derived.

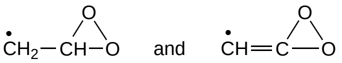
Introduction

Cyclic oxygenated hydrocarbons are important intermediates in chemical processes such as combustion, photochemical oxidation, and biological degradation of hydrocarbons. Many biological molecules including sugars, starches, nucleic acid segments, etc., include cyclic ethers in addition to alcohol moieties. The initial breakdown products of cellulose and similar natural materials in pyrolysis and combustion are cyclic and bicyclic oxygenated hydrocarbons (often radicals). Reactions of alkyl radicals with molecular oxygen in combustion processes form peroxy species, which react to form cyclic ethers[1] and hydroperoxides. Thermodynamic properties of these radical intermediates are the controlling parameters for pseudoequilibrium concentrations of these peroxy species, which in turn affect the overall rates of subsequent reactions leading to products in the combustion process.[2] These reactions can strongly influence flame speeds and completeness of conversion or mineralization (formation of CO_2 and H_2O).

Cyclic peroxy intermediates are formed in reactions of allylic and propargyl radicals with O_2, which are important in biological,[3] combustion,[1,4] and atmospheric photochemical oxidation systems.[5] For instance, the reaction of an allylic radical and O_2 initially forms an allylic peroxy radical, $CH_2{=}CHCH_2OO^\bullet$, which may isomerize to form primary and secondary alkyl radicals of cyclic peroxides:

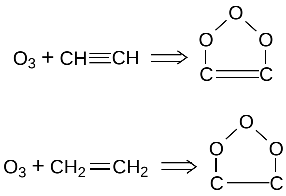


Cyclic peroxides are also formed in the reaction of vinyl, acetylenic, and phenyl radicals with O_2. Here the reactions initially form a peroxy radical ($CH_2{=}CHOO^\bullet$ or $CH{\equiv}COO^\bullet$) that reacts to form a three-membered ring, dioxirane alkyl radicals:



These radicals further react to form carbonyl and alkoxy radicals, via cleavage of the weak O−O bond.

Reactions of ozone with alkynes and alkenes in the atmosphere is another example where thermodynamic properties of cyclic oxygenated hydrocarbons are important. The reactions of ozone with alkynes and alkenes are assumed to proceed by addition to form a primary ozonide:[6,7]



Ideal gas thermodynamic properties of 22 oxygenated heterocyclic compounds of three- to six-membered rings were reported by Dorofeeva.[8,9] Enthalpies of formation of 10 cyclic oxygenated hydrocarbons (furan, oxirane, oxetane, 3,4-dihydro-2*H*-pyran, tetrahydrofuran, tetrahydro-2*H*-pyran, 1,3-dioxolane, 1,4-dioxane, 1,3-dioxane, and 1,3,5-trioxane) in her paper were adopted from experimental values which were originally quoted by Pedley *et al.*[10] Data on $\Delta H_f°_{298}$ for 12 other three- to six-membered ring species (oxirene, dioxirane, 1,2-dioxetane, 2,3-dihydrofuran, 2,5-dihydrofuran, 1,2-dioxolane, 1,2,3-trioxolane, 1,2,4-trioxolane, 3,6-dihydro-2*H*-pyran, 3,6-dihydro-1,2-dioxin, 2,3-dihydro-1,4-dioxin, and 1,4-dioxin) in Dorofeeva's work

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were estimated using a difference method, which is consistent with group additivity.[11] For instance, the value of $\Delta H_f{}^\circ{}_{298}$(3,6-dihydro-2*H*-pyran) was assumed to be the same as $\Delta H_f{}^\circ{}_{298}$(3,4-dihydro-2*H*-pyran). The enthalpy of formation of oxirene, as the second example, was estimated on the basis of the difference values between -CH$_2$- and -O- groups of similar ring compounds:

$$\underset{\text{unknown}}{\Delta H_f{}^\circ{}_{298}(\text{oxirene})} - \Delta H_f{}^\circ{}_{298}(\text{cyclopropene}) = \Delta H_f{}^\circ{}_{298}(\text{oxirane}) - \Delta H_f{}^\circ{}_{298}(\text{cyclopropane})$$

The enthalpy of formation of dioxirane was also estimated by applying this enthalpy difference method:

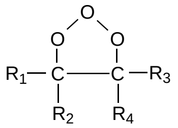
$$\underset{\text{unknown}}{\Delta H_f{}^\circ{}_{298}(\text{dioxirane})} - \Delta H_f{}^\circ{}_{298}(\text{oxirane}) = \Delta H_f{}^\circ{}_{298}(\text{dimethyl peroxide}) - \Delta H_f{}^\circ{}_{298}(\text{methoxyethane})$$

We shall show that the difference method does not yield accurate results for small ring species, i.e., three- to five-membered rings.

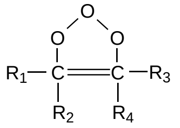
In this work we compare the $\Delta H_f{}^\circ{}_{298}$ data obtained from the semiempirical molecular orbital method PM3[12,13] with values previously reported. The experimentally-determined enthalpies of formation of 10 cyclic oxygenated hydrocarbons listed above are used as reference data to calibrate PM3-determined enthalpies of formation. An empirical equation is then obtained and used to calculate enthalpies of formation for 12 new cyclic oxygenated hydrocarbons: 1,3-dioxetane, dioxirene, 1,2-dioxolene, 1,3-dioxolene, 1,2,3-trioxolene, 1,2-dioxane, 3,4-dihydro-1,2-dioxin, 2,4-dihydro-1,3-dioxin, 1,2,4-trioxane, and 1,2,3-trioxane, 1,2,4-trioxene, 1,2,3-trioxane.

Structural parameters and fundamental frequencies resulting from either experiments or ab initio calculations have been adopted in Dorofeeva's work to calculate entropies and heat capacities for 13 oxygen heterocyclics.[8,9] Vibrational frequencies of remaining molecules in her work were estimated on the basis of the force constants evaluated from related compounds. The frequencies of 1,2-dioxolane were calculated, for instance, using 20 force constants transferred from tetrahydrofuran and 1,2,4-trioxolane. It is known that the PM3 method provides an economical way to obtain molecular structural parameters, fundamental frequencies, and subsequent thermodynamic properties.[14] We are, therefore, interested in comparing PM3-determined values with the data reported by Dorofeeva. We also evaluate and report the uncertainties of entropies and heat capacities obtained using the PM3 method.

Benson's group additivity technique is commonly used for the estimation of gas phase enthalpies of formation, heat capacities, and entropies.[11,15] The method assumes that the properties for a chemical substance are the sum of the contributions from each polyvalent atom (central atoms) in that molecule. Ring corrections are needed for ring compounds as group values are derived from noncyclic (chain) species. Groups for ring species considered in the present study are derived. The ring group corrections, once obtained, allow determination of the thermodynamic properties for cyclic compounds with alkyl substituents, which frequently appear in atmospheric oxidation systems. Examples are alkyl-substituted ozonides:



and



Thermodynamic properties ($\Delta H_f{}^\circ{}_{298}$, $S^\circ{}_{298}$, and $C_p(T)$, $300 \leq T/\text{K} \leq 1500$) on a total of 34 cyclic oxygenated hydrocarbons, which include 22 previously studied species and 12 new species listed above, are calculated in this study. The corresponding ring groups for use in group additivity are also derived.

Calculation Method

Thermodynamic properties are calculated for compounds in an ideal gas standard state at 1 atm. The standard state for molecules with optical isomers is defined as an equilibrium mixture of enantiomers at the total pressure 1 atm.

Optimized molecular geometry, moments of inertia for external rotation, and vibrational frequencies were obtained using the PM3[12,13] method in the MOPAC 6.0[16] computer package. The restricted Hartree−Fock method with the self-consistent-field molecular orbital treatment using the PM3 parameter set is employed for the calculations of all molecules. It should be noted that PM3 parameters were optimized to reproduce experimental data on enthalpies of formation and molecular geometries observed at 298 K, not the energies of molecules (E_{eq}) or equilibrium geometry at 0 K.[17]

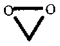
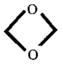
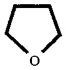
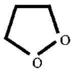
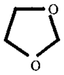
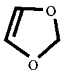
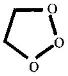
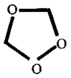
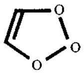
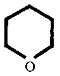
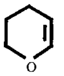
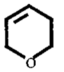
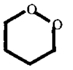
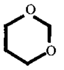
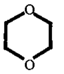
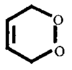
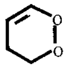
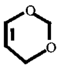
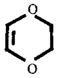
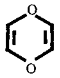
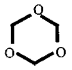
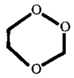
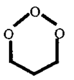
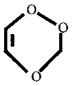
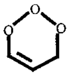
Enthalpies of formation of 10 cyclic oxygenated hydrocarbons (furan, oxirane, oxetane, 3,4-dihydro-2*H*-pyran, tetrahydrofuran, tetrahydro-2*H*-pyran, 1,3-dioxiolane, 1,4-dioxane, 1,3-dioxane, and 1,3,5-trioxane) have been previously determined by experiments.[10] These enthalpy values are used as reference data to calibrate PM3-determined enthalpies of formation ($\Delta H_f{}^\circ{}_{298,\text{PM3}}$). Enthalpies of formation for species where no experimental data exist are obtained using the PM3 method and corrected by this scaling equation. Calculations of standard entropies and heat capacities are implemented by MOPAC 6.0 with its internal programs which are based on the statistical mechanics. The anharmonicity of ring inversion (puckering) of oxetane, tetrahydrofuran, 2,3-dihydrofuran, 2,5-dihydrofuran, 1,3-dioxolane, and 1,3,5-trioxane is considered to be important in the determination of entropies and heat capacities.[8,9] Contributions to $S^\circ{}_{298}$ and $C_p(T)$ from ring inversions of these compounds calculated by Dorofeeva[8,9] using direct summation over energy levels are adopted in this work to replace the corresponding harmonic ring puckering frequencies (one from each molecule) determined using the PM3 method.

The absolute standard deviation (s) of enthalpies of formation determined in this work is calculated by root-mean-square: $s = [\Sigma\delta_i{}^2/(n-1)]^{1/2}$. Experimentally determined enthalpies of formation of the 10 molecules listed above are used as reference data in the calculation of the $s_{\Delta H_f{}^\circ{}_{298}}$ value of regressed, PM3-determined $\Delta H_f{}^\circ{}_{298}$ values. The $\Delta H_f{}^\circ{}_{298}$ data estimated by Dorofeeva are used neither in the calibration of PM3-determined $\Delta H_f{}^\circ{}_{298}$ nor in the calculation of absolute standard deviation (s).

Limited experimental data on entropies and heat capacities of these molecules are available. The entropy and heat capacity data of 22 molecules reported by Dorofeeva are therefore used as reference data to calculate the absolute standard deviations of entropies at 298 K and heat capacities from 300 to 1500 K resulting from the PM3 method. The absolute standard deviations (s) for entropies and heat capacities determined in this work are also calculated by root-mean-square.

Cyclic group parameters are derived using the thermodynamic properties from the literature or those obtained in the present study as described later for each molecule. Derivation of cyclic group values utilizes noncyclic group values reported by Benson and Cohen[11,18] and authors' reassignments based on recent literature data[4,19−23] on standard enthalpies of formation for corresponding compounds.

TABLE 1: Vibrational Frequencies (ν, cm^{-1}) and Moments of Inertia (I, 10^{-40} $g \cdot cm^2$), Calculated Using the PM3 Method

1		Oxirane	ν: 793, 893, 916, 932, 1015, 1072, 1142, 1176, 1300, 1358, 1575, 3038, 3053, 3063, 3064. I: 32.50, 39.08, 60.57.
2		Oxirene	ν: 669, 748, 844, 937, 1021, 1195, 1948, 3245, 3295. I: 26.16, 29.34, 55.50.
3		Dioxirane	ν: 750, 923, 924, 1006, 1193, 1265, 1552, 2938, 2949. I: 27.97, 37.38, 59.78.
4[a]		Oxetane	ν: 263, 825, 840, 873, 949, 957, 976, 999, 1012, 1064, 1116, 1190, 1207, 1262, 1314, 1374, 1397, 1440, 3001, 3007, 3045, 3049, 3057, 3122. I: 70.87, 71.10, 125.96.
5		1,2-Dioxetane	ν: 250, 800, 830, 840, 948, 977, 980, 1012, 1085, 1207, 1288, 1290, 1373, 1420, 2982, 2997, 3038, 3038. I: 61.87, 72.24, 123.38.
6		1,3-Dioxetane	ν: 234, 906, 914, 922, 923, 947, 988, 1005, 1059, 1213, 1229, 1334, 1360, 1427, 2956, 2960, 2970, 2974, I: 59.91, 66.05, 114.9.
7		Dioxirene	ν: 441, 775, 842, 863, 927, 980, 1011, 1276, 1339, 1756, 3154, 3180. I: 51.38, 60.52, 111.90.
8[a]		Tetrahydrofuran	ν: 75, 116, 679, 716, 780, 828, 932, 975, 1001, 1022, 1026, 1066, 1075, 1108, 1117, 1127, 1132, 1282, 1290, 1303, 1359, 1377, 1392, 1413, 1433, 2964, 2968, 2984, 2998, 3033, 3036, 3070, 3075. I: 117.68, 122.22, 217.55.
9[a]		2,3-Dihydrofuran	ν: 220, 442, 732, 766, 826, 840, 924, 951, 981, 1034, 1037, 1057, 1079, 1089, 1173, 1258, 1312, 1369, 1393, 1417, 1789, 2980, 2996, 3038, 3066, 3111, 3163. I: 103.96, 107.84, 201.22.
10[a]		2,5-Dihydrofuran	ν: 209, 395, 756, 760, 796, 889, 939, 954, 977, 982, 1003, 1046, 1074, 1080, 1152, 1242, 1322, 1348, 1377, 1390, 1816, 2960, 2964, 3011, 3013, 3137, 3155. I: 103.99, 107.98, 201.22.
11		Furan	ν: 502, 516, 764, 774, 872, 877, 883, 944, 979, 1026, 1069, 1102, 1290, 1313, 1486, 1611, 1697, 3128, 3134, 3166, 3178. I: 89.96, 92.47, 182.43.
12[b]		1,2-Dioxolane	ν: 85, 165, 649, 666, 784, 794, 905, 999, 1000, 1042, 1058, 1084, 1092, 1119, 1123, 1291, 1334, 1343, 1383, 1387, 1421, 2961, 2962, 2996, 3029, 3030, 3076. I: 110.65, 121.72, 213.21.
13[a]		1,3-Dioxolane	ν: 143, 172, 683, 738, 831, 908, 995, 956, 986, 998, 1038, 1073, 1085, 1100, 1142, 1275, 1288, 1350, 1365, 1380, 1403, 2917, 2972, 2983, 2987, 3037, 3040. I: 109.5, 110.95, 201.57.
14		1,2-Dioxolene	ν: 183, 416, 686, 747, 759, 880, 886, 952, 981, 998, 1048, 1052, 1191, 1348, 1366, 1393, 1789, 2956, 2999, 3098, 3165. I: 95.70, 109.32, 199.61.
15		1,3-Dioxolene	ν: 216, 436, 712, 776, 864, 865, 917, 919, 941, 999, 1036, 1098, 1248, 1252, 1349, 1386, 1780, 2939, 2955, 3127, 3148. I: 96.12, 97.41, 188.01.
16		1,2,3-Trioxolane	ν: 113, 239, 450, 578, 718, 750, 832, 976, 1003, 1044, 1064, 1069, 1111, 1301, 1330, 1374, 1384, 2965, 2978, 3041, 3045. I: 105.80, 112.96, 200.04.
17		1,2,4-Trioxolane	ν: 147, 248, 619, 666, 785, 895, 904, 942, 980, 1034, 1058, 1140, 1150, 1324, 1355, 1360, 1375, 2905, 2909, 2981, 2989. I: 96.09, 113.82, 192.88.
18		1,2,3-Trioxolene	ν: 203, 393, 609, 619, 749, 777, 861, 904, 962, 991, 1280, 1381, 1806, 3103, 3123. I: 92.73, 102.87, 195.60.
19		Tetrahydro-2H-pyran	ν: 182, 225, 356, 479, 482, 620, 823, 871, 936, 948, 958, 970, 1002, 1038, 1076, 1080, 1112, 1133, 1137, 1141, 1150, 1157, 1278, 1319, 1321, 1346, 1365, 1373, 1380, 1404, 1411, 1414, 2941, 2944, 2959, 2971, 2978, 3039, 3041, 3042, 3050, 3055. I: 179.03, 187.20, 323.64.
20		3,4-Dihydro-2H-pyran	ν: 153, 238, 406, 519, 534, 735, 775, 872, 932, 941, 967, 993, 1025, 1051, 1052, 1089, 1108, 1130, 1148, 1150, 1293, 1330, 1341, 1370, 1390, 1412, 1434, 1855, 2951, 2958, 2978, 3033, 3035, 3054, 3070, 3092. I: 162.17, 176.05, 312.14.
21		3,6-Dihydro-2H-pyran	ν: 127, 277, 366, 532, 539, 704, 789, 864, 952, 968 983, 995, 1026, 1040, 1053, 1088, 1099, 1110, 1138, 1164 1262, 1379, 1346, 1353, 1383, 1392, 1428, 1873, 2924, 2943 2959, 3025, 3034, 3041, 3060, 3081. I: 165.55, 172.94, 313.30.
22		1,2-Dioxane	ν: 226, 228, 372, 462, 498, 630, 693, 870, 907, 948, 979, 982, 1043, 1081, 1089, 1117, 1127, 1133, 1142, 1149, 1289, 1327, 1347, 1352, 1370, 1375, 1400, 1411, 2944, 2953, 2972, 2981, 3034, 3042, 3044, 3050. I: 177.58, 181.37, 319.11.
23		1,3-Dioxane	ν: 170, 250, 362, 484, 516, 644, 862, 897, 938, 974, 985, 1009, 1032, 1047, 1107, 1110, 1120, 1125, 1128, 1158, 1279, 1307, 1330, 1343, 1365, 1369, 1378, 1406, 2890, 2943, 2945, 2987, 3022, 3042, 3043, 3063. I: 171.50, 172.33, 307.14.
24		1,4-Dioxane	ν: 168, 278, 349, 510, 512, 672, 833, 929, 963, 977, 986, 1021, 1036, 1041, 1076, 1091, 1117, 1124, 1129, 1150, 1302, 1306, 1334, 1359, 1366, 1371, 1378, 1379, 2953, 2955, 2965, 2967, 3041, 3044, 3048, 3051. I: 165.84, 182.59, 312.98.
25		3,6-Dihydro-1,2-dioxin	ν: 196, 300, 394, 501, 541, 718, 741, 855, 902, 975, 1021, 1022, 1038, 1064, 1067, 1097, 1114, 1153, 1275, 1330, 1351, 1376, 1418, 1868, 2936, 2936, 3024, 3024, 3070, 3089. I: 159.50, 171.20, 305.83.
26		3,4-Dihydro-1,2-dioxin	ν: 120, 278, 405, 503, 535, 695, 741, 825, 899, 952 979, 1021, 1046, 1082, 1095, 1114, 1129, 1146, 1316, 1347 1376, 1389, 1445, 1857, 2949, 2964, 3036, 3041, 3063, 3089. I: 161.82, 169.81, 310.45.
27		2,4-Dihydro-1,3-dioxin	ν: 165, 278, 408, 520, 568, 758, 827, 897, 937, 965 993, 1015, 1031, 1054, 1078, 1099, 1111, 1159, 1274, 1322 1340, 1366, 1418, 1838, 2908, 2943, 3016, 3025, 3076, 3107 I: 154, 161, 294.
28		2,3-Dihydro-1,4-dioxin	ν: 174, 228, 434, 556, 557, 769, 793, 872, 933, 974 998, 1012, 1043, 1056, 1081, 1102, 1110, 1200, 1316, 1330 1359, 1375, 1405, 1840, 2958, 2971, 3038, 3042, 3081, 3099 I: 150, 170, 301.
29		1,4-Dioxin	ν: 142, 386, 475, 597, 654, 774, 779, 876, 898, 921 1026, 1036, 1044, 1047, 1137, 1182, 1316, 1383, 1814, 188 3078, 3082, 3096, 3101. I: 135.11, 155.73, 290.84.
30[a]		1,3,5-Trioxane	ν: 223, 232, 369, 499, 501, 656, 927, 930, 934, 938, 957, 1054, 1071, 1076, 1079, 1105, 1141, 1146, 1236, 1325, 1328, 1337, 1360, 1361, 2887, 2889, 2891, 3018, 3018, 302 I: 159.06, 159.80, 286.41.
31		1,2,4-Trioxane	ν: 213, 245, 369, 475, 491, 660, 705, 884, 960, 988, 998, 1025, 1034, 1085, 1099, 1110, 1121, 1160, 1299, 1323, 133 1367, 1371, 1379, 2901, 2952, 2965, 3017, 3040, 3048, I: 162.30, 174.04, 301.83.
32		1,2,3-Trioxane	ν: 213, 244, 369, 475, 491, 660, 705, 884, 960, 988, 998, 1025, 1034, 1085, 1099, 1110, 1121, 1160, 1299, 1323, 1337, 1367, 1371, 1379, 2901, 2952, 2965, 3017, 3040, 3048 I: 162.30, 174.04, 301.83.
33		1,2,4-Trioxene	ν: 109, 296, 433, 514, 528, 678, 773, 865, 874, 951, 984, 1009, 1042, 1072, 1130, 1203, 1282, 1367, 1423, 1804, 2913, 3004, 3071, 3095. I: 147.41, 161.58, 289.06.
34		1,2,3-Trioxene	ν: 161, 303, 366, 409, 483, 576, 680, 753, 865, 907, 991, 1022, 1041, 1069, 1095, 1123, 1319, 1344, 1423, 1845, 2947, 3030, 3067, 3107, I: 151.24, 164.60, 294.66.

[a] One ring-puckering frequency is not listed. [b] Frequencies calculated at the RHF/6-31G* level of theory for 1,2-dioxolane (scaled by 0.9): 114, 326, 657, 685, 800, 901, 912, 930, 959, 1010, 1112, 1155, 1224, 1243, 1245, 1306, 1333, 1387, 1478, 1493, 1508, 2915, 2917, 2930, 2956, 2981, and 2986.

TABLE 2: Thermodynamic Properties[a] of Cyclic Oxygenated Hydrocarbons

	compound	$\Delta H_f°_{298}$	$S°_{298}$	C_{p300}	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}
1	oxirane (σ = 2, OI = 1)[b]									
	this work	−8.81	58.14	11.58	15.09	18.25	20.85	24.78	27.60	31.88
	ref 8[c]	**−12.57**	**57.98**	**11.30**	**14.74**	**17.90**	**20.55**	**24.57**	**27.46**	**31.28**
2	oxirene (σ = 2, OI = 1)									
	this work	**44.63**	57.50	11.22	13.44	15.22	16.62	18.69	20.18	22.49
	ref 8	40.63	**58.70**	**13.00**	**15.12**	**16.68**	**17.86**	**19.62**	**20.89**	**22.91**
3	dioxirane (σ = 2, OI = 1)									
	this work	**−2.47**	57.81	10.47	12.71	14.69	16.30	18.69	20.34	22.75
	ref 8	8.36	**57.69**	**10.53**	**12.80**	**14.78**	**16.38**	**18.73**	**20.35**	**22.72**
4	oxetane (σ = 2, OI = 1)									
	this work	−25.20	64.78	14.82	20.27	25.20	29.27	35.38	39.71	46.24
	ref 8[c]	**−19.24**	**64.87**	**14.80**	**20.07**	**24.91**	**28.99**	**35.24**	**39.70**	**46.35**
5	1,2-dioxetane (σ = 2, OI = 1)									
	this work	−6.38	62.90	14.25	18.58	22.36	25.42	29.98	33.05	37.64
	ref 8	2.39	**62.23**	**13.62**	**17.80**	**21.57**	**24.71**	**29.49**	**32.73**	**37.53**
6	1,3-dioxetane (σ = 2, OI = 1)									
		−57.24	64.10	14.00	18.30	22.20	25.30	29.90	33.10	37.70
7	dioxirene (σ = 2, OI = 1)									
		25.08	61.36	12.81	15.91	18.47	20.49	23.38	25.33	28.12
8	tetrahydrofuran (σ = 2, OI = 1)									
	this work	−46.87	71.53	19.54	26.81	33.39	38.85	47.09	52.94	61.72
	ref 8[c]	**−44.02**	**72.26**	**18.45**	**25.59**	**32.13**	**37.64**	**46.07**	**52.08**	**60.97**
9	2,3-dihydro-furan (σ = 1, OI = 1)									
	this work	**−23.52**	69.40	17.19	23.44	28.91	33.37	40.02	44.70	51.67
	ref 8	−17.92	**69.92**	**17.86**	**24.01**	**29.40**	**33.82**	**40.46**	**45.14**	**52.03**
10	2,5-dihydro-furan (σ = 2, OI = 1)									
	this work	**−20.90**	67.69	17.69	23.93	29.38	33.81	40.40	45.03	51.93
	ref 8	−16.73	**67.95**	**18.20**	**24.41**	**29.80**	**34.20**	**40.79**	**45.42**	**52.24**
11	furan (σ = 2, OI = 1)									
	this work	−5.19	64.21	15.75	20.97	25.38	28.91	34.05	37.58	42.76
	ref 8[c]	**−8.34**	**63.87**	**15.74**	**21.22**	**25.77**	**29.34**	**34.45**	**37.91**	**42.95**
12	1,2-dioxolane (σ = 2, OI = 2)									
	this work	**−27.42**	71.93	18.81	24.91	30.28	34.68	41.22	45.80	52.89
	ref 8	−21.51	**68.67**	**18.51**	**24.78**	**30.26**	**34.73**	**41.37**	**46.01**	**52.79**
13	1,3-dioxolane (σ = 2, OI = 1)									
	this work	−74.38	72.37	17.48	23.64	29.11	33.58	40.20	44.82	51.63
	ref 8[c]	**−71.22**	**71.66**	**17.08**	**22.89**	**28.22**	**32.72**	**39.56**	**44.39**	**51.47**
14	1,2-dioxolene (σ = 1, OI = 1)									
		−4.62	68.16	17.18	22.24	26.48	29.87	34.80	38.20	43.15
15	1,3-dioxolene (σ = 2, OI = 1)									
		−49.03	66.11	16.87	22.00	26.32	29.76	34.75	38.18	43.16
16	1,2,3-trioxolane (σ = 1, OI = 1)									
	this work	**−7.09**	71.28	18.84	23.71	27.78	31.00	35.68	38.88	43.56
	ref 8	−23.90	**71.87**	**18.72**	**23.54**	**27.62**	**30.89**	**35.65**	**38.92**	**43.64**
17	1,2,4-trioxolane (σ = 2, OI = 2)									
	this work	**−59.12**	69.85	17.77	22.78	27.03	30.43	35.35	38.71	43.53
	ref 8	−50.19	**68.17**	**16.55**	**21.44**	**25.77**	**29.32**	**34.54**	**38.12**	**43.24**
18	1,2,3-trioxolene (σ = 1, OI = 1)									
		16.72	68.21	16.94	20.72	23.65	25.89	29.02	31.10	34.02
19	tetrahydro-2*H*-pyran (σ = 1, OI = 1)									
	this work	−52.28	74.43	23.83	32.96	41.17	48.00	58.32	65.67	76.67
	ref 9[c]	**−53.39**	**73.72**	**23.86**	**32.77**	**40.87**	**47.73**	**58.27**	**65.80**	**76.94**
20	3,4-dihydro-2*H*-pyran (σ = 1, OI = 2)									
	this work	−31.00	74.89	22.48	30.44	37.45	43.22	51.90	58.06	67.23
	ref 9[c]	**−29.90**	**74.36**	**22.17**	**29.96**	**36.96**	**42.82**	**51.73**	**58.04**	**67.35**
21	3,6-dihydro-2*H*-pyran (σ = 1, OI = 2)									
	this work	**−29.24**	75.12	22.52	30.49	37.51	43.29	51.98	58.13	67.29
	ref 9	−29.90	**74.54**	**22.75**	**30.69**	**37.69**	**43.49**	**52.26**	**58.46**	**67.58**
22	1,2-dioxane (σ = 2, OI = 2)									
		−32.96	73.79	23.12	31.11	38.13	43.88	52.48	58.54	67.52
23	1,3-dioxane (σ = 1, OI = 1)									
	this work	−79.06	73.84	22.66	30.71	37.84	43.68	52.39	58.50	67.54
	ref 9[c]	**−81.81**	**72.44**	**21.50**	**29.05**	**36.04**	**42.01**	**51.19**	**57.71**	**67.25**
24	1,4-dioxane (σ = 2, OI = 1)									
	this work	−74.95	72.31	22.53	30.62	37.76	43.61	52.33	58.44	67.49
	ref 9[c]	**−75.48**	**71.53**	**22.16**	**29.82**	**36.80**	**42.70**	**51.70**	**58.08**	**67.43**
25	3,6-dihydro-1,2-dioxin (σ = 2, OI = 2)									
	this work	**−9.80**	72.73	21.62	28.49	34.35	39.09	46.09	50.96	58.13
	ref 9	−4.78	**71.34**	**20.91**	**27.74**	**33.65**	**38.50**	**45.73**	**50.78**	**58.11**
26	3,4-dihydro-1,2-dioxin (σ = 1, OI = 2)									
		−11.45	75.07	21.78	28.54	34.34	39.04	46.02	50.89	58.08
27	2,4-dihydro-1,3-dioxin (σ = 1, OI = 1)									
		−57.44	72.62	21.31	28.22	34.15	38.94	46.01	50.92	58.12
28	2,3-dihydro-1,4-dioxin (σ = 2, OI = 2)									
	this work	**−53.62**	72.78	21.25	28.13	34.04	38.82	45.89	50.81	58.03
	ref 9	−57.36	**72.07**	**20.46**	**27.39**	**33.30**	**38.19**	**45.49**	**50.58**	**57.99**

TABLE 2 (Continued)

	compound	$\Delta H_f°_{298}$	$S°_{298}$	C_{p300}	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}
29	1,4-dioxin ($\sigma = 4$, OI = 1)									
	this work	**−30.87**	68.72	19.74	25.50	30.23	34.00	39.43	43.16	48.57
	ref 9	−33.46	**69.42**	**19.54**	**25.37**	**30.14**	**33.89**	**39.28**	**42.95**	**48.23**
30	1,3,5-trioxane ($\sigma = 3$, OI = 1)									
	this work	−109.62	70.89	21.71	28.68	34.68	39.51	46.58	51.45	58.48
	ref 9[c]	**−111.35**	**68.95**	**19.69**	**26.23**	**32.22**	**37.26**	**44.88**	**50.20**	**57.85**
31	1,2,4-trioxane ($\sigma = 1$, OI = 2)									
		−59.82	74.68	22.00	28.90	34.80	39.60	46.60	51.40	58.40
32	1,2,3-trioxane ($\sigma = 1$, OI = 1)									
		−13.05	74.80	23.40	30.10	35.70	40.30	47.00	51.60	58.50
33	1,2,4-trioxene ($\sigma = 1$, OI = 2)									
		−38.08	74.68	20.80	26.50	31.20	34.90	40.20	43.80	49.00
34	1,2,3-trioxane ($\sigma = 1$, OI = 1)									
		9.14	73.60	21.90	27.50	31.90	35.40	40.50	44.00	49.10

[a] For the compounds where two sets of data are listed, the numbers in bold are selected in the derivation of ring group values in Table 3. [b] σ, symmetry number; OI, number of optical isomers. Assignments of σ and OI are consistent with those of Dorofeeva in refs 8 and 9. [c] Enthalpies of formation taken from ref 10.

TABLE 3: Ring Group Values of Cyclic Oxygenated Hydrocarbons

molecule	$\Delta H_f°_{298}$	$S°_{298}$	C_{p300}	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}
oxirane	26.83	31.08	−2.08	−2.66	−2.40	−2.11	−2.05	−1.80
oxirene	56.42	34.08	1.20	1.42	1.38	1.06	0.02	−0.51
dioxirane	41.96	32.57	−2.77	−2.77	−2.67	−2.65	−2.98	−3.59
oxetane	25.16	28.55	−4.08	−4.28	−3.64	−3.02	−2.45	−1.90
1,2-dioxetane	31.39	26.93	−4.16	−4.52	−4.23	−3.83	−3.37	−3.53
1,3-dioxetane	24.96	27.90	−3.82	−2.99	−1.75	−1.03	−1.07	−0.83
dioxirene	19.97	26.50	−2.59	−1.83	−1.03	−0.81	−1.28	−1.25
tetrahydrofuran	5.20	26.52	−5.93	−5.71	−4.67	−3.72	−2.69	−1.86
2,3-dihydrofuran	8.02	24.65	−4.52	−4.04	−3.43	−2.94	−2.44	−2.32
2,5-dihydrofuran	2.89	25.11	−3.76	−3.07	−2.16	−1.58	−1.35	−1.04
furan	−6.11	26.49	−4.98	−4.06	−3.03	−2.30	−1.85	−1.71
1,2-dioxolane	12.49	22.57	−4.77	−4.49	−3.79	−3.16	−2.56	−2.59
1,3-dioxolane	12.18	26.66	−5.20	−5.16	−4.03	−3.09	−2.53	−1.81
1,2-dioxolene	−2.05	23.73	−3.70	−2.83	−2.00	−1.61	−1.72	−1.82
1,3-dioxolene	15.69	22.67	−4.85	−3.57	−2.73	−2.27	−2.16	−2.56
1,2,3-trioxolane	15.74	25.79	−1.26	−2.42	−2.38	−1.99	−1.83	−2.24
1,2,4-trioxolane	27.41	23.57	−5.65	−4.78	−3.63	−2.86	−2.64	−2.76
1,2,3-trioxolene	2.14	22.57	−0.66	−0.66	−0.05	0.25	−0.26	−0.38
tetrahydro-2*H*-pyran	1.01	17.18	−6.02	−5.48	−4.18	−2.98	−1.56	−0.48
3,4-dihydro-2*H*-pyran	1.04	18.29	−5.71	−5.04	−4.12	−3.29	−2.24	−1.76
3,6-dihydro-2*H*-pyran	−4.12	19.14	−4.20	−3.64	−2.57	−1.72	−0.99	−0.33
1,2-dioxane	7.10	18.27	−5.66	−5.11	−4.17	−3.36	−2.52	−2.40
1,3-dioxane	6.59	16.64	−6.28	−5.95	−4.46	−3.15	−1.97	−0.83
1,4-dioxane	3.32	16.35	−4.60	−4.98	−3.80	−2.62	−1.54	−0.44
3,6-dihydro-1,2-dioxin	4.44	18.72	−5.45	−4.66	−3.81	−3.16	−2.65	−2.68
3,4-dihydro-1,2-dioxin	−2.87	19.46	−4.09	−3.38	−2.44	−1.87	−1.61	−1.46
2,4-dihydro-1,3-dioxin	7.12	19.05	−4.98	−3.63	−2.33	−1.54	−1.25	−1.15
2,3-dihydro-1,4-dioxin	2.02	17.07	−5.74	−4.93	−4.10	−3.35	−2.57	−2.48
1,4-dioxin	−1.88	20.17	−4.06	−2.03	−0.46	0.29	0.08	0.15
1,3,5-trioxane	20.65	16.83	−7.01	−5.72	−3.63	−2.19	−1.53	−0.62
1,2,4-trioxane	7.04	18.53	−4.65	−4.05	−2.93	−2.11	−1.77	−1.82
1,2,3-trioxane	11.77	19.26	−2.05	−2.83	−2.53	−1.96	−1.58	−1.87
1,2,4-trioxene	3.81	23.14	−5.47	5.84	−5.50	−5.01	−4.46	−4.16
1,2,3-trioxene	3.87	21.54	−1.69	−2.71	−2.59	−2.23	−2.11	−2.07

Results and Discussion

Vibrational frequencies and moments of inertia are listed in Table 1. Thermodynamic properties, $\Delta H_f°_{298}$, $S°_{298}$, and $C_p(T)$ ($300 \leq T/\mathrm{K} \leq 1500$), are listed in Table 2. Parameters of ring groups are listed in Table 3.

The comparison of experimentally- versus PM3-determined enthalpies of formation is illustrated in Figure 1. A regressed line with an R^2 value equal to 0.993 is obtained in eq 1:

$$\Delta H_f{}^{\circ}{}_{298,\mathrm{expt}} = -1.642 + 0.882\Delta H_f{}^{\circ}{}_{298,\mathrm{PM3}} \qquad (1)$$

The standard deviation of the scaled PM3 enthalpies of formation using eq 1 versus experimental values is 3.16 kcal/mol. Enthalpies of formation of this work listed in Table 2 are calculated using eq 1. Absolute differences between enthalpies of formation obtained using eq 1 versus those reported by Dorofeeva range from 0.5 (1,4-dioxane) to 16.8 kcal/mol (1,2,3-trioxolane).

There is no experimental data on $\Delta H_f°_{298}$(1,2,3-trioxolane). It was estimated by Dorofeeva to be −23.90 kcal/mol[8] using the difference method described above. The value determined using eq 1 is, however, −7.09 kcal/mol. Jungkamp and Seinfeld[24] recently reported enthalpies of formation for the three trioxy compounds: HOOOH, CH_3OOOH, and C_2H_5OOOH to be −21.82, −21.34, and −28.52 kcal mol^{-1}, respectively. These values are determined using ab initio calculations at the G2, G2M, and G2M/MP2 levels of theory, respectively. The $\Delta H_f°_{298}$ data calculated by PM3 for these three species are −27.39, −22.86, and −25.92 kcal mol^{-1}, and after being scaled by eq 1, they are −25.80, −21.80, and −24.50 kcal mol^{-1},

TABLE 4: Comparison of Enthalpies of Formation (kcal/mol) for HOOOH, CH_3OOOH, and C_2H_5OOOH

	data in ref 24	PM3, unscaled (diff)	PM3, scaled[a] (diff)
HOOOH	−21.82	−27.39 (−5.57)	−25.80 (−3.98)
CH_3OOOH	−21.34	−22.86 (−1.52)	−21.80 (−0.46)
C_2H_5OOOH	−28.52	−25.92 (+2.6)	−24.50 (+4.02)

[a] Scaled using eq 1; see text.

TABLE 5: Group Values Used To Derive the Ring Corrections in Table 3

group	$\Delta H_f°_{298}$	$S°_{298}$	C_{p300}	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	note
C/H2/O2	−20.80	9.42	5.50	6.95	8.25	9.35	11.07	12.34	*a*
C/C/CD/H2	−4.80	9.80	5.12	6.86	8.32	9.49	11.22	12.48	ref 18
C/C/H2/O	−8.10	9.80	4.99	6.85	8.30	9.43	11.11	12.33	ref 11
C/C2/H2	−5.00	9.42	5.50	6.95	8.25	9.35	11.07	12.34	ref 18
C/CD/H2/O	−6.76	9.80	5.12	6.86	8.32	9.49	11.22	12.48	ref 18
C/CD2/H2	−4.30	10.20	4.70	6.80	8.40	9.60	11.30	12.60	ref 18
CD/H/O	2.03	6.20	4.75	6.46	7.64	8.35	9.10	9.56	*b*
CD/C/H	8.55	7.97	4.16	5.03	5.81	6.50	7.65	8.45	ref 18
CD/CD/H	6.78	6.38	4.46	5.79	6.75	7.42	8.35	9.11	ref 18
O/C/cd	−23.62	9.70	3.91	4.31	4.60	4.84	5.32	5.80	*c*
O/C2	−23.20	8.68	3.40	3.70	3.70	3.80	4.40	4.60	ref 18
O/CD2	−19.85	10.00	3.40	3.70	3.70	3.80	4.40	4.60	*d*
O/CD/O	1.64	10.12	3.50	3.87	3.95	4.15	4.73	4.89	*e*
O/C/O	−6.40	8.54	3.90	4.31	4.60	4.84	5.32	5.80	*f*
O/O2	9.30	9.40	2.20	3.64	4.20	4.34	4.62	4.90	*g*

[a−g] The groups derived by authors on the basis of the following: [a] $\Delta H_f°_{298}$ ($CH_2(OH)_2$) = −96.6 kcal mol^{-1} (Melius, C. F. *BAC-MP4 Heats of Formation and Free Energies*, Sandia National Laboratories, Livermore, CA, 1993). [b] O/CD/H = −37.9 and $\Delta H_f°_{298}$(vinyl alcohol)[19,22] = −29.8 kcal mol^{-1}. [c] $\Delta H_f°_{298}$($CH_3CH_2OCHCH_2$)[23] = −33.63 kcal mol^{-1} [d] $\Delta H_f°_{298}$($CH_2CHOCHCH_2$)[23] = −3.27 kcal mol^{-1}. [e] O/H/O = −16.3 and $\Delta H_f°_{298}$(CH_2CHOOH)[4] = −6.37 kcal mol^{-1}. [f] $\Delta H_f°_{298}$(CH_3OOH)[20] = −32.2 kcal mol^{-1}. [g] $\Delta H_f°_{298}$(HOOOH) = −22.94 kcal mol^{-1} and $\Delta H_f°_{298}$ (CH_3OOOH) = −23.8 kcal mol^{-1}, authors' unpublished results.

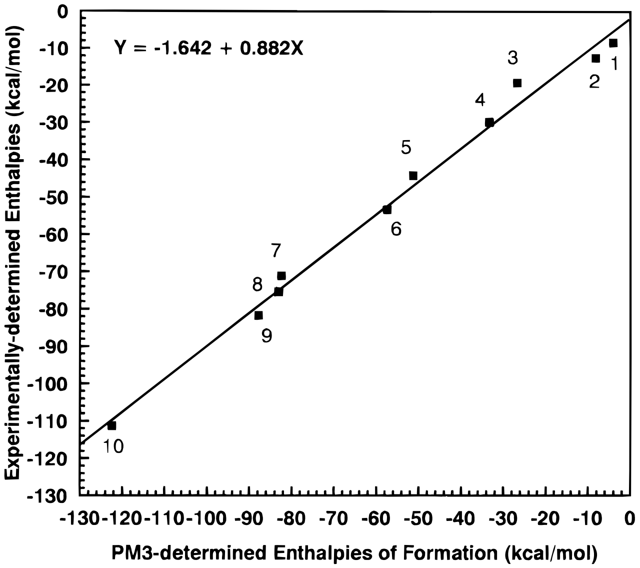


Figure 1. Comparison of PM3-determined and experimentally-determined enthalpies of formation (1, furan; 2, oxirane; 3, oxetane; 4, 3,4-dihydro-2*H*-pyran; 5, tetrahydrofuran; 6, tetrahydro-2*H*-pyran; 7, 1,3-dioxiolane; 8, 1,4-dioxane; 9, 1,3-dioxane; 10, 1,3,5-trioxane).

respectively, as shown in Table 4. The maximum deviation of scaled PM3-calculated $\Delta H_f°_{298}$ data from the values reported by Jungkamp *et al*. is 4.02 kcal mol^{-1}. The PM3-determined $\Delta H_f°_{298}$(1,2,3-trioxolane) value with 4.02 kcal/mol uncertainty, −7.09 ± 4.02 kcal mol^{-1}, indicates that Dorofeeva's data, −23.90 kcal mol^{-1}, could be ca. 12.8 kcal mol^{-1} too low.

The enthalpies of formation of two other molecules, dioxirane and 1,2-dioxolane, determined using eq 1 are also significantly lower than Dorofeeva's values by 10.83 and 5.91 kcal/mol, respectively. The experimental data on $\Delta H_f°_{298}$ of these two molecules are again not available. A study[25] of enthalpies of formation of cyclic alkyl peroxides using ab initio calculations at the MP4SDTQ/6-31G*//MP2/6-31G* level of theory combined with the isodesmic reactions results in $\Delta H_f°_{298}$(dioxirane) = −2.91 ± 1.34 kcal/mol and $\Delta H_f°_{298}$(1,2-dioxolane) = −27.43 ± 0.91 kcal/mol. These values are more consistent with the values determined using eq 1, $\Delta H_f°_{298}$(dioxirane) = −2.47 kcal/mol and $\Delta H_f°_{298}$(1,2-dioxolane) = −27.42 kcal/mol and are ≥7 kcal/mol different from the Dorofeeva's $\Delta H_f°_{298}$ data. We include these two $\Delta H_f°_{298}$ values determined at the MP4SDTQ/6-31G* level of theory in the data of Figure 1 and recalculate the standard deviation (*s*) of regressed PM3-determined $\Delta H_f°_{298}$ to be 2.89 kcal/mol.

The standard deviation of the PM3-determined entropy versus Dorofeeva's data is 1.15 cal mol^{-1} K^{-1} (eu). PM3-determined entropies of five species (oxirene, 1,2,4-trioxolane, 1,3-dioxane, 3,6-dihydro-1,2-dioxin, and 1,3,5-trioxane) differ from those in Dorofeeva's work by more than 1.0 but less than 2.0 eu. For the remaining 16 molecules, the entropy difference is smaller than 1 eu. The largest difference in the entropies is 3.26 eu for 1,2-dioxolane, which mainly results from difference in vibrational frequencies. The frequencies of 1,2-dioxolane were calculated[8,9] using 20 force constants transferred from tetrahydrofuran and 1,2,4-trioxolane. The vibrational contribution to entropy ($S°_{298,vib}$) of 1,2-dioxolane is 8.27 eu from the PM3-calculated vibrational frequencies, while it is 5.07 eu from Dorofeeva's frequencies.

Vibrational frequencies of 1,2-dioxolane are further calculated at the RHF/6-31G* level of theory using the *Gaussian 94*[26] system of programs. The default optimization criteria and the analytical method for vibrational frequency calculation are employed. The value of $S°_{298,vib}$ is 6.29 eu from the frequencies obtained at the RHF/6-31G* (scaled by 0.9),[27] which is 1.98 eu lower than the PM3 $S°_{298,vib}$ and 1.22 eu higher than Dorofeeva's value. At this step, we adopt Dorofeeva's data on entropies and heat capacities for 1,2-dioxolane in the derivation of the ring group values.

The standard deviations of PM3-determined heat capacities from Dorofeeva's data for temperatures of 300−1500 K are all smaller than 1.0 cal mol^{-1} K^{-1}: 0.79, 0.91, 0.92, 0.83, 0.82, 0.62, 0.45, and 0.29 cal mol^{-1} K^{-1} for $C_{p,300}$, $C_{p,400}$, $C_{p,500}$, $C_{p,600}$, $C_{p,800}$, $C_{p,1000}$, and $C_{p,1500}$, respectively. The deviation is more than 1 cal mol^{-1} K^{-1} for four molecules: oxirene, 1,2,4-trioxolane, 1,3-dioxane, and 1,3,5-trioxane. The largest difference observed is that for $C_{p,500}$ of 1,3,5-trioxane as 2.46 cal mol^{-1} K^{-1}, which results from the differences in vibrational frequencies. Vibrational frequencies of 1,3,5-trioxane adopted by Dorofeeva are experimentally-determined.[28]

A recent ab initio study[29] by Vacek *et al*. indicates that the C_{2v} structure of oxirene is a transition state, with an imaginary frequency corresponding to a ring-opening normal coordinate, according to DFT (BLYP, B3LYP) calculations and the MP4 and CCSD(T) methods with large spd basis sets. Other methods (RHF, MP2, CISD, and CCSD(T)) indicate it is a true minimum.[29] At the highest level of theory performed by Vacek *et al.*, CCSD(T) with a basis set of triple-ζ quality including multiple pdf shells, oxirene is a true minimum with the lowest harmonic vibrational frequency in the range of 139−163 cm^{-1}. The lowest vibrational frequency adopted by Dorofeeva is, however, 450 cm^{-1},[8] which is also supported by the calculations at the RHF/QZ3P(f,d) level of theory.[29] We conclude that the vibrational frequencies of oxirene are still not well characterized since significant controversy exists between different levels of theory. At this step, the entropy and heat capacity data of oxirene reported by Dorofeeva are adopted in the derivation of ring groups.

Ring Correction Groups of Group Additivity Method. The selection of thermodynamic properties to derive values for ring group corrections is described as follows. The experimental data for enthalpies of formation of 10 molecules described above are selected. The values of $\Delta H_f°_{298}$(dioxirane), $\Delta H_f°_{298}$(1,2-dioxetane), and $\Delta H_f°_{298}$(1,2-dioxolane) determined by ab initio study and isodesmic reactions are used. Enthalpies of formation determined using eq 1 are used for the remaining molecules. Values of entropies and heat capacities reported by Dorofeeva are adopted to derive the group contributions wherever available; otherwise, the values obtained using the PM3 method are used. The diffrences between PM3-determined and literature $S°_{298}$ and $C_p°$ values are, however, insignificant except for those of 1,2-dioxolane ($S°_{298}$) and 1,3,5-trioxolane ($C_p°_{500}$).

Some enthalpy corrections for ring groups in Table 3 have negative values, resulting from the use of group values listed in Table 5. Benson states the ring correction derived from group additivity reflects the strain energy of the corresponding cyclic compound since group values are derived from open-chain, “unstrained” compounds. However, he also recognizes the difficulty in separating strain energy from resonance energy using group additivity for some ring compounds. The ring strain of benzene, if calculated with a Benson type analysis, is −33.0 kcal mol^{-1}.[11] The negative enthalpy corrections for several ring groups in Table 3 may result from the combination of resonance and ring strain, such as that that occurs in furan, phenol, and other vinyl or unsaturated ether compounds.[11] Resonance through chemical bonds on unsaturated carbon and adjacent oxygen atoms is evidenced by the weaker O−H bonds (ca. 85 kcal mol^{-1})[30] in $CH_2{=}CHOH$, $CH{\equiv}COH$, and phenol compared to that in $CH_3O{-}H$ and $CH_3CH_2O{-}H$ (bond energy = 104 kcal mol^{-1}).[31]

We report the ring correction values for use in group additivity, based on the group values listed in Table 5. Additional study is needed to separate and identify ring strain and resonance effects in oxygenated hydrocarbon species, and this may lead to redefinition of several oxygen−carbon−hydrogen groups and subsequent revision of ring groups for some cyclic oxygenated hydrocarbons.

Conclusion

Thermodynamic properties ($\Delta H_f°_{298}$, $S°_{298}$, and $C_p(T)$, $300 \leq T/K \leq 1500$) of 34 cyclic oxygenated hydrocarbons are calculated using the PM3 method and scaled using eq 1, including 12 species which were not previously studied. The standard deviations of PM3-determined $\Delta H_f°_{298}$ and $S°_{298}$ are evaluated as 2.89 kcal/mol and 1.15 cal mol^{-1} K^{-1}. The standard deviations of PM3-determined heat capacities are determined to be less than 0.92 cal mol^{-1} K^{-1}. Ring groups corresponding to the 34 compounds are derived using thermodynamic properties selected from literature or this work. The PM3 method is a convenient and economic approach compared to ab initio methods. It is, therefore, valuable to determine the deviations of ideal gas thermodynamic properties for cyclic oxygenated hydrocarbons using the PM3 method. Enthalpies of formation obtained using the PM3 method after calibration are particularly valuable when no other data are available.

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