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The low-temperature heat capacity and ideal gas thermodynamic properties of isobutyl *tert*-butyl ether

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Abstract

The heat capacities of isobutyl *tert*-butyl ether in crystalline, liquid, supercooled liquid, and glassy states were measured by vacuum adiabatic calorimetry over the temperature range from (7.68 to 353.42) K. The purity of the substance, the glass-transition temperature, the triple point and fusion temperatures, and the enthalpy and entropy of fusion were determined. Based on the experimental data, the thermodynamic functions (absolute entropy and changes of the enthalpy and Gibbs free energy) were calculated for the solid and liquid states over the temperature range studied and for the ideal gas state at T = 298.15 K. The ideal gas heat capacity and other thermodynamic functions in wide temperature range were calculated by statistical thermodynamics method using molecular parameters determined from density-functional theory. Empirical correction for coupling of rotating groups was used to calculate the internal rotational contributions to thermodynamic functions. This correction was found by fitting to the calorimetric entropy values.

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1. Introduction

Tertiary ethers have a number of desirable physicochemical properties that make them perspective for using as fuel additives [1]. First, they have a high octane number, therefore adding the ethers to a gasoline increases its octane rating that helps to prevent an engine from a detonation. Second, an addition of combined oxygen to the gasoline promotes more complete combustion of the fuel that reduces an emission of such exhaust pollutants as carbon monoxide, nitrogen oxides, volatile organic compounds and solid particles. Methyl *tert*-butyl ether (MTBE) has been widely used all over the world for the past 20 years to replace toxic lead compounds as octane enhancers. Despite some desirable properties, MTBE has high volatility in the summer season and has been found to contaminate ground and drinking water. It is likely that heavier tertiary ethers having lower volatility and solubility in water will soon mainly replace MTBE as oxygenating fuel additive. Key thermodynamic properties (enthalpies of combustion and formation, heat capacity, enthalpy of vaporization, and saturated vapor pressure) for alternative ethers need to be considered in the objective selection of them as the octane enhancing additives to the engine fuels.

Reference [2] reports our determination of the lowtemperature heat capacities of *n*-propyl *tert*-butyl ether (NPTBE) and isopropyl *tert*-butyl ether (IPTBE) by

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vacuum adiabatic calorimetry and calculation of thermodynamic functions $S^{\circ}(T)$, $H^{\circ}(T) - H^{\circ}(0)$ and $G^{\circ}(T) - H^{\circ}(0)$ in the ideal gas state at T = 298.15 K. In Ref. [3], the standard enthalpies of formation and ideal gas thermodynamic functions of NPTBE and IPTBE were calculated based on DFT (density-functional theory). Both experimental and calculation methods were combined in [4,5] for studying ethyl *tert*-butyl ether (ETBE) and ethyl *tert*-amyl ether (ETAE) in wide temperature range from (5 to 1000) K. In this paper, we report an application of these methods to isobutyl *tert*butyl ether (IBTBE) that is promising fuel additive and can also be used for extracting pure isoolefins from the gas hydrocarbons fraction in oil processing.

2. Experimental

2.1. Methods and results

The IBTBE was prepared in a reaction between isobutanol and isobutylene at T = 313 K in the presence of a helium cationite Levatit S-100 as a selective catalyst. The reaction product was purified from residual of alcohol and isobutylene by washing with distilled water and blowing through with nitrogen under vacuum. Then the ether was dried over Na₂SO₄ and rectified in the vacuum. According to a gas-liquid chromatography, sample purity was 0.9992 mass fraction at analysis sensitivity 0.0001 mass fraction. The total amount of impurities was determined by calorimetric fractional melting as described in [6] and found to be $8 \cdot 10^{-4}$ mole fraction. The major impurities were isobutanol and isobutylene.

The heat capacity of IBTBE was measured in a fully automated setup [7] that consisted of a vacuum adiabatic calorimeter, data acquisition and control system, and a personal computer. The sample of the ether was put in a stainless steel cylindrical container (volume ~ 1 cm³) which was supplied with a brass lid and sealed by means of an indium gasket. The temperature of the calorimeter was measured using (rhodium + iron) resistance thermometer ($R_{\rm O} \sim 100 \ \Omega$) calibrated on ITS-90. An accuracy of the temperature measurement is $\pm 5 \cdot 10^{-3}$ K. The temperature difference between the calorimeter and the adiabatic shield was measured by a four-junction (copper + 0.001 mass of iron) - Chromel thermocouple. The data acquisition system controlled the adiabatic condition of experiment with a stability of (1–3) mK throughout the whole temperature interval. A small cryostat with the calorimeter was placed directly in transport Dewar flasks that made it possible to cut down cooling agents (liquid helium and nitrogen). The cryostat was evacuated by a cryosorption using a carbon adsorber. The heat capacity of IBTBE, Csat,m, was measured at the saturated vapor pressure over the temperature range from (7.68 to 353.42) K. The accuracy of the $C_{\text{sat},m}$ values are about 2% between the temperatures from (7.6 to 15) K, (0.5 to 1)% in the temperature range from (20 to 80) K, and (0.2 to 0.3)% above 80 K. The difference between $C_{\text{sat},m}$ and $C_{\text{p},m}$ values that was evaluated at T = 298.15 K, was smaller than the uncertainties of $C_{\text{sat},m}$ and not taken into account for the whole temperature interval studied.

The solid phase of IBTBE was formed by cooling the liquid sample from the room temperature at a rate of $(1-2) \cdot 10^{-3}$ K \cdot s⁻¹ followed by quenching it at T = 77.4 K during 24 h. The heat capacity curve (figure 1) reveals a glass, supercooled liquid, and crystalline phase of the ether. During the transitions of the glass into the supercooled liquid, spontaneous liberation of the heat took place at the temperatures from (30 to 34) K higher than the glass-transition temperature. This phenomenon was caused by crystallization of the sample. To obtain the stable crystalline phase, the solid specimen was annealed at the temperatures by (10 to 15) K below the triple point for 24 h and then quenched at T = 77.4 K for the same period.

Table 1 contains the $C_{p,m}/R$ values of the IBTBE in the crystalline, liquid, supercooled liquid, and glassy states. The heat capacity values could not be measured over the whole range of the supercooled liquid. They were obtained only for the temperature intervals by 23 K above glass-transition temperature, T_{gl} and 7.6 K below the triple point temperature, T_{tp} .

The purity and the triple point temperature of the ether were determined from fractional melting study the dependence of the equilibrium fusion temperatures, T_i , on the reciprocal fraction of the sample melted, $1/F_i$. Three experiments were performed to obtain the $T_i = f(1/F_i)$ dependence. An example is given in table 2.



FIGURE 1. Experimental molar heat capacity, $C_{p,m}$, of isobutyl *tert*butyl ether as a function of temperature, T, where T_{gl} and T_{tp} denote the temperatures of the glass transition and triple point. In the insert, a dependence of $C_{p,m}/T$ on T^2 is given for the helium range of the temperatures.

TABLE 1

Experimental molar heat capacity $C_{p,m}$ of isobutyl *tert*-butyl ether ($M = 130.231 \text{ g} \cdot \text{mol}^{-1}$, mass of the sample used = 0.738214 g, $R = 8.314472 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T/K	$C_{\mathrm{p},m}/R$	T/K	$C_{\mathrm{p},m}/R$	T/K	$C_{\mathrm{p},m}/R$	T/K	$C_{\mathrm{p},m}/R$
			Cr	vstal			
7.68	0.1610	42.60	5.753	83.57	10.71	121.09	15.01
8.33	0.2096	43.66	5.883	86.51	11.13	123.02	15.23
8.97	0.2666	44.72	6.044	87.51	11.22	123.99	15.37
9.61	0.3342	45.78	6.155	88.51	11.30	124.96	15.45
10.26	0.3993	46.84	6.301	89.50	11.44	125.92	15.57
11.02	0.4978	47.90	6.429	90.50	11.55	126.91	15.66
11.92	0.6213	48.96	6.574	91.51	11.68	127.10	15.70
12.83	0.7564	50.01	6.683	92.51	11.82	127.90	15.74
13.74	0.8960	51.07	6.804	93.50	11.92	128.89	15.79
14.65	1.048	52.12	6.953	94.49	12.05	129.13	15.86
15.57	1.205	53.17	7.098	95.48	12.20	130.13	15.94
16.48	1.374	54.22	7.249	96.48	12.32	132.12	16.22
17.41	1.542	55.27	7.404	97.47	12.42	133.10	16.28
18.34	1.716	56.31	7.596	98.47	12.52	134.08	16.35
19.27	1.887	57.36	7.759	99.46	12.63	136.02	16.55
20.20	2.069	58.41	7.765	100.45	12.73	136.98	16.67
21.22	2.258	59.46	/.853	101.44	12.86	137.94	16./1
22.29	2.460	63.63	8.445	102.44	13.00	138.89	16.84
23.35	2.658	64.68	8.509	103.44	13.07	139.84	16.85
24.42	2.863	65.72	8.6/9	104.44	13.17	140.78	16.94
23.49	2.070	67.80	0.795 8.005	105.45	13.29	141./1	17.08
20.33	3.238	68.84	8.903	100.41	13.41	142.05	17.14
27.03	3.433	60.88	0.933	107.39	13.55	143.30	17.23
20.70	3.817	70.92	9.070	109.35	13.04	145.41	17.20
30.84	4 013	70.92	9.325	110.32	13.74	146.33	17.34
31.91	4.015	74.01	9.603	111.32	13.05	140.33	17.40
32.98	4 346	75.04	9 780	112.29	14 07	149.06	17.61
34.05	4 521	76.07	9.890	113.28	14 17	150.86	17.73
35.12	4.677	77.10	9.993	114.26	14.27	151.76	17.85
36.19	4.841	79.16	10.30	115.24	14.39	152.66	17.92
37.26	5.007	80.19	10.41	116.22	14.49	153.55	18.03
38.34	5.151	80.56	10.38	117.20	14.59	156.22	$(18.43)^{a}$
39.41	5.300	81.22	10.50	118.17	14.69	157.08	(18.48)
40.47	5.449	82.25	10.65	119.15	14.81	157.95	(18.74) ^a
41.54	5.596	83.28	10.73	120.12	14.94		
			Lia	quid			
163.93	25.91	194.89	27.28	210.40	27.94	221.89	28.50
165.92	26.00	196.77	27.35	211.12	27.98	222.60	28.50
167.90	26.08	198.65	27.40	211.83	28.02	223.33	28.47
169.88	26.16	200.52	27.48	212.55	28.03	224.04	28.58
171.84	26.25	201.82	27.61	213.26	28.09	224.76	28.60
173.80	26.38	202.53	27.56	213.97	28.11	225.48	28.60
175.75	26.47	203.25	27.57	214.69	28.09	226.20	28.63
177.69	26.50	203.96	27.62	215.40	28.15	226.92	28.70
1/9.63	26.59	204.67	27.71	216.12	28.15	227.65	28.70
181.56	26.69	205.41	27.68	216.87	28.12	228.42	28.82
183.49	26.78	206.12	27.76	217.59	28.17	229.14	28.78
185.40	20.84	200.84	27.83	218.30	28.22	229.80	28.82
187.31	20.95	207.55	27.80	219.02	28.37	230.39	28.81
107.21	27.05 27.11	200.27	∠7.00 27.02	219.73	20.39	231.31	20.94 28.01
193.00	27.11	200.20	27.92	220.43	20.41	232.04	20.71
234 20	28.97	255.09	30.08	221.17	31 44	316 58	20.91
235.65	29.10	256.20	30.19	280.69	31 30	318 24	33 40
236.37	29.19	256.95	30.23	282.66	31.55	319 91	33 54
237.10	29.14	257.70	30.15	283.22	31.55	321.57	33.59
237.82	29.13	258.45	30.21	284.18	31.61	323.26	33.77
238.55	29.30	259.20	30.26	284.95	31.71	324.94	33.87
239.27	29.28	259.95	30.37	285.74	31.68	326.61	33.96

TABLE 1	(continued)
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T/K	$C_{\mathrm{p},m}/R$	T/K	$C_{\mathrm{p},m}/R$	T/K	$C_{\mathrm{p},m}/R$	T/K	$C_{\mathrm{p},m}/R$
240.05	29.26	260.71	30.34	287.30	31.75	328.29	34.05
240.77	29.32	261.46	30.41	287.56	31.80	329.99	34.13
241.50	29.34	262.22	30.50	288.43	31.83	331.66	34.24
242.22	29.42	263.85	30.51	288.86	31.78	333.33	34.34
242.94	29.49	264.62	30.60	290.42	31.86	335.19	34.39
243.67	29.45	265.39	30.60	290.43	31.95	336.85	34.50
244.39	29.45	266.16	30.70	291.99	31.93	338.51	34.63
245.12	29.57	266.93	30.71	295.17	32.10	340.16	34.76
246.57	29.71	267.70	30.78	298.38	32.29	341.81	34.88
247.30	29.56	268.48	30.82	299.98	32.36	343.47	35.02
248.03	29.71	269.26	30.84	301.59	32.45	345.13	35.07
248.76	29.81	270.82	30.89	303.21	32.54	346.78	35.16
249.49	29.82	273.20	31.03	304.86	32.67	348.44	35.24
250.22	29.86	274.00	31.05	306.49	32.74	350.08	35.43
251.77	29.83	274.80	31.06	308.30	32.85	351.76	35.56
252.51	29.87	275.61	31.14	309.95	32.95	353.42	35.71
253.24	29.95	276.58	31.23	311.60	33.00		
253.98	30.04	277.39	31.20	313.27	33.16		
254.72	30.13	279.03	31.40	314.92	33.25		
			Glass, supe	ercooled liquid			
80.42	11.01	97.47	13.43	114.06	19.53	131.57	24.66
81.39	11.15	98.41	13.56	114.91	23.32	132.51	24.72
82.32	11.24	99.31	13.77	115.82	23.82	133.45	24.76
83.29	11.45	100.20	13.69	116.80	24.01	134.39	24.80
84.28	11.54	101.10	13.86	117.80	24.05	135.33	24.82
85.22	11.71	101.97	14.11	118.80	24.10	136.26	24.88
86.13	11.69	102.84	14.17	119.80	24.14	137.20	25.00
87.04	11.89	103.72	14.31	120.79	24.17	149.71	25.26
87.98	12.09	104.61	14.46	121.77	24.23	151.77	25.34
88.93	12.20	105.51	14.61	122.76	24.30	153.82	25.48
89.88	12.38	106.42	14.80	123.76	24.31	155.87	25.56
90.83	12.49	107.34	15.00	124.76	24.33	157.90	25.66
91.79	12.57	108.29	15.20	125.75	24.40	159.92	25.74
92.74	12.73	109.25	15.50	126.75	24.40	161.93	25.82
93.68	12.91	110.23	15.63	127.74	24.47	163.93	25.91
94.62	12.98	111.21	16.12	128.73	24.56	165.92	26.00
95.55	12.98	112.18	16.71	129.70	24.62	167.90	26.08
96.51	13.21	113.14	17.57	130.64	24.64	169.88	26.16

^{*a*} Given in parentheses are the heat capacity $C_{p,m}$ values in the region just before the fusion.

TABLE 2

Equilibrium melting temperatures T_i^a , reciprocal of the sample fraction melted $1/F_i^a$, the $T_{i(calc)}$ values calculated from the linear dependence of T_i on $1/F_i$ for isobutyl *tert*-butyl ether.

T_i/K	$q_{ m i}/{ m J}^b$	$1/F_i$	$T_{i(\text{calc})}/\text{K}$
162.142 ^a	5.399	8.95 ^a	162.144
162.239 ^a	5.399	4.47^{a}	162.235
162.266 ^a	5.396	2.98^{a}	162.266
162.280 ^a	5.355	2.24 ^a	162.281
162.288 ^a	5.316	1.80^{a}	162.290
162.297 ^a	5.343	1.50 ^a	162.296
162.307 ^a	5.366	1.28^{a}	162.301
162.314	5.375	1.12	162.304
162.321	5.366	1.0	162.306
		0.00	162.327

^{*a*} The T_i and $1/F_i$ values were used for calculation of N_2 , T_{tp} , A_{cr} and B_{cr} in the range of $1/F_i$ from 1.2 to ≤ 10 according to [8]. ^{*b*} The q_i denotes a quantity of energy used for melting of the F_i

substance's fraction.

The Mastrangelo and Dornte method [9] did not indicate the presence of any solution in the solid state of the sample. Table 3 lists mean values of $T_{\rm tp}$, mole

TABLE 3

The values of triple point temperature, $T_{\rm tp}$, enthalpy, $\Delta_{\rm fus}H_m$, and entropy, $\Delta_{fus}S_m$, of fusion, total amount of impurities, N_2 , and cryoscopic constants $A_{\rm cr}$ and $B_{\rm cr}$, glass transition temperature, $T_{\rm gl}$, and temperature interval of the vitrification, $\Delta T_{\rm gl}$, of isobutyl *tert*butyl ether

$T_{\rm tp}/{\rm K}$	162.33 ± 0.01
$\Delta_{\rm fus} H_m/(\rm kJ\cdot mol^{-1})$	8.65 ± 0.02
$\Delta_{\rm fus}S_m/({\rm J}\cdot{\rm K}^{-1}\cdot{\rm mol}^{-1})$	53.29 ± 0.15
N_2 /mole fractions	0.0008 ± 0.0001
$A_{\rm cr}/{\rm K}^{-1}$	0.03948 ± 0.00012
$B_{\rm cr}/{\rm K}^{-1}$	0.00280 ± 0.00001
$T_{\rm gl}/{ m K}$	114.1
$\Delta T_{\rm gl}/{ m K}$	110.2–116.8

		· · · · ·	•	• •		
T_1/K	T_2/K	$\Delta H_{\rm tot}/({\rm J}\cdot{\rm mol}^{-1})$	$\Delta H_{\rm emp}/({\rm J}\cdot{\rm mol}^{-1})$	$\Delta H_3/(\mathbf{J} \cdot \mathbf{mol}^{-1})$	$\Delta H_4/(\mathbf{J} \cdot \mathbf{mol}^{-1})$	$\Delta_{\rm fus}H_m/({\rm J}\cdot{\rm mol}^{-1})$
156.874	168.902	13350	2460	843	1420	8627
153.095	170.580	15427	3564	1414	1785	8664
153.505	169.384	14771	3233	1352	1525	8661
					mean	8651 + 24

TABLE 4 The molar enthalpy of fusion, $\Delta_{fus}H_m$, of isobutyl *tert*-butyl ether calculated by equation (1)^{*a*}

^{*a*} The meanings of enthalpy increments ΔH_{tot} , ΔH_{emp} , ΔH_3 and ΔH_4 are given in text under equation (1).

fractions of impurities, N_2 , and cryoscopic constants A_{cr} and B_{cr} calculated from three independent experiments. Melting point depressions amount from (0.017 to 0.020) K. The N_2 values obtained by chromatographic and calorimetric methods are in good agreement. The glass-transition temperature T_{gl} was found graphically as an inflexion point of the C_p -curve for the transition of glass to the supercooled liquid. A correlation between the glass-transition and triple point temperatures of IBTBE, $T_{\rm gl} \approx 2/3T_{\rm tp}$, is typical for glasses [10]. The enthalpy of fusion, $\Delta_{fus}H_m$, of IBTBE was determined calorimetrically based on the total enthalpy absorbed during the fusion with a correction for the normal heat capacities of the crystal and liquid that the substance had in the fusion region. The $\Delta_{fus}H_m$ value was obtained from the equation:

$$\Delta_{\rm fus} H_m = \Delta_{\rm tot} H - \Delta H_1 - \Delta H_2 - \Delta H_{\rm emp},\tag{1}$$

where $\Delta_{tot}H$ is the total enthalpy absorbed in heating the calorimeter from initial temperature $T_1 < T_{tp}$ to final temperature $T_2 > T_{tp}$, ΔH_1 and ΔH_2 are the heating enthalpies calculated from the normal heat capacities of the crystal and liquid in the temperature intervals from T_1 to T_{tp} and T_{tp} to T_2 , respectively, ΔH_{emp} is the enthalpy increment needed for heating the empty calorimeter from T_1 to T_2 . The enthalpy of fusion of IBTBE is listed in table 4.

2.2. Treatment of the experimental data

The heat capacity of IBTBE was extrapolated to $T \rightarrow 0$ with the equation:

$$C_{\mathbf{p},m} = A_{\mathbf{D}}T^3. \tag{2}$$

The coefficient $A_{\rm D} = (3.042 \pm 0.001) \cdot 10^{-3} \text{ J} \cdot \text{K}^{-4} \cdot \text{mol}^{-1}$ was calculated by the least-squares method (LSM) from $C_{\rm p,m}$ data in the temperature interval from (7.68 to 12.82) K. The root-mean-square (RMS) deviation between the calculated and experimental $C_{\rm p,m}$ values ($\pm 1.9\%$) lies within the limits of experimental errors. Thus, the temperature dependence $C_{\rm p,m}(T)$ corresponds to the Debye equation (2) and $C_{\rm p,m} = 0$ and $S_m^\circ = 0$ at $T \rightarrow 0$.

The experimental heat capacities were divided into several intervals and fitted with polynomials of the following form:

$$C_{p,m} = \sum A_i \{ (T - A_k) / B_k \}^i,$$
(3)

where $(T - A_k)/B_k$ is the normalizing term. The RMS deviation between the calculated and experimental $C_{p,m}$ values is equal to 0.24% that corresponds to the experimental errors at T > 80 K. Smoothed values of $C_{p,m}/R$ and thermodynamic functions $S_m^{\circ}(T)/R$, $\{H_m^{\circ}(T) - H_m^{\circ}(0)\}/RT$, and $\Phi_m^{\circ}(T)/R$ are listed in table 5 for the whole temperature interval studied. Table 6 lists the standard ideal gas values of the thermodynamic functions and entropy and free Gibbs energy of formation of IBTBE at T = 298.15 K. The errors of the functions were estimated by the law of the random errors accumulation [11] based upon the uncertainties of the heat capacity measurements. In the calculation of the ideal gas thermodynamic functions, the enthalpy and entropy of vaporization, $\Delta_{vap}H_m^{\circ}$ (T), and $\Delta_{vap}S_m^{\circ}(T)$, and entropy of compression of the ideal gas, $R \cdot \ln\{p(298.15)/101.325 \text{ kPa}\}$, have been used. The values of these entropies were calculated using the $\Delta_{\text{vap}}H_m^{\circ}(T) = (39.12 \pm 0.20) \text{ kJ} \cdot \text{mol}^{-1}$ value measured calorimetrically [12] and saturated vapor pressure of IBTBE (our unpublished data), respectively. The thermodynamic consistency of the results of the vaporization calorimetry and vapor pressure studies was proved by satisfactory agreement between $\Delta_{\rm vap} H^{\circ}_{\rm m}(T)$ values measured calorimetrically and those calculated from the (p, T) data (39.24 ± 0.56) $kJ \cdot mol^{-1}$. The standard Gibbs free energy of formation was calculated from

$$\Delta_{\rm f} G^{\circ}_{\rm m}(g) = \Delta_{\rm f} H^{\circ}_{\rm m}(g) - T \cdot \Delta_{\rm f} S^{\circ}_{\rm m}(g) \tag{4}$$

using the experimental value of absolute entropy (table 6), and calorimetric value of the enthalpy of formation in liquid state, $\Delta_f H^{\circ}_m(l)$, [13] and enthalpy of vaporization of IBTBE [12], which led to $\Delta_f H^{\circ}_m(298.15, g) = (-369.9 \pm 1.6) \text{ kJ} \cdot \text{mol}^{-1}$. The function $\Delta_f S^{\circ}_m(g)$ in equation (4) is the difference between the values of absolute entropies of the final and initial products in reaction

$$16 \cdot C(cr, graphite) + 18 \cdot H_2(g) + O_2(g) = 2 \cdot (CH_3)_2 CHCH_2 OC(CH_3)_3(g).$$
(5)

The absolute entropies of the initial products were taken from [14].

TABLE 5 Smoothed molar thermodynamic properties of isobutyl *tert*-butyl ether $(R = 8.314472 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$

T/K	$C_{\mathrm{p},m}/R$	$\{H_m^\circ(T)-H_m^\circ(0)\}$	$)\}/RT S_m^{\circ}(T)/R$	$\Phi_m^\circ(T)/R^a$
		Crysta	l	
5	0.04573	0.0115	0.0152	0.0037
10	0.3659	0.0914	0.1220	0.0306
15	1.109	0.2999	0.4027	0.1028
20	2.027	0.6151	0.8453	0.2302
25	2.971	0.9925	1.400	0.4075
30	3.857	1.397	2.021	0.6240
35	4.662	1.812	2.677	0.8650
40	5.388	2.210	3.347	1.137
45	6.060	2.601	4.022	1.421
50	6.700	2.978	4.693	1.715
55	7.326	3.346	5.362	2.016
60	7.942	3.702	6.026	2.324
65	8.549	4.052	6.685	2.633
70	9.152	4.395	7.340	2.945
75	9.748	4.732	7.992	3.260
80	10.34	5.063	8.640	3.577
85	10.93	5.392	9.285	3.893
90	11.52	5.716	9.926	4.210
95	12.10	6.036	10.57	4.534
100	12.68	6.354	11.20	4.846
110	13.82	6.981	12.46	5.479
120	14.91	7.597	13.71	6.113
130	15.96	8.201	14.95	6.749
140	16.90	8.788	16.16	7.372
150	17.72	9.357	17.36	8.003
160	18.35	9,900	18.52	8.620
162.33	18.47	10.02	18.79	8.770
		Linuis	1	
162.22	25.82	16 42	25.20	8 770
102.55	23.65	16.45	25.20	0.770
1/0	20.10	10.87	20.40	9.550
100	20.03	17.39	21.92	10.55
200	27.00	1/.09	29.50	11.47
200	27.40	10.50	30.77	12.41
210	27.92	10.01	32.11	13.30
220	28.30	19.23	34.60	14.19
230	20.03	20.02	34.09	15.05
240	29.51	20.05	33.93 27.14	15.90
250	29.62	20.41	20 22	10.75
200	20.85	20.78	20.47	17.34
270	21.29	21.15	39.47	10.52
200	21.00	21.50	40.00	19.10
290	31.90	21.83	41./1 42.50 ± 0.08	19.80
296.15	32.32 ± 0.0	$0\ 22.15 \pm 0.04$	42.39 ± 0.08	20.40 ± 0.2
210	32.43 22.05	22.19	42.81 12 00	20.02 21.25
220	52.95 22.57	22.33	40.00	21.33
320	33.32 24.12	22.07	44.93	22.00 22.77
240	34.12 24.76	23.20	43.97	22.11
250	25 12	23.33	47.00	23.47
550	33.42	23.00	40.01	2 4. 13

^{*a*} $\Phi_m^{\circ}(T) = S_m^{\circ}(T) - \{H_m^{\circ}(T) - H_m^{\circ}(0)\}/T.$

3. Theoretical calculations

3.1. Methods of calculations

The DFT calculations were performed using the Gaussian 98 software package [15]. The structural parameters were fully optimized at the B3LYP/6-

TABLE 6

Calorimetrically derived thermodynamic functions in ideal gas state of isobutyl *tert*-butyl ether, the standard entropy, $\Delta_{\Gamma}S_m^{\circ}(T)(g)$, and free energy of formation, $\Delta_{\Gamma}G_m^{\circ}(T)(g)$, where $\Delta_{\text{vap}}H_m^{\circ}(T)$ and $\Delta_{\text{vap}}S_m^{\circ}(T)$ are the enthalpy and entropy of vaporization and $R \cdot \ln \{p(T)/101.325 \text{ kPa}\}$ is ideal gas entropy of compression at T = 298.15 K

, 2 15 1	
$\overline{\Delta_{\mathrm{vap}}H_m^\circ(T)}/(\mathrm{kJ}\cdot\mathrm{mol}^{-1})$	39.12 ± 0.20
$\Delta_{\mathrm{vap}} S^{\circ}_{m}(T) / (\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathrm{mol}^{-1})$	131.21 ± 0.67
$R \cdot \ln\{p(T)/101.325 \text{ kPa}\}/(J \cdot K^{-1} \cdot \text{mol}^{-1})$	-28.45
$S_m^{\circ}(T)(g)/(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathrm{mol}^{-1})$	456.96 ± 0.89
$\{H_m^{\circ}(T) - H_m^{\circ}(0)\}(g)/(k\mathbf{J} \cdot \mathbf{mol}^{-1})$	93.98 ± 0.23
$\{G_m^{\circ}(T) - H_m^{\circ}(0)\}(g)/(\mathrm{kJ}\cdot\mathrm{mol}^{-1})$	-42.26 ± 0.35
$\Delta_{\mathbf{f}} S^{\circ}_{m}(T)(g)/(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1})$	-866.5 ± 0.9
$\Delta_{\rm f} G^{\circ}_m(T)(g)/({\rm kJ}\cdot{\rm mol}^{-1})$	-111.6 ± 1.6

31G(d,p) level. Vibrational frequencies, zero-point energies, and thermal corrections were calculated at the same level. The scaling factors of 0.958 and 0.975 were applied to C–H stretchings and to all other frequencies, respectively. These values were obtained from fitting the experimental vibrational fundamentals of some ethers.

The barriers for internal rotation of CH₃ and C(CH₃)₃ rotors were determined from optimization of corresponding transition states. Potential functions for internal rotation of i-C₃H₇ and i-C₄H₉ rotors were determined by scanning the torsional angles from 0° to 360° at 15° increments and allowing all other structural parameters to be optimized at the B3LYP/6-31G(d,p) level. The calculated energy values were fitted to the torsional potential, which is a cosine-based Fourier function:

$$V(\phi) = V_0 + 1/2 \sum_{n} V_n (1 - \cos n\phi).$$
 (6)

The entropies, $S_m^{\circ}(T)$, heat capacities, $C_{p,m}^{\circ}(T)$, and enthalpies, $H_m^{\circ}(T) - H_m^{\circ}(0)$, (100 K $\leq T \geq 1500$ K) were calculated by standard statistical thermodynamics formulae using the rigid-rotor harmonic-oscillator approximation with correction for internal rotation. The torsional frequencies were omitted in the calculation of thermodynamic functions. Internal rotational contribution for each rotor was calculated by direct summation over the energy levels obtained by diagonalizating the one-dimensional Hamiltonian matrix associated with potential function from equation (6).

Enthalpy of formation, $\Delta_{f}H^{\circ}_{m,298}$, was calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level using isodesmic reactions and available recommended $\Delta_{f}H^{\circ}_{m,298}$ values for ethers [16].

3.2. Enthalpy of formation

The enthalpy of formation of IBTBE, (-369.9 ± 1.6) kJ · mol⁻¹, was obtained from available experimental data (see Section 2.2). To check the reliability of this value, in this work, the enthalpy of formation of IBTBE was calculated using the isodesmic reactions with group balance. From our previous studies [3,5], it was shown

TABLE 7

Enthalpies of reactions $(\Delta_r H_{m,298}^\circ)$ and enthalpies sof formation $(\Delta_{\rm f} H^{\circ}_{m.298})$ of isobutyl *tert*-butyl ether calculated at B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level from isodesmic reactions

Reaction	$\Delta_{ m r} H^{\circ}_{m,298}$	$\Delta_{ m f} H^\circ_{m,298}$
	kJ·mol ^{−1}	$kJ \cdot mol^{-1}$
i-Bu–O– t -Bu + Me–O–Et =	-4.8	-369.3
Pr–O– <i>t</i> -Bu + Me–O– <i>i</i> -Pr		
i-Bu–O– t -Bu + Me–O–Pr =	-3.2	-371.7
Bu–O–t-Bu + Me–O–i-Pr		
i-Bu–O– t -Bu + Me–O– i -Pr =	1.2	-371.4
Pr–O–t-Bu + Me–O–t-Bu		
i-Bu–O– t -Bu + Me–O–Et =	0.1	-371.1
<i>i</i> -Pr–O– <i>t</i> -Bu + Me–O–Pr		
i-Bu–O– t -Bu + Et–O–Et =	0.1	-369.3
<i>i</i> -Pr–O– <i>t</i> -Bu + Et–O–Pr		
i-Bu–O– t -Bu + Et–O–Pr =	0.3	-370.6
<i>i</i> -Pr–O– <i>t</i> -Bu + Pr–O–Pr		
Average		-370.6
Average value corrected for		-370.3
mixture of TG and TT conformers		
Experimental ^a		-369.9 ± 1.6

^a Calculated using experimental data from Refs. [12,13] (see Section 2.2).

that such calculations led to reasonable accuracy and even allowed to adjust recommended values derived from calorimetric measurements.



FIGURE 2. Torsional potential functions of isobutyl tert-butyl ether plotted against angle of rotation about C-O and C-C bonds. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. Line is Fourier expansion with the coefficients listed in table 8.

TABLE 8

Moments of inertia, vibrational frequencies and internal rotational molecular constants of isobutyl tert-butyl ether calculated at B3LYP/6-31G(d,p) level

TG conformer			
Point group: C_1	Moments of inertia:		
Symmetry number: $\sigma = 1$	$I_A = 29.6826 \cdot 10^{-39} \text{ g} \cdot \text{cm}^2$		
Ground electronic state: $\tilde{X}^{1}A$	$I_B = 104.1552 \cdot 10^{-39} \mathrm{g \cdot cm^2}$		
Molar mass: 130.2296	$I_C = 112.0862 \cdot 10^{-39} \text{ g} \cdot \text{cm}^2$		
	$I_A I_B I_C = 346525 \cdot 10^{-117} \text{ g}^3 \cdot \text{cm}^6$		

Vibrational frequencies:^a 3007, 3001, 3000, 2994, 2993, 2990, 2985, 2981, 2972, 2967, 2927, 2920, 2918, 2911, 2906, 2904, 2886, 2854, 1501, 1491, 1489, 1479, 1477, 1476, 1467, 1466, 1464, 1461, 1450, 1405, 1399, 1387, 1378, 1372, 1371, 1347, 1304, 1252, 1251, 1228, 1203, 1174, 1162, 1130, 1087, 1022, 1017, 955, 944, 936, 915, 913, 902, 889, 877, 814, 735, 501, 480, 446, 417, 382, 356, 331, 288, 270^b, 259, ^b 245, 238, ^b 216, ^b 206, ^b 141,^b 123, 65,^b 16^b

^a Scaling factor of 0.958 was used for C-H stretchings and 0.975 for other modes.

^b Instead of these torsional modes, the contributions due to the internal rotation were calculated using the following coefficients V_n in equation (6), reduced moment of inertia I_r and symmetry number of rotor σ_m

rotor σ_m : CH₃ group: $I_r = 0.5230 \cdot 10^{-39}$ g · cm², $\sigma_m = 3$, $V_3 = 1169$ cm⁻¹, CH₃ group: $I_r = 0.5222 \cdot 10^{-39}$ g · cm², $\sigma_m = 3$, $V_3 = 1103$ cm⁻¹, CH₃ group: $I_r = 0.5217 \cdot 10^{-39}$ g · cm², $\sigma_m = 3$, $V_3 = 1122$ cm⁻¹, CH₃ group: $I_r = 0.5230 \cdot 10^{-39}$ g · cm², $\sigma_m = 3$, $V_3 = 1121$ cm⁻¹, CH₃ group: $I_r = 0.5174 \cdot 10^{-39}$ g · cm², $\sigma_m = 3$, $V_3 = 1042$ cm⁻¹, t-C₄H₉ group: $I_r = 7.6485 \cdot 10^{-39}$ g · cm², $\sigma_m = 3$, $V_3 = 980$ cm⁻¹, i-C₄H₉ group: $I_r = 7.3771 \cdot 10^{-39}$ g · cm², $\sigma_m = 1$, $V_1 = 3973.1$, $V_r = 15645$ V = 7261 V = -1730 V = 1200 V = 7.2 (in $V_2 = -1564.5$, $V_3 = 726.1$, $V_4 = -173.0$, $V_5 = 120.0$, $V_6 = 7.2$ (in cm^{-1}), *i*-C₃H₇ group: $I_r = 7.4922 \cdot 10^{-39} \text{ g} \cdot \text{cm}^{-1}$, $\sigma_m = 1$, $V_1 = -438.1$, $V_2 = 230.8$, $V_3 = 1680.2$, $V_4 = 74.4$, $V_5 = 25.2$, $V_6 = -79.7$ (in cm^{-1}).

Fifty five isodesmic reactions were used to estimate the $\Delta_{\rm f} H^{\circ}_{m,298}$ value. The calculated values varied from (-347 to -389) kJ · mol⁻¹ with the average value of -369 kJ · mol⁻¹. Since among these 53 reactions, there were not well-balanced reactions with rather large values of enthalpies of reactions, $\Delta_{\rm r} H^{\circ}_{m,298}$, finally six reactions with small values of $\Delta_{\rm r} H^{\circ}_{m.298}$ were chosen (Table 7). As is seen from table 7, all reactions lead to close values and the average value agrees with experimental one

TABLE 9

Comparison between experimental (calorimetric), Sexp and calculated, Scale values of the absolute entropy of isobutyl tert-butyl ether in ideal gas state

<i>T</i> /K	$\frac{S_{\exp}}{(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1})}$	$S_{calc}/(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathrm{mol}^{-1})$	$S_{\exp} - S_{calc} / (\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathrm{mol}^{-1})$
298.15	456.96 ± 0.89	456.92	0.04
313	466.88 ± 1.65	466.82	0.06
323	473.37 ± 1.47	473.44	-0.07
333	479.92 ± 1.35	480.03	-0.11
343	486.53 ± 1.31	486.57	-0.04
353	493.21 ± 1.28	493.08	0.13

within its uncertainty. A more positive value was obtained with correction for conformational energy difference based on Boltzman averaging.

It is worth stressing that the estimated $\Delta_{\rm f} H_{m,298}^{\circ}$ value, -349.3 kJ·mol⁻¹, for IPTBE was used in last three reactions in table 7. This value was calculated from isodesmic and homodesmotic reactions [3] and was quite different from the recommended experimental value of (-358.1 ± 3.0) kJ·mol⁻¹ [16]. When used in isodesmic reactions, the estimated value leads to good agreement with experiment for NPTBE [3], ETBE ethyl [5], and IBTBE (Table 7). Thus it may be concluded that wellbalanced isodesmic reactions for ethers yield the $\Delta_{\rm f} H_{m,298}^{\circ}$ values of calorimetric accuracy. For IBTBE, theoretical calculations support the experimental value; this latter was adopted in further calculations of $\Delta_{\rm f} H_m^{\circ}(T)$ and $\Delta_{\rm f} G_m^{\circ}(T)$.

3.3. Geometry, vibrational frequencies, and torsional potentials

The DFT calculations predict the existence of two stable low energy conformers of IBTBE: the *trans*-*gauche* (*TG*) and *trans-trans* (*TT*) conformers with C_1 and C_s symmetry, respectively. (*TG*) conformer is 1.1 kJ \cdot mol⁻¹ (95 cm⁻¹) more stable than (*TT*). Both conformers have *trans* location of bulky groups relative to the C–O bond [(CH₃)₂CHCH₂–OC(CH₃)₃]:



and different relative positions of bulky groups around the C–C bond $[(CH_3)_2CH-CH_2OC(CH_3)_3]$:



Calculated potential energy curves as a function of torsion angles $\varphi(C-O)$ and $\varphi(C-C)$ are shown in figure 2. For rotation about the C-C bond, the minima on the potential curve at 0° and 120° correspond to the *TT* and *TG* conformers, respectively. Moments of inertia for the optimized geometry, vibrational frequencies, and coefficients V_n in the expansion for the torsional potentials (equation (6)) are given in table 8. The thermodynamic functions of IBTBE (Section 3.4) were calculated for an equilibrium mixture of *TG* and *TT*

TABLE 10 Ideal gas thermodynamic properties of isobutyl *tert*-butyl ether (R = 8.314472, $p^{\circ} = 101.325$ kPa)

-	• • •	•	•			
Т	$C^{\circ}_{\mathrm{p},m}(T)/R^a$	$S_m^\circ(T)/R$	$\Phi^\circ_m(T)/R^b$	$\{H^\circ_m(T)-H^\circ_m(0)\}/RT$	$\Delta_f H^\circ_m(T)/RT$	$\Delta_f G^\circ_m(T)/RT$
100	11.01	36.89	29.72	7.18	-407.70	-324.23
150	14.62	42.06	32.99	9.08	-278.59	-186.81
200	17.77	46.71	35.85	10.86	-213.61	-116.46
250	20.91	51.01	38.45	12.55	-174.55	-73.31
298.15	24.02	54.96	40.80	14.15	-149.22	-44.86
300	24.14	55.10	40.89	14.22	-148.40	-43.94
350	27.38	59.07	43.20	15.87	-129.55	-22.55
400	30.50	62.93	45.43	17.50	-115.23	-6.23
450	33.43	66.69	47.58	19.11	-103.94	6.67
500	36.13	70.36	49.68	20.68	-94.76	17.13
600	40.91	77.38	53.72	23.66	-80.66	33.08
700	44.95	84.00	57.57	26.42	-70.26	44.70
800	48.42	90.23	61.27	28.96	-62.19	53.53
900	51.42	96.11	64.82	31.30	-55.71	60.47
1000	54.02	101.67	68.23	33.44	-50.37	66.06
1100	56.28	106.93	71.51	35.42	-45.87	70.64
1200	58.23	111.91	74.67	37.24	-42.04	74.46
1300	59.93	116.64	77.72	38.92	-38.72	77.69
1400	61.41	121.14	80.66	40.48	-35.83	80.46
1500	62.70	125.42	83.50	41.92	-33.29	82.84

^{*a*} At temperatures from 150 K to 500 K thermodynamic functions can be calculated using equation $C_{p,m}^{\circ}(T)/R = a_1 + a_2T^{-2} + a_3T + a_4T^2 + a_5T^3$ with $a_1 = 10.890$, $a_2 = -2.680 \cdot 10^4$, $a_3 = 1.361 \cdot 10^{-2}$, $a_4 = 1.516 \cdot 10^{-4}$, $a_5 = -1.550 \cdot 10^{-7}$.

$${}^{\circ} \Phi_m^{\circ}(T) = S_m^{\circ}(T) - \{H_m^{\circ}(T) - H_m^{\circ}(0)\}/T$$

conformers. We did not take into account the difference between geometry and vibrational frequencies of TGand TT conformers of IBTBE because this results in insignificant changes of $S_{\rm m}^{\circ}(T)$ and $C_{\rm p,m}^{\circ}(T)$ values (0.05 and 0.15 J · K⁻¹ · mol⁻¹, respectively, at T = 298.15 K).

3.4. Thermodynamic functions

Thermodynamic functions, $S_m^{\circ}(T)$, $C_{p,m}^{\circ}(T)$, and $H_m^{\circ}(T) - H_m^{\circ}(0)$, were calculated within the framework of the rigid-rotor harmonic-oscillator approximation for all rotation and vibration modes, except for internal rotation modes for which the independent-rotor model was employed. This model results in overestimated values of thermodynamic functions as compared with $S_m^{\circ}(T)$ and $C_{p,m}^{\circ}(T)$ values determined from calorimetric measurements for alkyl ethers [3]. The greater is the number of rotors, the greater are the discrepancies between calculated and experimental values. Especially large discrepancies are found for *tert*-alkyl ethers. It is most likely that the increased error is associated with the independent-rotor assumption.

As in our previous works [3,5], in this work the contribution to the thermodynamic functions due to coupling of rotor potentials was taken into account by multiplying the partition function for uncoupling internal rotations by the empirical factor K_{r-r} The K_{r-r} value of 0.843 was found by fitting to the calorimetric entropies of IBTBE. The difference between experimental and thus calculated entropies is shown in table 9. It should be noted that the employed procedure for correction of the thermodynamic relations between calculated values of $S_m^{\circ}(T)$, $C_{p,m}^{\circ}(T)$, and $H_m^{\circ}(T) - H_m^{\circ}(0)$. Table 10 lists the thermodynamic properties of

Table 10 lists the thermodynamic properties of IBTBE calculated using molecular constants from table 8 and accepted below the $\Delta_{\rm f} H^{\circ}_{m,298}$ value. Since the calculated entropy values were fitted to the calorimetric ones, their uncertainty is close to the uncertainty of the experimental values at temperatures (298.15 to 350) K and should not exceed (3 to 5) J \cdot K⁻¹ \cdot mol⁻¹ at higher temperatures. The uncertainty of calculated $C^{\circ}_{\rm p,m}(T)$ values is estimated to be from (5 to 8) J \cdot K⁻¹ \cdot mol⁻¹.

4. Conclusions

The heat capacity of isobutyl *tert*-butyl ether has been measured in an adiabatic, fully automated calorimeter over the temperature range (7.68 to 353.42) K. The substance was in the glassy, supercooled liquid, crystalline and liquid states. The purity of the substance, the glass-transition temperature, the triple point and fusion temperatures, and the enthalpy and entropy of fusion were determined. The thermodynamic functions (absolute entropy and changes of the enthalpy and Gibbs free energy) were calculated for the solid and liquid states over the temperature range studied and for the ideal gas state at T = 298.15 K.

The ideal gas thermodynamic properties of IBTBE were calculated over the temperature range (0 to 1500) K by combining the DFT results with absolute entropies determined from calorimetric investigation. The B3LYP method provides a good way to calculate the structure and vibrational frequencies of the molecules, and torsional potential of independent rotors. A multi-dimensional model for the energy levels of internal rotation has not yet been solved and so an empirical correction for rotor-rotor coupling was used. Since the calculated entropy values were fitted to the experimental ones, the accuracy of calculated thermodynamic functions was believed to be rather high. As to enthalpy of formation values, this work and our previous calculations [3,5] demonstrate that DFT results applied to isodesmic reactions lead to values whose accuracy is comparable with experimental.

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