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Cyclic alkylene carbonates. Experiment and first principle calculations for prediction of thermochemical properties

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ABSTRACT

The standard molar enthalpies of formation of ethylene carbonate, propylene carbonate, and butylene carbonate were measured using combustion calorimetry. *Ab initio* calculations of molar enthalpies of formation of alkylene carbonates were performed using the G3MP2 method. The calculated values are in excellent agreement with available experimental data. Ring strain corrections were quantified for the refinement of the group-contribution method for prediction of enthalpies of formation and vaporization of alkylene carbonates.

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1. Introduction

The alkylene carbonates (or 1,2-glycol carbonates, or cyclic acid esters) have become increasingly attractive not only for their unique physico-chemical properties but also for the relative simplicity of their manufacturing [1]. They are long-term commercially available solvents used in many industrial applications such as cleaning, degreasing, paint stripping, gas treating, and textile dyeing [2]. Cyclic alkylene carbonates, such as ethylene carbonate, propylene carbonate, and their linear analogue, dimethyl carbonate, as well as their mixtures are widely used as solvents of electrolytes in lithium-ion batteries [3]. Our recent research has revealed specific features of propylene carbonate towards asymmetric hydrogenation with self-assembling catalysts [4] and for palladium-catalyzed substitution reactions [5]. Alkylene carbonates are biodegradable and non-toxic, thus they could be considered as possible "green" solvents. There is great interest in the computation of heat balances, equilibrium yields and feasibilities of processes, using the thermodynamic properties of organic compounds. Despite the practical importance of carbonates, relevant thermodynamic information is rather limited [6–10]. The aim of this work was an experimental and computational study of the enthalpies of formation for a series of alkylene carbonates (figure 1). This paper extends our previous experimental research of organic carbonates [11–14].

2. Experimental

2.1. Materials

Samples of alkylene carbonates of commercial purity were obtained from Huntsman Corporation and were further purified by fractional distillation at reduced pressures. The purity analyses were performed using a gas chromatograph (GC) with a flame ionization detector. A HP-5 capillary column (stationary phase cross-linked 5% PH ME silicone) was used in all our experiments. The column was 30 m long, 0.32 mm inside diameter, and had a film thickness of 0.25 μm. The flow rate of the carrier gas (nitrogen) was maintained at $7.2 \ \text{dm}^3 \cdot \text{h}^{-1}$. The starting temperature for the GC was $T = 323 \ \text{K}$ for the first 180 s followed by heating to $T = 523 \ \text{K}$ at the rate of $10 \ \text{K} \cdot \text{min}^{-1}$. No impurities greater than 0.0002 mass fraction were detected in all samples used in this work.

2.2. Combustion calorimetry

An isoperibol bomb calorimeter was used for measurements of energy of combustion of alkylene carbonates. The detailed

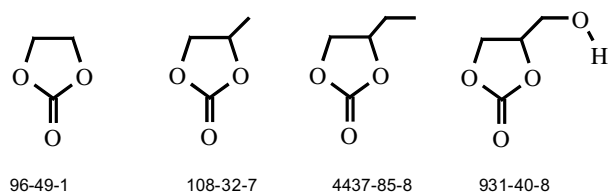*S.P. Verevkin et al. / J. Chem. Thermodynamics 40 (2008) 1428–1432*

1429

FIGURE 1. Structures of alkylene carbonates studied in this work: ethylene carbonate [CAS-number 96-49-1], propylene carbonate [CAS-number 108-32-7], butylene carbonate [CAS-number 4437-85-8], and glycerine carbonate [CAS-number 931-40-8].

experimental procedure has been described previously [15]. In this study, we used commercially available 1 cm^3 polyethylene bulbs (Fa. NeoLab, Heidelberg, Germany) as sample containers for the liquid carbonates. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. The energy equivalent of the calorimeter ε_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39i, N.I.S.T.). Correction for nitric acid formation was based on the titration with 0.1 mol · dm^{-3} NaOH (aq). The atomic masses used were those recommended by the IUPAC Commission [16]. The sample masses were reduced to vacuum, taking into consideration the density values given in table 1. Five to six successful combustion experiments (without soot traces) were carried out for each compound. For converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states, the conventional procedure [17] was applied.

2.3. Computations

Standard *ab initio* molecular orbital calculations were performed with the Gaussian 03 Rev.04 series of programs [18]. Energies were obtained at the G3MP2 level of theory. The G3 theory is a procedure for calculating energies of molecules containing atoms of the first and second rows of the periodic chart based on *ab initio* molecular orbital theory. A modification of the G3 theory that uses reduced orders of Moller–Plesset perturbation theory is the G3MP2 theory [19]. This method saves considerable computational time compared to G3 theory with some losses in accuracy, but it is much more accurate than G2MP2 model predicts. For all the species included in this study, full geometry optimizations were carried out at the HF/6-31G(d) level. The corresponding harmonic vibrational frequencies were evaluated at the same level of theory to confirm that the optimized structures found correspond to potential energy minima and to evaluate the corresponding zero-point vibrational energies, ZPE, and the thermal corrections at $T = 298$ K. The values of ZPE were scaled by the empirical factor 0.8929. All the minima found at the HF/6-31G(d) level were again fully re-optimized at the MP2(FULL)/6-31G(d) level. The G3MP2

theory uses geometries from second-order perturbation theory and scaled zero-point energies from Hartree–Fock theory followed by a series of single-point energy calculations at the MP2(Full), QCISD(T) and MP2/GTMP2Large levels of theory (for details, see reference [19]). The enthalpy value of the compounds studied at $T = 298$ K was evaluated according to standard thermodynamic procedures [20].

3. Results and discussion

3.1. Enthalpies of formation from combustion calorimetry

Results of combustion experiments for alkylene carbonates are summarized in tables 2 to 4. Values of the standard specific energies of combustion $\Delta_c u°$, together with their mean, are also given in table 2. To derive $\Delta_f H_m°$ (l or cr) from $\Delta_c H_m°$, molar enthalpies of formation of H$_2$O (l): $-(285.830 \pm 0.042)$ kJ · mol^{-1} and CO$_2$ (g): $-(393.51 \pm 0.13)$ kJ · mol^{-1} were taken, as assigned by *CODATA* [21]. Table 5 lists the derived standard molar enthalpies of combustion, and standard molar enthalpies of formation of alkylene carbonates. The total uncertainties were calculated according to the guidelines presented by Olofsson [22]. The uncertainties assigned to $\Delta_f H_m°$ were twice the overall standard deviation and included the uncertainties of calibration, combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H$_2$O and CO$_2$.

The enthalpy of combustion of butylene carbonate is reported for the first time (see table 5). Previous calorimetric determinations of the standard molar enthalpy of formation, $\Delta_f H_m°$ (cr), of ethylene carbonate were reported by Silvestro and Lenchitz [8]: $-(580.9 \pm 1.3)$ kJ · mol^{-1}, Vasil'eva *et al.* [9]: $-(581.6 \pm 0.4)$ kJ · mol^{-1}, and Calhoun [10]: $-(586.3 \pm 3.8)$ kJ · mol^{-1}. All literature and our values were in close agreement (see table 1). However, our experimental results for the heat of combustion of ethylene carbonate (-584.8 ± 0.6) kJ · mol^{-1} were found to be in disagreement with the work of Choi and Joncich [7]: $-(682.8 \pm 2.1)$ kJ · mol^{-1} and Vogdanis *et al.* [6]: $-(590.9)$ kJ · mol^{-1}.

The standard molar enthalpy of formation, $\Delta_f H_m°$(l), of propylene carbonate determined by combustion calorimetry is $-(631.8 \pm 2.1)$ kJ · mol^{-1} and $-(613.4 \pm 1.3)$ kJ · mol^{-1} as reported by Choi and Joncich [7] and Vasil'eva *et al.* [9], respectively. Our value of $\Delta_f H_m°$(l) determined in a combustion experiment was $-(614.1 \pm 0.8)$ kJ · mol^{-1}, which agrees well with the value reported by Vasil'eva *et al.* [9], and resolves the conflict between the literature results for the standard molar enthalpy of propylene carbonate.

3.2. Vapour pressures, sublimation and vaporization enthalpies

Vapour pressures of alkylene carbonates were measured in our previous work [11] using the transpiration method [23–25]. Molar

TABLE 1
Formula, density ρ ($T = 293$ K), massic heat capacity c_p ($T = 298.15$ K), and expansion coefficients $(\delta V/\delta T)_p$ of the materials used in this study

Compounds	Formula	ρ^a/(g · cm^{-3})	$c_p{}^b$/(J · K^{-1} g^{-1})	$10^{-6} \cdot (\delta V/\delta T)_p{}^c$/(dm^3 · K^{-1})
Ethylene carbonate	C$_3$H$_4$O$_3$	1.32	1.33	0.1
Propylene carbonate	C$_4$H$_6$O$_3$	1.23 [31]	1.20	1.0
Butylene carbonate	C$_5$H$_8$O$_3$	1.14	1.20	1.0
Polyethene^d	CH$_{1.93}$	0.92	2.53	0.1
Cotton^e	CH$_{1.774}$O$_{0.887}$	1.50	1.67	0.1

^{a} Measured with a pycnometer.
^{b} From reference [11].
^{c} Estimated.
^{d} From 13 combustion experiments, $\Delta_c u° = -(46361.0 \pm 3.1)$ J · g^{-1}.
^{e} From 10 combustion experiments, $\Delta_c u° = -(16945.2 \pm 4.2)$ J · g^{-1}.

TABLE 2
Results for typical combustion experiments at $T = 298.15$ K ($p° = 0.1$ MPa) of the ethylene carbonate[a]

m(substance)/g[b]	1.032182	1.068698	1.030644	1.012889	1.017638	1.008019	1.036652
m'(cotton)/g[b]	0.003649	0.00356	0.004035	0.003655	0.004068	0.003501	0.004235
ΔT_c/K[c]	0.92930	0.96230	0.92873	0.91161	0.91689	0.90804	0.93439
$(\varepsilon_{calor}) \cdot (-\Delta T_c)$/J	−13755.6	−14243.9	−13747.1	−13493.6	−13571.8	−13440.8	−13830.8
$(\varepsilon_{cont}) \cdot (-\Delta T_c)$/J	−15.93	−16.62	−15.96	−15.59	−15.69	−15.52	−16.03
ΔU_{corr}/J[d]	15.52	16.14	15.51	15.2	15.29	15.12	15.6
$-m' \cdot \Delta_c u'$/J	61.83	60.32	68.37	61.93	68.93	59.32	71.76
$\Delta_c u°$(cr)/(J·g^{-1})	−13267.2	−13272.3	−13272.4	−13261.1	−13269.2	−13275.4	−13273.0

[a] For the definition of the symbols, see reference [17], calorimeter: $T_h = 298.15$ K; V(bomb) = 0.2664 dm^3; p^i(gas) = 3.04 MPa; m^i(H$_2$O) = 1.00 g.
[b] Masses obtained from apparent masses.
[c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\varepsilon_{cont}) \cdot (-\Delta T_c) = (\varepsilon_{cont}^i) \cdot (T^i - 298.15 \text{ K}) + (\varepsilon_{cont}^f) \cdot (298.15 \text{ K} - T^f + \Delta T_{corr.})$.
[d] ΔU_{corr}, the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in reference [17]; ε_{calor}=14802.0 ± 1.0 J·K^{-1}.

TABLE 3
Results for typical combustion experiments at $T = 298.15$ K ($p° = 0.1$ MPa) of the propylene carbonate[a]

m(substance)/g[b]	0.497919	0.491504	0.575586	0.529713	0.53881
m'(cotton)/g[b]	0.003551	0.003376	0.003686	0.003179	0.003722
m''(polythen)/g[b]	0.283244	0.297263	0.291872	0.292214	0.290877
ΔT_c/K[c]	1.49185	1.52777	1.61265	1.55741	1.56596
$(\varepsilon_{calor}) \cdot (-\Delta T_c)$/J	−22083.3	−22615.0	−23871.4	−23053.7	−23180.3
$(\varepsilon_{cont}) \cdot (-\Delta T_c)$/J	−27.5	−28.25	−30.12	−28.8	−28.61
ΔU_{decomp}HNO$_3$/J	43.00	44.20	45.99	44.20	44.79
ΔU_{corr}/J[d]	9.99	10.13	11.21	10.56	25.36
$-m' \cdot \Delta_c u'$/J	60.17	57.21	62.46	53.87	63.07
$-m'' \cdot \Delta_c u''$/J	13131.48	13781.41	13531.48	13547.33	13485.35
$\Delta_c u°$(liq)/(J·g^{-1})	−17806.4	−17803.1	−17808.5	−17795.6	−17799.0

[a] For the definition of the symbols, see reference [17], calorimeter: $T_h = 298.15$ K; V(bomb) = 0.2664 dm^3; p^i(gas) = 3.04 MPa; m^i(H$_2$O) = 1.00 g.
[b] Masses obtained from apparent masses.
[c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\varepsilon_{cont}) \cdot (-\Delta T_c) = (\varepsilon_{cont}^i) \cdot (T^i - 298.15 \text{ K}) + (\varepsilon_{cont}^f) \cdot (298.15 \text{ K} - T^f + \Delta T_{corr.})$.
[d] ΔU_{corr}, the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in reference [17], ε_{calor} = 14802.6 ± 1.0 J·K^{-1}.

TABLE 4
Results for typical combustion experiments at $T = 298.15$ K ($p° = 0.1$ MPa) of the butylene carbonate[a]

m(substance)/g[b]	0.393786	0.603616	0.441995	0.367577	0.30439
m'(cotton)/g[b]	0.003535	0.003363	0.003386	0.003395	0.003536
m''(polythen)/g[b]	0.288258	0.302798	0.288243	0.294574	0.29045
ΔT_c/K[c]	1.47442	1.82201	1.5434	1.45614	1.35243
$(\varepsilon_{calor}) \cdot (-\Delta T_c)$/J	−21825.3	−26970.5	−22846.3	−21554.7	−20019.4
$(\varepsilon_{cont}) \cdot (-\Delta T_c)$/J	−27.01	−34.62	−28.43	−26.57	−24.46
ΔU_{decomp}HNO$_3$/J	44.79	52.56	44.79	42.41	40.02
ΔU_{corr}/J[d]	8.62	11.78	9.27	8.37	7.48
$-m' \cdot \Delta_c u'$/J	59.9	56.99	57.38	57.53	59.92
$-m'' \cdot \Delta_c u''$/J	13363.93	14038.02	13363.23	13656.75	13465.55
$\Delta_c u°$(liq)/(J·g^{-1})	−21268.1	−21281.3	−21267.4	−21264.1	−21258.7

[a] For the definition of the symbols, see reference [17], calorimeter: $T_h = 298.15$ K; V(bomb) = 0.2664 dm^3; p^i(gas) = 3.04 MPa; m^i(H$_2$O) = 1.00 g.
[b] Masses obtained from apparent masses.
[c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\varepsilon_{cont}) \cdot (-\Delta T_c) = (\varepsilon_{cont}^i) \cdot (T^i - 298.15 \text{K}) + (\varepsilon_{cont}^f) \cdot (298.15 \text{K} - T^f + \Delta T_{corr.})$.
[d] ΔU_{corr}, the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in reference [17], ε_{calor} = 14802.6 ± 1.0 J·K^{-1}.

enthalpies of vaporization of the compounds given in table 5 (column 4) were obtained from the temperature dependence of the vapour pressure. The molar enthalpy of sublimation of ethylene carbonate was measured in the same way.

3.3. Calculation of the gaseous enthalpies of formation

Values of vaporization and sublimation enthalpies of alkylene carbonates, derived in our previous work [11] (table 5), can now be used together with the results from our combustion experiments for further calculation of the gaseous standard enthalpies of formation, $\Delta_f H_m°$(g) at $T = 298.15$ K. The resulting values of $\Delta_f H_m°$(g) of alkylene carbonates are given in the last column in table 5.

3.4. Quantum chemical calculations for carbonates

Results of *ab initio* molecular orbital methods for calculation of the enthalpy of formation of alkyl carbonates have not been yet reported in the literature. The G3MP2 total energies at $T = 0$ K and enthalpies at $T = 298.15$ K of the molecules studied in this work are given in table 6. We calculated enthalpies of formation of alkylene carbonates using atomization [26] and bond separation reactions [27]. For the latter method, we have chosen the following two reactions:

$$C_nH_{2n}O_3 + (n+3)CH_4 \rightleftharpoons 3CH_3OH + nC_2H_6 \qquad (1)$$
$$C_nH_{2n}O_3 + (n+6)CH_4 \rightleftharpoons 3H_2O + (n+3)C_2H_6 \qquad (2)$$

TABLE 5
Thermochemical data at $T = 298.15$ K ($p° = 0.1$ MPa) for alkylene carbonates

Compounds	State	$\Delta_c H_m°/(\text{kJ·mol}^{-1})$	$\Delta_f H_m°/(\text{kJ·mol}^{-1})$	$\Delta_l^g H_m°/(\text{kJ·mol}^{-1})$[a]	$\Delta_f H_m°(\text{g})/(\text{kJ·mol}^{-1})$
Ethylene carbonate	cr	−1167.4 ± 0.4	−584.8 ± 0.6	74.1 ± 0.6[b]	−510.7 ± 0.9
				62.8 ± 0.1	
Propylene carbonate	liq.	−1817.4 ± 0.6	−614.1 ± 0.8	60.2 ± 0.1	−553.9 ± 0.8
Butylene carbonate	liq.	−2470.8 ± 1.0	−640.1 ± 1.2	63.4 ± 0.2	−576.7 ± 1.2
Glycerine carbonate	liq.			85.9 ± 0.2	

[a] From reference [11].
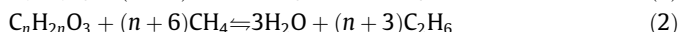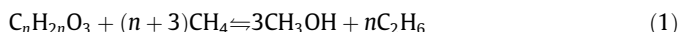[b] Enthalpy of sublimation.

TABLE 6
G3MP2 total energies at $T = 0$ K and enthalpies at $T = 298.15$ K (in Hartree) of the molecules studied in this work

Compounds	E_0	H_{298}
Ethylene carbonate	−341.955390	−341.949504
Propylene carbonate	−381.198374	−381.191084
Butylene carbonate	−420.432786	−420.424070
Glycerine carbonate	−456.337492	−456.329067

Enthalpies of these reactions calculated by the G3MP2 method and experimental enthalpies of formation $\Delta_f H_m^\circ(g)$, of methane, methanol, water, and ethane from Pedley et al. [28], were used to determine enthalpies of formation of alkylene carbonates. Comparison of the calculated and experimental data is given in table 7. Enthalpies of formation of alkylene carbonates derived via the atomization procedure. Both the bond separation reactions 1 and 2 were practically indistinguishable. They were also in an excellent agreement with the available experimental results as shown in table 7.

3.5. Structure–energy relationships: strain enthalpies H_S of alkylene carbonates

Conventional-strain enthalpy, H_S, of a molecule is defined as the difference between its experimental enthalpy of formation, $\Delta_f H_m^\circ(g)$, and the calculated sum of the Benson-type increments [29,30] for this molecule. The system of group additive increments based on the standard enthalpies of formation, $\Delta_f H_m^\circ(g)$, and molar enthalpies of vaporization, $\Delta_l^g H_m$, was established recently [13].

The summary of the group additivity values (GAV) is given in table 8. The new experimental values for $\Delta_f H_m^\circ(g)$ and $\Delta_l^g H_m$ of the cyclic alkyl carbonates (table 5) and increments from table 8 were used for the estimation of the strain enthalpies, $H_S = (\Delta_f H_m^\circ(g) - \Sigma$ increments), of these carbonates. The results on H_S are presented in table 9. Cyclic alkyl carbonates listed in table 9 present a typical example of similarly shaped molecules with the five-membered ring, where an alkyl substituent (methyl or ethyl) is attached to the ring. Hence the strain, H_S, of a molecule is expected to provide insight into the energetic interactions of an alkyl substituent R with the ring.

The strain enthalpies for all alkyl carbonates studied were found to be approximately 40 kJ · mol^{-1} and could be considered equal within the uncertainties of the experiment as expected for similarly shaped five-membered ring derivatives. The H_S value reflects the intrinsic strain, typical for the cyclic molecules, due to non-bonded interactions from steric effects of the carbon and oxygen atoms constituting the ring. No additional interactions of an alkyl substituent R with the ring could be detected. These strains in cyclic alkylene carbonates are also comparable to the strain, $H_S = 38.1$ kJ · mol^{-1}, of the cylopentane (see table 9). Such a similarity of strains in alkylene carbonates proves the consistency of the experimental data involved in the interpretation. For this reason, an additional correction term, which takes into account the strain of the five-membered ring (table 9), should be introduced for the prediction of $\Delta_f H_m^\circ(g)$.

Similar analyses were performed on vaporization enthalpies, $\Delta_l^g H_m$. As can be seen in table 9, the corrections for a five-membered

TABLE 7
Results of calculation of the standard enthalpies of formation $\Delta_f H_m^\circ(g)$ for the alkylene carbonates in the gaseous phase at $T = 298.15$ K

Compounds	$\Delta_f H_m^\circ$/(kJ · mol^{-1}) Atomization	$\Delta_f H_m^\circ$/(kJ · mol^{-1}) Equation (1)	$\Delta_f H_m^\circ$/(kJ · mol^{-1}) Equation (2)	$\Delta_f H_m^\circ$/(kJ · mol^{-1})[a] G3MP2	$\Delta_f H_m^\circ$/(kJ · mol^{-1}) Exp
Ethylene carbonate	−508.4	−509.5	−508.5	−508.8	−510.7 ± 0.9
Propylene carbonate	−552.3	−552.9	−551.9	−552.4	−553.9 ± 0.8
Butylene carbonate	−573.7	−573.8	−572.8	−573.4	−576.7 ± 1.2
Glycerine carbonate	−699.0		−699.5	−699.3	
Di-methyl carbonate	−569.5	−571.3	−570.4	−570.4	−571.0 ± 0.4 [13]
Di-ethyl carbonate	−638.4	−639.2	−638.3	−638.6	−637.9 ± 0.8 [13]
Methyl-cyclohexyl carbonate	−662.9	−661.5	−660.5	−661.6	−657.6 ± 4.2 [13]

[a] Average value from columns 2, 3, and 4.

TABLE 8
Group-additivity values for the calculation of enthalpy of formation, $\Delta_f H_m^\circ$, and enthalpy of vaporization, $\Delta_l^g H_m$, for alkylene carbonates at $T = 298.15$ K

Increment	$\Delta_f H_m^\circ(g)$/(kJ · mol^{-1})	$\Delta_l^g H_m$/(kJ · mol^{-1})	Increment	$\Delta_f H_m^\circ(g)$/(kJ · mol^{-1})	$\Delta_l^g H_m$/(kJ · mol^{-1})
C–(C)(H)$_3$	−41.32	5.69	C(O)(H$_3$)	−41.32	5.69
C–(C)$_2$(H)$_2$	−22.90	4.88	C(O)(H$_2$)(C)	−32.50	2.64
C–(C)$_3$(H)	−11.12	2.61	C(O)(H)(C$_2$)	−31.85	−1.28
C–(C)$_4$	−3.89	−0.47	C(O)(C$_3$)	−21.75	−6.30
(C–C)$_{1-4}$	2.34	0.10	Ph(O)	95.00	27.71
CO(O$_2$)	−487.64	27.04	Five-membered ring	39.5	25.3

TABLE 9
Strain in alkylene carbonates at $T = 298.15$ K

Compounds	$\Delta_f H_m^\circ(g)_{exp}$/(kJ · mol^{-1})	Σ_{incr}/(kJ · mol^{-1})[a]	H_S/(kJ · mol^{-1})[b]	$\Delta_l^g H_{m\,exp}$/(kJ · mol^{-1})	Σ_{incr}/(kJ · mol^{-1})[c]	GAV/(kJ · mol^{-1})[d]
Ethylene carbonate	−510.7 ± 0.9	−552.6	41.9	62.8 ± 0.1 [11]	24.4	30.5
Propylene carbonate	−553.9 ± 0.8	−553.9	39.4	60.2 ± 0.1 [11]	32.3	26.1
Butylene carbonate	−576.7 ± 1.2	−576.7	39.5	63.4 ± 0.2 [11]	34.1	24.4
Cyclopentane	−76.4 ± 0.8 [28]	−114.5	38.1	28.7 ± 0.1 [28]	39.1	4.3

[a] Sum of the increments from table 8, column 2.
[b] $H_S = (\Delta_f H_m^\circ(g) - \Sigma$ increments) was calculated as the difference between columns 2 and 3 from this table.
[c] Sum of the increments from table 8, column 3.
[d] GAV was calculated as the difference between columns 5 and 6 from this table.

ring for propylene carbonate (26.1 kJ · mol^{-1}) and butylene carbonate (24.4 kJ · mol^{-1}) are nearly the same, but significantly different from the unsubstituted five-membered ring correction of ethylene carbonate (30.5 kJ · mol^{-1}). This discrepancy demonstrates that the interactions of an alkyl substituent R with the ring are not negligible for this thermodynamic property. Thus an additional correction term for the alkyl substituted five-membered ring (table 9) should be included for the prediction of $\Delta_l^g H_m$. Surprisingly, the five-membered ring corrections for the unsubstituted five-membered ring for ethylene carbonate (30.5 kJ · mol^{-1}) and its alkyl derivatives are substantially larger (see table 9) than those of cyclopentane (4.3 kJ · mol^{-1}).

4. Conclusions

The group-additivity methods serve as a valuable tool for many scientists and engineers whose work involves thermodynamic characterization of elementary and overall reaction processes. New experimental thermochemical results for alkylene carbonates have been determined and extended available data for this chemical family. The use of the modern first principle calculations allowed the validation of the mutual consistency of the experimental data. Strain corrections derived in this work are useful for the prediction of the thermochemical properties of a broad range of organic compounds containing carbonate moiety.

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