Conformational studies of aliphatic secondary ozonides (propene, 1-butene and 1-heptene) by means of FTIR spectroscopy

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Abstract: Ozonization reaction of simple alkenes was studied by means of FT infrared absorption gas spectroscopy. The reaction was performed at 95 K in neat films of the reactants. IR absorption spectra of the gaseous products were recorded. The spectra were analyzed combining experimental results with theoretical calculations performed at B3LYP 6-311++G (3df, 3pd) level. We found that among all theoretically predicted conformers of propene secondary ozonide, only one which has the O-O half-chair configuration for the five membered ring and the radical attached in the *equatorial* position was present in the sample. Samples of 1-butene and 1-heptene secondary ozonides consist from two conformers of very similar energy (ΔH=0.3 kJ/mol). The most stable conformer for both ozonides is the one with O-O half-chair configuration of the five membered ring and the radical attached in *equatorial* position and the aliphatic chain in *gauche* position. The second stable conformer has the aliphatic chain in *anti* position.

1   Introduction

The ability of ozone to cleave double bonds in olefins has been known for more than 50 years. Understanding of these reactions is very important in atmospheric chemistry. Ozone, together with the hydroxyl radical OH and the nitrate radical NO_3 are the main oxidant species of atmospheric unsaturated hydrocarbons, where reaction with the olefins

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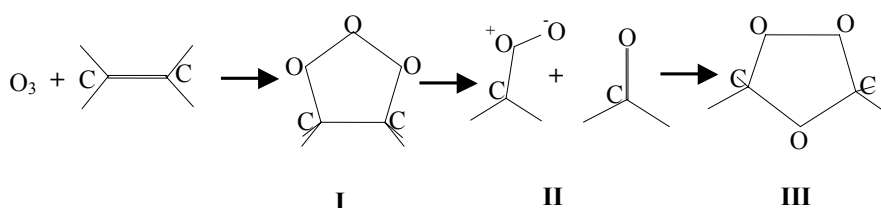
Fig. 1 *Criegee* mechanism of ozonization reaction of alkenes.

results in the break down of the double bond and forming carbonyl compounds. The alkene ozonization reaction is believed to proceed under so called *Criegee* three-step mechanism (see Fig. 1). During the different stages of the reaction, the primary ozonide (POZ) I, carbonyl oxide (COX) II and the secondary ozonide (SOZ) III are formed. The fate of the reaction depends on many parameters, such as type of radical, conformation of alkene, temperature of the reaction, environmental effects, internal energy as well as reactions with other molecular species surrounding the reactants. Despite numerous studies of the reaction by different spectroscopic techniques the precise mechanism of the reaction is still unknown [1–4].

It's well established experimentally, that POZ is a highly unstable intermediate, which rapidly dissociates into the carbonyl compound (CC) and COX, often known as the *Criegee* intermediate (CI). The further fate of the reaction depends on the environmental effects [2]. In the gas phase many different reaction pathways are possible such as dissociation or rearrangement of the CI followed by a bimolecular reaction with CC or residual CI, which leads to a rather complicated reaction sequence. In the condense phase, the carbonyl compound and *Criegee* intermediates readily recombine to form a secondary ozonide. However, other competing processes may occur in the condensed phase. Suenram and Lovas have reported the detection of dioxirane from ethene ozonolysis [1].

It has been experimentally shown that SOZ is more stable then POZ [5]. At room temperature SOZ can remain stable from a few hours up to a few days, after that it eventually dissociates into formic acid and aldehyde. Stability of SOZ is dependent on size and configuration of the radical. Unfortunately, not much is known about the spatial structure of the SOZ molecules.
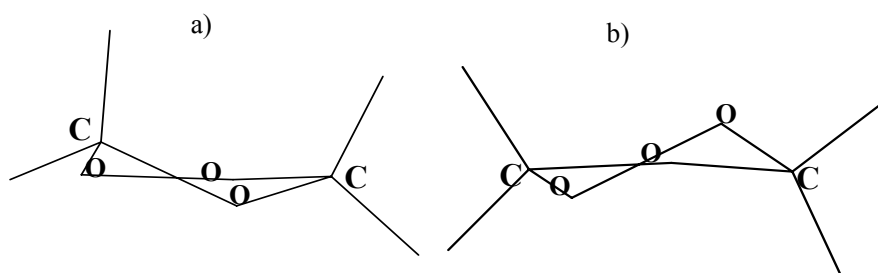
Fig. 2 Conformations of five membered ring of secondary ozonides: a) C-O half-chair conformation; b) O-O half-chair conformation.

In the late 1960's the so called Bauld-Bailey theory was proposed. It concerns the five membered ring geometry of the SOZ molecules as well as substitution positions on the ring. According to this theory the five membered ring of SOZ is in the so called C-O half-chair configuration (see Fig. 2a) [5, 6]. The position of substitution depends on the initial conformation of the reactants. In the early 1970's, the Bauld-Bailey theory was revised by Kuczkowski [7, 8]. The revision was based on new experimental microwave data. According to Kuczkowski's theory, SOZ is more stable in the O-O half-chair ring conformation (see Fig. 2b) and for the case of the 1-alkene SOZ, *cis* configuration (also called *equatorial*) of aliphatic chain [5–8] was considered stable. This configuration of the aliphatic chain and five membered ring for propene SOZ were supported by early *ab initio* calculations [8]. From a theoretical point of view the *ab initio* calculations of this molecular species containing such a strained five membered ring was a challenging task where the results of calculations should be treated with care. In conformational analysis, such calculations usually are combined with experimental data taken from vibrational and rotational spectra [9]. Unfortunately, for such unstable molecules as SOZ'es such an approach is not possible. Indeed the SOZ molecules in the ozonization reaction are formed along with other products of the reaction, thus making vibrational spectra of such mixtures difficult to interpret. Herein a new method for obtaining IR absorption spectra of pure gaseous SOZ molecules of simple alkenes is reported. Combining such spectral data with Density Functional Theory (DFT) calculations allows us to define the geometrical structure of the titled SOZ molecules.

2   Experimental

The experiments were carried out at the infrared beam line BL73 at the Swedish National Laboratory of Synchrotron Radiation – MAX-lab. The ozonization reaction was performed in the condensed phase in a home made liquid nitrogen cooled stainless steel double walled reactor. The inner part of the reactor is cooled by liquid nitrogen placed in between the walls. All ozonization reactions took place on the walls of the reactor at the temperature of 77 K. After the reaction, the reactor was slowly warmed up and the products after each 20 K temperature increase were pumped out to the temperature controlled infrared gas cell equipped with White Optics and cooled back down to the temperature of the reactor. After acquiring the FTIR spectrum, the products were pumped out of the cell. After increasing the temperature of the reactor and cell by 20 K, a new batch of the products were introduced into the cell. The highest yield's for propene SOZ was at 220 K, for 1-butene SOZ - at 240 K and for 1-heptene SOZ – at 295 K. In a similar fashion the secondary ozonides were purified by the removal of the by-products of the reaction at temperatures of their fusion: acetaldehyde - 150 K, formaldehyde - at 156 K, propanal - at 180 K, hexanal - at 220 K. The temperature of the reactor was monitored by a platinum thermometer. The pressure of the gaseous product in the cell was approximately 0.05 torr. The base length of the cell was 2.85 meters. The total length of the optical path was 68.4 meters. The cell is described in detail elsewhere [10, 11].

Infrared absorption spectra of the reaction products were collected on a Bruker IFS 120 HR spectrometer with a 4 cm^{-1} resolution, using glowbar as a source. A spectral resolution up to 0.003 cm^{-1} was used in some experiments. Unfortunately, for 1-butene SOZ rotational structure is partly resolvable and for 1-heptene SOZ – is not due to low rotational constants. In the case of propene, the SOZ rotational structure was resolvable and shall be published as a separate paper. The absorption spectra were measured in the spectral region 600-4000 cm^{-1}. For the conformational analysis a closer look at the spectral region of 900-1200 cm^{-1} was taken, where the spectral bands for the different vibrations of the five membered ring are located. Spectral bands for the CH stretch spectral region for all of the title compounds are located closely to similar frequencies and cannot be used for our analysis. Scans of 128 were averaged to obtain the spectra. It took approximately 70 seconds for each spectrum, which was found to be a reasonable registration time for such unstable molecules as the secondary ozonides. The spectra of the products were recorded in the 180-300 K temperature range.

3   Results and discussion

Conformational diversity of secondary ozonides of 1-alkenes is influenced by three different factors. Foremost, the five membered ring can adopt various puckering forms. The conformations of such a ring can be classified into an envelope (E) form in which one atom lies out of the plane of the other atoms, and twist (T) form in which two consecutive atoms lie on opposite faces of the plane of the other three atoms. Theoretically the five membered ring of the secondary ozonides can have two different T forms while the E form (C$_s$ symmetry) is rarely possible due to strong dipole-dipole interactions in the ring. Both T forms are presented in Fig. 2. The so called C-O half chair conformer (C$_1$ symmetry) has consecutive C and O atoms being out of plane with the other three atoms of the ring. The O-O half chair conformer (C$_2$ symmetry) has two consecutive O atoms being out of plane of the other atoms of the ring.

Secondly, the aliphatic chain of 1-alkene ozonide can be attached to the ring in two different so-called *axial* and *equatorial* positions. In the *axial* position, the chemical bond between the ring carbon and aliphatic carbon atom is parallel (or close to parallel) to the normal vector of the ring plane. In the *equatorial* position the C-C bond lies in the ring plane. It is notable, that contrary to the examples of six membered ring's, those that are five membered rings containing COCOO, the definition of *axial* and *equatorial* conformers is not exact due to the fact that the C-C bond is never parallel or perpendicular to the ring plane and visually it is quite difficult to distinguish the *axial* conformer from the *equatorial*. Nevertheless, these notations are still in use in conformational analysis of the SOZ molecules.

Finally, the aliphatic chain attached to the ring can have different conformations by itself. The energetic barrier of rotation around a single CC (σ) bond is generally very low. So, the hindered rotation around each CC bond can result in different conformers. In the most stable conformation, the neighboring methyl or methylene groups lie as far

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apart from each other as possible with a dihedral CCCC angle of 180 degrees. It is well established that different staggered conformers can be formed only as result of rotations around the two closest to the ring CC bonds of aliphatic chains. In the case of an aliphatic group attached to the COCOO ring, only one such CC bond is left in the aliphatic chain and only a rotation around this bond can cause the formation of the so called *anti* and *gauche* conformers. It has been experimentally and theoretically shown that the alkane's energy differences between *anti* and *gauche* conformers are 3.7-3.8 kJ/mol [10]. For that of the aliphatic chain attached to COCOO ring, this value can be very different due to interactions between the ring and terminal methyl group of the aliphatic chain attached to the ring.

These three reasons make the conformational picture of SOZ molecules quite complicated. For the conformational studies we have chosen the three following secondary ozonides: propene, 1-butene and 1-heptene SOZ. For the propene SOZ only the first two factors influence the conformational diversity and for the 1-butene and 1-heptene SOZ molecules all three factors are important.
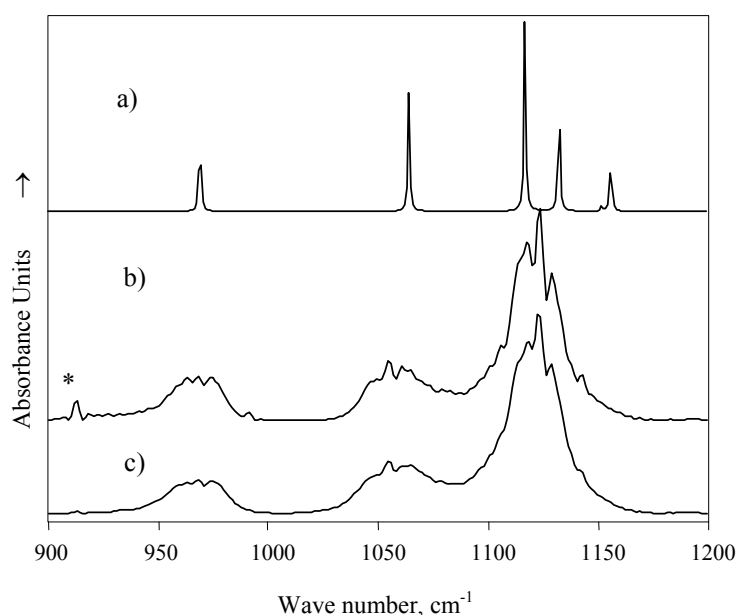
3.1 Propene SOZ

The only experimental attempt to define the geometrical structure of propene ozonide was made by L. Kuczkowski et al in 1974 [8], by collection of a microwave absorption spectra of gaseous propene SOZ at 195 K. In this study only one conformer of the molecule had been observed, possessing the O-O half chair conformation and having a single methyl constituent in an *equatorial* position. The authors of this work do not rule out the presence of an *axial* conformer but they believe that this apparently is much less abundant.

Some studies of the propene ozonization reaction have been made by means of gas infrared absorption spectroscopy [8, 13–15]. But this approach is not suitable for conformational analysis of secondary ozonides. The secondary ozonide is only a minor product in the ozonization of alkenes in the gas phase. According to the *Criegee* mechanism, the primary ozonide is formed in first step and it is in an excited state. In order for the primary ozonide to convert to the secondary ozonide it has to be collisionally cooled, otherwise it will directly decompose in to smaller final products of the reaction. Collisional cooling is not very efficient in the gas phase. So, SOZ as a major product of the reaction can be formed only in the condensed phase.

The experimental approach taken in this study is to perform the ozonization reaction in the condensed phase and to separate the secondary ozonide from the other by-products of the reaction by selective evaporation, thus obtaining the infrared absorption spectrum of the gaseous secondary ozonide at various fixed temperatures.

The infrared absorption spectrum of gaseous propene ozonide at 295 K and 220 K is presented in Fig. 3 (bottom and middle curves). The relative intensities of the spectral bands are the same in both spectra. For a conformational mixture, such similarities of relative intensity of vibrational spectral bands may occur in two cases. Either conformers in the mixture have nearly the same stability or the stability is very different and due

Fig. 3 IR absorption spectra of propene SOZ: a) theoretically (B3LYP 6- 311++G(3df, 3pd)) calculated spectra of the most stable O-O half-chair *equatorial* conformer; b) and c) experimental spectra of gaseous sample at 220 K and 295 K, respectively. * - denotes propene spectral band.

to *Boltzmann* distribution only one conformer dominates in the mixture. In order to determine which conformer or conformers are present in the sample, quantum chemical calculations at DFT B3LYP level, using 6-311++G (3df, 3pd) basis set were performed. It was prepared big number of input files with the initial conformers, having structures of C-O half chair *axial*, C-O half chair *equatorial*, O-O half chair *axial* and O-O half chair *equatorial*. In all cases, optimization of the geometry lead to only two staggered conformers, either O-O half chair *equatorial* or O-O half chair *axial*, where the former is more stable. Both theoretically calculated structures are presented in Fig. 4.

Energy difference between these two conformers was found to be ΔH=3.3 kJ/mol. In the experimental spectrum where a 5% noise adjustment is taken in to account for the thermodynamic equilibrium, it should be possible to observe the spectral bands of O-O half chair *axial* conformer. However, in the experimental spectra of the gaseous propene ozonide at 295 K and 220 K, no changes were observed for the relative intensities of the spectral bands. This can be best explained by the relative abundance of only one conformer in the sample. Perhaps, the theoretical calculations performed for the molecule containing such a strained five membered ring underestimated the energy difference between both conformers. The assignment of experimental spectral bands based on our theoretical calculations is presented in Table 1. The calculated spectrum is presented in Fig. 3. The experimental band in the spectral region 1070-1130 cm^{-1} seems to consist of 3 components, while DFT calculations predict for the *equatorial* conformer of propene SOZ only two bands at 1117 and 1132 cm^{-1}. The DFT calculated rotational constants for
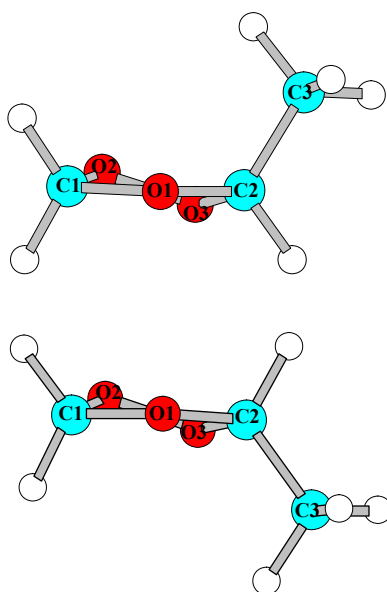
Fig. 4 Theoretically (B3LYP 6-311++G (3df, 3pd)) calculated structures of the staggered conformers of propene secondary ozonide. Top: O-O half-chair *axial*, τ(OOCC)= 87.8 °; Bottom: O-O half-chair *equatorial*, τ(OOCC)= 160.4 °.

this molecule are rather large (0.25, 0.1 and 0.08 cm^{-1}), which makes the vibro-rotational spectral bands partly resolvable even in the spectrum with 4 cm^{-1} resolution. According to these calculations, the band at 1117 cm^{-1} should be nearly c-type and the band at 1132 cm^{-1} nearly b-type. Convolution of these two experimental bands gives a spectral contour with three maxima. The main spectral features of the experimental and calculated spectra resemble each other, which indicates the sufficiency of the chosen level of theoretical calculations.

Table 1 Theoretically calculated and experimental infrared absorption spectral bands of propene SOZ in spectral region of the five membered ring vibrations.

Theoretical O-O half chair *equatorial*		Appr. assignment	Experimental	
ν, cm^{-1}	I, a.u.		ν, cm^{-1}	I, a.u.
969	45.5	-O(1)-C(1)-, -C(1)-O(2)- asym. stretch	968	18
1064	61.7	-O(1)-C(1)-, -C(2)-O(2)- sym. stretch	1059	28
1117	100.3	-O(1)-C(2)- stretch, -C(3)H3 rocking	1119	100
1132	64.7	-O(1)-C(2)-, -C(2)-O(3)- sym. stretch	1128	72
1151	2.5	-C(1)H2 rocking		
1156	30	-C(3)H3 deformation		

"a.u." means arbitrary units

3.2   1-butene and 1-heptene SOZes

The conformational problem in 1-butene and 1-heptene SOZ molecules is more complex than that in the propene SOZ due to (I) the possible rotation of the aliphatic chain around the first CC bond from the ring and (II) the possible rotation of the terminal ethyl group of the aliphatic chain around the C-C bond. The 1-heptene SOZ has a longer aliphatic chain than 1-butene SOZ. So, interaction between the radical and the five-member ring is expected to be different in both ozonides. Between a large variety of possible conformers of 1-butene and 1-heptene SOZ we have chosen for theoretical analysis only those, which are formed from the rotation of the radical around the first C-C bond from the ring. Staggered conformers due to rotation of the radical around the other C-C bonds (even around last but one CC bond) should be much higher in energy, similar to conformational picture of alkanes [9].

Table 2 DFT calculated (B3LYP\6-311++G(3df, 3pd)) relative potential energies (ΔH) of all staggered conformers of propene, 1-butene and 1-heptene ozonides.

Conformer	ΔH, kJ/mol(τ_{OCCC})		
	Propene SOZ	1-butene SOZ	1-heptene SOZ
O-O half chair *equatorial*		0 (-66.1 °)	0 (-66.3 °)
O-O half chair *equatorial*		0.3 (-177.6 °)	0.3 (-177.8 °)
O-O half chair *equatorial*	0	1.7 (56.9 °)	2.3 (57.3 °)
O-O half chair *equatorial*			3.8(-65.9 °, τ_{CCCC} = 66.1°)
O-O half chair *equatorial*			3.9(-66.5°, τ_{CCCC} = - 66.2°)
O-O half chair *axial*		2.1 (175.5^o)	2.5 (174.6°)
O-O half chair *axial*	3.3	3.2 (62.5°)	3.6 (62.9°)
O-O half chair *axial*		6.3 (-60.4°)	6.9 (-60.4°)

Results of our calculations are presented in Table 2. Similar to the case of 1-propene SOZ, O-O half chair *equatorial* conformers are much more stable then O-O half chair *axial* conformers. The calculations show that the energy difference between the two most stable O-O half chair *equatorial anti* and *gauche* conformers of 1-butene and 1-heptene secondary ozonide is very small – ~0.3 kJ/mol. For the notation of an *anti* conformer we use the conformer with the torsional angle between the ring plain and the first CC bond of the aliphatic chain being around 180°, while notation for the *gauche* conformer – is set with the torsional angle being around 60°. The calculated structures of these conformers are presented in Fig. 5 and Fig. 6. Experimental FTIR absorption spectra of gaseous 1-butene and 1-heptene SOZ molecules together with theoretically calculated IR absorption spectra of O-O half chair *equatorial anti* and *gauche* conformers of both compounds are presented in Fig. 7 and 8. The experimental and theoretically calculated spectral bands together with assignments are listed in Table 3 and Table 4.

Table 3 Theoretically calculated and experimental infrared absorption spectral bands of 1-butene SOZ in spectral region of the five membered ring vibrations.

| Theoretical | | | | Assignment | Experimental | |
| O-O half chair *equatorial* (-66.1°) | | O-O half chair *equatorial* (-177.6°) | | | | |
ν, cm^{-1}	I. a.u.	ν, cm^{-1}	I. a.u.		ν, cm^{-1}	I, a.u.
936	13			-O(2)-C(1)-, -O(3)-C(2)- stretch	931	13
936	13			-C(4)H3 rocking	958	38
		983	49	C(1)-O(1)-, -O(1)-C(2)- sym. stretch	982	44
		1001	12	-C(3)-C(4)- stretch	997	28
1027	23			-C(3)-C(4)- stretch	1028	12
1066	56	1068	33	-O(1)-C(1)-, -C(1)-O(2)- sym. stretch	1064	86
		1097	100	-O(1)-C(2)- stretch, -C(2)-C(3)-C(4)- deformation in plain	1099	100
1109	100			-O(1)-C(2)-, -C(2)-O(3)- sym. stretch -C(2)-C(3)-C(4)- deformation in plain	1120	92
1131	23			-C(2)-O(1)-stretch. -C(2)-C(3)-C(4)- deformation out of plain		
		1139	21	-C(2)-O(3)-stretch. -C(2)-C(3)-C(4)- deformation in plain		

"a.u." means arbitrary units

As in the case of 1-propene SOZ, the relative intensities of the spectral bands are similar in both spectra. The experimental data together with results of the theoretical calculations leads to the conclusion, that in our gaseous samples both conformers of 1-butene and 1-heptene SOZ molecules are abundant. Experimental FTIR absorption spectra of gaseous 1-butene and 1-heptene SOZ molecules together with theoretically calculated IR absorption spectra of O-O half chair *equatorial anti* and *gauche* conformers of both compounds are presented in Fig. 7-8. Nearly all vibrational spectral bands of both conformers partly or completely overlap. The spectral region of 1000-1200 cm^{-1},
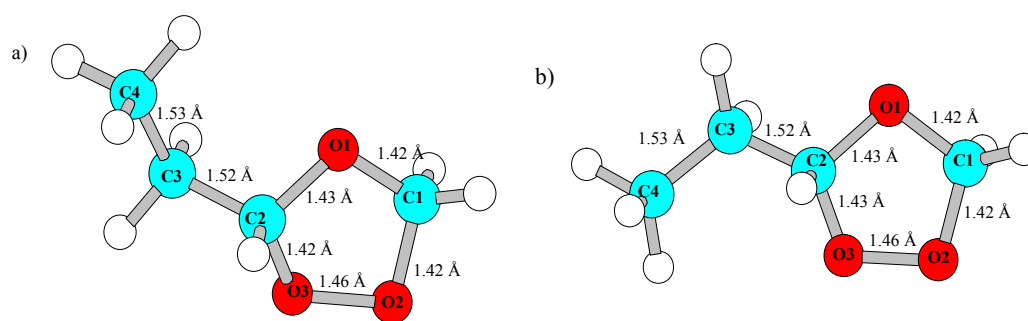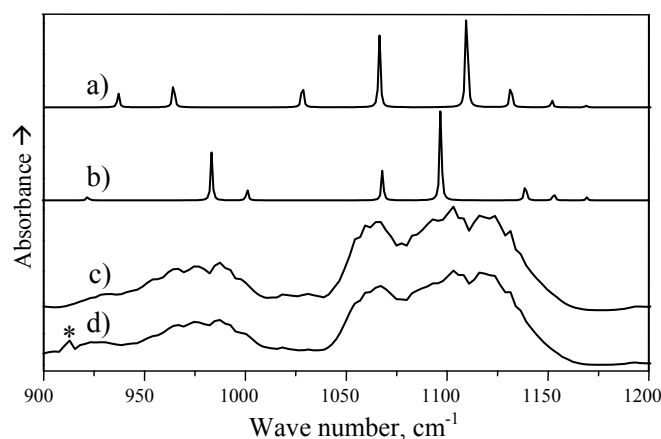
Fig. 5 Theoretically (B3LYP 6-311++G (3df, 3pd)) calculated structure of the most stable 1-butene SOZ conformers: a) *gauche* conformer: ∠O1C2C3C4=-66.1°; b) *anti* conformer: ∠O1C2C3C4=-177.6°. The enthalpy difference between them δH = -0.31 kJ/mol.
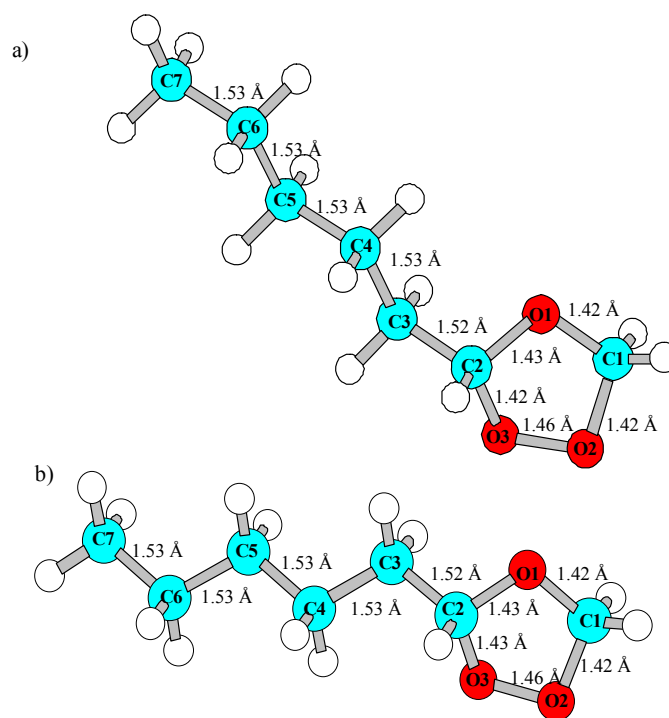
Fig. 6 Theoretically (B3LYP 6-311++G (3df, 3pd)) calculated structure of the most stable 1-heptene SOZ conformers: a) *gauche* conformer: ∠ O1C2C3C4=-66.3°; b) *anti* conformer: ∠O1C2C3C4=-177.8°. The enthalpy difference between them δH = - 0.29 kJ/mol.

where the spectral bands of different ring vibrations are located, is the most sensitive to the conformations of the ozonides. In this spectral region we can expect some not overlapping bands, belonging to the different conformers. According to the calculations, the bands at 982, 997 and 1099 cm^{-1} can be attributed to the *anti* conformer, while bands located at 931, 958, 1028 and at 1120 cm^{-1} - to *gauche* conformer of 1-butene SOZ.

Table 4 Experimental and theoretical infrared absorption spectral bands of 1-heptene SOZ.

Theoretical				Assignment	Experimental	
O-O half chair *equatorial* (-66.3°)		O-O half chair *equatorial* (-177.8°)				
ν, cm^{-1}	I. a.u.	ν, cm^{-1}	I. a.u.		ν, cm^{-1}	I, a.u.
		972	41	-O(1)-C(1)-, -C(1)-O(2)- asym. stretch	966	20
996	11			-C(3,4,5,6)H2 twisting, -C(7)H3 rocking	995	17
1000	8			-C(3)-C(4)-C(5)-C(6)-C(7)- skeleton in plain		
		1013	11	-C(3,4,5,6)H2 twisting		
		1025	10	-C(6)-C(7)-, -C(4)-C(5)- asym. stretch		
1044	5			-C(3)-C(4)-, -C(6)-C(7)- sym. stretch		
		1046	2	-C(3)-C(4)- stretch		
1056	11			-C(3)-C(4)-C(5)-C(6)-C(7)- chain stretch		
		1064	10	-C(4)-C(5)-C(6)- chain stretch	1062	63
1067	59			-O(1)-C(1)-, -C(1)-O(2)- sym. stretch		
1073	16.8			-C(2)-C(4)-C(5)-C(6)-C(7) skeleton in plain	1074	25
		1076	83.7	-O(2)-C(1)-, -C(1)-O(1)- sym. stretch		
1116	100	1116	100	-O(1)-C(2)-, -C(2)-O(3)- sym. stretch, -C(2)-C(3)- stretch.	1109	100
1142	9	1141	11	-C(2)-C(3)-C(4)-C(5)-C(6)-C(7)- skeleton out of plain	1128	33

Fig. 7 IR absorption spectra of 1-butene SOZ in frequency range of the ring vibrations: a) theoretically (B3LYP 6-311++G (3df, 3pd)) calculated spectrum of 1- butene SOZ *gauche* conformer; b) theoretically calculated spectrum of 1-butene SOZ *anti* conformer, c) experimental spectrum of gaseous sample at 240 K, d) experimental spectrum of gaseous sample at 295 K. * - denotes 1-butene band.
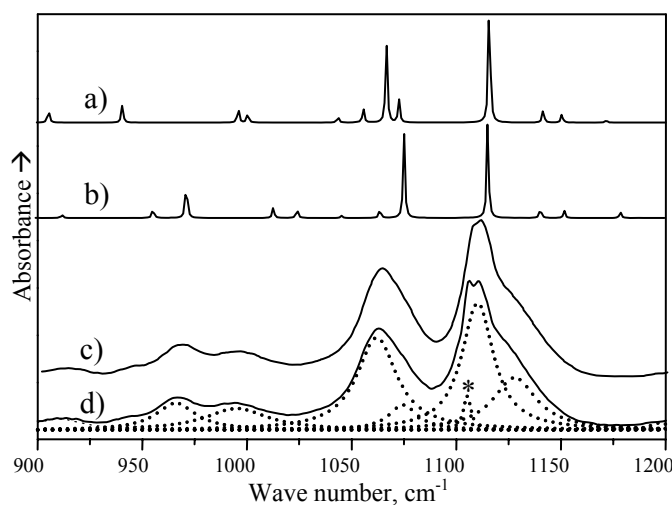
Fig. 8 IR absorption spectra of 1-heptene SOZ in spectral region of the ring vibrations: a) theoretically (B3LYP 6-311++G(3df, 3pd)) calculated spectrum of 1-heptene SOZ *gauche* conformer; b) theoretically calculated spectrum of 1-heptene SOZ *anti* conformer, c) and d) experimental spectrum of gaseous sample at 250 and 295 K respectively.
∗ - denotes formic acid spectral band.

This spectral region for 1-heptene SOZ is even more complicated than in the case of 1-butene SOZ. Two spectral bands near 1108 cm^{-1} are present in the spectrum (Fig. 8) of 1-heptene SOZ, but the band at 1105 cm^{-1} seems to be a –CO– stretching band of the impurity, formic acid. The asymmetric band at 1070 cm^{-1} seems to be an overlapping of spectral bands. By fitting this band with two Lorentzian contours we found that this asymmetrical band is consistent with two overlapping bands. According to the calcula-

tions the first one at 1062 cm^{-1} can be attributed to –CO– stretch vibration of 1-heptene SOZ *gauche* conformer, while the second band at 1074 cm^{-1} is attributed to the –CO– stretch vibration of 1-heptene SOZ *anti* conformer. The aliphatic chain deformation band at 995 cm^{-1} was attributed to the *gauche* conformer, while another ring's –CO– vibration at 966 cm^{-1} was attributed to the *anti* conformer.

4   Conclusions

It was found that all infrared absorption bands of gaseous 1-propene ozonide can be attributed to only one conformer. By combining the experimental spectra with results of the DFT calculations (B3LYP 6-311+G (3df, 3pd)) it was found that this conformer is characterized by O-O half chair configuration of the five membered ring and the methyl group attached to the ring in the *equatorial* position. Among all the theoretically predicted conformers for 1-butene and 1-heptene secondary ozonides only two of them were spectroscopically observed. According to the DFT calculations, these conformers are: O-O half chair *equatorial anti* and *gauche*. The infrared spectral bands of both conformers nearly completely overlap in the spectra. Only in the spectral region of the ring vibrations (1000-1200 cm^{-1}) the bands could be attributed to the *gauche* and *anti* conformers.

Comparison of the experimental and theoretical spectra of 1-butene SOZ'es allows us to assign spectral bands at 982 and 1099 cm^{-1} to the five membered ring vibrations of the *anti* conformer, while the bands at 931 and 1120 cm^{-1} were assigned to the ring vibrations of *gauche* conformer. In the case of 1-heptene SOZ – the bands at 966 and 1074 cm^{-1} – to the ring and chain vibrations respectively of *anti* conformer and a band at 995 cm^{-1} to the chain and 1062 cm^{-1} – to the ring vibrations of the *gauche* conformer. The relative intensity of the bands belonging to the *gauche* and *anti* conformers is not temperature dependent in the 230-300 K temperature range. The DFT calculations support this experimental result. According to the calculations the potential energy difference between *gauche* and *anti* conformers of 1-butene ozonide and 1-heptene ozonide is only 0.3 kJ/mol, with *gauche* being the more stable than *anti*. Such small energy difference indicates about the weakness of interaction between the five membered ring and the aliphatic chain. In order to have more experimental evidences about this conformational picture of both ozonides, some matrix isolation experiments with hot nozzle and annealing techniques should be carried out. Such experiments are now under way in this lab.

Acknowledgment

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