4036 *J. Phys. Chem. A* **2008,** *112,* 4036−4045

Structure−Energy Relationships in Unsaturated Esters of Carboxylic Acids. Thermochemical Measurements and ab Initio Calculations

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Received: December 6, 2007; In Final Form: February 5, 2008

Standard molar enthalpies of formation in the gaseous state of a series of alkyl 3-methylbut-2-enoates have been obtained from combustion calorimetry and results from the temperature dependence of the vapor pressure measured by the transpiration method. To verify the experimental data, we have performed ab initio calculations of all compounds. Enthalpies of formation derived from the G3MP2 method are in excellent agreement with the experimental results. Quantitative analysis of strain effects in alkyl 3-methylbut-2-enoates was discussed in terms of deviations of $\Delta_f H^\circ_m$(g) from the group additivity rules. Energetics of the cis−trans isomerization of carboxylic acid derivatives was studied using G3MP2 and DFT methods. Values of strain and cis−trans corrections derived in this work provide further improvement on the group-contribution methodology for prediction of the thermodynamic properties of compounds relevant to biodiesel.

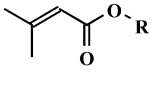
Introduction

Alkyl esters of long-chain fatty acids are called biodiesel. These esters can be obtained from vegetable oils or animal fats by transesterification with alcohols. The flow and combustion properties of biodiesel are similar to petroleum-based diesel and, thus, can be used either as a substitute for diesel fuel or more commonly in fuel blends. Derived from renewable sources, biodiesel can be used without any modification in engine design.

Typically, biodiesel from vegetable oils is composed of a blend of fatty acid esters. More than 30% of these esters are unsaturated.[1] This has prompted interest in the thermochemical properties of the unsaturated and saturated aliphatic esters.[2−3] This effort complements and extends earlier work on a number of aliphatic esters by our group.[4−9]

Direct studies of typical biodiesels are currently difficult because laboratory experiments would have to be carried out on complex, largely involatile mixtures and also because the modeling and simulation is not sufficiently developed to be able to tackle such large molecules.[10] Hence, we have chosen to work on model compounds, alkyl 3-methylbut-2-enoates, which encapsulate the essential chemical motifs of the unsaturated esters in real biodiesel and can therefore be used to provide insight into the thermochemistry of the natural product.

In this work, we explore the thermochemistry of alkyl 3-methylbut-2-enoates



where R = Me, Et, Pr, iPr, Bu, iBu, Pe including the vaporization enthalpies, $\Delta_l^g H_m$, and the standard enthalpies of formation in the liquid state, $\Delta_f H^\circ_m$(l), using experimental methods (combustion calorimetry and vapor pressure measurements). For the validation of the experimental data on unsaturated esters, high-level ab initio calculations of $\Delta_f H^\circ_m$(g) of these molecules have been performed using the *GAUSSIAN-03* program package. Absolute electronic energy values of the molecules have been obtained using the G3MP2 method. Because less than 0.02% of known organic species have had their enthalpies of formation measured,[11] the application of quantum methods is both inevitable and desirable provided that reasonable accuracy can be obtained. In this context, combined computational and experimental studies will help to reveal the accuracy of ab initio methods toward parent compounds.

Experimental Section

Materials. Samples of methyl 3-methylbut-2-enoate and of ethyl 3-methylbut-2-enoate were of commercial origin (Aldrich, Alfa). Samples of iso-propyl, propyl-, iso-butyl, butyl, and pentyl 3-methylbut-2-enoates were prepared by modified procedure[12] as follows.

To the solution of 3-methylbut-2-enoic acid (10.01 g, 0.1 mol), *p*-toluenesulfonic acid (500 mg, 0.003 mol) and H_2SO_4 (1 g, 0.01 mol) in benzene (50 mL) the corresponding alcohol (0.08 mol) was added. The vigorously stirred reaction mixture was heated under reflux for 6−8 h. A Dean-Starck apparatus was used for the continuous removal of the reaction water. After the reaction was complete, solvent was removed under reduced pressure. The product was purified by column chromatography (silica, ethyl acetate/hexane 1:4) and additionally by fractional distillation in vacuum.

Chromatographic purification of esters was accomplished using flash column chromatography on Macherey-Nagel silica gel 60 (230−400 mesh ASTM) with mixtures of solvents as mobile phases. TLC was carried out on Merck plates with aluminum backing and silica gel 60 F_{254}. NMR spectra were recorded with a Bruker ARX 300 spectrometer. Chemical shifts

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10.1021/jp7115033 CCC: $40.75

are reported in ppm (δ) and referred to internal TMS for ^{1}H NMR, deuterated solvents for ^{13}C NMR. The degree of purity was determined using GC on a capillary column HP-5 (stationary phase crosslinked 5% phenyl methyl silicone) with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 mm. The standard temperature program of the GC was $T = 333$ K for 180 s followed by a heating rate of 0.167 K·s^{-1} to $T = 523$ K. The temperature of the injector was 353 K. GC and mass spectrometric analyses were performed by the analytic laboratory of Leibniz-Institut für Katalyse e.V. at the University of Rostock.

Small amounts (about 1%) of isomeric alkyl 3-methylbut-2-enoates have been detected and identified by GC-MS in samples of iso-propyl, propyl-, iso-butyl, butyl, and pentyl 3-methylbut-2-enoates prepared according to the procedure in ref 12. Such a small amount of isomeric impurity in a sample usually does not impact the results of thermochemical studies within the boundaries of experimental uncertainties. That is why no additional corrections were applied by data treatment. It was not possible to remove small amounts of water (about 400 ppm) from the sample prepared for thermochemical measurements. The exact amount of water in each sample was measured by using Karl Fisher titration, and the appropriate corrections to the mass of sample have been performed.

Measurements of the Vapor Pressures using the Transpiration Method. Vapor pressures were determined using the method of transpiration in a saturated nitrogen stream,[13,14] and enthalpies of vaporization were obtained applying the Clausius−Clapeyron equation. 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 diameter of 1 mm provided a surface that was sufficient for the 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 optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The mass of compound collected within a certain time interval was determined by dissolving it in a suitable solvent with a certain amount of internal standard (hydrocarbon). This solution was analyzed using a gas chromatograph equipped with an autosampler. Uncertainty of the sample amount determined by GC analysis was assessed to be within 1−3%. The saturation vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of 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

$$p_i^{\text{sat}} = m_i \cdot R \cdot T_{\text{a}} / V \cdot M_{i;} \qquad V = V_{\text{N}_2} + V_i; \qquad (V_{\text{N}_2} \gg V_i) \quad (1)$$

where $R = 8.314472$ J·K^{-1}·mol^{-1}, m_i is the mass of transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase. V_{N_2} is the volume of transporting gas and T_{a} is the temperature of the soap bubble meter. The volume of transporting gas, V_{N_2}, was determined from the flow rate and time measurements. Data of p_i^{sat} have been obtained as a function of temperature and were fitted using following equation[14]

$$R \cdot \ln p_i^{\text{sat}} = a + \frac{b}{T} + \Delta_{\text{l}}^{\text{g}} C_{\text{p}} \cdot \ln\left(\frac{T}{T_0}\right) \quad (2)$$

where a and b are adjustable parameters and $\Delta_{\text{l}}^{\text{g}} C_{\text{p}}$ is the difference of the molar heat capacities of the gaseous and the liquid phase, respectively. T_0 appearing in eq 2 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, from eq 2 the expression for the vaporization enthalpy at temperature T is derived:

$$\Delta_{\text{l}}^{\text{g}} H_{\text{m}}(T) = -b + \Delta_{\text{l}}^{\text{g}} C_{\text{p}} \cdot T \quad (3)$$

Values of $\Delta_{\text{l}}^{\text{g}} C_{\text{p}}$ have been calculated according to a procedure developed by Chickos.[15] Experimental results and parameters a and b are listed in Table 1. The errors in the enthalpies of vaporization are calculated from eq 2 by using the method of least-squares, and uncertainties in values of $\Delta_{\text{l}}^{\text{g}} C_{\text{p}}$ are not taken into account. We have checked the experimental and calculation procedures with measurements of vapor pressures of n-alcohols.[14] It turned out that vapor pressures derived from the transpiration method were reliable within 1−3% and their accuracy was governed by reproducibility of the GC analysis. To assess the uncertainty of the vaporization enthalpy, we approximated the experimental data with the linear equation ln (p_i^{sat}) = $f(T^{-1})$ using the method of least-squares. The uncertainty in the enthalpy of vaporization was assumed to be identical to the average deviation of experimental ln(p_i^{sat}) values from this linear correlation. Experimental results are presented in Table 1.

Combustion Calorimetry. An isoperibol bomb calorimeter was used for the measurement of energy of combustion of esters. From a practical point of view, careful encapsulation of a sample is important in combustion calorimetry of liquids. In the present study, we used commercially available polyethene bulbs (NeoLab, Heidelberg) of 1 cm^3 volume as the sample container for liquids in order to reduce the capillary effect and make the encapsulation easier. The liquid specimen was transferred to polyethene bulbs with a syringe. The narrow neck of the container was compressed with special tweezers and was sealed outside the glovebox by heating with hot air. Then, the loaded container was placed in the bomb and burned in oxygen at a pressure of 3.04 MPa. Results from combustion experiments are given in Tables 2 and 3. The detailed procedure has been described previously.[16] 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.). From nine experiments, ϵ_{calor} was measured to be (14807.1 ± 0.70) J·K^{-1}. Correction for nitric acid formation was based on the titration with 0.1 mol·dm^{-3} NaOH (aq.). The atomic weights used were those recommended by the IUPAC Commission.[17] The sample masses were reduced to vacuum, taking into consideration the density values measured with a pycnometer (see Table 2). For converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states, the conventional procedure[18] was applied.

Results and Discussion

The enthalpy of formation in the gaseous phase of any compound is made up of two contributions: $\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{g}) = \Delta_{\text{l}}^{\text{g}} H_{\text{m}} + \Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{l})$, where $\Delta_{\text{l}}^{\text{g}} H_{\text{m}}$ is the enthalpy of vaporization and $\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{l})$ is the enthalpy of formation in the liquid state. There is surprisingly little known about the $\Delta_{\text{l}}^{\text{g}} H_{\text{m}}$ and $\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{l})$ of esters of aliphatic unsaturated carboxylic acids in

TABLE 1: Vapor Pressures, *p*, and Enthalpies of Vaporization, $\Delta_l^g H_m$, of Alkyl 3-Methyl-but-2-enoates Obtained by the Transpiration Method

T/K[a]	m/mg[b]	$V(N_2)$[c]/dm^3	flow/(dm^3·h^{-1})	p/Pa[d]	$(p_{exp} - p_{calc})$/Pa	$\Delta_l^g H_m$/(kJ·mol^{-1})	T/K[a]	m/mg[b]	$V(N_2)$[c]/dm^3	flow/(dm^3·h^{-1})	p/Pa[d]	$(p_{exp} - p_{calc})$/Pa	$\Delta_l^g H_m$/(kJ·mol^{-1})
methyl 3-methyl-but-2-enoate [CAS 924-50-5];							iso-propyl 3-methyl-but-2-enoate [CAS 25859-51-2];						
$\Delta_l^g H_m$ (298.15 K) = (46.90 ± 0.19) kJ·mol^{-1}							$\Delta_l^g H_m$ (298.15 K) = (50.01 ± 0.17) kJ·mol^{-1}						
$\ln(p/\text{Pa}) = \frac{282.395}{R} - \frac{66906.7}{R(T/\text{K})} - \frac{67.1}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$							$\ln(p/\text{Pa}) = \frac{301.2}{R} - \frac{74902.2}{R(T/\text{K})} - \frac{80.7}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
274.2	2.2	0.250	0.79	200.4	2.2	48.51	278.5	4.4	0.825	2.20	97.2	1.86	52.43
277.2	2.5	0.224	0.79	251.7	2.3	48.31	281.5	4.5	0.678	2.20	123.9	0.45	52.19
277.2	2.4	0.224	0.79	248.0	−1.3	48.31	284.5	5.5	0.660	2.20	154.6	−2.77	51.95
280.2	2.9	0.204	0.79	322.8	10.9	48.11	287.5	5.9	0.550	2.20	195.1	1.03	51.71
280.2	3.2	0.229	0.81	301.5	−10.5	48.11	290.5	6.4	0.477	2.20	241.0	−1.26	51.46
283.2	3.2	0.185	0.79	387.1	−1.0	47.91	293.5	7.3	0.440	2.20	300.2	−1.24	51.22
283.2	3.3	0.189	0.76	386.5	−1.6	47.91	298.4	8.1	0.348	2.20	430.0	−7.29	50.83
283.2	3.6	0.202	0.81	386.2	−1.9	47.91	303.4	10.4	0.312	2.20	589.2	1.57	50.42
286.2	3.4	0.158	0.79	473.8	−6.4	47.71	308.4	11.0	0.238	2.20	793.0	2.44	50.02
286.2	3.8	0.175	0.81	468.9	−11.2	47.71	313.4	9.4	0.147	2.20	1092.0	12.98	49.61
289.2	4.8	0.177	0.76	603.1	12.1	47.50							
289.2	5.2	0.189	0.81	604.1	13.2	47.50							
289.2	5.1	0.189	0.81	593.3	2.4	47.50							
292.2	4.8	0.151	0.76	704.2	−19.4	47.30							
292.2	5.4	0.162	0.81	733.0	9.5	47.30							
292.2	4.9	0.148	0.81	726.8	3.3	47.30							
295.2	5.3	0.135	0.81	858.9	−22.7	47.10							
295.2	6.6	0.162	0.81	894.8	13.3	47.10							
298.2	6.5	0.135	0.81	1062.2	−6.8	46.90							
301.2	8.0	0.135	0.81	1298.8	8.7	46.70							
304.2	9.7	0.135	0.81	1562.7	12.7	46.50							
ethyl 3-methyl-but-2-enoate [CAS 638-10-8];							n-propyl 3-methyl-but-2-enoate [Beilstein Registry 6774200];						
$\Delta_l^g H_m$ (298.15 K) = (49.30 ± 0.19) kJ·mol^{-1}							$\Delta_l^g H_m$ (298.15 K) = (53.00 ± 0.19) kJ·mol^{-1}						
$\ln(p/\text{Pa}) = \frac{291.2}{R} - \frac{71776.7}{R(T/\text{K})} - \frac{75.4}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$							$\ln(p/\text{Pa}) = \frac{305.1}{R} - \frac{77056.7}{R(T/\text{K})} - \frac{82.4}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
273.9	6.3	1.77	7.09	72.5	1.4	51.13	278.3	4.6	1.37	2.54	62.2	0.1	54.13
275.4	7.1	1.77	7.09	82.0	1.3	51.01	281.3	5.3	1.18	2.54	80.1	0.3	53.88
276.5	7.7	1.77	7.09	88.4	0.6	50.93	284.3	6.6	1.16	2.54	103.5	1.6	53.63
278.2	8.7	1.77	7.09	98.9	−1.7	50.80	287.3	6.9	1.03	2.54	128.0	−1.3	53.39
279.0	3.9	0.71	2.85	105.2	−1.8	50.74	290.3	8.0	0.933	2.54	160.3	−2.8	53.14
280.3	10.4	1.77	7.09	117.1	−1.4	50.65	293.3	8.9	0.852	2.54	201.3	−3.3	52.89
282.1	5.3	0.761	2.85	135.2	−0.9	50.51	296.3	10.1	0.761	2.54	257.3	2.0	52.65
283.3	5.4	0.720	2.88	149.0	−0.1	50.42	299.3	11.1	0.679	2.54	321.0	4.3	52.40
286.3	7.4	0.785	2.85	181.5	−4.9	50.19	302.3	12.0	0.591	2.54	390.0	−0.8	52.15
287.2	7.2	0.713	2.85	197.8	−1.4	50.13	305.3	13.3	0.510	2.54	480.0	0.2	51.90
288.2	7.7	0.720	2.88	211.3	−3.0	50.05	308.3	13.4	0.426	2.54	582.6	−3.6	51.66
290.1	3.3	0.256	1.02	247.1	1.4	49.91	311.3	13.4	0.337	2.54	717.6	4.8	51.41
292.1	11.6	0.791	2.88	286.9	3.9	49.76							
293.2	8.3	0.516	1.11	315.3	9.7	49.67							
294.4	4.4	0.256	1.02	334.7	2.7	49.58							
295.7	15.7	0.850	3.40	361.0	−1.9	49.48							
297.1	5.2	0.256	1.02	392.0	−7.0	49.38							
298.2	6.0	0.267	1.07	439.0	9.5	49.30							
302.3	7.5	0.256	1.02	563.8	1.8	48.99							
303.2	8.2	0.267	1.07	599.9	4.4	48.92							
306.2	9.6	0.256	1.02	726.5	6.6	48.69							
307.2	10.5	0.267	1.07	761.0	−5.1	48.62							
310.2	12.2	0.256	1.02	915.8	−4.9	48.39							
312.2	13.8	0.256	1.02	1041.5	3.4	48.24							
314.1	14.2	0.229	0.92	1198.1	36.7	48.10							
314.2	16.1	0.267	1.07	1165.8	−2.4	48.09							
315.0	16.3	0.256	1.02	1230.9	6.8	48.03							
316.0	17.3	0.267	1.07	1252.4	−44.9	47.95							
317.2	17.9	0.252	0.92	1374.9	−15.0	47.86							
318.2	32.8	0.428	0.92	1481.7	10.3	47.79							
319.1	21.3	0.267	1.07	1536.5	−11.8	47.72							

TABLE 1 (Continued)

T/K[a]	m/mg[b]	$V(\mathrm{N_2})$[c]/ dm^3	flow/ (dm^3·h^{-1})	p/Pa[d]	$(p_{\mathrm{exp}} - p_{\mathrm{calc}})$/ Pa	$\Delta_l^g H_m$/ (kJ·mol^{-1})
n-butyl 3-methyl-but-2-enoate [CAS 54056−51-8]; $\Delta_l^g H_m$ (298.15 K) = (56.62 ± 0.27) kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = \frac{314.4}{R} - \frac{84050.0}{R(T/\mathrm{K})} - \frac{92.0}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$						
278.9	1.5	2.44	5.43	9.9	−0.1	58.40
282.5	1.6	1.81	5.43	14.0	0.3	58.06
285.8	1.5	1.35	1.50	17.7	−0.6	57.76
290.1	1.6	0.933	1.51	26.4	0.3	57.37
294.6	2.2	0.935	1.52	38.0	0.4	56.95
297.5	2.3	0.785	1.57	46.7	−0.4	56.68
299.4	3.0	0.925	1.59	53.4	−1.1	56.51
299.8	2.3	0.666	1.41	56.0	−0.2	56.47
302.6	3.0	0.687	1.59	70.4	1.2	56.22
303.3	1.8	0.378	1.51	74.3	1.4	56.15
306.3	2.9	0.503	1.59	92.4	1.9	55.87
307.2	3.1	0.506	1.52	98.8	2.2	55.79
311.3	5.3	0.662	1.59	128.6	−0.1	55.41
312.2	3.2	0.385	1.54	132.8	−4.1	55.33
315.3	6.0	0.565	1.61	169.8	1.1	55.05
316.2	3.9	0.341	1.46	181.1	2.0	54.96
316.3	6.4	0.580	1.58	176.8	−3.4	54.95
318.3	6.6	0.514	1.62	202.8	−2.7	54.77
318.3	5.4	0.410	1.59	210.4	4.9	54.77
318.3	9.9	0.767	1.59	204.2	−1.3	54.77
319.3	6.5	0.477	1.51	216.9	−2.3	54.68
321.3	5.8	0.375	1.61	245.4	−3.8	54.49
323.3	9.4	0.527	1.76	284.9	2.2	54.31
n-pentyl 3-methyl-but-2-enoate [Beilstein Registry Number 8048681]; $\Delta_l^g H_m$ (298.15 K) = (61.83 ± 0.40) kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = \frac{331.0}{R} - \frac{91737.6}{R(T/\mathrm{K})} - \frac{100.3}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$						
288.6	1.9	3.71	4.95	7.3	0.1	62.80
291.3	2.1	3.30	4.95	9.0	−0.2	62.53
293.5	2.2	2.89	4.96	10.9	−0.2	62.30
296.4	2.4	2.47	4.95	14.2	0.0	62.01
298.5	2.5	2.07	4.96	17.0	0.1	61.80
300.4	2.2	1.61	4.83	19.8	0.0	61.61
303.4	2.1	1.23	2.55	25.0	−0.4	61.31
305.3	2.5	1.21	4.85	30.2	0.8	61.12
308.4	2.4	0.936	2.55	38.1	0.6	60.81
310.3	2.5	0.801	1.92	44.4	1.1	60.62
313.2	8.2	2.252	2.73	52.6	−1.3	60.33
315.4	2.5	0.561	1.92	63.9	0.6	60.11
323.3	6.7	0.865	2.73	110.5	0.1	59.32
323.3	3.8	0.501	2.73	108.3	−2.1	59.32
iso-butyl 3-methyl-but-2-enoate [CAS 30434−54-9]; $\Delta_l^g H_m$ (298.15 K) = (54.68 ± 0.22) kJ·mol^{-1} $\ln(p/\mathrm{Pa}) = \frac{313.8}{R} - \frac{81600.4}{R(T/\mathrm{K})} - \frac{90.3}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$						
279.6	2.1	1.22	2.87	27.7	−0.3	56.36
282.5	2.1	0.961	2.88	35.9	0.1	56.10
284.4	2.4	0.931	2.87	41.8	−0.2	55.92
285.6	3.2	1.105	2.88	46.9	0.5	55.82
288.5	2.7	0.721	2.88	59.4	0.6	55.55
291.5	3.5	0.745	2.88	76.1	1.6	55.28
293.5	5.5	1.029	2.87	86.6	−0.4	55.10
293.5	5.9	1.077	2.87	87.8	0.8	55.10
293.6	2.7	0.480	1.15	90.8	3.1	55.09
295.5	2.4	0.382	1.15	100.6	−0.8	54.92
297.4	6.4	0.886	2.87	116.1	−0.8	54.75
298.4	2.6	0.345	1.15	122.7	−3.2	54.66
300.5	2.6	0.288	1.15	144.7	−2.2	54.47
303.3	3.2	0.288	1.15	181.2	1.7	54.22
304.3	2.9	0.230	0.92	196.9	4.2	54.13
306.4	4.0	0.288	1.15	218.8	−4.2	53.94
307.4	4.9	0.335	2.87	232.7	−6.2	53.85
308.3	4.6	0.297	1.15	250.4	−3.7	53.77
309.3	5.3	0.307	0.92	273.4	1.5	53.68
310.4	5.2	0.288	1.15	288.2	−4.6	53.58
313.4	6.3	0.288	1.15	350.1	−6.8	53.30
314.3	5.9	0.253	0.92	369.1	−9.4	53.22
317.3	6.3	0.215	0.92	463.3	4.7	52.95
320.4	5.7	0.161	0.92	563.9	7.2	52.67
323.5	63.7	1.44	2.87	704.3	31.8	52.39

[a] Temperature of saturation. [b] Mass of transferred sample, condensed at $T = 243$ K. [c] Volume of nitrogen, used to transfer 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.

the literature. Practically all available experimental results are from measurements of enthalpies of combustion made in the 1930s by Schjanberg.[19] Only several recent studies[20−23] have somewhat extended the available database. In this context, a systematic investigation of the homologues series of alkyl 3-methylbut-2-enoates seems to be highly desirable.

Vapor Pressures and Enthalpies of Vaporization. A summary of vapor pressures and vaporization enthalpies of alkyl 3-methylbut-2-enoates measured in this work is presented in Table 1. The only comparison is possible with the data measured using the static apparatus with a membrane zero-manometer.[22] The vaporization enthalpies reported in that work[22] were not adjusted to the reference temperature, 298.15 K. That is why we treated experimental results from ref 22 using eqs 2 and 3, and calculated $\Delta_l^g H_m$ (298.15 K) for the sake of comparison with our results (see Figure 2). Unfortunately, the values of $\Delta_l^g H_m$ (298.15 K) for methyl-, propyl-, and butyl- 3-methylbut-2-enoates obtained from Van-Chin-Syan et al.[22] are systematically lower by 6−7 kJ·mol^{-1} in comparison to our results (see Figure 1). At the same time, the vaporization enthalpy $\Delta_l^g H_m$ (298.15 K) of pentyl 3-methylbut-2-enoate is in close agreement with our result. The reason for such a disagreement is not quite clear now. Thus, it is required to check the consistency of the

TABLE 2: Formula, Density ρ (T = 293 K), Purity, Massic Heat Capacity c_p (T = 298.15 K), and Expansion Coefficients $(\delta V/\delta T)_p$ of Alkyl 3-Methyl-but-2-enoates and Auxiliary Materials Used in the Present Study

compounds	formula	purity % mol	ρ g·cm^{-3}	$c_p{}^a$ J·K^{-1} g^{-1}	$10^{-6}\cdot(\delta V/\delta T)_p{}^b$ dm^3·K^{-1}
methyl ester	$C_6H_{10}O_2$	99.99	0.935	1.91	1.0
ethyl ester	$C_7H_{12}O_2$	99.99	0.922	1.95	1.0
propyl ester	$C_8H_{14}O_2$	98.60	0.917	1.98	1.0
butyl ester	$C_9H_{16}O_2$	98.76	0.912	2.00	1.0
iso-propyl ester	$C_8H_{14}O_2$	98.53	0.917	1.93	1.0
polythene^c	$CH_{1.93}$		0.92	2.53	0.1
cotton^d	$CH_{1.774}O_{0.887}$		1.50	1.67	0.1

[a] Calculated using procedure suggested by Chickos and Acree.[15] [b] Estimated. [c] From 10 combustion experiments, $\Delta_c u° = -(46352.1 \pm 4.0)$ J·g^{-1}. [d] From 10 combustion experiments, $\Delta_c u° = -(16945.2 \pm 4.2)$ J·g^{-1}.

experimental data set on $\Delta_l^g H_m$ (298.15 K) of alkyl 3-methyl-but-2-enoates with the help of any correlation procedure.

Correlation of Enthalpies of Vaporization with the Number of C Atoms in Esters. The correlation of enthalpies of vaporization with the number of C atoms in the series of homologues is a valuable test to check the internal consistency of the experimental results. Vaporization enthalpies $\Delta_l^g H_m$ appear to be a linear function of the number of carbon atoms of the aliphatic esters[6] and aliphatic nitriles.[24] The plot of $\Delta_l^g H_m$ (298.15 K) against the number of C atoms in the alkyl 3-methylbut-2-enoates (alkyl = Me, Et, Pr, Bu, and Pe) is presented in Figure 1. As can be seen in Figure 1, the first representative, methyl 3-methylbut-2-enoate, is slightly out of the linear correlation. Such an anomaly has also been observed for aliphatic esters[6] and aliphatic nitriles,[24] and this fact might be caused by the high dipole moment of these species. The dependence of vaporization enthalpy for the linear alkyl 3-methylbut-2-enoates on the total number of C atoms in a molecule $n \geq 6$ is expressed by the following equation

$$\Delta_l^g H_m\ (298.15\ \mathrm{K})/\ \mathrm{kJ\cdot mol}-^{1} = 20.9 + 4.02n \qquad (r = 0.9957) \quad (4)$$

from which enthalpy of vaporization $\Delta_l^g H_m$ (298.15 K) other linear representatives of this series with n > 10 can be calculated.

It is well established[25] that introduction of the double C=C bond in a linear molecule instead of the single C−C bond does not impact vaporization enthalpies very much. For example, the differences between vaporization enthalpies of hexane and hexene (or decane and decene) are only on the level of 1 kJ·mol^{-1}. To check the validity of this observation for the esters, we have presented in Figure 1 the comparison of our data on $\Delta_l^g H_m$ for unsaturated esters with those for linear aliphatic alkyl acetates. As can be seen, our data for alkyl 3-methylbut-2-enoates are in line with those for alkyl acetates within 1 kJ·mol^{-1}. At the same time, the values of $\Delta_l^g H_m$ (298.15 K) for alkyl 3-methylbut-2-enoates obtained from Van-Chin-Syan et al.[22] are definitely out of correlation (except for pentyl 3-methylbut-2-enoate).

Correlation of Enthalpies of Vaporization with Kovat's Indices. The correlation of the enthalpies of vaporization with Kovat's indices of organic compounds is another valuable method to study the systematic behavior in homologous series. Kovat's index is the retention characteristics acknowledged among analytic chemists for the identification of the individual compounds in diverse mixtures. In Kovat's index, n-alkanes serve as the standards and logarithmic interpolation is utilized defined by

$$J_x = \frac{\lg(t_x) - \lg(t_N)}{\lg(t_{N+1}) - \lg(t_N)} \cdot 100 + 100\cdot N \qquad (5)$$

where x refers to the adjusted retention time, N is the number of carbon atoms of the n-alkane eluting before, and $(N + 1)$ is the number of carbon atoms of the n-alkane eluting after the peak of interest. According to the established GC procedure, all retention times are corrected for the "dead" retention time adjusted from the retention times of the homologues n-hydrocarbons.[26]

The vaporization enthalpy $\Delta_l^g H_m$ appears to be a linear function of Kovat's indices in homologous series of alkanes, alcohols, and aliphatic esters.[6] We have used Kovat's indices available from the literature[27] for three stationary phases, SE-30, and OV-225, and DC-230, in order to test how the results fit into a systematic dependence on Kovat's indices. It can be seen from the Figure 2 that the data for $\Delta_l^g H_m$ (298.15 K) fit very well in the linear correlation, again except for methyl 3-methylbut-2-enoate. The following empirical equation for the enthalpy of vaporization of the linear and also branced alkyl 3-methylbut-2-enoates (except for methyl 3-methylbut-2-enoate) is suggested

$$\Delta_l^g H_m\ (298.15\ \mathrm{K})\ /(\mathrm{kJ\cdot mol^{-1}}) = 7.9 + 0.045\cdot J_x \qquad (r = 0.9851)\ \text{for SE-30} \quad (6)$$

$$\Delta_l^g H_m\ (298.15\ \mathrm{K})\ /(\mathrm{kJ\cdot mol^{-1}}) = -0.7 + 0.043\cdot J_x \qquad (r = 0.9914)\ \text{for OV-225} \quad (7)$$

$$\Delta_l^g H_m\ (298.15\ \mathrm{K})\ /(\mathrm{kJ\cdot mol^{-1}}) = 11.4 + 0.041\cdot J_x \qquad (r = 0.9855)\ \text{for OV-225} \quad (8)$$

where J_x is the Kovat's index of an ester. This linear relationship can be used as evidence of the internal consistency of our experimental results for vaporization enthalpies.

Thus, values of vaporization enthalpies of alkyl 3-methylbut-2-enoate derived in this work show internal consistency and they can be used with high reliability for further calculation of the standard enthalpies of formation, $\Delta_f H_m^\circ$(g) at 298.15 K.

Enthalpies of Formation $\Delta_f H_m^\circ$(l) at 298.15 K of Alkyl 3-Methylbut-2-enoates. Results of typical combustion experiments for esters are summarized in Table 3 (extended experimental tables are given in the Supporting information). The means of individual values of the standard massic energies of combustion $\Delta_c u°$, were derived as a rule from 5−8 independent experiments. To derive $\Delta_f H_m^\circ$(l) from the molar enthalpy of combustion $\Delta_c H_m^\circ$, molar enthalpies of formation of H_2O (l): −(285.830 ± 0.042) kJ·mol^{-1} and CO_2 (g): −(393.51 ± 0.13) kJ·mol^{-1} have been used as assigned by *CODATA*.[28] Table 4 lists the derived standard molar enthalpies of combustion and standard molar enthalpy of formation of the esters derived in this work. The total uncertainty was calculated according to the guidelines presented by Olofsson.[29] The uncertainty assigned to $\Delta_f H_m^\circ$ is twice the overall standard deviation and includes 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.

Some previous experimental values of $\Delta_f H_m^\circ$(l) for methyl, propyl, butyl, and pentyl 3-methylbut-2-enoates have been determined by Van-Chin-Syan et al.[22] using combustion calorimetry with the static bomb. Their values are systematically

TABLE 3: Results for Typical Combustion Experiments at $T = 298.15$ K ($p^\circ = 0.1$ MPa) of the Alkyl 3-Methylbut-2-enoates[a]

	methyl-	ethyl-	propyl-	iso-propyl-	butyl-
m (substance)/g [b]	0.33505	0.4336	0.427197	0.383103	0.356069
m'(cotton)/g [b]	0.001111	0.003215	0.001122	0.001133	0.001407
m''(polythen)/g [b]	0.365043	0.28195	0.28717	0.321762	0.290332
ΔT_c/K[c]	1.8139	1.80439	1.84823	1.85715	1.72999
$(\epsilon_{calor})\cdot(-\Delta T_c)$/J	−26 858.6	−26 717.8	−27 367	−27 499	−25 616.1
$(\epsilon_{cont})\cdot(-\Delta T_c)$/J	−33.89	−33.74	−34.7	−34.92	−32.14
ΔU_{decomp} HNO_3/J	50.47	49.57	50.77	51.36	48.98
ΔU_{corr}/J[d]	9.23	9.25	9.19	9.16	8.24
$-m'\cdot\Delta_c u'$/J	18.83	54.48	19.01	19.2	23.84
$-m''\cdot\Delta_c u''$/J	16 923.76	13 071.48	13 313.49	14 917.21	13 460.08
$\Delta_c u^\circ\cdot$(l)/(J·g^{-1})	−29 518.4	−31 288.7	−32 793.3	−32 724.8	−34 002.2

[a] For the definition of the symbols see ref 18, macrocalorimeter: $T_h = 298.15$ 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] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\epsilon_{cont})\cdot(-\Delta T_c) = (\epsilon^i_{cont})\cdot(T^i - 298.15\text{ K}) + (\epsilon^f_{cont})\cdot(298.15\text{ K} - T^f + \Delta T_{corr.})$. [d] ΔU_{corr}, the correction to standard states, is the sum of items 81−85, 87−90, 93, and 94 in ref 18.

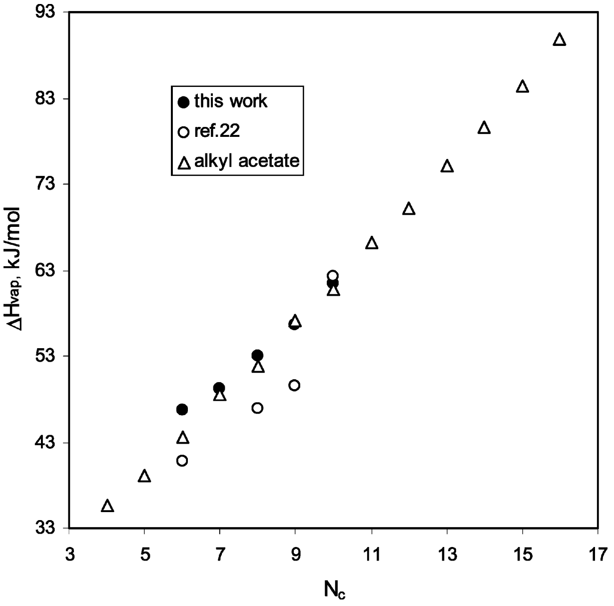


Figure 1. Correlation of enthalpies of vaporization of alkyl 3-methylbut-2-enoates and n-alkyl acetates[6] with the number of C atoms in esters.

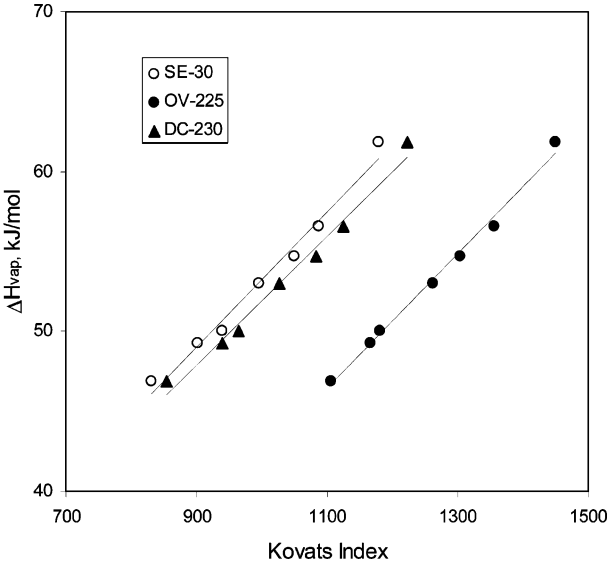


Figure 2. Correlation of enthalpies of vaporization of alkyl 3-methylbut-2-enoates (alkyl = Me, Et, Pr, iPr, Bu, iBu, Pe) with Kovat's indices at 423 K.[27] ○, SE-30; ▲, DC-230, ●, OV-225.

in disagreement by about 20 kJ·mol^{-1} with the result obtained in this work (see Figure 3). There was apparently something wrong with the data treatment of the combustion results published in the ref 22 because some years later the same authors presented revision of their data[22] and the recalculated data became closer to the result obtained in this work (see Figure 3). But, the agreement between the two data sets still remains very poor. One of the possible reasons for the disagreement of the combustion results could be traces of water, which (in contrast to our work) were not determined and taken into account in the refs 22 and 23.

Correlation of $\Delta_f H^\circ_m$(l) of Alkyl 3-Methylbut-2-enoates with Those $\Delta_f H^\circ_m$(l) of Analogous n-Alkyl Acetates. Taking into account the reactivity and thermal lability of the unsaturated esters, which could aggravate purification and thermochemical measurements, evidence of the reliability of the results derived in this work seems to be desirable. Values of $\Delta_f H^\circ_m$(l) of alkyl 3-methylbut-2-enoate derived in this work could be checked for internal consistency using enthalpies of formation of n-alkyl acetates where reliable experimental data is available from the literature.[30] Such a procedure has been applied for the benzyl derivatives successfully.[31] Indeed, considering the general structures of alkyl esters of the carboxylic acids ($R_1-CO_2-R_2$), it is obvious that the alkyl 3-methylbut-2-enoates under study in this work, are parents to the structures of the n-alkyl acetates because of the common alkyl R_2. Thus, the correlation of the enthalpies of formation of alkyl 3-methylbut-2-enoate with those for n-alkyl-acetates should give a linear correlation if the data used for the correlation are consistent. It can be seen from Figure 4 that data involved in comparison fit very well into the linear correlation with correlation coefficient $r = 0.9990$. This near-perfect relationship can subsequently be used at least as an indication of the internal consistency of our experimental results.

Thus, values of enthalpies of formation of alkyl 3-methylbut-2-enoate derived in this work show internal consistency and they have been used for calculation of the standard enthalpies of formation, $\Delta_f H^\circ_m$(g) at 298.15 K.

Correlation of $\Delta_f H^\circ_m$(g) of Alkyl 3-Methylbut-2-enoates with Those $\Delta_f H^\circ_m$(g) of Analogous n-Alkyl Acetates. Gaseous enthalpies of formation $\Delta_f H^\circ_m$(g) of alkyl 3-methylbut-2-enoates were derived in this work as the sum of the own experimental results of $\Delta_f H^\circ_m$(l) and of enthalpies of vaporization listed in Table 4. The set of the $\Delta_f H^\circ_m$(g) of alkyl 3-methylbut-2-enoates derived in this work could be further checked for internal consistency using gaseous enthalpies of formation of n-alkyl acetates in the same way as it has just been performed for the enthalpies of formation in the liquid state. As can be seen from Figure 5, methyl, ethyl, propyl, and butyl esters involved in comparison fit well in to the linear correlation with correlation coefficient $r^2 = 0.9994$. At the same time, the point for the R_2 = iso-propyl is slightly out of correlation.

TABLE 4: Thermochemical Data at $T = 298.15$ K ($p° = 0.1$MPa) for Alkyl 3-Methyl-but-2-enoates Studied in This Work (kJ·mol^{-1})

compounds	$\Delta_c H^\circ_m$ (l)	$\Delta_f H^\circ_m$ (l)	$\Delta_l^g H_m$	$\Delta_f H^\circ_m$ (g)/(exp)	$\Delta_f H^\circ_m$ (g)(calc)^a	$H_S{}^b$
methyl ester	−3372.8 ± 1.3	−417.5 ± 1.5	46.9 ± 0.2	−370.6 ± 1.5	−387.9	17.3
ethyl ester	−4014.5 ± 2.1	−455.0 ± 2.3	49.3 ± 0.2	−405.7 ± 2.3	−421.6	16.0
propyl ester	−4669.6 ± 2.6	−479.4 ± 2.8	53.0 ± 0.2	−426.4 ± 2.8	−443.1	16.7
butyl ester	−5319.0 ± 2.6	−509.3 ± 2.9	56.6 ± 0.3	−452.6 ± 2.9	−464.6	12.0
iso-propyl ester	−4657.5 ± 3.2	−491.4 ± 3.4	50.0 ± 0.2	−441.4 ± 3.4	−441.4	19.8

[a] Calculated as the sum of strain-free increments (see text). [b] Strain enthalpy $H_S = \Delta_f H^\circ_m(g)(exp) - \Delta_f H^\circ_m(g)(calc)$

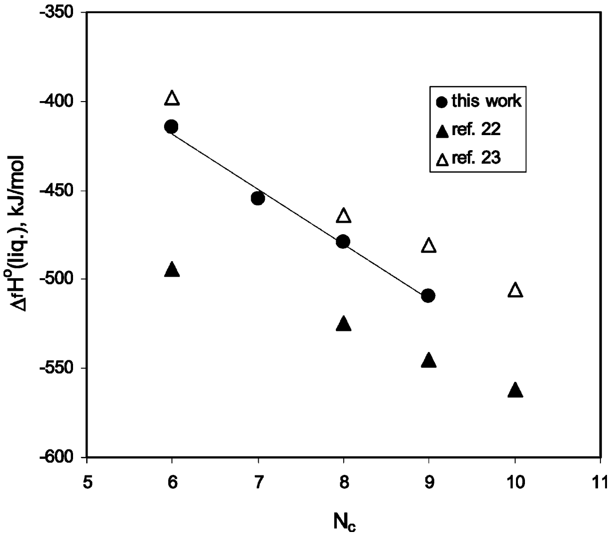


Figure 3. Correlation of enthalpies of formation in liquid phase of alkyl 3-methylbut-2-enoates (alkyl = Me, Et, Pr, Bu) with the number of C atoms in esters.

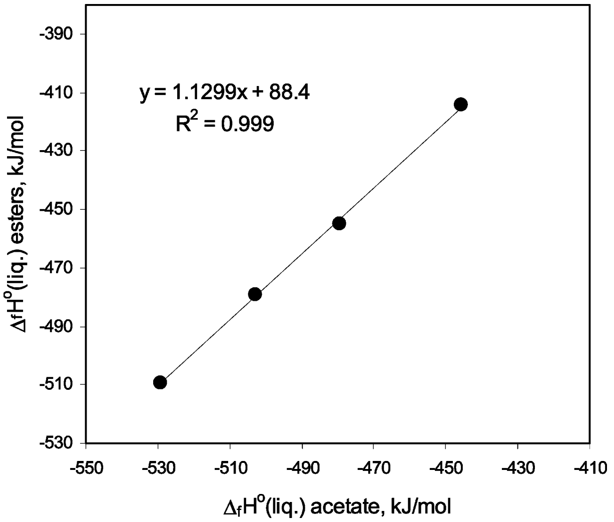


Figure 4. Correlation of $\Delta_f H^\circ_m$(l) of alkyl 3-methylbut-2-enoates with those $\Delta_f H^\circ_m$(l) of analogous n-alkyl acetates[30] (alkyl = Me, Et, Pr, Bu).

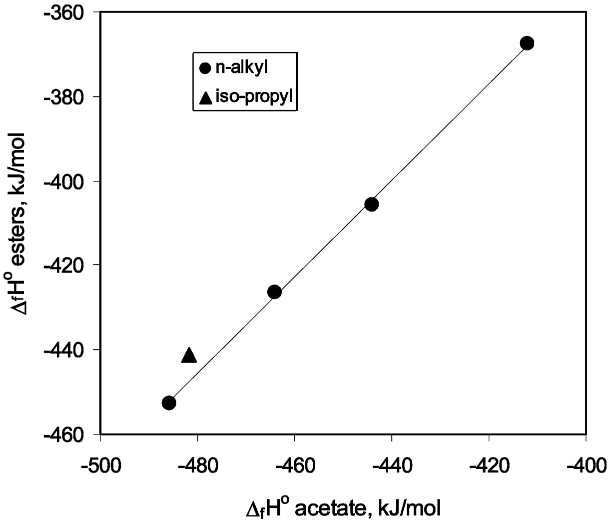


Figure 5. Correlation of $\Delta_f H^\circ_m$(g) of alkyl 3-methylbut-2-enoates with those $\Delta_f H^\circ_m$(g) of analogous n-alkyl acetates[30] (alkyl = Me, Et, Pr, Bu, iPr).

However, as will be discussed below, a possible explanation for such a deviation could be sterical repulsions of the methyl substituents in iso-propyl 3-methylbut-2-enoate, which are expected to be substantially large as those in iso-propyl acetate.

Structure−Energy Relationships. Nonbonded Interactions and Strain Enthalpies H_S of Alkyl 3-Methylbut-2-enoates. The conventional strain-enthalpy, H_S, of a molecule is defined as the difference between its experimental enthalpy of formation $\Delta_f H^\circ_m$(g) and the calculated sum of the Benson-type increments[32,33] for this molecule. Indeed, the alkyl 3-methylbut-2-enoates listed in Table 4 present a typical example of similarly shaped molecules ($R_1-CO_2-R_2$), where an alkyl substituent R_2 is attached to the carboxyl group. Hence the strain, H_S, of a molecule is expected to provide insight into the energetic interact-ions of an alkyl substituent R_2 with the (R_1-CO_2-) moiety.

The system of strain-free increments[34] is based on the standard enthalpies of formation $\Delta_f H^\circ_m$(g) of simple homologous ("strainless") molecules. Strain-free group additivity increments for hydrocarbons[34] are well-defined. Their advantage with respect to the classic Benson increments[32] is the possibility to determine strain enthalpies directly. All of the increments necessary in this work are as follows:[33,34] $CH_3[C] = -42.05$ kJ·mol^{-1}; $CH_2[2C] = -21.46$ kJ·mol^{-1}; $CH[3C] = -9.04$ kJ·mol^{-1}; $C_dH_2[C_d] = 26.4$ kJ·mol^{-1}; $C_dH[C, C_d] = 36.0$ kJ·mol^{-1}; $C_d[2C, C_d] = 42.7$ kJ·mol^{-1} (C_d represents the double bonded C atoms). Strain-free group additivity increments for ester:[9] $CO_2[2C] = -327.05$ kJ·mol^{-1}; $CH3[CO_2] = -42.05$ kJ·mol^{-1}; $CH_2[CO_2, C] = -17.4$ kJ·mol^{-1}; $CH[CO_2, 2C] = -7.4$ kJ·mol^{-1}; $CH_3[O] = -42.05$ kJ·mol^{-1}; $CH_2[O, C] = -33.8$ kJ·mol^{-1}; $CH[O, C] = -31.3$ kJ·mol^{-1}; $C_dH[CO_2, C_d] = 22.7$ kJ·mol^{-1}(derived from n-butyl acrylate[20]). Using the group-additivity parameters given and the values of $\Delta_f H^\circ_m$(g) of compounds (Table 4) derived in this research, the values of strain enthalpies $H_S = (\Delta_f H^\circ_m(g) - \Sigma$ increments) of alkyl 3-methylbut-2-enoates have been estimated. These resulting strain interactions are listed in the last column of Table 4.

All studied n-alkyl 3-methylbut-2-enoates are noticeably strained about 15 kJ·mol^{-1}; refer to Table 4. These strains are equal (within the boundaries of their experimental uncertainties) as expected for linear alkyl derivatives. Indeed, according to Figure 6, the origin of strain in n-alkyl 3-methylbut-2-enoates is mainly due to the nonbonded repulsions of oxygen lone pairs (and also possibly of the π electrons of the double bond) with

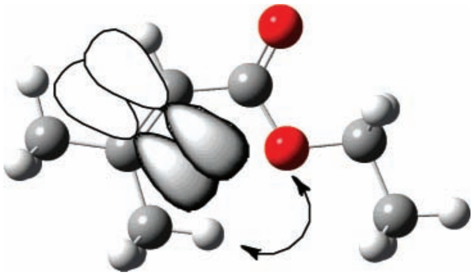


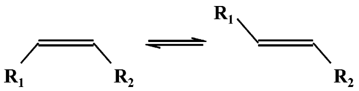
Figure 6. Steric repulsions of substituents in ethyl 3-methylbut-2-enoate.

the methyl substituent in the 3 position. At the same time, the linear substituent R_2 is out of interactions due to free rotation and it is hardly able to contribute to the strain.

Such a similarity of strains in n-alkyl derivatives again proves the consistency of the procedure and the experimental data involved in the interpretation. It makes oneself conspicuous, that the strain of the ester with the branched R_2, namely iso-propyl 3-methylbut-2-enoate, $H_S = 19.8$ kJ·mol^{-1}, is somewhat larger than that for the ester with the linear R_2. This strain reflects the intrinsic strain, typical for the branched molecules, due to nonbonded sterical interactions of methyl groups and attached to the secondary carbon atom.[35,36] Thus, this additional strain is apparently the reason for outlying of the appropriate point for the iso-propyl derivative on Figure 6 as discussed above.

Structure−Energy Relationships. The Relative Stability of cis and trans Isomers. Because of the fact that biodiesel from vegetable oils is composed of a blend of unsaturated and saturated fatty acid esters, the position of the double bond in the molecule is not fixed and could occur at any part of the alkyl chain, close to or distant from the carboxyl group. Following, diverse cis and trans isomers are naturally presented in the biodiesel. In order to predict the energetics of unsaturated esters as well as of biodiesel, the knowledge of the appropriate corrections for cis−trans interactions is required.

One of the basic rules of organic chemistry is that trans isomers of alkenes are more stable than the cis forms. This orientation is readily explained by the short $CH_3\cdots CH_3$ distance in *cis*-but-2-ene. Allowing for the bond distortions, the nonbonded repulsions between the methyl groups stabilize the trans form of about 4−5 kJ·mol^{-1} (see Table 5). However it is well known[37] that attachment of halogens to the 1 and 2 positions of the ethane stabilizes the cis form. Unfortunately, experimental evidence of cis−trans preferences in the unsaturated carboxylic acid derivatives are limited or of a questionable quality. For this reason, we decided to use ab initio methods for study of the following reaction of cis−trans isomerization



where R_1 = Me or Et and R_2 = Me or Et, COOH, or $COOCH_3$.

Taking into account the similarity of the molecules under calculations, the relative energies calculated using the composite G3MP2 and DFT methods are expected to predict the more stable structure correctly. A systematic quantum mechanical study of the possible conformations and their relative stabilities has been conducted. The molecules were considered as a two-rotor system having internal rotation about C−C and C−O bonds with the possibility of hindered rotation of the alkyl group. The most stable conformers of the cis and trans configurations of each species involved in the reaction isomerization were taken into account for the calculation of cis−trans conversion presented in the Table 5. As can be seen in this table, for alkenes, unsaturated carboxylic acids, and unsaturated esters the trans isomer is 5−7 kJ·mol^{-1} more stable than the cis isomer according to the ab initio calculations. The results from both G3MP2 and DFT methods are generally indistinguishable, and they are also acceptable close to the experimental data available only for alkenes (see Table 5).

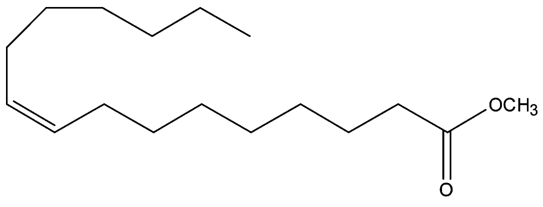
TABLE 5: Study of the Reaction Enthalpy $\Delta_r H_{cis\to trans}$ of the cis−trans Isomerization in the Carboxylic Acid Derivatives

	$\Delta_r H_{cis\to trans}$ (in kJ·mol^{-1})		
compounds	G3MP2	DFT[a]	$\Delta_r H_{cis\to trans}$,exp (in kJ·mol^{-1})
$CH_3{-}CH{=}CH{-}CH_3$	−5.1	−6.1	−4.3[48]
$CH_3{-}CH{=}CH{-}CH_2{-}CH_3$	−5.2	−6.6	−4.9[48]
$CH_3{-}CH_2{-}CH{=}CH{-}CH_2CH_3$	−5.3	−7.2	−4.0[49]
$HOOC{-}CH{=}CH{-}CH_3$	−7.4	−7.4	
$HOOC{-}CH{=}CH{-}CH_2{-}CH_3$	−7.3	-7.0	
$HC_3OOC{-}CH{=}CH{-}CH_3$	−7.3	−7.3	
$HC_3OOC{-}CH{=}CH{-}CH_2{-}CH_3$	−7.2	−7.9	

[a] B3LYP/6-31G(d).

Our calculations performed for the but-2-ene, 2-butenoic acid, and methyl 2-butenoate provide the effect of cis−trans interactions of Me, −COOH, or COOMe with the terminal CH_3 group, which are represenatative of relatively short molecules. Because unsaturated esters in biodiesel are usually long-chained molecules, it is of interest to study whether extension of the alkyl chains to the left and to the right side of the double bond (formally, exchange methyl with methylene group) impacts the cis−trans interactions or not? From a general point of view, the methylene group possess somewhat less spatial requirements in comparison to the methyl group; thus, it is reasonable to expect that cis−trans interactions in molecules such as pentene-2 or hexene-3, 2-penetenoic acid, or methyl 2-pentenoate (see Table 5) should be less intensive. However, according to the result from our ab initio calculations listed in Table 5, the trans isomers of the latter molecules are in the same way 5−7 kJ·mol^{-1} more stable than the cis isomer. Following, the individual corrections for the strain of the cis isomer given in Table 5 could be simply applied for the longer molecules that are parent of the structures studied in this work.

Although the corrections for strain determined in this work are moderate, these values are useful for further improvement on the group-contribution methodology for estimation of the thermodynamic properties of unsaturated esters of carboxylic acids. The derived values of increments and H_S can be applied for the prediction of the energy content of biofuels and for modeling and simulation of the thermochemistry and kinetics of decomposition reactions of biofuels.[10] For instance, gaseous enthalpy of formation for (Z)-9-hexadecenoic acid, methyl ester (one of the unsaturated esters detected in the babassu biodiesel[1])



could be calculated with the help of the aforementioned group contributions:

TABLE 6: Results of G3MP2 Calculation of the Standard Enthalpy of Formation $\Delta_f H^\circ_m$ (g) at 298.15 K for the Alkyl 3-Methyl-but-2-enoates (in kJ·mol^{-1})

	G3MP2					
		bond separation				
compounds	atomization	1	2	3	$\Delta_f H^\circ_{m\ G3MP2}$[a]	$\Delta_f H^\circ_{m\ exp}$
methyl ester	−373.4	−371.1	−372.4	−371.9	−372.2 ± 1.0	−370.6 ± 1.5
ethyl ester	−407.0	−404.2	−405.6	−405.0	−405.5 ± 1.2	−405.7 ± 2.3
propyl ester	−427.4	−424.2	−425.5	−424.9	−425.5 ± 1.4	−426.4 ± 2.8
butyl ester	−448.4	−444.6	−445.9	−445.4	−446.1 ± 0.8	−452.6 ± 2.9
iso-propyl ester	−445.3	−442.0	−443.4	−442.8	−443.4 ± 1.4	−441.4 ± 3.4
iso-butyl ester	−457.7	−453.9	−455.3	−454.8	−455.4 ± 1.6	

[a] Calculated as the average from atomization and bond separation procedures (see text).

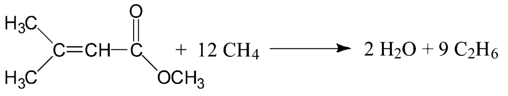
$$\Delta_f H^\circ_m\,(g) = CH_3[C] + 11 \times CH_2[2C] + CH_2[CO_2, C] + CH_3[O]$$

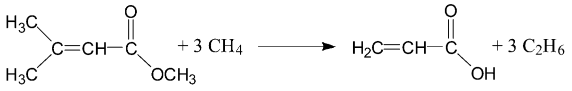
$$CO_2[2C] + 2 \times C_dH[C, C_d] + \text{cis-correction (alkenes)}$$

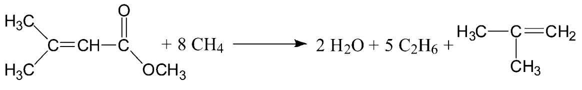
Quantum Chemical Calculations for Alkyl 3-Methylbut-2-enoates. Combination of quantum methods with thermochemical experiments has become very common in recent literature.[38−40] It has been shown hat ab initio calculations are suitable to predict the formation enthalpies of norbornane[41] or substituted benzenes.[42,43] For this reason, experimental enthalpies of formation $\Delta_f H^\circ_m$(g) of alkyl 3-methylbut-2-enoates have been compared with those obtained from high-level ab initio methods.

Calculations were made with the *Gaussian 03* Rev.04 suite of programs.[44] The DFT methods require a moderate expense of time and provide good results for normal frequencies of molecules, whereas the electronic energies of the molecules are not always predicted in a satisfying way. Family compound-G* methods provide more reliable results concerning electronic energies and are therefore preferably used for calculating thermodynamic quantities such as enthalpies of formation and enthalpies of reaction.[38−40] In this work, we have applied a G3MP2 method for predicting the gaseous enthalpies of the formation of esters. 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)/6-31G(d), QCISD(T)/6-31G(d), and MP2/GTMP2Large levels of theory (for details see ref 45). The enthalpy values of the studied compounds at $T = 298$ K were evaluated according to the standard thermodynamic procedures.[46]

In this work, we calculated enthalpies of formation of alkyl 3-methylbut-2-enoates with the help of an atomization procedure[47] as well as using three following bond-separation reactions (methyl ester is given as an example):


(1)


(2)


(3)

Using the enthalpies of reactions 1−3 calculated by G3MP2 methods together with the enthalpies of formation, $\Delta_f H^\circ_m$(g), for other reactions participants taken from Pedley et al.,[30] the enthalpies of formation of alkyl 3-methylbut-2-enoates have been calculated (see Table 6). The experimental enthalpy of formation $\Delta_f H^\circ_m$(g) for acrylic acid available in the literature is uncertain.[50] In this work, we have evaluated $\Delta_f H^\circ_m(g) = -323.3 \pm 1.8$ kJ·mol^{-1} of acrylic acid (see calculations in the Supporting Information) and used this value in the bond separation reaction (2).

Enthalpies of formation of alkyl 3-methylbut-2-enoates calculated by the G3MP2 method using the bond separation reactions 1−3 as well as using the atomization procedure are indistinguishable within 1−2 kJ·mol^{-1}. For this reason, we decided to take the average of this values. These averaged values, $\Delta_f H^\circ_m(g)_{G3MP2}$, are given in the Table 6, and they are in excellent agreement with the experimental data derived in this work (see Table 4).

Conclusions

The purpose of this work was to establish a consistent set of experimental thermochemical quantities for unsaturated esters of carboxylic acids. Values of strain and cis−trans corrections derived in this work provide further improvement on the group-contribution methodology for prediction of the thermodynamic properties of compounds relevant to biodiesel. One of the ab initio methods from G* series - G3MP2 (moderate on the scale of time-consuming) could be further recommended for calculation of enthalpies of formation of parent unsaturated and saturated esters of carboxylic acids.

Acknowledgment. V. E., A. T., and S. K. acknowledge gratefully a research scholarship from the Research Training Group "New Methods for Sustainability in Catalysis and Technique" of German Science Foundation (DFG).

Supporting Information Available: Spectroscopic data, results from combustion calorimetry (Tables S1−S5), total energies at 0 K and enthalpies at 298.15 K (in Hartree) of the molecules studied in this work (Table S6), and calculation of the gaseous enthalpy of formation of acrylic acid. This material is available free of charge via the Internet at http://pubs.acs.org.

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