

ОБЩАЯ И ФИЗИЧЕСКАЯ ХИМИЯ

UDC 541.1; 541.11

THEORETICAL AB INITIO CALCULATION OF ENTROPY AND HEAT CAPACITY OF DIALKYLSULFONES IN THE GAS PHASE

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The present study describes the theoretical ab initio calculation of entropy, heat capacity and internal energy for a series of dialkylsulfones (dimethyl-, ethylmethyl-, diethyl sulfones). The thermodynamic properties of dialkylsulfones have been calculated by combining quantum mechanics with statistical thermodynamics by using Gaussian 09 software package. Geometry optimizations of isolated sulfone's molecules are performed by the restricted Hartree-Fock (RHF) and the density functional theory (DFT/B3PW91) methods with 6-311++G(d,p) extended basis set. The approximations of the methodology are those of the rigid-rotor/harmonic oscillator formalism. Because theoretically calculated entropy, heat capacity and heat content are sensitive to vibrational frequencies, the appropriate scaling factor has been used to recalculate harmonic vibration modes.

Figs. 3, tables 4, references 23.

Sulfones are sulfur-containing compounds having an important role in atmospheric, industrial, and biological reactions [1, 2]. Recently, sulfones are widely studied as a possible medium in lithium-ion batteries [3-6]. Since lithium batteries work in a wide temperature range, it is important to investigate their thermochemical parameters. The determination of thermochemical data for molecules by either calorimetric or spectroscopic measurements is a tedious task and requires careful control of the experimental conditions. Even in the best of cases the remaining error bars can be non-negligible. On the other hand, computational approaches offer the possibility to compute these data directly. Since accuracy of the thermochemical data is quite important in many areas of chemistry, e.g., combustion processes, industrial process design, etc., a variety of methods have been developed for their determination. *Ab initio* calculations provide highly appropriate way to calculate

various thermodynamic properties, such as the entropy, heat capacity and thermal energy. In [7] the thermodynamic properties of crystalline dimethyl sulfone (DMSO₂) have been experimentally reported. Recently, in our laboratory the various physicochemical properties of DMSO₂ and diethyl sulfone (DESO₂) and their solutions have been studied by the means of densimetry, surface tension, calorimetry and dielectric relaxation spectroscopy [8-10].

The present study is focused on the thermochemical studies of dialkylsulfones. It should be noted that thermochemical values obtained in this study have been calculated without using adjustable parameters – they are entirely *ab initio*.

The evolution of *ab initio* calculations methods, coupled with increasing of computer resources, has allowed the high accuracy prediction of various thermodynamic properties, such as entropy, enthalpy and heat capacity by statistical mechanics. An important characteristic of *ab initio* computational methodology is the ability to approach the exact description – that is, the focal point – of the molecular electronic structure in a systematic manner [11]. The basic quantities of statistical thermodynamics are the molecular partition functions, which include contributions from all degrees of freedom of a molecule resulting from translational, rotational, vibrational, and electronic degrees of freedom. The approximations of the methodology are those of the rigid-rotor/harmonic oscillator formalism.

Over the last decade, several studies at different computational levels have been performed to estimate entropy and heat capacity of molecules at various temperatures [12-19]. It was shown, that entropy could be calculated to within $1 \text{ J K}^{-1} \text{ mol}^{-1}$ [12]. In [18] gas-phase standard enthalpies of formation, S-H bond dissociation enthalpies, and gas-phase acidities for a large number of small sulfur-containing molecules were calculated by density functional theory approaches. These studies show that theoretical predictions have achieved the level of accuracy which can compete with experimental measurements in accuracy. The theoretical *ab initio* calculation of entropy, heat capacity, and heat content for a series of alkanes have been performed [14], the data have shown good agreement with experimental values. Since dimethyl, ethylmethyl- and diethyl sulfones have the similar geometries as corresponding alkanes, the same methodology was applied to perform this study.

In the present work, the structural parameters and vibrational spectra of isolated DMSO₂, DESO₂ and ethylmethyl sulfone (EMSO₂) using restricted Hartree-Fock (RHF) and density functional theory (DFT/B3PW91) methods with extended 6-311++G(d,p) basis set have been calculated. All internal vibrational modes were treated within the harmonic oscillator approach. The thermochemical values (entropy, heat capacity, internal energy) reported in this paper all refer to the ideal gaseous state at 1 atm. The thermodynamic data provide helpful information for the further study on the title compounds, when these are used as a reactant to take part in a new reaction.

Computational part

Calculations of thermodynamic properties of dialkylsulfones have been carried out using Gaussian 09 program package [20]. Geometry optimizations of isolated DMSO₂, DESO₂ and EMSO₂ molecules in their ground states in the gas phase were performed using restricted Hartree-Fock (HF) and density functional theory (DFT). Becke's three-parameter hybrid functional combined with the gradient-correlation functional of Perdew-Wang denoted B3PW91, was employed in the computations using DFT. The all-electron 6-311++G(d,p) basis set including polarization and diffuse functions was employed. Following the geometry optimization, frequencies were calculated using the same method at a stationary point. Energy minima were confirmed by the absence of imaginary vibration frequency.

The thermodynamic properties of molecules have been calculated by combining quantum mechanics with statistical thermodynamics. Two key ideas of statistical thermodynamics are the Boltzmann distribution and the partition function. The main approximation is to use a single molecule in the gas phase, that is, in vacuum, in order to get access to the molecular partition function [21]. For the present compounds the translational, rotational and vibrational contributions to the internal energy, entropy and heat capacity have been considered. It should be noted that electronic contribution is neglected.

The thermochemical values reported in this paper all refer to the ideal gaseous state at 1 atm, the harmonic approximation has been used to treat the molecular vibrations, and temperature was changed from 100 K up to 1000 K.

The following equations were employed to calculate the internal energy (U), constant-volume molar heat capacity (C_v) and entropy (S), of the molecule at zero Kelvin and the specified temperature (T):

$$U = E_{\text{pot}} + E_{\text{ZPE}} + E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}}, \quad (1)$$

where E_{pot} is the potential energy and E_{ZPE} is the zero point energy of the molecule at 0 K. E_{trans} , E_{rot} , and E_{vib} are the thermal energy corrections due to the effects of molecular translation, rotation, and vibration at the specified temperature, respectively.

The constant-volume heat capacity and entropy can be also written as sums

$$C_v = C_{v,\text{trans}} + C_{v,\text{rot}} + C_{v,\text{vib}} \quad (2)$$

$$S = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}}. \quad (3)$$

Translational contribution to the heat capacity $C_{v,\text{trans}}$ is $(3/2)R$, and overall rotation gives an additional $(3/2)R$, vibrational contribution to the heat capacity depends on frequencies and temperature:

$$C_{v,\text{vibr}} = R \sum_{i=1}^{N_{\text{vibr}}} e^{\Theta_{v,i}/T} \left(\frac{\Theta_{v,i}/T}{e^{\Theta_{v,i}/T} - 1} \right)^2, \quad (4)$$

where R is the universal gas constant, θ_v is the vibrational temperature ($\theta_v = hv/k_B$, where h is Planck constant, k_B is Boltzmann constant and v is frequency of i th vibration).

The translation, rotational and vibrational components of entropy must be calculated individually at each temperature of interest. On the other hand translational component of the entropy depends on the mass of molecules, rotational component depends on the principal moments of inertia and vibrational contribution depends on the frequency [21]. Since harmonic vibrational frequencies overestimate experimental data, the appropriate scaling factors were used in all calculations.

GaussView 5.0 program has been used to visualize molecule structures and IR spectra [22].

Results and discussion

Before performing thermochemical calculations, geometry optimizations on isolated DMSO₂, EMSO₂ and DESO₂ molecules have been performed at various level of theory (RHF and B3PW91) to identify the most stable conformers. All further calculations have been done only for this conformer. In Fig. 1 the optimized structures of above mentioned sulfones, performed by RHF/6-311++G(d,p) method are presented. Following the geometry optimization, vibrational analysis for these stable conformers was performed at the same levels of theory.

The main geometrical and spectral parameters are summarized in Table 1. Reliability of RHF/6-311++G(d,p) and B3PW91/6-311++G(d,p) methods have been checked by comparison calculated structural parameters of DMSO₂ with the experimentally determined geometry [23]. In contrast to DMSO₂ there is no experimental data reported in literature for EMSO₂ and DESO₂ molecules. The S-O, S-C, C-H bonds lengths in EMSO₂ and DESO₂ are relatively longer than in DMSO₂, but bond angles OSO and CSC are smaller. This difference in homologous series can be explained by the larger electron-donating effect of ethyl group in comparison with methyl group. In all molecules the configuration of sulfur is distorted tetrahedral. The global minimum energy obtained by RHF/6-311++G(d,p) method for DMSO₂, EMSO₂ and DESO₂ are calculated as -626.4781319, -665.523929 and -704.569573 Hartree, respectively. The calculated values of energy are lower in the B3PW91/6-311++G(d,p) method. Calculated dipole moments at both level of theory are increasing in series DESO₂<EMSO₂<DMSO₂. As a result of calculations B3PW91method predicts the dipole moment closer to experimental value than RHF method at the same 6-311++G(d,p) basis set.

The thermodynamic parameters supply helpful and extra information about the dialkylsulfones. The values of some thermodynamic parameters, such as zero-point vibrational energy, rotational constants, rotational temperature, thermal energy, molar heat capacity and entropy of DMSO₂, EMSO₂ and DESO₂ obtained by RHF and B3PW91 methods with 6-311+G(d,p) basis sets are presented in Table 2. Because the values of zero-point vibrational energy, thermal energy, molar heat

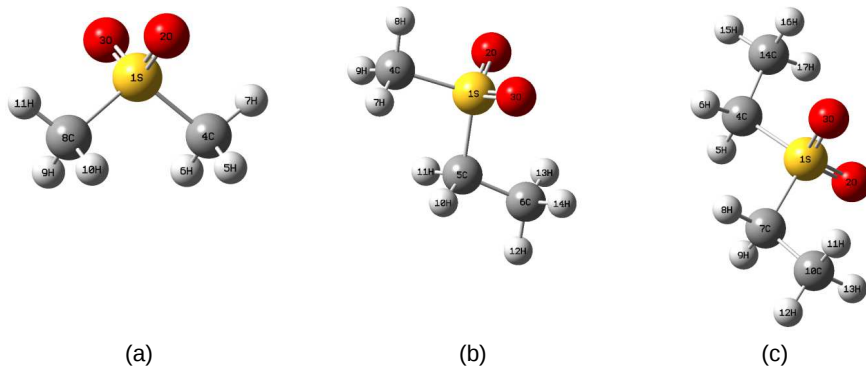


Fig. 1. Optimized structures of DMSO2 (a), EMSO2 (b) and DESO2 (c).

capacity and entropy are sensitive to vibrational frequencies, in this study the appropriate scaling factors have been used in the step of frequency calculations. It is widely known that the calculated ‘unscaled’ harmonic frequencies overestimate experimental values due to the lack of electron correlation, insufficient basis sets and anharmonicity. It should be noted that scaling factors equal 0.909 for RHF/6-311++G(d,p) and 0.963 for B3PW91/6-311++G(d,p) level of theory were taken into account to receive good agreement between observed and calculated wavenumbers.

Table 1

The main geometrical and spectral parameters for DMSO₂, EMSO₂ and DESO₂ optimized at RHF/6-311++G(d,p) and B3PW91/6-311++G(d,p) levels

	DMSO ₂		EMSO ₂		DESO ₂	
Parameters	RHF	B3PW91	RHF	B3PW91	RHF	B3PW91
r(S ₁ -O ₃), Å	1.4314 (1.431 [23])	1.4614	1.4332	1.4635	1.4351	1.4656
r(S ₁ -O ₂), Å	1.4314 (1.431 [23])	1.4614	1.4332	1.4635	1.4351	1.4656
r(S ₁ -C ₄), Å	1.7741 (1.777 [23])	1.7962	1.7749	1.7967	1.7856	1.8119
r(C ₄ -H ₅), Å	1.0814	1.0899	1.0822	1.0907	1.0836	1.0930
∠(OSO)	119.71 (121.0 [23])	120.49	119.36	120.09	119.01	119.71
∠(CSC)	104.61 (103.1 [23])	103.93	104.37	103.74	104.22	103.73
Dipole Moment, D	5.41 (4.44 [23])	4.90	5.28	4.79	5.13	4.65
Energy, Hartree	-626.478132	-628.364211	-665.523929	-667.676128	-704.569573	-706.987854

The temperature dependence of the thermodynamic properties: constant-volume heat capacity, entropy and thermal energy for DMSO₂, EMSO₂ and DESO₂ were also determined by RHF/6-311++G(d,p) and B3PW91/6-311++G(d,p) methods. In Table 3 energy, heat capacity and entropy calculated for several temperatures from 100 to 1000 K in 100 K intervals at B3PW91/6-311++G (d,p) level are listed.

It can be observed that these thermodynamic functions are increasing with temperature ranging from 100 to 1000 K. This tendency is due to increasing vibrational contributions to the total entropy and total heat capacity with temperature. The increasing of molar mass, size and number of vibrational modes of molecules in the series of DMSO₂-EMSO₂-DESO₂ leads to the increasing in vibrational contributions to the total energy, entropy and total heat capacity as expected. The translational and rotational contributions to the total entropy are also increasing.

Table 2

**Calculated thermodynamic parameters of DMSO₂, EMSO₂ and DESO₂
at 298.15 K at RHF/6-311++G(d,p) and B3PW91/6-311++G(d,p) levels**

	RHF/6-311 + + G(d,p)			B3PW91/6-311 + + G(d,p)		
Parameter	DMSO ₂	EMSO ₂	DESO ₂	DMSO ₂	EMSO ₂	DESO ₂
Zero-point vibrational energy ($kcal\cdot mol^{-1}$)	51.8509	69.2004	86.5228	51.2655	68.5544	81.0185
Rotational constants (GHz)						
	4.6917	4.5501	4.3986	4.5133	4.3781	4.2330
	4.2916	2.3327	1.4711	4.1669	2.2907	1.4511
	4.1767	2.2942	1.4521	4.0855	2.2611	1.4353
Rotational temperatures (K)						
	0.2252	0.2184	0.2111	0.2166	0.2101	0.2032
	0.2060	0.1120	0.0706	0.2000	0.1099	0.0696
	0.2005	0.1101	0.0697	0.1961	0.1085	0.0689
Energy ($kcal\cdot mol^{-1}$)						
Translational	0.889	0.889	0.889	0.889	0.889	0.889
Rotational	0.889	0.889	0.889	0.889	0.889	0.889
Vibrational	53.943	72.171	90.389	53.487	71.683	85.290
Total	55.721	73.949	92.389	55.264	73.461	87.067
Molar heat capacity ($cal\cdot mol^{-1}\cdot K^{-1}$)						
Translational	2.981	2.981	2.981	2.981	2.981	2.981
Rotational	2.981	2.981	2.981	2.981	2.981	2.981
Vibrational	15.564	20.554	25.557	16.327	21.378	27.949
Total	21.526	26.516	31.518	22.288	27.340	33.910
Entropy ($cal\cdot mol^{-1}\cdot K^{-1}$)						
Translational	39.534	39.948	40.312	39.534	39.948	40.312
Rotational	24.372	26.981	27.928	24.462	27.052	27.991
Vibrational	11.249	17.384	23.851	12.024	18.581	26.978
Total	75.155	84.314	92.091	76.020	85.581	95.281

The correlation equations between heat capacity, entropy, energy and temperatures were fitted by quadratic equation ($property = a + bT + dT^2$) and the corresponding fitting coefficients and coefficient of determination (R^2) for these thermodynamic properties are listed in Table 4. The temperature dependence of entropy, heat capacity, and energy, as well as corresponding correlation plots are shown in Fig. 2 and 3.

Table 3

Thermodynamic properties at different temperatures at B3PW91/6–311++G (d,p) level for DMSO2, EMSO2 and DESO2.

T(K)	E (kcal.mol ⁻¹)	C _V (cal.mol ⁻¹ .K ⁻¹)	S (cal.mol ⁻¹ .K ⁻¹)
		DMSO2	
100	51.99	10.21	56.95
200	53.35	16.72	67.50
300	55.31	22.39	76.17
400	57.81	27.60	83.91
500	60.80	32.00	91.01
600	64.18	35.60	97.53
700	67.90	38.57	103.55
800	71.88	41.07	109.14
900	76.10	43.21	114.34
1000	80.51	45.05	119.20
		EMSO2	
100	69.43	12.99	62.55
200	71.12	20.47	75.34
300	73.51	27.47	85.76
400	76.60	34.26	95.18
500	80.33	40.14	103.92
600	84.60	45.01	112.05
700	89.31	49.05	119.60
800	94.39	52.47	126.650
900	99.78	55.38	133.26
1000	105.45	57.89	139.41
		DESO2	
100	82.09	16.32	67.34
200	84.17	25.17	82.83
300	87.13	34.08	95.50
400	90.98	42.78	107.09
500	95.64	50.23	117.91
600	100.98	56.35	127.99
700	106.88	61.42	137.37
800	113.24	65.69	146.13
900	119.99	69.31	154.31
1000	127.08	72.40	161.90

Table 4

Least-squares fitted coefficients of quadratic equation (property= $a+bT+dT^2$) and the corresponding coefficients of determination (R^2) for heat capacity, entropy and thermal energy of DMSO2, EMSO2 and DESO2 at RHF/6-311++G(d,p) and B3PW91/6-311++G(d,p) levels

	RHF/6-311++G(d,p)				B3PW91/6-311++G(d,p)			
DMSO2	a	b	d	R^2	a	b	d	R^2
E	51.0514	0.0107	$1.9064 \cdot 10^{-5}$	0.9996	50.3737	0.0116	$1.8811 \cdot 10^{-5}$	0.9995
Cv	3.2503	0.0699	$-2.8615 \cdot 10^{-5}$	0.9998	3.5328	0.0718	$-3.0663 \cdot 10^{-5}$	0.9996
S	47.9304	0.0981	$-2.8851 \cdot 10^{-5}$	0.9995	47.8768	0.1017	$-3.0784 \cdot 10^{-5}$	0.9994
EMSO2								
E	68.2455	0.0123	$2.5246 \cdot 10^{-5}$	0.9995	67.5428	0.0133	$2.4898 \cdot 10^{-5}$	0.9996
Cv	3.9123	0.0869	$-3.3341 \cdot 10^{-5}$	0.9998	4.2985	0.0888	$-3.5413 \cdot 10^{-5}$	0.9998
S	51.1401	0.1180	$-3.2561 \cdot 10^{-5}$	0.9995	51.6322	0.1220	$-3.4724 \cdot 10^{-5}$	0.9995
DESO2								
E	85.4899	0.0140	$3.1255 \cdot 10^{-5}$	0.9996	79.7525	0.0163	$3.1405 \cdot 10^{-5}$	0.9995
Cv	4.6436	0.1037	$-3.7921 \cdot 10^{-5}$	0.9995	5.1312	0.1116	$-4.4476 \cdot 10^{-5}$	0.9996
S	53.4617	0.1380	$-3.6327 \cdot 10^{-5}$	0.9995	53.9138	0.1487	$-4.1246 \cdot 10^{-5}$	0.9996

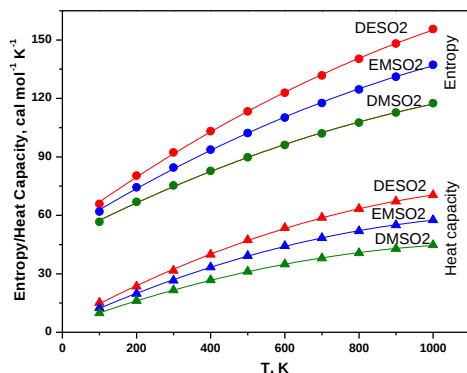


Fig. 2. Temperature dependence of molar entropy and heat capacity of DMSO2, EMSO2 and DESO2 calculated at RHF/6-311++G(d,p) level.

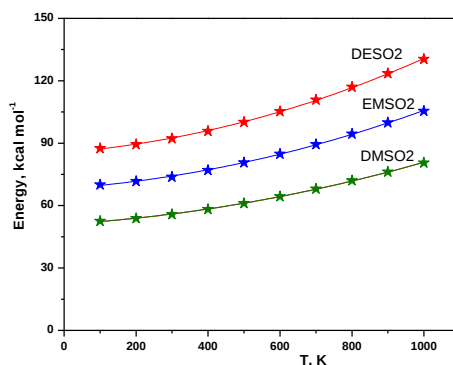


Fig. 3. Temperature dependence of thermal energy of DMSO2, EMSO2 and DESO2 calculated at RHF/6-311++G(d,p) level.

The thermodynamic data provide helpful information for the further study on the title compounds, when these are used as a reactant to take part in a new reaction. They can be used to estimate the direction of chemical reactions involving sulfones, thermochemistry of these reactions etc. It should be only noted, that all thermodynamic calculations have been performed in the gas phase.

This work was partially supported by the RA MES State Committee of Science.

**ԴԻԱԿԵԼՍՈՒԼՖՈՆՆԵՐԻ ԷՆՏՐՈՊԻԱՅԻ ԵՎ ՋԵՐՄՈՒՆԱԿՈՒԹՅԱՆ
ՏԵՍԱԿԱՆ ՔՎԱՆՏԱՔԻՄԻԱԿԱՆ ՈՐՈՇՈՒՄԸ ԳԱՋ ՖԱԶՈՒՄ**

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Իրականացվել է դիալկիլսուլֆոնների (դիմեթիլ-, էթիլմեթիլ-, դիէթիլսուլֆոնների) էնտրոպիայի, ջերմունակության և ներքին էներգիայի տեսական քվանտաքիմիական հաշվարկը: Դիալկիլսուլֆոնների նշված թերմոդինամիական հատկությունները հաշվարկվել են քվանտային մեխանիկայի և վիճակագրական թերմոդինամիկայի համակցումով Gaussian 09 ծրագրային փաթեթի օգնությամբ: Մեկուսացված մոլեկուլների երկրաչափության օպտիմիզացիան իրականացվել է Հարթրի-Ֆոկի սահմանափակ (RHF) և խտության ֆունկցիոնալի տեսության (DFT/B3PW91) մեթոդներով՝ 6-311++G(d,p) ընդլայնված բազիսային հավաքածուով: Կիրառվել է կոշտ ուռուր/հարմոնիկ օսցիլյատորի մոտավորությունները: Քանի որ տեսականորեն հաշվարկված էնտրոպիայի և ջերմունակության արժեքները զգալուն են տատանողական հաճախությունների նկատմամբ, օգտագործվել է համապատասխան մասշտաբային գործակիցը՝ վերահաշվարկելու հարմոնիկ հաճախությունները:

**ТЕОРЕТИЧЕСКИЙ РАСЧЕТ ЭНТРОПИИ И ТЕПЛОЕМКОСТИ
ДИАЛКИЛСУЛЬФОНОВ В ГАЗОВОЙ ФАЗЕ**

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Проведен теоретический квантово-химический расчет энтропии, теплоемкости и внутренней энергии диалкилсульфонов (диметил-, этилметил-, диэтилсульфоны). Термодинамические свойства диалкилсульфонов были рассчитаны путем комбинирования квантовой механики со статистической термодинамикой с использованием программного пакета Gaussian 09. Оптимизация геометрии изолированных молекул сульфонов проводилась ограниченным методом Хартри-Фока (RHF) и методами теории функционала плотности (DFT/B3PW91) с расширенным базисным набором 6-311++G(d,p). Методология расчета основана на формализме жесткого ротора/гармонического осциллятора. Так как теоретически рассчитанные энтропия и теплоемкость чувствительны к колебательным частотам, соответствующий коэффициент масштабирования использовался для перерасчета гармонических колебаний.

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