Organic Carbonates: Experiment and ab Initio Calculations for Prediction of Thermochemical Properties

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This work has been undertaken in order to obtain data on thermodynamic properties of organic carbonates and to revise the group-additivity values necessary for predicting their standard enthalpies of formation and enthalpies of vaporization. The standard molar enthalpies of formation of dibenzyl carbonate, *tert*-butyl phenyl carbonate, and diphenyl carbonate were measured using combustion calorimetry. Molar enthalpies of vaporization of these compounds were obtained from the temperature dependence of the vapor pressure measured by the transpiration method. Molar enthalpy of sublimation of diphenyl carbonate was measured in the same way. Ab initio calculations of molar enthalpies of formation of organic carbonates have been performed using the G3MP2 method, and results are in excellent agreement with the available experiment. Then the group-contribution method has been developed to predict values of the enthalpies of formation and enthalpies of vaporization of organic carbonates.

1. Introduction

There is no need to discuss the importance of carbon dioxide as a C_1 feedstock. Some of the most interesting synthetic targets starting from CO_2 are organic carbonate according to recent reports of successful CO_2 conversion by heterogeneous and homogeneous catalysis.[1,2] From the standpoint of the protection of the environment and development of green processes organic carbonates have become a growing interest in recent times. Organic carbonates can be used to manufacture many products, primarily polycarbonates and polyurethanes, but also pesticides and herbicides, pharmaceutical products, polyimide films, and electrolytic fluids for lithium batteries. It also may be used as a fuel additive, and as a solvent it is more environmentally benign than other carbonating and methylating agents such as phosgene, dimethyl sulfate, and methyl halides. Organic carbonates are biodegradable and nontoxic; thus, they could be considered as a 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 very restricted (see Table 1). The aim of this work was an experimental and computational study to gain thermochemical properties of alkyl carbonates. This paper extends our previous experimental studies of a series of carbonates[3,4] directed to the systematic evaluation of the group-additivity contributions for a broad range of organic compounds.[5−9]

2. Experimental Section

2.1. Materials. The samples of dibenzyl carbonate [CAS no. 3459-92-5] and *tert*-butyl-phenyl carbonate [CAS no. 6627-89-0] (purchased from Aldrich) having a mass-fraction purity of about 0.99 were purified by repeated distillation in vacuum. The solid sample of diphenyl carbonate [CAS no. 102-09-0] (Merck) was purified by repeated sublimation in vacuum. Gas chromatography (GC) showed no traceable amounts of impurities in dialkyl carbonates samples after they were purified. The samples were analyzed with a Hewlett-Packard gas chromatograph 5890 series II with a flame ionization detector and Hewlett-Packard 3390A integrator. The dimensions of the capillary column HP-5 (stationary phase cross-linked 5% PH ME silicone) were the following: the column length, inside diameter, and film thickness were 25 m, 0.32 mm, and 0.25 μm, respectively. The flow rate of a carrier gas (nitrogen) was 12.1 $cm^3 \cdot s^{-1}$. The starting point for the GC temperature program was 323 K with a heating rate of 0.167 $K \cdot s^{-1}$ up until reaching 523 K temperature.

2.2. Combustion Calorimetry. An isoperibol bomb calorimeter was used for the measurement of energy of combustion of dialkyl carbonates. The detailed procedure has been described previously.[15] In the present study, we used commercially available polyethylene bulbs (Fa. NeoLab, Heidelberg, Germany) of 1 cm^3 as sample containers for *tert*-butyl phenyl carbonate. Successful combustion experiments with the samples of dibenzyl carbonate were performed only by addition of 5−6 drops of oil. However, it was observed that, after addition of the oil, this solid compound (melting temperature 303 K) becomes a liquid within several minutes during weighing of the sample in the crucible. Thus, the combustion experiments with dibenzyl carbonate were referred to the liquid state. 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, NIST). Correction for nitric acid formation was based on the titration with 0.1 $mol \cdot dm^{-3}$ NaOH(aq). The atomic weights used were those recommended by the IUPAC Commission.[16] The sample masses were reduced to vacuum, taking into consideration the density values given in Supporting Information Table S1. 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. Vapor Pressure Measurements of Carbonates. Vapor pressures of dialkyl carbonates were determined using the

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TABLE 1: Compilation of Thermochemical Data for Dialkyl Carbonates at 298 K (in $kJ \cdot mol^{-1}$)

compounds	$\Delta_c H^\circ_m$	$\Delta_f H^\circ_m$(l)	$\Delta^g_l H_m$	$\Delta_f H^\circ_m$(g)
dimethyl carbonate (l)		−608.7 ± 0.4[a]	38.02 ± 0.38[b]	−570.7 ± 0.6
diethyl carbonate (l)		−681.5 ± 0.8[c]	44.35 ± 0.44[b]	−637.2 ± 0.9
dipropyl carbonate (l)			53.22 ± 0.58[b]	
dibutyl carbonate (l)			62.88 ± 0.76[b]	
di-*t*-butyl carbonate (cr)			65.44 ± 0.22[d,e] 49.2[f,g]	
methyl-cyclohexyl carbonate (l)		−708.8 ± 2.1[h]	51.2 ± 3.6[h]	−657.6 ± 4.2
dicyclohexyl carbonate (cr)		−830.5 ± 5.9[h]	66.8 ± 5.4[e,h]	−763.7 ± 8.0
dibenzyl carbonate (l)	−7436.8 ± 1.7	−466.7 ± 2.6	96.7 ± 1.3[b]	−370.0 ± 2.9
t-butyl-phenyl carbonate (l)	−5731.3 ± 1.9	−598.1 ± 2.4	67.57 ± 0.56	−530.5 ± 2.5
diphenyl carbonate (cr)	−6142.7 ± 1.7	−402.1 ± 2.4	104.5 ± 1.1[e] 80.93 ± 0.64	−297.6± 2.6

[a] Ref 10. [b] Ref 4. [c] Ref 11. [d] Ref 12. [e] Enthalpy of sublimation. [f] Enthalpy of vaporization was calculated with help of the enthalpy of fusion, $\Delta^l_{cr} H_m$, which was assessed using the modified (ref 13) Walden's rule: $\Delta^l_{cr} H_m(T_{fus}) = 54.4\ (J \cdot K^{-1} \cdot mol^{-1}) T_{fus}$ (K) and adjusted (ref 14) to $T = 298.15$ K. [g] Melting temperature $T_m = 321$ K from ref 48. [h] Ref 47.

TABLE 2: Results for Typical Combustion Experiments at $T = 298$ K ($p^\circ = 0.1$ MPa)[a]

compound	dibenzyl carbonate	*tert*-butyl phenyl carbonate	diphenyl carbonate
$\varepsilon_{calor}/J \cdot K^{-1}$	14802.0 ± 1.0	14807.1 ± 0.9	14802.0 ± 1.0
m (substance)/g[b]	0.440316	0.42597	0.346791
m' (cotton)/g[b]	0.003863	0.002935	0.003111
m'' (auxiliary)/g[b]	0.04121[b]	0.290685[b]	
ΔT_c/K[c]	1.04507	1.76344	0.67499
$(\varepsilon_{calor})(-\Delta T_c)$/J	−15469.2	−26111.4	−9991.23
$(\varepsilon_{cont})(-\Delta T_c)$/J	−17.05	−32.52	−10.63
ΔU_{dec} HNO_3/J		48.98	
ΔU_{corr}/J[d]	8.93	10.38	6.77
$-m'\Delta_c u'$/J	65.46	49.73	52.72
$-m''\Delta_c u''$/J	1904.87	13476.45	
$\Delta_c u^\circ/(J \cdot g^{-1})$	−30675.6[e,f]	−29481.8	−28669.6
$\Delta_c u^\circ/(J \cdot g^{-1})$[d]	−30675.9 ± 0.3	−29482.7 ± 3.6	−28663.4 ± 2.3

[a] For the definition of the symbols see ref 17, calorimeter: $T_h = 298.15$ K; V(bomb) = 0.2664 dm^3; p^i(gas) = 3.04 MPa; $m^i(H_2O) = 1.00$ g. [b] Masses obtained from apparent masses. [c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\varepsilon_{cont})(-\Delta T_c) = (\varepsilon^i_{cont})(T^i - 298.15\ K) + (\varepsilon^f_{cont})(298.15\ K - T^f + \Delta T_{corr})$. [d] ΔU_{corr}, the correction to standard states, is the sum of items 81−85, 87−90, 93, and 94 in ref 17. [e] Combustion experiments are referred to the liquid state (see text). [f] Average value of the standard specific energy of combustion for each compound.

method of transpiration[18,19] in a saturated nitrogen stream. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with a diameter of the glass spheres of 1 mm provide surface large enough for rapid vapor−liquid equilibration. At constant temperature (±0.1 K), a nitrogen stream was passed through the U-tube and the transported amount of material was collected in a cooling trap. The flow rate of the nitrogen stream was measured using a soap bubble flow meter and was optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The amount of condensed substance was determined by GC analysis using an external standard (hydrocarbon n-C_nH_{2n+2}). The saturation vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of the product collected within a definite period of time. Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated with the equation

$$p_i^{sat} = m_i R T_a / V M_i; \quad V = V_{N2} + V_i; \quad (V_{N2} \gg V_i) \qquad (1)$$

where $R = 8.314472\ J \cdot K^{-1} \cdot mol^{-1}$, m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase. V_{N2} is the volume of the carrier gas, and T_a is the temperature of the soap bubble meter. The accuracy of the volume V_{N2} measurements from the flow rate was assessed to be ±0.001 dm^3. The volume of the carrier gas V_{N2} was determined from the flow rate and the time measurement. It was established that the total uncertainty of the data for this experimental technique was within the range from 1% to 3% with the main source of errors attributed to the reproducibility of GC measurements.

2.3. Computations. Standard ab initio molecular orbital calculations were performed with the Gaussian 03 revision 04 series of programs.[20] Energies were obtained at the G3MP2 level of theory. G3 theory is a procedure for calculating energies of molecules containing atoms of the first and second row of the periodic chart based on ab initio molecular orbital theory. A modification of G3 theory that uses reduced orders of Møller−Plesset perturbation theory is G3MP2 theory.[21] No corrections for internal rotors have been taken into account. The enthalpy values of at $T = 298$ K were evaluated according to standard thermodynamic procedures.[22]

3. Results and Discussion

3.1. Enthalpies of Formation from Combustion Calorimetry. Results of typical combustion experiments for dialkyl carbonates are summarized in Table 2. Values of the standard specific energies of combustion $\Delta_c u^\circ$, together with their mean, are also given in Table 2. To derive $\Delta_f H^\circ_m$(l or cr) from $\Delta_c H^\circ_m$, molar enthalpies of formation of H_2O(l): −(285.830 ± 0.042) $kJ \cdot mol^{-1}$ and CO_2(g): −(393.51 ± 0.13) $kJ \cdot mol^{-1}$ were taken, as assigned by CODATA.[23] Table 1 lists the derived standard molar enthalpies of combustion and standard molar enthalpies of formation of dialkyl carbonates. The total uncertainties were calculated according to the guidelines presented by Olofsson.[24] The uncertainties assigned to $\Delta_f H^\circ_m$ are twice the overall standard deviation and include the uncertainties from calibration, from the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H_2O and CO_2.

Enthalpies of combustion of dibenzyl carbonate and *tert*-butyl-phenyl carbonate have been measured for the first time (see Table 1). Previous determination of the standard molar enthalpy of combustion of diphenyl carbonate was made by Sinke et al.[25] Their value, $\Delta_c H_m^\circ = -(6143.6 \pm 1.9)$ kJ·mol^{-1}, is in excellent agreement with our result (see Table 1). Three very imprecise combustion experiments with an average value $\Delta_c H_m^\circ = -(6138.6 \pm 22.6)$ kJ·mol^{-1} were reported recently,[26] which is also in agreement with our new combustion result.

3.2. Vapor Pressures, Sublimation, and Vaporization Enthalpies. Vapor pressures of dialkyl carbonates measured in this work (Table 3) were treated with eqs 2 and 3 in order to derive their enthalpies of vaporization or sublimation, respectively:

$$R \ln p_i^{\text{sat}} = a + \frac{b}{T} + \Delta_l^g C_p \ln\left(\frac{T}{T_0}\right) \qquad (2)$$

$$\Delta_l^g H_m(T) = -b + \Delta_l^g C_p T \qquad (3)$$

where p_i^{sat} is vapor pressure, a and b are adjustable parameters (Table 1), T_0 is an arbitrarily chosen reference temperature (T_0 is 298 K in this work), and $\Delta_l^g C_p$ is the difference of the molar heat capacities of the gaseous and the liquid phase. Values of $\Delta_l^g C_p$ were calculated using the group-contribution method of Chickos and Acree.[27] When the vapor pressures were measured over the solid sample (for diphenyl carbonate), eqs 2 and 3 give the expression for the sublimation enthalpy, $\Delta_{cr}^g H_m$, at temperature T. Values of $\Delta_{cr}^g C_p$ required for the data treatment in this case have been derived using the experimental isobaric molar heat capacity $C_p^{cr} = 263.1$ J·mol^{-1}·K^{-1} of diphenyl carbonate[25] according to a procedure developed by Chickos and Acree.[28] In order to assess the uncertainty of the vaporization enthalpy, the experimental data were approximated with the linear equation $\ln(p_i^{\text{sat}}) = f(T^{-1})$ using the method of least-squares. Combined standard uncertainty of the measurement result for vaporization enthalpy was estimated by combining the individual standard uncertainties of deviation of experimental $\ln(p_i^{\text{sat}})$ values from this linear correlation, as well as of additional uncertainties of temperature and gas-flow measurements using the usual "root-sum-of-squares" method.[7] However, it was established that the main source of errors was attributed to the reproducibility of GC mass determination. The uncertainties assigned to $\Delta_{cr}^g H_m$ or $\Delta_l^g H_m$ are twice the combined standard deviation according to the common thermochemical practice.[7]

The experimental vapor pressures of all dialkyl carbonates as well as their enthalpies of vaporization (or sublimation) (see Table 3) were studied for the first time. Only a very rough estimate, $\Delta_{cr}^g H_m = 90.0 \pm 8.4$ kJ·mol^{-1}, was reported by Carson et al.[29] for diphenyl carbonate; however, our experimental result, $\Delta_{cr}^g H_m = 104.5 \pm 1.1$ kJ·mol^{-1}, does not fulfill their expectation. In order to give support to our experimental result on sublimation enthalpy of diphenyl carbonate, we have performed additional vapor pressure measurements over the liquid diphenyl carbonate and we have derived its enthalpy of vaporization (see Table 1).

A valuable test of consistency of the experimental data on sublimation and vaporization enthalpies measured for diphenyl carbonate provides a comparison with an experimental value of enthalpy of fusion, $\Delta_{cr}^l H_m = 23.4 \pm 1.3$ kJ·mol^{-1}, available[29] for the solid diphenyl carbonate. Indeed, in this work, the sample of diphenyl carbonate was investigated by the transpiration method in both ranges, above and below its temperature of melting $T_m = 351.9$ K.[25] The values $\Delta_{cr}^g H_m(298 \text{ K})$ and $\Delta_l^g H_m(298.15 \text{ K})$ were derived (see Tables 1 and 3). Comparison of the enthalpy of fusion, $\Delta_{cr}^l H_m = 23.6 \pm 1.3$ kJ·mol^{-1}, calculated as the difference $\Delta_{cr}^g H_m - \Delta_l^g H_m$ (both values referred to $T = 298.15$ K) from Table 1 and the enthalpy of fusion $\Delta_{cr}^l H_m = 20.2 \pm 1.3$ kJ·mol^{-1} (adjusted to $T = 298$ K, according to well-established procedure[14]) demonstrate a quite acceptable agreement (because the uncertainties of the adjustment procedures are ill-defined,[14] they were not taken into account). Thus, the set of vaporization and sublimation enthalpies of diphenyl carbonate given in Tables 1 and 3 possess internal consistency.

3.3. Calculation of the Gaseous Enthalpies of Formation. Values of vaporization and sublimation enthalpies of dialkyl carbonates derived in this work (Table 3) can now be used together with the results from our combustion experiments for further calculation of the gaseous standard enthalpies of formation, $\Delta_f H_m^\circ(g)$ at 298.15 K. The resulting values of $\Delta_f H_m^\circ(g)$ of dialkyl carbonates are given in the last column in Table 1.

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. We have calculated the enthalpies of formation of dialkyl carbonates with help of the standard atomization reactions[30] as well as using the bond separation reactions.[31] For the latter method we have chosen the following two reactions:

$$C_nH_{2n}O_3 + (n+3)CH_4 \rightleftharpoons 3CH_3OH + nC_2H_6 \qquad (4)$$

$$C_nH_{2n}O_3 + (n+6)CH_4 \rightleftharpoons 3H_2O + (n+3)C_2H_6 \qquad (5)$$

With the use of enthalpies of these reactions calculated by the G3MP2 method and enthalpies of formation $\Delta_f H_m^\circ(g)$ for methane, methanol, water, and ethane recommended by Pedley et al.,[32] enthalpies of formation of dialkyl carbonates have been calculated (see Table 4). There were three possible arrangements (cis−cis, cis−trans, and trans−trans) of dialkyl carbonates toward the double bond of the carbonyl group. Conformational analysis for the carbonates under study has revealed the large energetic discrepancies among conformers. However, computations of the equilibrium mixture of conformers (assumption of the equal entropies) have shown that the most stable conformer is presented in such a mixture in the amount of 98−99%. The preliminary calculations revealed that cis−cis isomer was energetically favored (e.g., for dimethyl carbonate the stabilizing effect was 12.5 kJ·mol^{-1}) (see Figure 1 in the Supporting Information). The latter most stable conformation was used in all further calculations. Comparison of the calculated and experimental data is given in Table 5. Enthalpies of formation of dialkyl carbonates derived with help of the atomization procedure and both of the bond separation reactions 4 and 5 are practically indistinguishable. They are also in an excellent agreement with the available experimental results (see Table 5). However, it should be mentioned that the composite G3MP2 method used in this work to predict enthalpies of formations of dialkyl carbonates is a quite time-consuming method. For small molecules such a dimethyl carbonate a required job CPU time was 52 min only for the longest step 4 with QCISD(T)/6-31G(d). For middle size molecules such a di-*tert*-butyl carbonate a required job CPU time was already 96 h (the calculations were performed at university computational center with help of a Sun Fire 3800 UltraSparc III 900 MHz using two processors and 1800 Mb RAM). But already for dibenzyl carbonate it was not possible to complete our calculations within 3 weeks even using the resources of the university computational center. Following,

TABLE 3: Experimental Vapor Pressures, Enthalpy of Sublimation, or Enthalpy of Vaporizations of Dialkyl Carbonates Measured by the Transpiration Method

T/K[a]	m/mg[b]	$V_{(N2)}$/dm^3 [c]	flow of N_2/dm^3·h^{-1}	p/Pa[d]	$(p_{exp} - p_{calc})$/Pa	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$/kJ·mol^{-1}
tert-Butyl-phenyl carbonate; $\Delta_{l}^{g}H_m$ (298.15 K) = (67.57 ± 0.56) kJ·mol^{-1}						
$\ln(p/\text{Pa}) = \frac{336.92}{R} - \frac{96903.91}{(R \cdot T/\text{K})} - \frac{98.4}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
293.5	2.08	9.80	6.53	2.67	−0.03	68.03
296.5	2.25	7.88	6.59	3.59	0.01	67.73
299.5	2.08	5.54	6.59	4.71	0.00	67.44
302.5	2.42	4.89	6.52	6.21	0.05	67.14
305.4	2.44	3.81	6.52	8.05	0.12	66.86
308.4	2.71	3.26	6.52	10.43	0.19	66.56
311.3	2.99	2.84	6.56	13.16	0.12	66.28
313.3	1.70	1.37	4.12	15.64	0.29	66.08
314.4	2.99	2.24	6.56	16.69	−0.09	65.97
317.4	3.72	2.19	6.56	21.27	−0.02	65.68
318.6	2.52	1.37	4.12	23.20	−0.18	65.56
320.5	4.50	2.19	6.56	25.69	−1.37	65.37
323.5	4.66	1.73	4.16	33.76	−0.20	65.08
328.5	5.39	1.39	4.16	48.79	−0.23	64.58
333.5	5.38	0.970	4.16	69.54	−0.25	64.09
338.5	2.78	0.350	1.50	100.04	1.97	63.60
343.4	3.95	0.375	1.50	132.60	−2.64	63.12
348.5	5.64	0.370	1.48	191.87	5.19	62.62
Diphenyl carbonate; $\Delta_{cr}^{g}H_m$ (298.15 K) = (104.5 ± 1.1) kJ·mol^{-1}						
$\ln(p/\text{Pa}) = \frac{355.06}{R} - \frac{116536.55}{(R \cdot T/\text{K})} - \frac{40.22}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
308.2	1.33	301.8	6.75	0.051	0.00	104.14
310.1	0.86	139.8	6.79	0.071	0.00	104.06
313.2	0.71	82.22	6.75	0.099	0.00	103.94
318.1	1.32	83.08	6.79	0.184	0.00	103.74
323.2	1.16	37.69	6.79	0.353	0.01	103.54
328.1	0.91	16.98	6.75	0.612	−0.01	103.34
331.0	2.03	26.43	6.75	0.875	0.02	103.23
333.2	3.00	31.04	6.75	1.10	0.00	103.14
336.6	1.67	12.11	8.16	1.59	−0.01	103.00
338.0	2.56	15.30	6.75	1.91	0.04	102.94
341.0	1.83	8.12	6.75	2.57	0.00	102.82
341.2	2.03	8.98	8.16	2.61	−0.02	102.82
342.9	1.27	4.30	5.61	3.36	0.21	102.75
342.9	1.17	4.30	5.61	3.14	−0.01	102.75
343.0	1.84	6.75	6.75	3.11	−0.07	102.74
344.1	2.30	7.20	6.75	3.65	0.06	102.70
345.2	1.40	3.83	5.61	4.17	0.15	102.65
345.3	1.96	5.81	6.11	3.88	−0.16	102.65
345.9	1.70	4.30	5.61	4.56	0.26	102.63
345.9	1.70	4.30	5.61	4.56	0.26	102.63
346.5	2.30	5.51	6.75	4.79	0.19	102.60
347.5	1.42	3.18	5.61	5.10	0.03	102.56
348.3	2.20	4.61	6.75	5.43	−0.08	102.53
348.7	1.93	4.02	5.61	5.53	−0.20	102.51
350.6	1.29	2.15	5.61	6.95	0.01	102.44
350.8	2.26	3.94	8.16	6.62	−0.46	102.43
351.3	1.44	2.43	5.61	6.84	−0.60	102.41
Diphenyl carbonate; $\Delta_{l}^{g}H_m$ (298.15 K) = (80.93 ± 0.64) kJ·mol^{-1}						
$\ln(p/\text{Pa}) = \frac{348.22}{R} - \frac{110687.84}{(R \cdot T/\text{K})} - \frac{99.8}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
354.5	1.54	1.87	5.61	9.39	−0.07	75.31
355.0	1.49	1.75	3.63	9.73	−0.11	75.26
356.3	3.73	3.93	3.63	10.76	−0.03	75.13
357.2	1.83	1.81	3.63	11.58	0.12	75.04
357.2	1.84	1.87	5.61	11.46	0.00	75.04
358.0	1.86	1.78	5.61	12.10	−0.03	74.96
358.7	2.14	1.87	5.61	13.04	0.30	74.89
359.2	1.69	1.45	3.63	13.36	0.16	74.84
359.7	1.66	1.40	5.61	13.85	0.19	74.79

TABLE 3 (Continued)

T/K[a]	m/mg[b]	$V_{(N2)}$/dm^3 [c]	flow of N_2/dm$^3\cdot$h^{-1}	p/Pa[d]	$(p_{exp} - p_{calc})$/Pa	$\Delta_{cr}^{g}H_m$ or $\Delta_{l}^{g}H_m$/kJ·mol^{-1}
360.1	1.93	1.59	5.61	13.91	−0.14	74.75
361.1	2.23	1.70	6.79	15.18	0.13	74.66
362.8	2.05	1.40	5.61	16.95	0.04	74.49
363.3	1.98	1.27	3.63	17.93	0.43	74.44
365.1	2.05	1.21	5.61	19.46	−0.29	74.26
365.6	4.57	2.65	6.35	19.94	−0.48	74.21
367.3	1.95	0.97	3.63	23.12	0.25	74.04
367.6	2.77	1.40	5.61	22.89	−0.43	74.01
368.1	3.58	1.70	6.79	24.05	−0.05	73.96
368.9	3.10	1.40	5.61	25.39	0.00	73.88
371.0	2.79	1.12	5.61	28.76	−0.34	73.67
371.3	1.88	0.72	1.35	30.09	0.42	73.64
373.2	2.35	0.81	1.35	33.37	−0.23	73.44
373.7	3.66	1.21	5.61	34.43	−0.14	73.40
376.9	4.50	1.21	5.61	42.14	−0.10	73.08
377.2	2.21	0.58	1.35	43.31	0.28	73.05
378.2	2.18	0.54	1.35	46.47	0.57	72.94
379.2	2.11	0.49	1.35	49.08	0.29	72.84
381.5	2.09	0.43	1.35	56.20	0.13	72.61

[a] Saturation temperature. [b] Mass of transferred sample condensed at $T = 243$ K. [c] Volume of nitrogen used to transfer the mass m of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at the cooling temperature $T = 243$ K.

TABLE 4: Results of Calculation of the Standard Enthalpies of Formation $\Delta_f H_m^\circ$(g) for the Dialkyl Carbonates in the Gaseous Phase at 298 K in kJ·mol^{-1}

compounds	$\Delta_f H_m^\circ$(g) atomization	$\Delta_f H_m^\circ$(g) eq 4	$\Delta_f H_m^\circ$(g) eq 5	$\Delta_f H_m^\circ$(g) G3MP2[a]	$\Delta_f H_m^\circ$(g) exp
dimethyl carbonate	−569.5	−571.3	−570.4	−570.4	−570.7 ± 0.6
methyl-ethyl carbonate	−604.0	−605.3	−604.3	−604.5	
diethyl carbonate	−638.4	−639.2	−638.3	−638.6	−637.9 ± 0.9
methyl-propyl carbonate	−624.34	−625.2	−624.3	−624.6	
mehyl-*iso*-propyl carbonate	−643.0	−643.8	−642.9	−643.2	
methyl-butyl carbonate	−645.3	−645.7	−644.7	−645.2	
methyl-*tert*-butyl carbonate	−675.1	−675.5	−674.5	−675.0	
ethyl-propyl carbonate	−658.8	−659.2	−658.2	−658.7	
ethyl-*iso*-propyl carbonate	−677.4	−677.8	−676.8	−677.3	
dipropyl carbonate	−679.3	−679.1	−678.1	−678.8	
di-*iso*-propyl carbonate	−716.5	−716.3	−715.3	−716.0	
dibutyl carbonate	−721.2	−720.0	−719.0	−720.1	
di-*tert*-butyl carbonate	−780.0	−778.8	−777.9	−778.9	
ethylene carbonate	−508.4	−509.5	−508.5	−508.8	−510.7 ± 0.9[b]
propylene carbonate	−552.3	−552.9	−551.9	−552.4	−553.9 ± 0.8[b]
butylene carbonate	−573.7	−573.8	−572.8	−573.4	−576.7 ± 1.2[b]
methyl-cyclohexyl carbonate	−662.9	−661.5	−660.5	−661.6	−657.6 ± 4.2
dicyclohexyl carbonate[c]					−763.7 ± 8.0
tert-butyl-phenyl carbonate[c]					−530.5 ± 2.5
diphenyl carbonate[c]					−297.6 ± 2.6

[a] Average value from columns 2, 3, and 4. [b] Ref 54. [c] Calculation has been not completed due to our restricted computational capability.

an alternative group-additivity procedure is required for predicting thermochemical properties of dialkylcarbonates.

3.5. Additive Calculations of Thermodynamic Properties of Carbonates. The group-additivity methods[5−9] serve as a valuable tool for many scientists and engineers whose work involves thermodynamic characterization of elementary and overall reaction processes. Benson's group-additivity method[33] seems to have the most widespread acceptance at present and the overall best record for reliability of estimation techniques. A group is defined by Benson[33] as "a polyvalent atom (ligancy ≥2) in a molecule together with all of its ligands." In this work we endorse and follow Benson.

3.5.1. Additive Calculations of the Gaseous Enthalpies of Formation of Carbonates. Our approach for evaluation of the group-additivity values (GAV)s was similar to that of others[34] in that we began by deriving GAVs for the alkane groups using as a database the same set of thermodynamic properties for 68 compounds as has been used by Cohen.[34] The method of the polyfunctional least-squares was used to evaluate the additivity parameters. The group-contributions values, which are specific for alkanes C(C)(H$_3$), C(C$_2$)(H$_2$), C(C$_3$)(H), C(C$_4$), and correction for 1−4 C−C interactions (C−C)$_{1-4}$, are well-established[7]

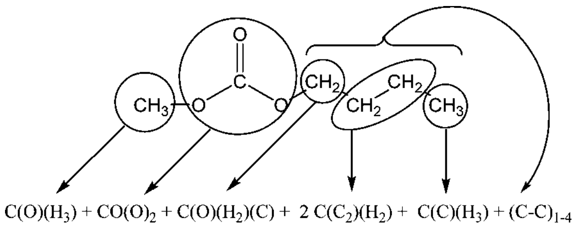
TABLE 5: Group-Additivity Values for the Calculation of Enthalpy of Formation, $\Delta_f H_m^\circ$, and Enthalpy of Vaporization, $\Delta_l^g H_m$, for Dialkyl Carbonates at $T = 298$ K (in kJ·mol^{-1})

increment	ΔH_m°(g)	$\Delta_l^g H_m$
C−(C)(H)$_3$	−41.32	5.69
C−(C)$_2$(H)$_2$	−22.90	4.88
C−(C)$_3$(H)	−11.12	2.61
C−(C)$_4$	−3.89	−0.47
(C−C)$_{1-4}$	2.34	0.10
CO(O$_2$)	−487.64	27.04
C(O)(H$_3$)	−41.32	5.69
C(O)(H$_2$)(C)	−32.50	2.64
C(O)(H)(C$_2$)	−31.85	−1.28
C(O)(C$_3$)	−21.75	−6.30
Ph(O)	95.00	27.71

TABLE 6: Results for Calculation of Enthalpies of Formation of Dialkyl Carbonates at 298 K (in kJ·mol^{-1})

compound	$\Delta_f H^\circ_m$(g) G3MP2	$\Delta_f H^\circ_m$(g) additive	Δ
dimethyl carbonate	−570.4	−570.3	−0.1
methyl-ethyl carbonate	−604.5	−602.8	−1.7
diethyl carbonate	−638.6	−635.3	−3.3
methyl-propyl carbonate	−624.6	−625.7	1.1
ethyl-propyl carbonate	−658.7	−658.2	−0.5
dipropyl carbonate	−678.8	−681.1	2.3
methyl-*iso*-propyl carbonate	−643.2	−643.4	0.2
ethyl-*iso*-propyl carbonate	−677.3	−675.9	−1.4
di-*iso*-propyl carbonate	−716.0	−716.6	0.6
dibutyl carbonate	−720.0	−722.2	2.2
di-*tert*-butyl carbonate	−778.9	−779.1	0.2
methyl-*tert*-butyl carbonate	−675.0	−674.7	−0.3
methyl-butyl carbonate	−645.2	−646.2	1.0
	average		±1.1

(see Table 5). With these values fixed, we then turned to organic carbonates to derive GAVs necessary for those compounds: $(CO)(O)_2$, $C-(C)(H)_2(O)$, $C-(C)_2(H)(O)$, $C-(C)_3(O)$. For example, for the prediction of the enthalpy of formation of methyl-butyl carbonate the following contributions should be accounted:



As a rule, the evaluation of the GAVs is based solely on experimental data, not on calculated values.[5−9] However, it has been a successful endeavor to combine experimental and ab initio methods for prediction of thermodynamic properties.[35−44] From the one side, the experimental results available now for organic carbonates (Table 1) are too restricted and they are not able to provide sufficient basis for the parametrization of the additive contributions. From the other side, the remarkable ability of the G3MP2 ab initio method to predict gaseous enthalpies of organic carbonates accurately (see Table 4) has encouraged us to involve the calculated data (Table 4) for deriving of the GAVs. For this purpose we have performed G3MP2 calculations of the diverse 13 dialkyl carbonates with the secondary, tertiary, and quaternary branching of the alkyl substituents. These compounds have constituted a matrix (see Table S6 in the Supporting Information), which has been solved using the method of the polyfunctional least-squares, and the group-additivity parameters have been evaluated (see Table 5). Now, using these GAVs, the gaseous enthalpy of formation of any arbitrarily large organic carbonate could be predicted. Analysis of the results presented in Table 6 shows that the average standard deviation of the selected data taken into correlation and predicted values are at the very acceptable level of 1 kJ·mol^{-1}.

3.5.2. Extension of the Benson's Methodology for Prediction of Enthalpies of Vaporization. Original works by Benson[33] and updating compilations[34] do not provide GAVs for calculation of vaporization enthalpies, $\Delta_l^g H_m$, at 298 K. There is not the fault of the empirical and half-empirical methods for estimation of the enthalpies of vaporization of organic compounds.[45,46] However, it seems to be logical to follow Benson's methodology for this thermodynamic property as well. In this work, we have applied for prediction of vaporization enthalpies of carbonates the same definition of groups and the same evaluation procedure as those for enthalpies of formation. The evaluation of the GAVs for prediction of the vaporization enthalpies, $\Delta_l^g H_m$, was based this time solely on experimental data (see Table 7); however, due to the lack of experimental data for carbonates with the tertiary and quaternary branching of the alkyl substituents, some additional compounds from the parent chemical family of esters have been involved (see Table 7). Group-additivity parameters have been evaluated using the method of least-squares, and they are given in Table 5. Results for predicted data presented in Table 7 show that the average standard deviations of the selected data taken into correlation and predicted values are also at the level of 1 kJ·mol^{-1}.

TABLE 7: Results for Calculation of Enthalpies of Vaporization of Dialkyl Carbonates and Esters at 298 K (in kJ·mol^{-1})

compound	$\Delta_l^g H_m$ exptl	$\Delta_l^g H_m$ additive	Δ
dimethyl carbonate	38.02[a]	38.42	−0.40
diethyl carbonate	44.35[a]	43.70	0.65
dipropyl carbonate	53.22[a]	53.46	−0.24
dibutyl carbonate	62.88[a]	63.42	−0.54
methyl acetate	32.60[b]	31.80	0.80
ethyl acetate	35.60[b]	34.44	1.16
propyl acetate	39.10[b]	39.32	−0.22
butyl acetate	43.60[b]	44.30	−0.70
iso-propyl acetate	37.20[c]	36.21	0.99
iso-propyl *iso*-butanoate	43.00[d]	44.51	−1.51
sec-butyl acetate	41.70[e]	41.19	0.51
tert-butyl acetate	38.00[c]	36.88	1.12
tert-amyl acetate	40.30[d]	41.96	−1.66
tert-amyl propionate	45.30[d]	46.84	−1.54
phenyl acetate	54.80[f]	53.82	0.98
tert-butyl-phenyl carbonate	67.57	65.52	2.05
diphenyl carbonate	80.93	82.46	−1.53
	average		±0.98

[a] Ref 4. [b] Ref 50. [c] Ref 49. [d] Ref 51. [e] Ref 52. [f] Ref 53.

3.5.3. Validation of the Experimental Results Available for Carbonates. The compilation of the available experimental data on carbonates is listed in Table 1. One needs a criterion to assess the reliability of the experimental results. One of the best flags to possible experimental errors is a large discrepancy between experimental and calculated values—especially if other, closely related compounds show no such discrepancy. In this context it was interesting to check some archival data available for the dialkyl carbonates. Experimental data for enthalpies of formation $\Delta_f H^\circ_m$(g) for methyl-cyclohexyl [CAS no. 25066-36-8] and dicyclohexyl carbonate [CAS no. 4427-97-8] were reported from combustion calorimetry and Knudsen effusion technique measurements[47] (see Table 1). Calculations of the $\Delta_f H^\circ_m$(g) for these compounds with the help of parameters listed in Table 5 provide the values of −675.3 and −780.3 kJ·mol^{-1}, respectively. The discrepancy between experimental and predicted values for both compounds is on the level of 16 ± 8 kJ·mol^{-1} and is quite acceptable taking into account the large experimental uncertainties. Thus, the data for methyl-cyclohexyl and dicyclohexyl carbonate seem to be reliable (within the boundaries of their experimental uncertainties).

The enthalpy of vaporization, $\Delta_l^g H_m$, of di-*tert*-butyl carbonate is possible to be derived from the available sublimation enthalpy (see Table 1). Calculations of the $\Delta_l^g H_m$ for this compound with the help of parameters listed in Table 5 provide the value of 48.6 $kJ \cdot mol^{-1}$, which is in a fair agreement with that of 49.2 $kJ \cdot mol^{-1}$ available from experiment.

4. Conclusions

Use of the experimental thermochemical methods with the modern first-principle calculations has made it possible to understand the interrelations of structure and energetics of organic carbonates. A combination of experimental and ab initio calculated results has allowed for revision of Benson's group-additivity method. The new derived values can be applied to the prediction of the thermochemical properties of a broad range the organic compounds containing the carbonate moiety.

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Supporting Information Available: Auxiliary quantities of the materials used in the present study (Table S1), results from combustion calorimetry (Tables S2−S4), total energies at 0 K and enthalpies at 298 K (in hartree) of the molecules studied in this work (Table S5), matrix of the parameters and experimental values involved in calculations of enthalpies of formation of dialkyl carbonates (Table S6), matrix of the parameters and experimental values involved in calculations of enthalpies of vaporization of dialkyl carbonates (Table S7), conformations and energies of the dimethyl carbonate and diethyl carbonate (Figure 1), and structures and computational details (G3MP2) on organic carbonates (Table S8). This material is available free of charge via the Internet at http://pubs.acs.org.

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