”ALEXANDRU IOAN CUZA” UNIVERSITY OF IASI

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CHEMISTRY DOCTORAL SCHOOL

Study of the chemical consumption of some volatile organic compounds under simulated atmospheric conditions. Theoretical and practical approaches

SUMMARY OF THE PHD THESIS

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I. INTRODUCTION

The atmosphere plays a critical role in sustaining life on Earth, providing the elements necessary for life as well as pollutants that can have harmful effects on human health and ecosystems. As a complex system, the atmosphere combines, transforms, and transports natural and anthropogenic emissions on a global scale. Studies in atmospheric chemistry have led to remarkable advances, including improving air quality, characterizing the formation of aerosols involved in acid rain, and studying ozone depletion. (*Report of the National Academies of Sciences, Engineering, and Medicine, 2016*).

Volatile organic compounds (VOCs) are emitted in significant quantities from both natural and anthropogenic sources. The European Directive 1999/13/EC defines them as "any compound containing at least one carbon atom and one or more hydrogen, oxygen, sulphur, phosphorus, silicon, nitrogen or halogens (chlorine, fluorine, bromine), with the exception of carbon oxides and inorganic carbonates". A VOC is also considered to be "any organic compound having a vapor pressure of 0.01 kPa or more at 293.15 K, or having an equivalent volatility under the specific conditions of use" (Council Directive 1999/13/EC of 11 March 1999).

VOCs can be classified into two main categories:

- biogenic volatile organic compounds (BVOCs), emitted by the biosphere and from biomass burning,
- anthropogenic volatile organic compounds (AVOCs), originating from industrial activities, transport and other human sources,

and can reach the atmosphere through:

- evaporation of oxygenated solvents or fuels used in industry, commerce or consumer products,
- incomplete combustion of hydrocarbons from fuels or oil depots,

- emissions from biological sources, such as biogenic compounds emitted by vegetation,
- atmospheric oxidation of hydrocarbons emitted into the air (*Mellouki et al., 2015*).

The major sources of BVOCs are forests (822 TgC/yr), shrubs (194 TgC/yr), crops (120 TgC/yr), oceans (5 TgC/yr) and other sources (soils, volcanoes, biomass fires - 9 TgC/yr) (*Guenther et al., 1995*). BVOCs can be divided into three main classes: terpenoids (*Pang, 2022*), oxygenated volatile organic compounds, and oxygen-free volatile organic compounds.

The study and quantification of VOCs and carbonyl compounds (CC) have become essential for environmental chemistry, as they affect air quality and human health. They contribute to the formation of tropospheric ozone and secondary organic aerosols (SOA) (*Chan et al., 2009; Szulejko and Kim, 2015*). OVOCs are generally more reactive than the hydrocarbons from which they originate, which has made them an intensively studied subject (*Mellouki et al., 2015*).

Recently, researchers attention has turned to methyl-butenols (MBOs), unsaturated alcohols with five carbon atoms, synthesized in the chloroplasts of conifers during the day (*Lerdau şi Gray, 2003*). The most studied of these is 2-methyl-3-buten-2-ol (MBO232), due to its high concentrations in certain regions and structural similarity to isoprene (*Goldan et al., 1993; Grosjean et al., 1993c*). North American pine forests emit MBO232 in quantities 5-8 times greater than isoprene (*Lehnert et al., 2020*). Other sources of MBOs include deciduous forests (e.g. birch, poplar), grasslands and agricultural crops (*Konig et al., 1995; Harley et al., 1998; Zhang et al., 2012*). Emissions increase on sunny, warm days, decreasing significantly in winter (*Koppmann, 2007*). Prenol (3-methyl-2-buten-1-ol) is a natural alcohol and one of the simplest terpenoids. It is a clear, colorless liquid with a fruity odor, occasionally used in perfumery. It occurs naturally in citrus fruits, cranberries, grapes, raspberries, tomatoes, coffee, hop oil, and white bread. An isomer of it, isoprenol (3-methyl-3-buten-1-ol), is also present in nature (*Belsito et al., 2010*).

Organic compounds containing the functional group >C=O (carbonyl) are classified as carbonyl compounds, which are divided into aldehydes and ketones and are emitted into the atmosphere from a variety of anthropogenic and natural sources. Natural sources include certain plants, chemical reactions generated by insect stress, volcanic emissions, animal husbandry and forest fires. On the other hand, anthropogenic sources of aldehydes and ketones include petroleum refining, the plastics industry, the production of paints and varnishes, mining, wastewater treatment plants and the roasting of coffee beans. Also, the burning of wood in households, the incineration of waste and the exploitation of fossil fuels to produce energy, heating and transport represent significant sources of carbonyls in the atmosphere (*Carlier et al., 1986*).

Unsaturated alcohols can be oxidized in the atmosphere by reactions with ozone, hydroxyl radicals during the day, and nitrate radicals at night. These reactions lead to the formation of carbonyls, carboxylic acids, and, in the presence of nitrous oxide, peroxyacyl nitrates (*Grosjean et al., 1993c*). The main carbonyl compounds resulting from these reactions are formaldehyde, acetone, acetaldehyde, glycolaldehyde, 2-hydroxy-2-methylpropanal, and various organic nitrates.

Carbonyl compounds and their photochemical oxidation play a key role in the formation of secondary organic aerosols. Secondary organic aerosols (SOA) constitute a major fraction of fine particles in the atmosphere and influence air chemistry, air quality and climate (*Ortiz et al., 2006; La et al., 2016*).

The motivation for choosing the topic "*Study of the chemical consumption of some volatile organic compounds under simulated atmospheric conditions. Theoretical and practical approaches*" derives from the desire to expand the field of knowledge regarding the atmospheric behavior of volatile organic compounds (VOCs), especially unsaturated alcohols of biogenic nature.

Objectives of the PhD thesis

The objectives of the thesis entitled "Study of the chemical consumption of some volatile organic compounds under simulated atmospheric conditions. Theoretical and practical approaches" were

- Determination of the rate constants for the reactions between a series of methyl-butenols and OH radicals and ozone.
- Evaluation of the impact of methyl butenol degradation on the atmosphere and estimation of the average lifetime of these compounds.
- Comparison of experimentally obtained reaction rate constants (under simulated atmospheric conditions) with theoretical values predicted by SAR models.
- Development of a rapid and sensitive solid phase derivatization method for the analysis of carbonyl compounds in the gas phase using various chromatographic techniques.

II. PERSONAL CONTRIBUTIONS

II.1 ESC-Q-UAIC REACTION CHAMBER AND RESEARCH INFRASTRUCTURE

II.1.1 ESC-Q-UAIC reaction chamber

The ESC-Q-UAIC reaction chamber (Environmental Simulation Chamber made of quartz from University ”Alexandru Ioan Cuza” of Iași) from the Integrated Center for Environmental Science Studies for the North-East Development Region (CERNESIM) of the ”Alexandru Ioan Cuza” University of Iași is made up of three quartz tubes, each measuring 1.4 m in length and 0.48 m in diameter (**Figure II.1**). The reactor has a total capacity of 760 ± 2 L. The evacuation of gases and suspended particles after the completion of an experimental session is carried out using an oil vacuum pump capable of reaching a minimum pressure of 4×10^{-3} mbar. The homogenization of the mixture inside the reaction vessel is achieved by two fans with Teflon blades, chemically inert. A series of temperature and pressure sensors are used to monitor physical parameters during the experimental session.

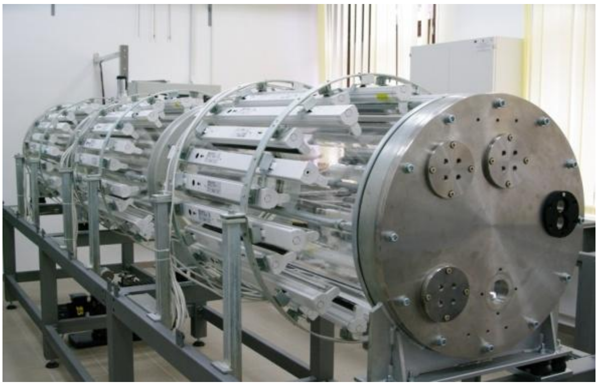


Figure II.1. ESC-Q-UAIC reaction chamber assembly

Around the quartz tubes are mounted 32 Philips TL-DK 36 W super actinic lamps with λ_{max}= 365 nm and 32 Philips UV-C TUV 30W/G30 T8 germicidal lamps with λ_{max}= 254 nm. The lamps are uniformly distributed outside the quartz tubes. The actinic radiation sources are used to simulate radiative conditions at the troposphere, their spectrum reproducing the solar radiation that reaches the troposphere (*Roman et al., 2022b, a*).

II.1.2 Gas chromatograph coupled to ion trap mass spectrometer

The gas chromatography-mass spectrometry tandem brings numerous advantages to the research and development of new methods and the identification of new compounds. The mass spectrometer is an important tool in instrumental analytical chemistry, as it provides a lot of information about the composition and structure of a substance in a sample and is a universal analytical detector for the GC technique. A gas chromatograph with a mass spectrometer detector and ion trap was used to identify and quantify carbonyl compounds (*Agilent 7890A GC, 2007*; *Agilent 240 Ion Trap GC/MS, 2011*) (**Figure II.2**).

Figure II.2 Agilent 7890A GC / Agilent 240 Ion Trap GC/MS gas chromatograph and the main components of the instrument (*Agilent 240 Ion Trap GC/MS, 2011*)

The carbonyl compounds in the analyzed samples were in liquid state, dissolved in a solvent suitable for gas chromatography. The ionization method used was internal ionization – the analytes eluted from the column entering directly into the ion trap, close to a filament that generates electrons. The mass analyzer used is the ion trap, an assembly of three electrodes separated by quartz rings, which form a cavity for ionization, fragmentation, storage and mass analysis (*Agilent 240 Ion Trap GC/MS, 2011*; *Nollet şi Lambropoulou, 2017*).

II.2 SUBSTANCES USED AND EXPERIMENTAL SET-UP

II.2.1 Substances used and experimental set-up in kinetic determinations

Two volatile organic compounds (methyl-butenols and reference compounds) will react with OH/ozone radicals, according to bimolecular (second-order) kinetics, then using the kinetic equation it is possible to determine the values of the reaction rate constants of methyl-butenols with OH/ozone radicals. All experiments were performed at 1000 mbar and 298 ± 2 K. After introducing the reactants into the reactor, their loss at the reactor wall was monitored over a period of 10 minutes using FT-IR. Monitoring of the reaction between methyl-butenol and OH/ozone radicals was performed over a period of 10–15 min for each experiment. For each methyl-butenol, reaction rate constants were determined using at least two references.

The results obtained revealed that the losses at the reactor walls and the losses due to photolysis processes for reactants and references were sometimes quite significant. The values of these wall loss constants were:

- 3-methyl-2-buten-1-ol (MBO321): $k_3 = (1{,}21 \pm 0{,}07) \times 10^{-4}\ s^{-1}$;
- 3-methyl-3-buten-1-ol (MBO331): $k_3 = (3{,}75 \pm 0{,}28) \times 10^{-5}\ s^{-1}$;
- 1,2-dihydroxybenzene: $k_4 = (1{,}51 \pm 0{,}15) \times 10^{-4}\ s^{-1}$;
- mesitylene: $k_4 = (4{,}22 \pm 0{,}19) \times 10^{-5}\ s^{-1}$;
- mesitylene: $k_{6\ (254nm)} = (1{,}40 \pm 0{,}05) \times 10^{-4}\ s^{-1}$.

The estimation of the initial concentrations of the solid phase reactants was performed based on the amount of compound introduced into the reactor, by weighing the glass support before and after. In the case of gases and liquids, the initial concentrations were determined from the injected volume.

OH radicals were generated in the reaction system by:

a) *photolysis of methylnitrite* (CH_3ONO) in the presence of NO at 365 nm;
b) *photolysis of hydrogen peroxide* (H_2O_2) at 254 nm.

Ozone was generated by photolysis of oxygen at λ=184.9 nm, being added to the reactor every 2-3 minutes.

The scavenger is a substance added in excess to the reaction system in order to react predominantly with the OH radicals formed as a result of the ozonolysis reaction of olefins, but not with ozone.

The tracer is a substance introduced into the O3-olefin system that reacts with the OH radicals formed during the olefin degradation processes.

II.2.2 Substances used and experimental working method in the determination of carbonyl compounds

Derivatization is a technique used in chemistry that transforms a chemical compound into a product with a modified chemical structure, called a derivative, which can be analyzed by various instrumental analytical methods. Derivatization in gas or liquid chromatography analysis can be defined as a procedural technique that primarily modifies the functionality of an analyte to allow chromatographic separations *(Mohd, 2012)*.

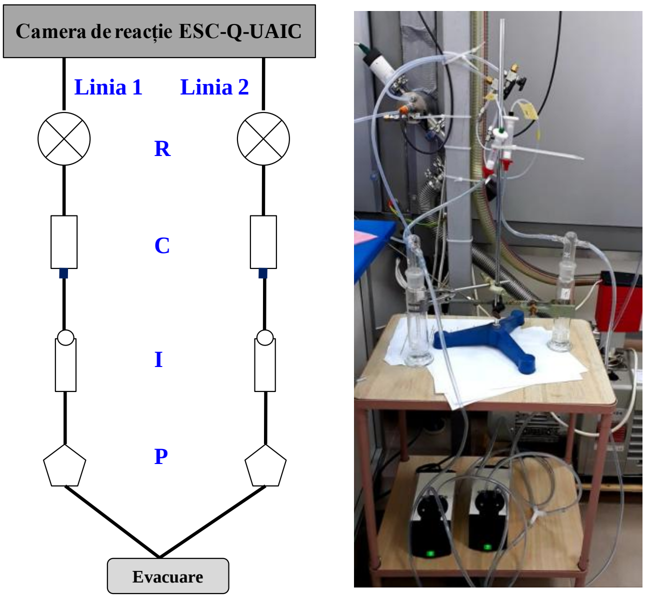
The experiments that were carried out to develop the method of derivatization of carbonyl compounds after passing some volumes of air through SPE C_{18} cartridges took place at a pressure of 1000 mbar and a temperature of (298±2) K. The sampling was carried out through two lines available on the side of the reaction chamber. C_{18} cartridges prepared a few hours in advance were used, so that the adsorbent layer was wet. The variants of connecting two cartridges in series were tested, as well as of connecting a cartridge connected to an impinger in series. The optimal variant was the one that also involved the use of an impinger because a better derivatization of carbonyl compounds in solution was observed. In **Figure II.3**, which shows the scheme and photograph of the system for sampling carbonyl compounds from the ESC-Q-UIAC reaction chamber directly onto C18 cartridges on which the derivatization agent was retained.

II.3 KINETIC STUDIES IN SIMULATED ATMOSPHERE INITIATED BY THE PRESENCE OF OH RADICALS

II.3.1 Determination of the rate constants of the gas-phase oxidation reaction initiated by OH radicals for the methyl-butenol series

A series of gas phase kinetic studies were performed using the relative kinetic technique (**Eq.I.7**) and the ESC-Q-UAIC reactor to simulate atmospheric conditions.

$$\ln\frac{[\mathrm{reagent}]_{t_0}}{[\mathrm{reagent}]_t} - (k_3 + k_5)\times(t - t_0) = \frac{k_1}{k_2}\times\ln\frac{[\mathrm{reference}]_{t_0}}{[\mathrm{reference}]_t} - (k_4 + k_6)\times(t - t_0) \qquad \textbf{Ec.I.7}$$



R-valve, **C**-cartridge, **I**-impinger, **P**-vacuum pump

Figure II.3 Sampling system used for capturing carbonyl compounds

II.3.1.1 Gas-phase reaction between 3-methyl-2-buten-1-ol (MBO321) and OH radicals

For the experimental evaluation of the rate constant of the gas phase reaction of 3-methyl-2-buten-1-ol with OH radicals, the following were used: i) four references (E-2-butene, mesitylene, propene and 1,2-dihydroxybenzene) for the experiments performed with methylnitrite, and ii) two references (*E*-2-butene and mesitylene) for the experiments performed in the presence of hydrogen peroxide. **Figure II.4** presents the distributions of the kinetic data related to the reaction studied using the photolysis of methyl nitrite (λ = 365 nm) as a source of OH radicals and the reaction studied using the photolysis of hydrogen peroxide (λ = 254 nm) as a source of OH radicals (*Rusu (Vasilache) et al., 2024a*).

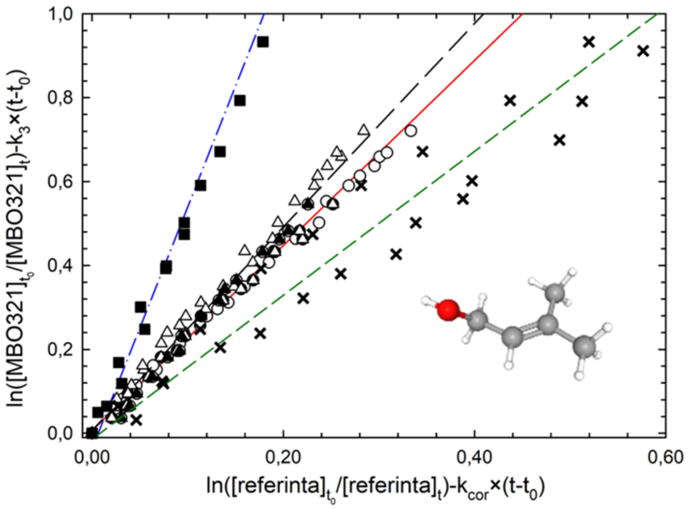


Figure II.4 Distribution of experimental kinetic data corresponding to the reaction of OH radicals with MBO321 versus (●/○) *E*-2-butene, (▲/Δ) mesitylene, (■) propene and (×) 1,2-dihydroxybenzene (empty symbols belong to low NO$_X$ conditions and filled symbols belong to high NO$_X$ conditions). Linear regression lines: red- MBO321 *vs*. *E*-2-butene, black- MBO321 *vs*. mesitylene, green- MBO321 *vs*. 1,2-dihydroxybenzene and blue- MBO321 *vs*. propene

II.3.1.2 Gas-phase reaction between 2-methyl-3-buten-2-ol (MBO232) and OH radicals

For the experimental evaluation of the rate constant of the gas phase reaction for 2-methyl-3-buten-2-ol with OH radicals, two references (*E*-2-butene and mesitylene) were used. For the generation of OH radicals, methylnitrite photolysis at λ = 365 nm and hydrogen peroxide photolysis at λ = 254 nm were used. The data obtained showed that for mesitylene there is a photolysis process when germicidal lamps are turned on (k_6 (254nm)) and another unimolecular loss process (k_4). E-2-butene and MBO232 (k_3) did not show losses by adsorption to the reactor walls or photolysis. **Figure II.5** presents the distributions of kinetic data related to the reaction studied using methylnitrite photolysis at λ = 365 nm as a source of OH radicals and related to the reaction studied using hydrogen peroxide photolysis at λ = 254 nm as a source of OH radicals (*Rusu (Vasilache) et al., 2024a*).

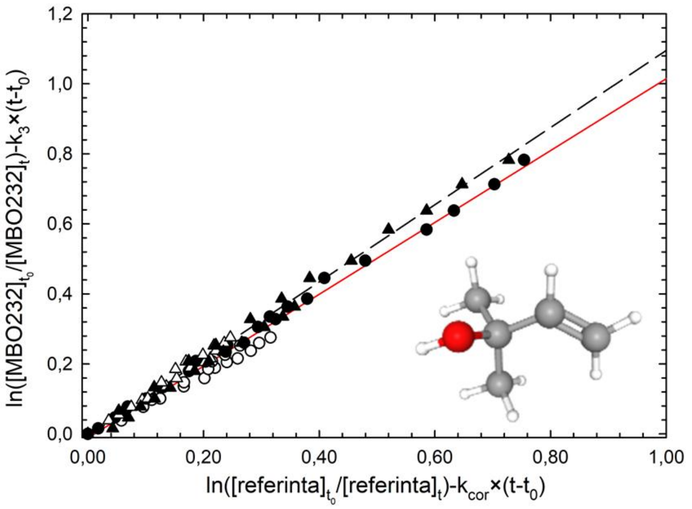


Figure II.5 Distribution of experimental kinetic data corresponding to the reaction of OH radicals with MBO232 versus (●/○) *E*-2-butene and (▲/Δ) mesitylene (empty symbols belong to low NO_X conditions and filled symbols belong to high NO_X conditions). Linear regression lines: red- MBO232 *vs*. *E*-2-butene and black- MBO321 *vs*. mesitylene

II.3.1.3 Gas-phase reaction between 2-methyl-3-buten-1-ol (MBO231) and OH radicals

For the experimental evaluation of the rate constant of the gas phase reaction of 2-methyl-3-buten-1-ol with OH radicals, three references (*E*-2-butene, 1,2-dihydroxybenzene and propene) were used for the experiments performed with methyl nitrite and two references (*E*-2-butene and mesitylene) for the experiments performed with hydrogen peroxide. For the generation of OH radicals, methyl nitrite photolysis at λ = 365 nm and hydrogen peroxide photolysis at λ = 254 nm were used. The data obtained showed that for mesitylene there is a photolysis process when the germicidal lamps are turned on (k_6 (254nm)). Also, the tests performed showed that 1,2-dihydroxybenzene (k_4) exhibits loss by adsorption to the reactor walls but not photolysis. *E*-2-butene, propene and MBO231 (k_3) did not show losses by adsorption to the reactor walls or photolysis. In **Figure II.6** are presented the distributions of kinetic data related to the reaction studied using the photolysis of methylnitrite at λ = 365 nm as a source of OH radicals and related to the reaction studied using the photolysis of hydrogen peroxide at λ = 254 nm as a source of OH radicals (*Rusu (Vasilache) et al., 2024a*).

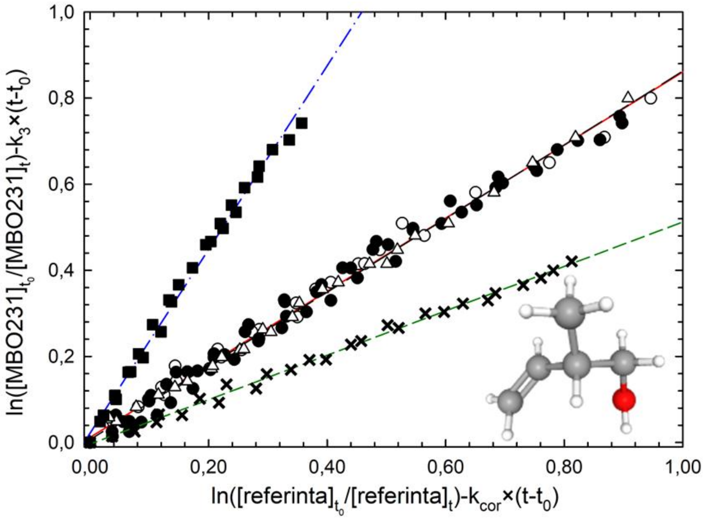


Figure II.6 Distribution of experimental kinetic data corresponding to the reaction of OH radicals with MBO231 versus (●/○) *E*-2-butene, (Δ) mesitylene, (■) propene and (×) 1,2-dihydroxybenzene (empty symbols belong to low NO_X conditions and filled symbols belong to high NO_X conditions). Linear regression lines: red- MBO231 *vs*. E-2-butene, black- MBO231 *vs*. mesitylene (overlaps with red), green- MBO231 *vs*. 1,2-dihydroxybenzene and blue- MBO231 *vs*. propene

II.3.1.4 Gas-phase reaction between 3-methyl-3-buten-1-ol (MBO331) and OH radicals

For the experimental evaluation of the rate constant of the gas phase reaction for 3-methyl-3-buten-1-ol with OH radicals, two references (*E*-2-butene and 1,2-dihydroxybenzene) were used for the experiments performed in the presence of methyl nitrite and two references (*E*-2-butene and mesitylene) for the experiments in which we introduced hydrogen peroxide. For the generation of OH radicals, methyl nitrite photolysis at λ = 365 nm and hydrogen peroxide photolysis at λ = 254 nm were used. The data obtained showed that for mesitylene there is a photolysis process when the germicidal lamps are turned on (k_6 (254nm)). Also, the tests performed showed that catechol (k_4) and MBO331 (k_3)

show losses by adsorption at the reactor walls but not photolysis. *E*-2-butene does not show losses by adsorption at the reactor walls or photolysis. **Figure II.7** presents the distributions of kinetic data related to the reaction studied using methylnitrite photolysis at λ = 365 nm as a source of OH radicals and related to the reaction studied using hydrogen peroxide photolysis at λ = 254 nm as a source of OH radicals (*Rusu (Vasilache) et al., 2024a*).

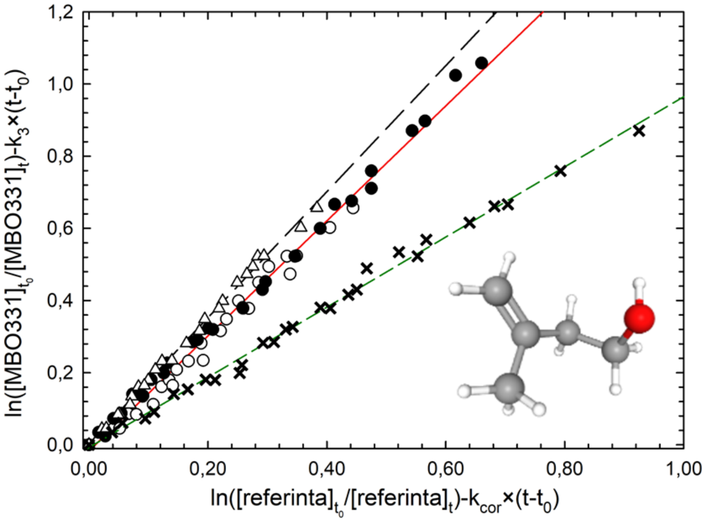


Figure II.7 Distribution of experimental kinetic data corresponding to the reaction of OH radicals with MBO331 versus (●/○) *E*-2-butene, (Δ) mesitylene and (×) 1,2-dihydroxybenzene (empty symbols belong to low NO_X conditions and filled symbols belong to high NO_X conditions). Linear regression lines: red- MBO331 *vs*. E-2-butene, black- MBO331 *vs*. mesitylene and green- MBO331 *vs*. 1,2-dihydroxybenzene

II.3.1.5 Gas-phase reaction between 3-methyl-3-buten-2-ol (MBO332) and OH radicals

For the experimental evaluation of the rate constant of the gas phase reaction for 3-methyl-3-buten-2-ol with OH radicals, two references (*E*-2-butene and 1,2-dihydroxybenzene) were used. For the generation of OH radicals, methylnitrite photolysis at λ = 365 was used. The obtained data showed that for catechol there is a loss process (k_4). E-2-butene and MBO332 (k_3) did not show losses by adsorption to the reactor walls or photolysis. In **Figure II.8**, the distributions of the kinetic data related to the reaction studied using methylnitrite photolysis at λ = 365 nm as a source of OH radicals are presented (*Rusu (Vasilache) et al., 2024a*).

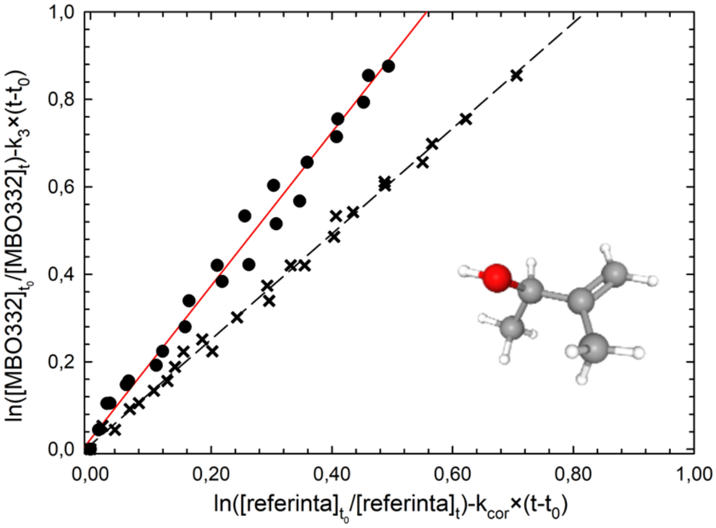


Figure II.8 Distribution of experimental kinetic data corresponding to the reaction of OH radicals with MBO332 versus (●) E-2-butene and (×) 1,2-dihydroxybenzene under high NO_X conditions. Linear regression lines: red- MBO332 *vs*. E-2-butene and black-MBO331 *vs*. 1,2-dihydroxybenzene

II.3.2 Experimental values of kinetic constants in the gas phase

Table II.1 presents the experimental values determined in the current study, for the kinetic constants of gas-phase reactions with respect to OH radicals, for the reaction rate constants of methyl-butenols with respect to the reference compounds, the average k_1 average values for each of the variants used in the generation of OH radicals and the weighted average $k_{1\ total}$ value that this study proposes for each of the investigated reactants (*Rusu (Vasilache) et al., 2024a*).

The experimental data obtained in the present study suggest that there is no dependence of the rate constants of the reaction of methyl-butenols with OH radicals on the NOx concentration. This conclusion is consistent with the data available in the literature for the reaction conditions in the presence or absence of NOx. The gas phase reaction rate constants with OH radicals for 3-methyl-2-buten-1-ol [(**5,31 ± 0,37**) × **10^{-11}** cm^3 $molecul^{-1}$ s^{-1}] and 3-methyl-3-buten-2-ol

[(**11,71 ± 1,29**) × **10^{-11}** cm^3 molecul^{-1} s^{-1}] (**Table II.2**) (*Rusu (Vasilache) et al., 2024a*).

Table II.1 Experimental results obtained for a series of methyl-butenols with OH radicals by the relative method (*Rusu (Vasilache) et al., 2024a*)

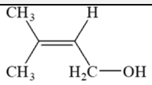
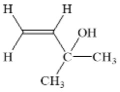
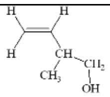
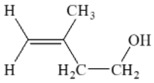
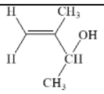
Methyl-butenol	**Source of OH radicals**	**Reference**	**$k_{1\ (mediu)} \times 10^{11}$ (cm^3 molecule^{-1} s^{-1})**	**$k_{1\ (total)} \times 10^{11}$ (cm^3 molecule^{-1} s^{-1})**
MBO321	CH_3ONO	propene	14,86±1,17	**14,55±0,93**
		1,2-dihydroxybenzene		
		mesitylene		
		E-2-butene		
	H_2O_2	*E*-2-butene	14,04±1,51	
		mesitylene		
MBO232	CH_3ONO	*E*-2-butene	6,48±0,70	**6,32±0,49**
		mesitylene		
	H_2O_2	*E*-2-butene	6,18±0,68	
		mesitylene		
MBO231	CH_3ONO	*E*-2-butene	5,46±0,48	**5,31±0,37**
		1,2-dihydroxybenzene		
		propene		
	H_2O_2	*E*-2-butene	5,13±0,56	
		mesitylene		
MBO331	CH_3ONO	*E*-2-butene	10,05±1,10	**10,04±0,78**
		1,2-dihydroxybenzene		
	H_2O_2	*E*-2-butene	10,04±1,10	
		mesitylene		
MBO332	CH_3ONO	*E*-2-butene	11,71±1,29	**11,71±1,29**
		1,2-dihydroxybenzene		

II.3.3 Reactivity of methyl-butenols

II.3.3.1 Comparison of experimental results vs. results obtained by SAR methods

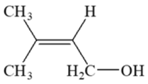
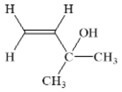
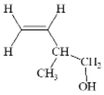
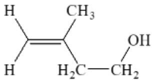
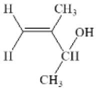
The average experimental values reported in this paper were compared with the values calculated using the different SAR approaches. **Table II.3** presents the results obtained and the values of the k_{EXP}/k_{SAR} ratio for methyl-butenols. Following the application of the least squares method to the experimental (k_{exp}) and estimated (k_{SAR}) reaction rate constants for the five methyl-butenols, the SAR estimates proposed by *Jenkin et al. (2018a)* show the best fit to the experimental data ($\Sigma((k_{EXP} - k_{SAR})/k_{EXP})^2 = 0.124$). Also, the method proposed by *Pfrang et al. (2008)* has the second best fit ($\Sigma((k_{EXP} - k_{SAR})/k_{EXP})^2 = 0.284$), followed by Kwok and Atkinson (1995) ($\Sigma((k_{EXP} - k_{SAR})/k_{EXP})^2 = 0.511$), *Peeters et al. (2007)* ($\Sigma((k_{EXP} - k_{SAR})/k_{EXP})^2 = 0.927$) and *AOPWINv1.92* ($\Sigma((k_{EXP} - k_{SAR})/k_{EXP})^2 = 1.060$) (*Rusu (Vasilache) et al., 2024a*).

Table II.2 The reaction rate constants corresponding to the reactions of methyl-butenols with OH radicals in air at a temperature of (298±2) K obtained in this work (*Rusu (Vasilache) et al., 2024a*) compared to the data from the literature

Methyl-butenol	**$k_{OH} \times 10^{11}$ (cm^3 molecule^{-1} s^{-1})**	**Method used**	**Reference**
 3-methyl-2-buten-1-ol	**14,55±0,93**	RR	this work (*Rusu (Vasilache) et al., 2024a*)
	15,00±1,00	RR	*Imamura et al., 2004*
 2-methyl-3-buten-2-ol	**6,32±0,49**	RR	this work (*Rusu (Vasilache) et al., 2024a*)
	6,40±0,60	AR	*Rudich et al., 1995*
	3,90±1,20	RR	*Fantechi et al., 1998a*
	6,90±1,00	RR	*Ferronato et al., 1998*
	5,67±0,13	RR	*Papagni et al., 2001*
	6,60±0,50	RR	*Imamura et al., 2004*
	6,61±0,66	AR	*Baasandorj și Stevens, 2007*
	5,60±0,60	RR	*Carrasco et al., 2007*
	6,49±0,82	RR	*Takahashi et al., 2010*
 2-methyl-3-buten-1-ol	**5,31±0,37**	RR	this work (*Rusu (Vasilache) et al., 2024a*)
 3-methyl-3-buten-1-ol	**10,04±0,78**	RR	this work (*Rusu (Vasilache) et al., 2024a*)
	9,70±0,70	RR	*Imamura et al., 2004*
	9,70±1,80	RR	*Cometto et al., 2008*
	9,40±0,40	AR	*Cometto et al., 2008*
 3-methyl-3-buten-2-ol	**11,71±1,29**	RR	this work (*Rusu (Vasilache) et al., 2024a*)

AR - absolute method; RR - relative method

Table II.3 Comparison of different SAR methods applied to reactions with OH radicals and the ratio between k_{SAR}/k_{exp}. k_{exp} is the average of the reaction rate constants obtained in this work (*Rusu (Vasilache) et al., 2024a*)

Methyl-butenol	**k_{EXP} (cm^3 molecule^{-1} s^{-1})**	**k_{SAR} (cm^3 molecule^{-1} s^{-1})**	**k_{EXP}/k_{SAR}**
 3-methyl-2-buten-1-ol	$14{,}55 \times 10^{-11}$	$14{,}27 \times 10^{-11}$ [a]	**1,02**
		$12{,}77 \times 10^{-11}$ [b]	1,14
		$8{,}50 \times 10^{-11}$ [c]	1,71
		$11{,}78 \times 10^{-11}$ [d]	1,24
		$9{,}06 \times 10^{-11}$ [e]	1,61
 2-methyl-3-buten-2-ol	$6{,}32 \times 10^{-11}$	$4{,}26 \times 10^{-11}$ [a]	1,49
		$7{,}32 \times 10^{-11}$ [b]	**0,86**
		$3{,}45 \times 10^{-11}$ [c]	1,83
		$5{,}24 \times 10^{-11}$ [d]	1,21
		$2{,}75 \times 10^{-11}$ [e]	2,30
 2-methyl-3-buten-1-ol	$5{,}31 \times 10^{-11}$	$3{,}30 \times 10^{-11}$ [a]	1,61
		$7{,}46 \times 10^{-11}$ [b]	0,71
		$3{,}45 \times 10^{-11}$ [c]	1,54
		$6{,}56 \times 10^{-11}$ [d]	**0,81**
		$3{,}30 \times 10^{-11}$ [e]	1,61
 3-methyl-3-buten-1-ol	$10{,}04 \times 10^{-11}$	$5{,}69 \times 10^{-11}$ [a]	1,83
		$11{,}15 \times 10^{-11}$ [b]	0,93
		$5{,}95 \times 10^{-11}$ [c]	1,75
		$10{,}63 \times 10^{-11}$ [d]	**0,98**
		$5{,}68 \times 10^{-11}$ [e]	1,83
 3-methyl-3-buten-2-ol	$11{,}71 \times 10^{-11}$	$8{,}95 \times 10^{-11}$ [a]	1,31
		$8{,}52 \times 10^{-11}$ [b]	1,37
		$5{,}95 \times 10^{-11}$ [c]	1,97
		$11{,}11 \times 10^{-11}$ [d]	**1,05**
		$5{,}86 \times 10^{-11}$ [e]	2,00

[a] *Kwok şi Atkinson, 1995*; [b] *Pfrang et al., 2008*; [c] *Peeters et al., 2007*; [d] *Jenkin et al., 2018a*; [e] *AOPWIN*$_{v1.92}$

II.3.3.2 Influence of structure on the reactivity of alkenols

The order of reactivity towards OH radicals in the gas phase of methyl-butenols is as follows:

$$k_{(MBO321)} > k_{(MBO332)} > k_{(MBO331)} > k_{(MBO232)} > k_{(MBO231)}$$

This reactivity is explained by the stability of the MBO-OH intermediates formed upon addition to the double bond. Based on literature data, **Figure II.9** shows the possible radical intermediates formed upon addition of OH radicals to the double bond of methyl-butenols (*Rusu (Vasilache) et al., 2024a*).

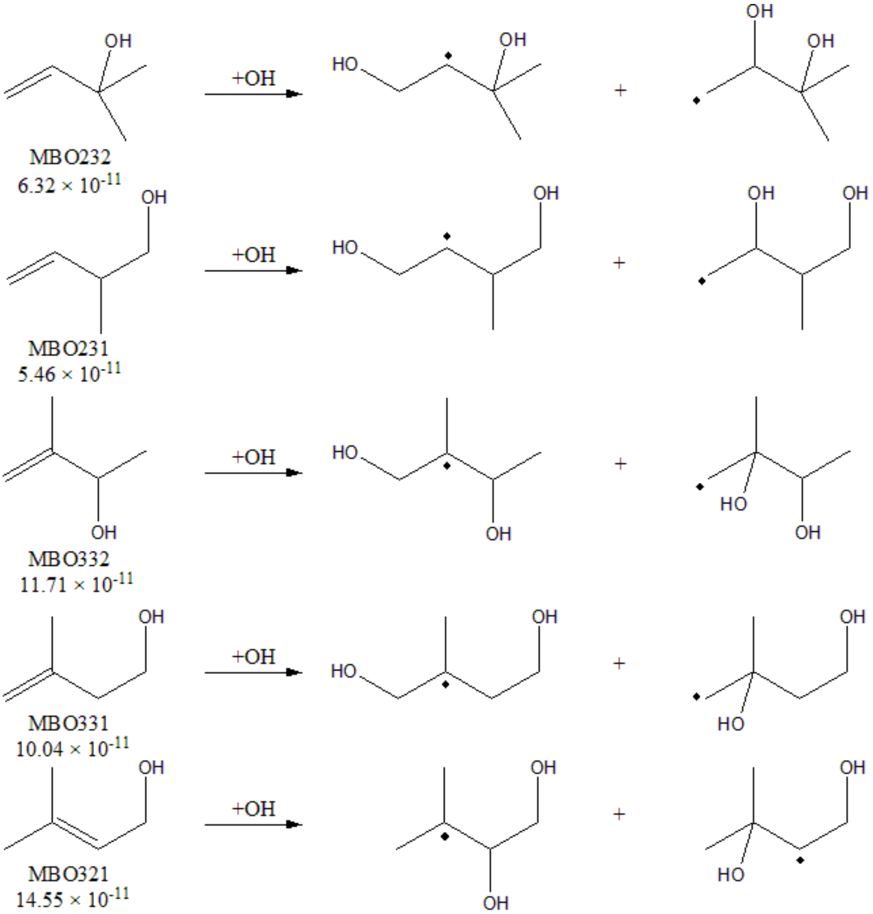


Figure II.9 Possible adducts formed following the interaction of OH radicals with methyl-butenols of interest

The increased reactivity of 3-methyl-2-buten-1-ol is explained by the stability of the adducts formed after the addition, thus a radical adducts Ctert(•) is formed at the first C(sp^2) of the double bond close to the OH group and a radical adduct Csec(•) at the second C(sp^2). The order of reactivity and stability of the radical adduct is as follows: Ctert(•) > Csec(•) > Cprim(•), thus explaining the difference in reactivity in the case of methyl-butenol isomers. The reactivity of unsaturated alcohols towards OH radicals is approximately 2 times higher than that of the corresponding simple alkenes, due to the strong electron-donating character of the hydroxyl group which increases the charge density on the double bond, as well as the polarizability of the π electrons, leading to an increase in the reaction rate constants (*Cometto et al., 2008*).

Also, the oxygen atom polarizes both the C—O bond and the O—H bond in saturated or unsaturated alcohols, but the presence of unsaturation in the compound leads to an increase in the polarizability of some bonds (*Cheptănaru, 2019*), thus alkenols react 5 to 18 times faster with OH radicals than saturated alcohols.

Table II.4 presents the $k_{alcohol}/k_{alkene}$ ratios for the unsaturated alcohol and the corresponding alkene with respect to OH radicals. The lowest ratio is observed between the reaction rate constant for 3-methyl-2-buten-1-ol and the corresponding alkene, 2-methyl-2-butene. The closer the ratio is to unity, the less substantial the change in the reaction rate of the unsaturated compound with respect to OH radicals. **Table II.4** also shows the values of the $k_{alcool\ unsat}/k_{alcool\ sat}$ reaction rate constant ratios, where the values differ considerably. The inclusion of a double bond in the structure of a tertiary alcohol (e.g. 2-methyl-butan-2-ol) increases its reactivity by up to ~ 18 times. It is also possible to observe an increase in the reactivity of methyl-butenols depending on the position of the hydroxyl group, the position of the double bond or the position of the branching. (*Rusu (Vasilache) et al., 2024a*)

II.3.4 Atmospheric implications and atmospheric lifetime calculation

The atmospheric influence of unsaturated alcohols in the atmosphere is derived from the average lifetimes calculated using reaction rate constants. The high reactivity of methyl-butenols can be observed from the relatively short lifetimes towards OH, NO3 radicals and Cl atoms. The dominant reaction of methyl-butenols during the day is the reaction with OH radicals, evidenced by the estimated average atmospheric lifetimes varying between 1.69 hours (MBO321) and 4.63 hours (MBO231). Globally, MBO emissions represent only a component of total BVOCs emissions, with a regional contribution.

Table II.4 Comparison of reaction rate constants (cm^3 molecules^{-1} s^{-1}) towards OH radicals of some unsaturated alcohols *vs*. homologous alkenes and of some unsaturated alcohols *vs*. homologous saturated alcohols at a temperature of 298±4 K (*Rusu (Vasilache) et al., 2024a*)

Unsaturated alcohols	$k_{OH}\times10^{11}$ *, a	Alkenes	$k_{OH}\times10^{11}$ *	$k_{alcohol}/k_{alkene}$	Saturated alcohols	$k_{OH}\times10^{11}$ *	$k_{alcool\ unsat}/k_{alcool\ sat}$
MBO321	**14,55**	2-methyl-2-butene	8,69 ^{b}	1,67	3-methyl-butan-1-ol	1,39 ^{d}	10,47
MBO331	**10,04**	2-methyl-1-butene	6,10 ^{c}	1,65			7,22
MBO332	**11,71**			1,92	3-methyl-butan-2-ol	1,25 ^{d}	9,37
MBO232	**6,23**	3-methyl-1-butene	3,18 ^{b}	1,99	2-methyl-butan-2-ol	0,36 ^{e}	17,56
MBO231	**5,31**			1,67	2-methyl-butan-1-ol	-	-

* cm^3 molecule^{-1} s^{-1}; ^{a} *Rusu (Vasilache) et al., 2024a*; ^{b} *Atkinson, 1986*; ^{c} *Atkinson și Arey, 2003;* ^{d} *Mellouki et al., 2004*; ^{e} *Jiménez et al., 2005*

II.4 KINETIC STUDIES IN SIMULATED ATMOSPHERE INITIATED BY THE PRESENCE OF OZONE

II.4.1 Determination of the rate constants of the ozone-initiated gas-phase oxidation reaction for the methyl-butenol series

The experiments were performed by two different methods, with scavenger and tracer for OH radicals. For the ozonolysis of compounds in which a tracer was used, the kinetic equation **Eq.II.13** was graphically represented to determine the k_1/k_2 ratio. **Eq.I.7** was used to determine the ratio of constants for the experiments in which scavenger was used.

$$\ln\frac{[\text{reagent}]_{t_0}}{[\text{reagent}]_t} - (k_3 + k_5)\times(t - t_0) = \frac{k_1}{k_2}\times\ln\frac{[\text{reference}]_{t_0}}{[\text{reference}]_t} - (k_4 + k_6)\times(t - t_0)$$

Ec.I.7

$$\mathbf{k_1/k_2} = \ln([MBO]_0/[MBO]_t) - (k'_1\times[OH] + k_3)\times(t-t_0) / \ln([R]_0/[R]_t) - k'_2\times[OH]\times(t-t_0)$$

Ec.II.13

II.4.1.1 Gas phase reaction between 3-methyl-2-buten-1-ol (MBO321) and ozone

For the experimental evaluation of the rate constant of the gas phase reaction of 3-methyl-2-buten-1-ol (MBO321) with ozone, two reference compounds (*E*-2-butene and cyclohexene) were used for the experiments performed in the presence of a tracer compound to evaluate the concentration of OH radicals formed during the investigated reactions. Also, the rate constant of the reaction with ozone was evaluated using three reference compounds (*E*-2-butene, cyclohexene and 2-methyl-2-butene) in the presence of a compound to limit the accumulation of OH radicals formed during the investigated reactions (scavenger). **Figure II.10** presents the distributions of the kinetic data related to the studied reaction with the selected reference compounds for the experiments with tracer and scavenger (*Rusu (Vasilache) et al., 2024b*).

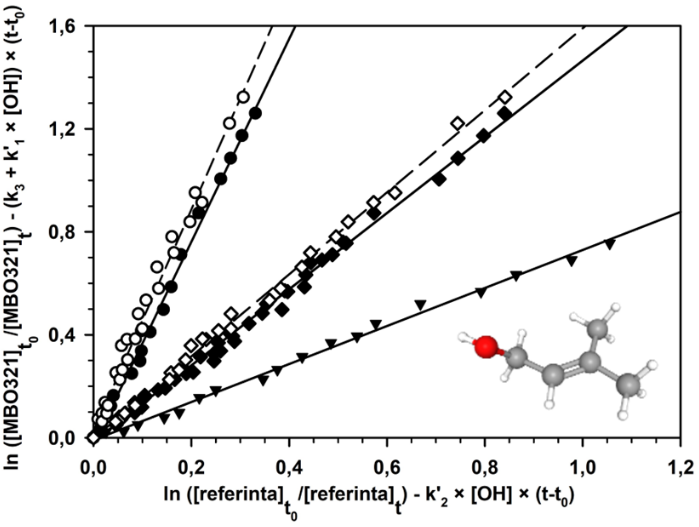


Figure II.10 Distribution of experimental kinetic data corresponding to the reaction of ozone with 3-methyl-2-buten-1-ol versus (◆/◇) E-2-butene, (●/○) cyclohexene and (▼) 2-methyl-2-butene (solid symbols and continuous regression line are data obtained for the scavenger method; empty symbols and dashed regression line are data obtained for the tracer method)

II.4.1.2 Gas-phase reaction between 2-methyl-3-buten-2-ol (MBO232) and ozone

For the experimental evaluation of the rate constant of the gas phase reaction of 2-methyl-3-buten-2-ol (MBO232) with ozone, two reference compounds (propene and 3-methyl-1-butene) were used. Experiments were performed only in the presence of a tracer compound to evaluate the concentration of OH radicals formed during the investigated reactions. In **Figure II.11**, the distributions of the kinetic data related to the studied reaction with the selected reference compounds are presented. The rate constant of the reaction of 2-methyl-3-buten-2-ol with ozone obtained in this study represents the weighted average of the constants determined for each reference compound (*Rusu (Vasilache) et al., 2024b*).

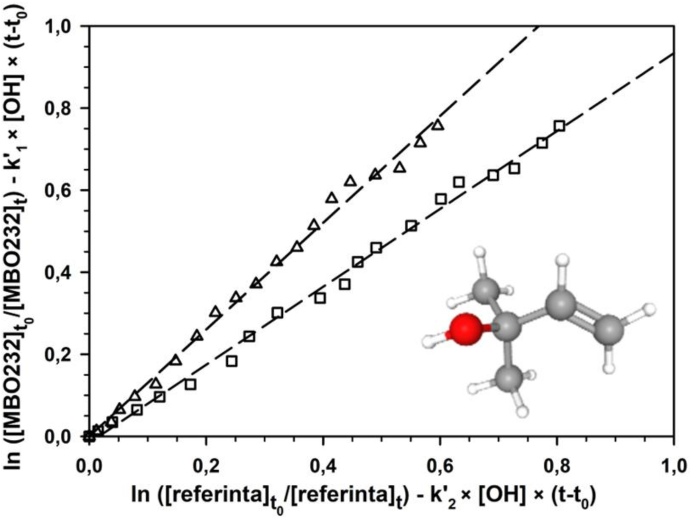


Figure II.11 Distribution of experimental kinetic data corresponding to the reaction of ozone with 2-methyl-3-buten-2-ol towards (□) propene and (Δ) 3-methyl-1-butene using mesitylene as OH tracer

II.4.1.3 Gas-phase reaction between 2-methyl-3-buten-1-ol (MBO231) and ozone

For the experimental evaluation of the rate constant of the gas phase reaction of 2-methyl-2-buten-1-ol (MBO231) with ozone, two referents (propene and ethene) were used both for the experiments performed in the presence of a tracer compound to evaluate the concentration of OH radicals formed during the investigated reactions (tracer), and in the presence of a compound to limit the accumulation of OH radicals formed during the investigated reactions (scavenger). **Figure II.12** presents the distributions of the kinetic data related to the studied reaction with the referents selected for the experiments with a tracer compound and scavenger (*Rusu (Vasilache) et al., 2024b*).

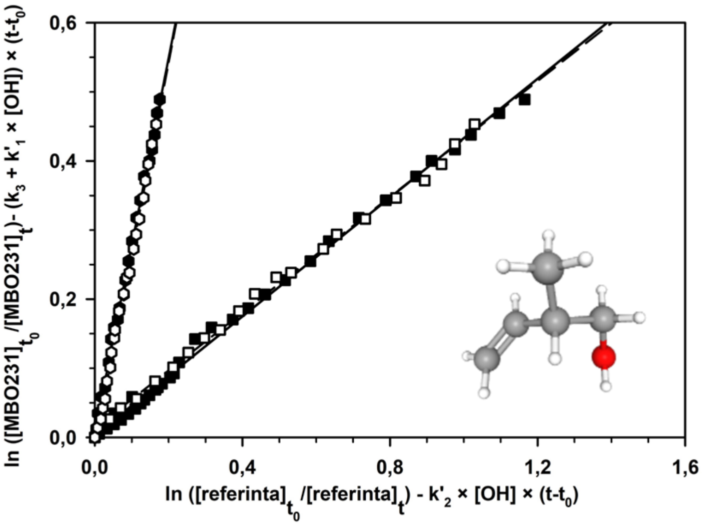


Figure II.12 Distribution of experimental kinetic data corresponding to the reaction of ozone with 2-methyl-3-buten-1-ol versus (■/□) propene and (█/□) ethene (solid symbols and continuous regression line are data obtained for the scavenger method; empty symbols and dashed regression line are data obtained for the tracer method)

II.4.1.4 Gas-phase reaction between 3-methyl-3-buten-1-ol (MBO331) and ozone

For the experimental evaluation of the rate constant of the gas phase reaction of 3-methyl-2-buten-1-ol (MBO331) with ozone, two reference compounds (propene and 3-methyl-1-butene) were used for the experiments performed in the presence of a tracer compound to evaluate the concentration of OH radicals formed during the investigated reactions (tracer). The rate constant of the reaction with ozone was also evaluated using three reference compounds (propene, 1-butene and 3-methyl-1-butene) in the presence of a compound to limit the accumulation of OH radicals formed during the investigated reactions (scavenger). **Figure II.13** presents the distributions of the kinetic data related to the studied reaction with the selected reference compounds for the experiments with a tracer compound and scavenger (*Rusu (Vasilache) et al., 2024b*).

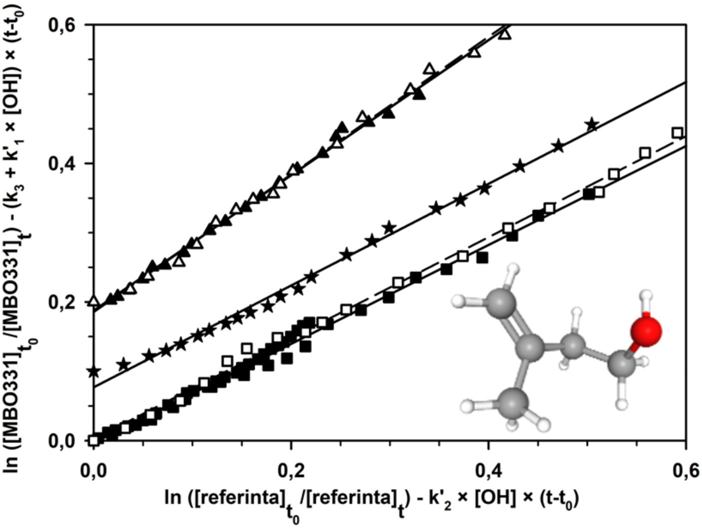


Figure II.13 Distribution of experimental kinetic data corresponding to the reaction of ozone with 3-methyl-3-buten-1-ol versus (■/□) propene, (★) 1-butene and (▲/△) 3-methyl-1-butene (solid symbols and continuous regression line are data obtained for the scavenger method; empty symbols and dashed regression line are data obtained for the tracer method)

II.4.1.5 Gas-phase reaction between 3-methyl-3-buten-2-ol (MBO332) and ozone

For the experimental evaluation of the gas phase reaction rate constant for 3-methyl-3-buten-2-ol (MBO332) with ozone, two reference compounds (propene and cyclohexene) were used. Experiments were performed only in the presence of a tracer compound to evaluate the concentration of OH radicals formed during the investigated reactions (tracer). **Figure II.14** presents the distributions of the kinetic data related to the studied reaction with the selected reference compounds (*Rusu (Vasilache) et al., 2024b*).

II.4.2 Experimental values of kinetic constants in the gas phase

Tables II.5 and **II.6** centralize the experimental data obtained for five methyl-butenols for which the gas phase reaction rate constants with respect to ozone were investigated at a temperature of 298 K and a total pressure of 1000 mbar in air. Thus, **Table II.5** presents the reactivity ratios determined by applying equation **Eq.I.7**, the substances used as compounds to limit the accumulation of OH radicals formed during the reactions and the references for each experiment, but also the average reaction rate constants ($k_{1\ average}$) for the compounds of interest. The average value of the reaction rate constant, $k_{1\ average}$, represents the weighted average of the values determined for each reactant and each reference compound used (*Rusu (Vasilache) et al., 2024b*).

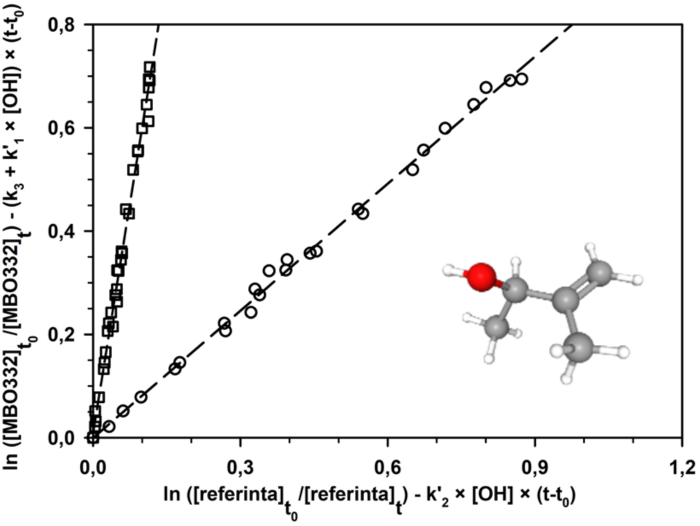


Figure II.14 Distribution of experimental kinetic data corresponding to the reaction of ozone with 3-methyl-3-buten-2-ol towards (□) propene and (○) cyclohexene using mesitylene as OH tracer

Table II.6 presents the experimental values determined for the ozonolysis constants of five unsaturated alcohols when a tracer compound is used to evaluate the concentration of OH radicals formed during the investigated reactions, as well as the $k_{1\ total\ average}$ values. The $k_{1\ total\ average}$ values were calculated as the weighted average of the values determined for each experiment with scavenger or OH tracer because no significant differences were observed between the average values obtained by the two methods (*Rusu (Vasilache) et al., 2024b*). The uncertainties assigned to the ratio values represent twice the standard deviation from the linear regression analysis, and the uncertainties for the k1 constant values also sum up the errors indicated in the literature of 15% at the recommended value.

Table II.5 Experimental results obtained by the relative method for the ozonolysis of some methyl-butenols using a compound that limits the accumulation of OH radicals formed during the investigated reactions

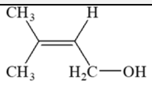
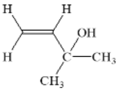
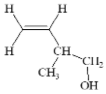
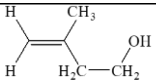
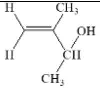
Methyl-butenol	**OH scavenger**	**Reference**	**$k_1 \times 10^{18}$ ($cm^3 molecule^{-1} s^{-1}$)**	**$k_{1\ average} \times 10^{18}$ ($cm^3 molecule^{-1} s^{-1}$)**
MBO321	CO	*E*-2-butene	302,05±49,02	302,84±23,54
	TMB	*E*-2-butene	294,92±44,68	
		cyclohexene	319,33±49,36	
		2-methyl-2-butene	297,65±45,76	
MBO231	CO	propene	4,37±0,68	4,26±0,38
	TMB	propene	4,23±0,64	
		ethene	4,20±0,64	
MBO331	CO	propene	7,75±1,20	7,29±0,56
	TMB	propene	7,29±1,10	
		3-methyl-1-butene	7,12±1,09	
		1-butene	7,07±1,09	

Table II.6 Experimental results obtained by the relative method for the ozonolysis of methyl-butenols using a tracer compound to evaluate the concentration of OH radicals formed during the investigated reactions

Methyl-butenol	**OH tracer**	**Reference**	**$k_1 \times 10^{18}$** ($cm^3 molecule^{-1} s^{-1}$)	**$k_{1average} \times 10^{18}$** ($cm^3 molecule^{-1} s^{-1}$)	**$k_{1total\ average} \times 10^{18}$** ($cm^3 molecule^{-1} s^{-1}$)
MBO321	TMB	*E*-2-butene	317,85±48,19	331,10±36,09	**311,27±19,72**
		cyclohexene	348,05±54,48		
MBO232		propene	9,59±1,47	9,55±1,04	**9,55±1,04**
		3-methyl-1-butene	9,50±1,46		
MBO231		propene	4,22±0,65	4,22±0,46	**4,25±0,29**
		ethene	4,22±0,65		
MBO331		propene	7,49±1,17	7,29±0,83	**7,29±0,46**
		3-methyl-1-butene	7,10±1,16		
MBO332		propene	59,933±9,17	62,87±6,78	**62,87±6,78**
		cyclohexene	66,44±10,09		

Table II.7 compares the reaction rate constants obtained in this study with the literature data, where available, obtained by absolute or relative methods. The results obtained through the investigations carried out during the doctoral internship will help to expand the kinetic database on the ozonolysis of biogenic compounds. In this study, the gas phase reaction rate constant against ozone for MBO332 was determined for the first time [(62,87 ± 6,78) × 10^{-18} cm^3 $molecule^{-1}$ s^{-1}] (*Rusu (Vasilache) et al., 2024b*).

Table II.7 The reaction rate constants corresponding to the reactions of methyl-butenols with ozone in air at a temperature of (298±2) K obtained in this work (*Rusu (Vasilache) et al., 2024b*) compared to the data in the literature

Methyl-butenol	**$k_{O3} \times 10^{18}$ (cm^3 $molecule^{-1}$ s^{-1})**	**Metoda utilizată**	**Reference**
 3-methyl-2-buten-1-ol	**311,51±19,73**	RR	this work
	439,00±37,00	AR	*Grosjean şi Grosjean, 1999*
 2-methyl-3-buten-2-ol	**9,55±1,04**	RR	this work
	10,00±0,30	AR	*Grosjean şi Grosjean, 1994*
	8,60±2,90	RR	*Fantechi et al., 1998a*
	8,30±1,00	AR	*Klawatsch-Carrasco et al., 2004*
 2-methyl-3-buten-1-ol	**4,25±0,29**	RR	this work
	3,74±0,62	AR	*Gai et al.,2011*
 3-methyl-3-buten-1-ol	**7,29±0,46**	RR	this work
	6,80±1,29	AR	*Gai et al.,2011*
 3-methyl-3-buten-2-ol	**62,87±6,78**	RR	this work

AR - absolute method; RR - relative method

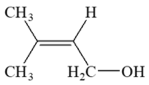
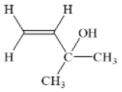
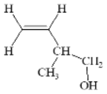
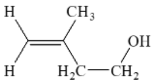
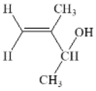
II.4.3 Reactivity of methyl-butenols

II.4.3.1 Comparison of experimental results vs. results obtained by SAR methods

In **Table II.8**, the experimental values for the gas-phase reactions of five methyl-butenols with ozone (k_{exp}) were compared with the calculated values obtained using five different SAR approaches (k_{SAR}) (*Rusu (Vasilache) et al., 2024b*). Following the application of the least squares method to the experimental (kexp) and estimated (kSAR) reaction rate constants for the five methyl-butenols, the SAR estimates proposed by *McGillen et al. (2011)* show the best fit to the experimental data ($\Sigma((k_{EXP} - k_{SAR})/k_{EXP})^2 = 0.55$). Also, the method proposed by

Calvert et al. (2000) has the second best fit ($\Sigma((k_{EXP} - k_{SAR})/k_{EXP})^2 = 0.60$), followed by Jenkin et al., 2020 ($\Sigma((k_{EXP} - k_{SAR})/k_{EXP})^2 = 0.64$), *Atkinson and Carter (1984)* ($\Sigma((k_{EXP} - k_{SAR})/k_{EXP})^2 = 0.78$) and *Pfrang et al. (2008)*, ($\Sigma((k_{EXP} - k_{SAR})/k_{EXP})^2 = 0.95$). After analyzing the obtained results, it is observed that the SAR method proposed by *McGillen et al. (2011)* estimates the rate constants for ozonolysis of aliphatic unsaturated organic compounds much closer to the experimental data than the other approaches mentioned above.

Table II.8 Comparison of different SAR methods applied to ozone reactions and the ratio of kSAR/kexp. kexp is the average of the reaction rate constants obtained in this work (*Rusu (Vasilache) et al., 2024b*)

Methyl-butenol	**k_{exp} (cm^3 molecule^{-1} s^{-1})**	**k_{SAR} (cm^3 molecule^{-1} s^{-1})**	**k_{SAR}/k_{exp}**
 3-methyl-2-buten-1-ol	$311{,}51 \times 10^{-18}$	$4{,}30 \times 10^{-16\,\mathrm{a)}}$	1,38
		$4{,}00 \times 10^{-16\,\mathrm{b)}}$	**1,29**
		$3{,}51 \times 10^{-17\,\mathrm{c)}}$	0,11
		$1{,}54 \times 10^{-16\,\mathrm{d)}}$	0,49
		$6{,}58 \times 10^{-16\,\mathrm{e)}}$	2,11
 2-methyl-3-buten-2-ol	$9{,}55 \times 10^{-18}$	$1{,}20 \times 10^{-17\,\mathrm{a)}}$	1,26
		$1{,}00 \times 10^{-17\,\mathrm{b)}}$	**1,05**
		$6{,}78 \times 10^{-17\,\mathrm{c)}}$	0,71
		$7{,}82 \times 10^{-18\,\mathrm{d)}}$	0,82
		$7{,}56 \times 10^{-18\,\mathrm{e)}}$	0,79
 2-methyl-3-buten-1-ol	$4{,}25 \times 10^{-18}$	$1{,}20 \times 10^{-17\,\mathrm{a)}}$	2,82
		$1{,}00 \times 10^{-17\,\mathrm{b)}}$	2,35
		$6{,}98 \times 10^{-18\,\mathrm{c)}}$	1,64
		$6{,}25 \times 10^{-18\,\mathrm{d)}}$	1,47
		$5{,}40 \times 10^{-18\,\mathrm{e)}}$	**1,27**
 3-methyl-3-buten-1-ol	$7{,}29 \times 10^{-18}$	$1{,}20 \times 10^{-17\,\mathrm{a)}}$	1,65
		$1{,}10 \times 10^{-17\,\mathrm{b)}}$	**1,51**
		$2{,}26 \times 10^{-17\,\mathrm{c)}}$	3,09
		$1{,}35 \times 10^{-17\,\mathrm{d)}}$	1,86
		$1{,}40 \times 10^{-17\,\mathrm{e)}}$	1,92
 3-methyl-3-buten-2-ol	$62{,}87 \times 10^{-18}$	$1{,}20 \times 10^{-17\,\mathrm{a)}}$	0,19
		$1{,}10 \times 10^{-17\,\mathrm{b)}}$	0,18
		$1{,}16 \times 10^{-17\,\mathrm{c)}}$	0,18
		$1{,}58 \times 10^{-17\,\mathrm{d)}}$	0,25
		$1{,}96 \times 10^{-17\,\mathrm{e)}}$	**0,32**

[a] *Atkinson și Carter, 1984*; [b] *Calvert et al., 2000*; [c] *Pfrang et al., 2008*; [d] *McGillen et al., 2011*; [e] *Jenkin et al., 2020*

II.4.3.2 Influence of structure on the reactivity of alkenols

The reaction of ozone with unsaturated compounds in the gas phase involves the electrophilic addition of ozone to the carbon-carbon double bond followed by the unimolecular decomposition of the 1,2,3-trioxolane adduct (primary ozonide) into two carbonyl compounds and two Criegee intermediates (**Figure II.15**).

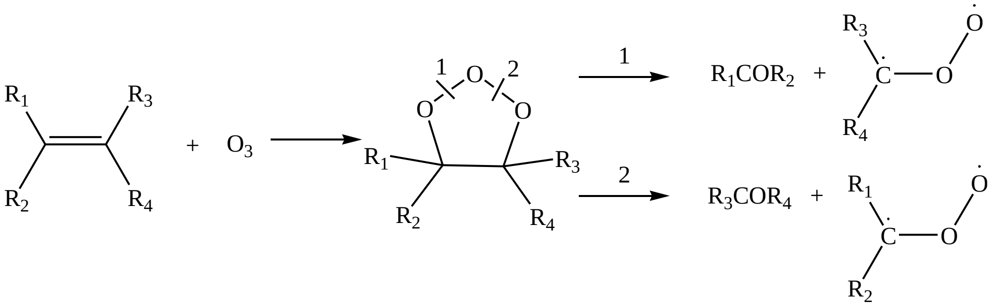


Figure II.15 Reaction of unsaturated compounds with ozone

The order of reactivity towards ozone in the gas phase of methyl-butenols is as follows:

$$k_{(MBO321)} > k_{(MBO332)} > k_{(MBO232)} > k_{(MBO331)} > k_{(MBO231)}$$

From the data presented in **Table II.9**, it is observed that among the methyl-butenols studied, 3-methyl-2-buten-1-ol (trisubstituted alcohol) has the highest reaction rate with ozone, then 3-methyl-3-buten-2-ol, 2-methyl-3-buten-2-ol and 3-methyl-3-buten-1-ol (disubstituted alcohols), and 2-methyl-3-buten-1-ol (monosubstituted alcohol) reacts the slowest, in accordance with other recommendations in the literature (*Kalalian et al., 2020*). Also, **Table II.15** presents the ratios of the reaction rate constants for methyl-butenol and the homologous alkene (k_{MBO} / k_{alkene}), respectively methyl-butenol and the homologous carbonyl (k_{MBO} / $k_{carbonyl}$). The presence of the OH functional group in the β position relative to the olefinic bond i) increases the reactivity of mono- and disubstituted methyl-butenols, such as the reactivity of MBO232 and MBO332 compared to the reactivity of the homologous alkenes 3-methyl-1-butene and 2-methyl-1-butene, respectively, and ii) decreases when the OH functional group is located in the γ position, as observed for MBO231 and MBO331.

Table II.9 Comparison of the reactivity of methyl-butenols towards ozone with the homologous alkenes and corresponding carbonyls (*Rusu (Vasilache) et al., 2024b*)

Unsaturated alcohols	**k_{OH}×10^{18} *, a**	**Alkenes**	**k_{OH}×10^{18} ***	**k_{MBO} / k_{alkene}**	**Carbonyls**	**k_{OH}×10^{18} ***	**k_{MBO} /$k_{ccarbonyl}$**
MBO321	311,51	2-methyl-2-butene	403,00[b]	0,77	3-methyl-2-butenal	1,82[e]	171,16
MBO331	7,29	2-methyl-1-butene	14,30[c]	0,51	-	-	-
MBO332	62,87			4,40	3-methyl-3-buten-2-one	11,80[f]	5,33
MBO231	4,25	3-methyl-1-butene	7,30[d]	0,58	-	-	-
MBO232	9,55			1,30	-	-	-

* cm^3 $molecule^{-1}$ s^{-1}; [a] *Rusu (Vasilache) et al., 2024a*; [b] *Calvert et al., 2015*; [c] *Avzianova și Ariya, 2002*; [d] *Shi et al., 2011*; [e] *Sato et al., 2004*; [f] *Wang et al., 2015*

II.4.4 Atmospheric implications and atmospheric lifetime calculation

The high reactivity of methyl-butenols can be observed through their relatively short lifetimes in relation to gas-phase reactions towards ozone, OH and/or NO_3 radicals and Cl atoms, as can be seen in **Table II.10**.

Table II.10 Average lifetimes calculated for methyl-butenols in this study for gas phase reactions with OH, NO3 radicals, ozone and Cl atoms (*Rusu (Vasilache) et al., 2024b*)

Methyl-butenol	**Reaction rate constant (cm^3 $molecules^{-1}$ s^{-1})**				**Lifetime [a] (hours)**				
	k_{OH}× 10^{11} *	**k_{O3}× 10^{18} ***	**k_{NO3}× 10^{13}**	**k_{Cl}× 10^{10}**	**$τ_{OH}$**	**$τ_{O3}$**	**$τ_{NO3}$**	**$τ_{Cl}$**	**$τ_{total}$**
MBO232	6,32	9,55	0,11[c]	2,64 [d]	3,89	41,55	50,51	105,22	3,22
MBO321	14,55	311,51	10,00 [c]	4,02 [e]	1,69	1,27	0,56	69,10	0,31
MBO331	10,04	7,29	2,70 [c]	4,13 [f]	2,45	54,43	2,06	67,26	1,08
MBO231	5,31	4,25	$(^-)$	3,51 [f]	4,63	93,37	$(^-)$	79,14	<4,18
MBO332	11,71	62,87	$(^-)$	$(^-)$	2,10	6,31	$(^-)$	$(^-)$	<1,58

* Values obtained in this work; **[a]** Average values of oxidant concentrations used in lifetime calculation: [OH] =1.13×10^6 radicals cm^{-3} (*Lelieveld et al., 2016*), [O_3] = 7 × 10^{11} molecules cm^{-3} (*Logan, 1985*), [NO_3] = 5 × 10^8 radicals cm^{-3} (*Shu și Atkinson, 1995*), [Cl] = 10^4 atoms cm^{-3} (*Wingenter et al., 1996*); [b]; [c] *Noda et al., 2002*; [d] *Takahashi et al., 2010*; [e] *Rodriguez et al., 2008*; [f] *Gai et al., 2011*; $(^-)$ unknown experimental data.

The reactions initiated in the gas phase by OH radicals and ozone have similar lifetimes for 3-methyl-2-buten-1-ol and 3-methyl-3-buten-2-ol. The emissions of methyl-butenols in the atmosphere are influenced by solar radiation, therefore their concentrations during the night are lower, so the main rapid consumption pathway would be during the day through the reaction with OH radicals (*Rudich et al., 1996*). The longest total lifetime is attributed to 2-methyl-3-buten-1-ol, since it has the lowest reactivity. Therefore, the studied compounds have high reactivity in the troposphere and, analyzing the estimated total lifetime, most methyl-butenols will be eliminated in the gas phase in the immediate vicinity of their emission sources.

II.5 RESULTS AND DISCUSSIONS FOR CARBONYL COMPOUND DETERMINATIONS

The objective of this study was to further develop the solid-phase derivatization method for the analysis of carbonyl compounds in the gas phase by gas chromatography. The method is based on solid-phase derivatization and was proposed to identify different carbonyl compounds formed in photo-oxidation processes carried out in an atmosphere simulation chamber. A mixture of 9 carbonyl compounds was thus prepared: formaldehyde, acetaldehyde, acetone, methylvinylketone, valeraldehyde, benzaldehyde, m-tolualdehyde, glyoxal and methylglyoxal in methanol and 50 μl (100 ppbv) were injected into the ESC-Q-UAIC reaction chamber filled with synthetic air. The sampling was performed on two sampling lines connected in series: a C_{18} solid phase cartridge on which the derivatization agent (PFBHA) was retained and an impinger containing an aqueous solution of the derivatization agent (c = 0.24 mg/ml). The samples were collected on the cartridges and impinged for 30 minutes.

The separation of the chromatographic peaks for the carbonyl-PFBHA derivatives was achieved using a gas chromatograph coupled to an ion trap mass spectrometer, but to visualize and integrate the peaks of the derivatives, the chromatograms were obtained after the selected ion (SIC-selected ion chromatogram), using the ions m/z=181÷181.9. The elution order of the compounds was: 1-formaldehyde, 2-acetaldehyde, 3-acetone, 4-methylvinylketone, 5-valeraldehyde, 6-benzaldehyde, 7-m-tolualdehyde, 8-

glyoxal and 9-methylglyoxal (**Figures II.16** and **II.17**), identifying all nine carbonyl compounds introduced into the atmosphere simulation chamber.

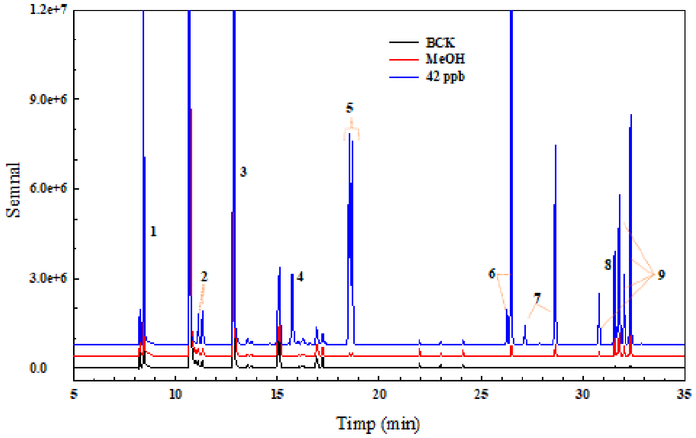


Figure II.16 SIC chromatograms obtained for line 1 (BCK-blank cartridge-C1, MeOH-cartridge C2, 42 ppb-cartridge C6)

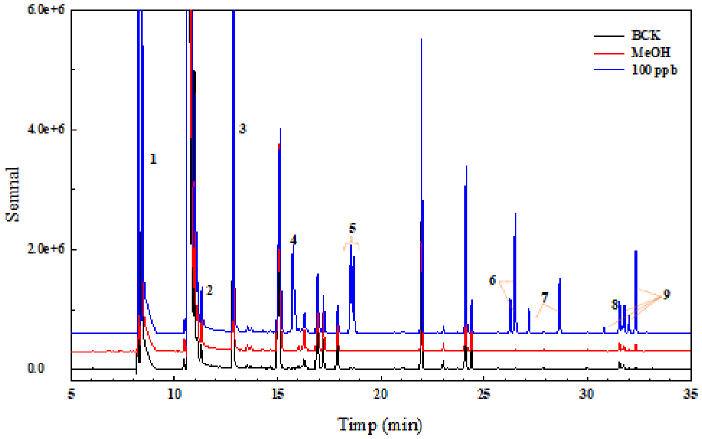


Figure II.17 SIC chromatograms obtained for line 2 (BCK-blank cartridge-C1, MeOH-cartridge C2, 100 ppb-cartridge C3)

The amount of carbonyl compound retained in the derivatizing agent loaded state depends on the volume of air collected, the sampling flow rate, and the amount of derivatizing agent retained. Comparing the SIC chromatograms obtained for the cartridge and the impinger solution, it can be concluded that using wet cartridges, the capture of carbonyl compounds can be observed after

30 minutes on C_{18} cartridges loaded with specific derivatizing agent, the reaction taking place in the solid layer with high yields.

To identify and quantify carbonyl compounds, we must consider certain factors such as the relative humidity inside the chamber, the cartridge preparation steps, the volume of solvent required for elution, etc

GENERAL CONCLUSIONS

Studies performed with the ESC-Q-UAIC reactor have made significant contributions to the understanding of the reactivity of volatile organic compounds in the atmosphere, opening new perspectives in the field of atmospheric chemistry. For example, the gas-phase reaction rate constants for five methyl butenols (3-methyl-2-buten-1-ol (MBO321), 2-methyl-3-buten-2-ol (MBO232), 2-methyl-3-buten-1-ol (MBO231), 3-methyl-3-buten-1-ol (MBO331), 3-methyl-3-buten-2-ol (MBO332) in reaction with OH radicals, as well as the values related to reactions with ozone for the selected compounds. The reproducibility of the data was ensured by using at least two reference compounds for each reaction studied, thus demonstrating the robustness of the methodology adopted.

Kinetic studies carried out under different NOx concentration conditions have shown that the values of the reaction rate constants of methyl butenols remain practically invariant, regardless of the low or high NOx level. Studies of the ozonolysis process have also shown that the choice of different scavenger compounds does not affect the reaction rate constant, and the use of mesitylene as a tracer to monitor the formation of OH radicals, together with reference compounds, has allowed precise correction of the experimental data.

The gas-phase reaction constants for the reaction of hydroxyl radicals (OH) with the compounds MBO231 and MBO332 and the experimental determination of the reaction constant between MBO332 and ozone are reported for the first time in this study.

The comparison of the results obtained with the values reported in the literature showed an excellent correlation, while contributing to the determination of three new reaction rate constants. In particular, the gas-phase reaction rate constants for MBO321 and MBO332 in the interaction with OH radicals and for MBO332 in the reaction with ozone were determined for the first time.

The experimental values were also compared with those obtained by structure-reactivity relationship (SAR) prediction models, and the differences found can be attributed to the way steric hindrances, identity factors, and group constants are evaluated.

From an atmospheric point of view, methyl butenols have significant local and regional impacts, with reactions with hydroxyl radicals and ozone being the main pathways of consumption of these compounds. Estimates of the average lifetimes of the major tropospheric oxidants vary from a few hours (0.19-14.30 h) to a few days (2-4 days), highlighting the importance of these processes in atmospheric dynamics.

The atmospheric lifetimes calculated for reactions with the major atmospheric oxidants indicate that the reaction with OH radicals is the main atmospheric degradation pathway of MBO compounds and that they are rapidly eliminated near their emission sources.

Another major objective of the thesis was the detection of carbonyl compounds formed after the photo-oxidation of methyl butenols in the presence of OH or O_3 radicals. The difficulties inherent in the direct analysis of polar compounds such as formaldehyde, glyoxal or methylglyoxal were overcome by converting them through the derivatization reaction into more stable and volatile forms suitable for analysis by gas chromatography. Tests on C18 cartridges showed that these compounds can be identified as oximes, and the optimized chromatographic conditions allowed the separation of derivatives for nine carbonyl compounds.

Future research will focus on improving the method for collecting carbonyl compounds on C18 cartridges, considering the influence of factors such as relative humidity, cartridge preparation steps, eluent volume, sampling time, and collection flow rate. The next step will be to obtain calibration curves for gas-phase analysis and to quantify the analytes of interest in real samples.

In conclusion, the results obtained not only validate the initial hypotheses, but also open new research directions in elucidating the atmospheric degradation mechanisms of methyl butenols, emphasizing the importance of studying the complex interactions between volatile organic compounds and oxidizing species in the atmosphere.

SELECTIVE BIBLIOGRAPHY

- Agilent 7890A Gas Chromatograph, *Operating Guide*, Agilent Technologies, **2007**
- Agilent 240 Ion Trap GC/MS, *Hardware Operation Manua*l, Agilent Technologies, **2011**
- Atkinson, R., Carter, W.P.L., *Kinetics and Mechanisms of the Gas-Phase Reactions of Ozone with Organic Compounds under Atmospheric Conditions*, Chemical Reviews, 84, 437–470, **1984**
- Atkinson, R., *Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds under Atmospheric Conditions*, Chemical Reviews, 86, 69–201, **1986**
- Atkinson, R., Arey, J., *Atmospheric Degradation of Volatile Organic Compounds Atmospheric Degradation of Volatile Organic Compounds*, Chemical Reviews, 103, 4605–4638, **2003**
- Avzianova, E.V., Ariya, P.A., *Temperature-dependent Kinetic Study for Ozonolysis of Selected Tropospheric Alkenes*, International Journal of Chemical Kinetics, 34, 678–684, **2002**
- Baasandorj, M., Stevens, P.S., *Experimental and theoretical studies of the kinetics of the reactions of OH and OD with 2-methyl-3-buten-2-ol between 300 and 415 K at low pressure***,** The Journal of Physical Chemistry A, 111, 640–649, **2007**
- Belsito, D., Bickers, D., Bruze, M., Calow, P., Greim, H., Hanifin, J.M., Rogers, A.E., Saurat, J.H., Sipes, I.G., Tagami, H., *A safety assessment of non-cyclic alcohols with unsaturated branched chain when used as fragrance ingredients*, Food and Chemical Toxicology, 48, S1–S42, **2010**
- Calvert, J. G., Atkinson, R., Kerr, J. A., Madronich, S., Moortgat, G. K., Wallington, T. J., Yarwood, G., *The Mechanisms of Atmospheric Oxidation of the Alkenes*, Oxford University Press, **2000**
- Calvert, J.G., Orlando, J.J., Stockwell, W.R., and Wallington, T.J., *The Mechanisms of Reactions Influencing Atmospheric Ozone*, Oxford University Press, **2015**
- Carlier, P., Hannachi, H., Mouvier , G., *The chemistry of carbonyl compounds in the atmosphere-a review*, Atmospheric Environment, 20, 2079-2099, **1986**
- Carrasco, N., Doussin, J.F., O'Connor, M., Wenger, J.C., Picquet-Varrault, B., Durand-Jolibois, R., Carlier, P., *Simulation chamber studies of the atmospheric oxidation of 2-Methyl-3-Buten-2-ol: Reaction with hydroxyl radicals and ozone under a variety of conditions*, Journal of Atmospheric Chemistry, 56, 33–55, **2007**
- Chan, A.W.H., Galloway, M.M., Kwan, A.J., Chhabra, P.S., Keutsch, F.N., Wennberg, P.O., Flagan, R.C., Seinfeld, J.H., *Photooxidation of 2-methyl-3-buten-2-ol (MBO) as a potential source of secondary organic aerosol*, Environmental Science and Technology, 43, 4647–4652, **2009**
- Cheptănaru, C., *Chimie organică*, Chișinău, **2019**
- Cometto, P.M., Dalmasso, P.R., Taccone, R.A., Lane, S.I., Oussar, F., Daële, V., Mellouki, A., Le Bras, G., *Rate coefficients for the reaction of OH with a series of unsaturated alcohols between 263 and 371*, The Journal of Physical Chemistry A, 112, 4444–4450, **2008**

- Directiva 1999/13/CE a consiliului din 11 martie 1999 privind reducerea emisiilor de compuși organici volatili datorate utilizării solvenților organici în anumite activități și instalații, Consiliul Uniunii Europene, **1999**
- Fantechi, G., Jensen, N.R., Hjorth, J., Peeters, J., *Determination of the rate constants for the gas- phase reactions of methylbutenol with OH radicals , ozone ,* NO_3 *radicals , and Cl atoms*, International Journal of Chemical Kinetics, 30, 589–594, **1998a**
- Ferronato, C., Orlando, J.J., Tyndall, G.S., *Rate and mechanism of the reactions of OH and Cl with 2-methyl-3-buten-2-ol*, Journal of Geophysical Research, 103,25579-25586, **1998**
- Gai, Y., Ge, M., Wang, W., *Kinetics of the gas-phase reactions of some unsaturated alcohols with Cl atoms and* O_3, Atmospheric Environment, 45, 53-59, **2011**
- Goldan, P.D., William, C.K., Fehsenfeld, F.C., *The observation of a* C_5 *alcohol emission in a North American pine forest*, Geophysical Research Letters, 20, 1039–1042, **1993**
- Grosjean D., Grosjean E., Williams E. L., *Atmospheric chemistry of unsaturated alcohols*, Environmental Science & Technology, 27, 2478-2405, **1993c**
- Grosjean E., Grosjean D., *The reaction of unsaturated aliphatic oxygenates with ozone*, Journal of Atmospheric Chemistry, 32, 205–232, **1999**
- Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, A.W., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P., *A global model of natural volatile organic compound emissions*, Journal of Geophysical Research, 100, 8873–8892, **1995**
- Harley, P., Fridd-Stroud, V., Greenberg, J., Guenther, A., Vasconcellos, P., *Emission of 2-methyl-3-buten-2-ol by pines: A potentially large natural source of reactive carbon to the atmosphere*, Journal of Geophysical Research , 103, 25479–25486, **1998**
- Imamura, T., Iida, Y., Obi, K., Nagatani, I., Nakagawa, K., Patroescu-Klotz, I., Hatakeyama, S., *Rate coefficients for the gas-phase reactions of OH radicals with methylbutenols at 298 K*, International Journal of Chemical Kinetics, 36, 379–385, **2004**
- Jenkin, M.E., Valorso, R., Aumont, B., Rickard, A.R., Wallington, T.J., *Estimation of rate coefficients and branching ratios for gas-phase reactions of OH with aliphatic organic compounds for use in automated mechanism construction*, Atmospheric Chemistry and Physics, 18, 9297–9328, **2018a**
- Jenkin, M.E., Valorso, R., Aumont, B., Newland, M.J., Rickard, A.R., *Estimation of rate coefficients for the reactions of* O_3 *with unsaturated organic compounds for use in automated mechanism construction*, Atmospheric Chemistry and Physics, 20, 12921–12937, **2020**
- Jiménez, E., Lanza, B., Garzón, A., Ballesteros, B., Albaladejo, J., *Atmospheric Degradation of 2-Butanol, 2-Methyl-2-Butanol, and 2,3-Dimethyl-2-Butanol: OH Kinetics and UV Absorption Cross Sections*, The Journal of Physical Chemistry A, 109, 10903–10909, **2005**
- Kalalian, C., El Dib, G., Singh, H.J., Rao, P.K., Roth, E., Chakir, A., *Temperature dependent kinetic study of the gas phase reaction of ozone with 1-penten-3-ol, cis-2-penten-1-ol and trans-3-hexen-1-ol: Experimental and theoretical data*, Atmospheric Environment, 223, 117306, **2020**

- Klawatsch-Carrasco, N., Doussin, J.F., Carlier, P., *Absolute rate constants for the gas-phase ozonolysis of isoprene and methylbutenol*, International Journal of Chemical Kinetics, 36, 152–156, **2004**
- Konig, G., Brunda, M., Puxbaum, H., Hewitt, C.N., Duckham, S.C., Rudolph, J., *Relative contribution of oxygenated hydrocarbons to the total biogenic VOC emissions of selected mid-european agricultural and natural plant species*, Atmospheric Environment, 29, 861–874, **1995**
- Koppmann, R., Volatile organic compounds in the atmosphere, Blackwell Publishing, **2007**
- Kwok, E.S.C., Atkinson, R., Estimation of hydroxyl radical reaction rate constants for gas phase organic compounds using a structure-reactivity relationship: An update. Atmospheric Environment, 29, 1685–1695, **1995**
- La, Y.S., Camredon, M., Ziemann, P.J., Valorso, R., Matsunaga, A., Lannuque, V., Lee-Taylor, J., Hodzic, A., Madronich, S., Aumont, B., *Impact of chamber wall loss of gaseous organic compounds on secondary organic aerosol formation: Explicit modeling of SOA formation from alkane and alkene oxidation*, Atmospheric Chemistry and Physics, 16, 1417–1431, **2016**
- Lehnert, A.-S., Perreca, E., Gershenzon, J., Pohnert, G., Trumbore, S. E., *Simultaneous Real-Time Measurement of Isoprene and 2-Methyl-3-Buten-2-Ol Emissions from Trees Using SIFT-MS*, Frontiers in Plant Science,11, **2020**
- Lelieveld, J., Gromov, S., Pozzer, A., Taraborrelli, D., *Global tropospheric hydroxyl distribution, budget and reactivity*. Atmospheric Chemistry and Physics, 16, 12477–12493, **2016**
- Lerdau, M., Gray, D., *Ecology and Evolution of Light-dependent and Light-independent Phytogenic Volatile Organic Carbon*, New Phytologist, 157, 199–211, **2003**
- Logan, J.A., *Tropospheric Ozone ' Seasonal Behavior , Trends , and Anthropogenic Influence*, Journal of Geophysical Research, 90, 463–482, **1985**
- McGillen, M.R., Archibald, A.T., Carey, T., Leather, K.E., Shallcross, D.E., Wenger, J.C., Percival, C.J., *Structure-activity relationship (SAR) for the prediction of gas-phase ozonolysis rate coefficients: An extension towards heteroatomic unsaturated species*, Physical Chemistry Chemical Physics, 13, 2842–2849, **2011**
- Mellouki, A., Oussar, F., Lun, X., Chakir, A., *Kinetics of the Reactions of the OH Radical with 2-Methyl-1-Propanol, 3-Methyl-1-Butanol and 3-Methyl-2-Butanol between 241 and 373 K*, Physical Chemistry Chemical Physics, 6, 2951–2955, **2004**
- Mellouki, A., Wallington, T.J., Chen, J., *Atmospheric Chemistry of Oxygenated Volatile Organic Compounds: Impacts on Air Quality and Climate*, Chemical Reviews, 115, 3984–4014, **2015**
- Mohd, M.A., *Advanced gas chromatography –progress in agricultural, biomedical and industrial applications*, IntechOpen, **2012**
- Noda, J., Nyman, G., Langer, S., *Kinetics of the gas-phase reaction of some unsaturated alcohols with the nitrate radical*, The Journal of Physical Chemistry A, 106, 945-951, **2002**
- Nollet, M.L., Lambropoulou D.A., *Chromatographic Analysis of the Environment-Mass Spectrometry Based Approaches* (Fourth edition), CRC Press,

Nollet, L. M.L., Lambropoulou D. A., *Chromatographic Analysis of the Environment-Mass Spectrometry Based Approaches* (Fourth edition), CRC Press, **2017**

- Ortiz, R., Hagino, H., Sekiguchi, K., Wang, Q., Sakamoto, K., *Ambient air measurements of six bifunctional carbonyls in a suburban area*, Atmospheric Research, 82, 709–718, **2006**
- Pang, J.Y.S., Novelli, A., Kaminski, M., Acir, I.H., Bohn, B., M.Carlsson, P.T., Cho, C., Dorn, H.P., Hofzumahaus, A., Li, X., Lutz, A., Nehr, S., Reimer, D., Rohrer, F., Tillmann, R., Wegener, R., Kiendler-Scharr, A., Wahner, A., Fuchs, H., *Investigation of the limonene photooxidation by OH at different NO concentrations in the atmospheric simulation chamber SAPHIR*, Atmospheric Chemistry and Physics, 22, 8497–8527, **2022**
- Papagni, C., Arey, J., Atkinson, R.,. *Rate constants for the gas-phase reactions of OH radicals with a series of unsaturated alcohols*, International Journal of Chemical Kinetics, 33, 142-147, **2001**
- Peeters, J., Boullart, W., Pultau, V., Vandenberk, S., Vereecken, L., *Structure-activity relationship for the addition of OH to (poly)alkenes: Site-specific and total rate constants*, The Journal of Physical Chemistry A, 111, 1618-1631, **2007**
- Pfrang, C., King, M.D., Braeckevelt, M., Canosa-Mas, C.E., Wayne, R.P., *Gas-phase rate coefficients for reactions of* NO_3*, OH,* O_3 *and* $O(^3P)$ *with unsaturated alcohols and ethers: Correlations and structure-activity relations (SARs)*, Atmospheric Environment, 42, 3018–3034, **2008**
- Report of the National Academies of Sciences, Engineering and Medicine, *The Future of Atmospheric Chemistry Research: Remembering Yesterday, Understanding Today, Anticipating Tomorrow*, The National Academies Press, **2016**
- Rodriguez, D., Rodriguez, A., Soto, A., Aranda, A., Diaz-De-Mera, Y., Notario, A., *Kinetics of the Reactions of Cl Atoms with 2-Buten-1-Ol, 2-Methyl-2-Propen-1-Ol, and 3-Methyl-2-Buten-1-Ol as a Function of Temperature*, Journal of Atmospheric Chemistry, 59, 187–197, **2008**
- Roman, C., Roman, T., Arsene, C., Bejan, I. G., and Olariu, R. I., *Gas-phase IR crosssections and single crystal structures data for atmospheric relevant nitrocatechols*, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 265, 120379, **2022a**
- Roman, C., Arsene, C., Bejan, I. G., and Olariu, R. I., *Investigations into the gas-phase photolysis and OH radical kinetics of nitrocatechols: implications of intramolecular interactions on their atmospheric behaviour*, Atmospheric Chemistry and Physics, 22, 2203–2219, **2022b**
- Rudich, Y., Talukdar, R., Burkholder, J.B., Ravishankara, A.R., *Reaction of methylbutenol with the OH radical: mechanism and atmospheric implications*, The Journal of Physical Chemistry, 99, 12188–12194, **1995**
- Rudich, Y., Talukdar, R.K., Fox, R.W., Ravishankara, A.R., *Rate coefficients for reactions of* NO_3 *with a few olefins and oxygenated olefins*, The Journal of Physical Chemistry, 100, 5374-5381, **1996**
- Rusu (Vasilache) A.-M.; Roman C.; Bejan I.G.; Arsene C.; Olariu R.I., Gas-Phase Kinetic Investigation of the OH-Initiated Oxidation of a Series of Methyl-Butenols under Simulated Atmospheric Conditions, Journal of Physical Chemistry A, 128, 24, 4838-4849, **2024a**

- Rusu (Vasilache) A.-M.; Roman C.; Bejan I.G.; Arsene C.; Olariu R.I., Gas-Phase Reaction Kinetic Study of a Series of Methyl-Butenols with Ozone under Atmospherically Relevant Conditions, Journal of Physical Chemistry A, 128, 32, 6745-6756, **2024b**
- Sato, K., Klotz, B., Taketsugu, T., Takayanagi, T., *Kinetic Measurements for the Reactions of Ozone with Crotonaldehyde and Its Methyl Derivatives and Calculations of Transition-State TheoryElectronic Supplementary Information (ESI) Available: The Stationary-Point Geometries Optimized at B3LYP/6-31G(d,p) F*, Physical Chemistry Chemical Physics, 6, 3969, **2004**
- Shi, Y., Xu, Y., Jia, L., *Arrhenius Parameters for the Gas-Phase Reactions of* O_3 *with Two Butenes and Two Methyl-Substituted Butenes over the Temperature Range of 295–351 K*, International Journal of Chemical Kinetics, 43, 238–246, **2011**
- Shu, Y., Atkinson, R., *Atmospheric lifetimes and fates of a series of sesquiterpenes*, Geophysical Research Letters, 100, 7275–7281, **1995**
- Szulejko, J. E. and Kim, K. H., *Derivatization techniques for determination of carbonyls in air*, Trends in Analytical Chemistry, 64, 29–41, **2015**
- Takahashi, K., Hurley, M.D., Wallington, T. J., *Kinetics and mechanisms of OH-initiated oxidation of small unsaturated alcohols*, International Journal of Chemical Kinetics, 42, 151-158, **2010**
- US EPA, *Estimation Programs Interface SuiteTM for Microsoft® Windows*, v 4.11 https://www.epa.gov/ (accessed **2022 -04 -06**)
- Wang, J., Zhou, L., Wang, W., Ge, M., *Gas-Phase Reaction of Two Unsaturated Ketones with Atomic Cl and* O_3 *: Kinetics and Products*, Physical Chemistry Chemical Physics , 17, 12000–12012, **2015**
- Wingenter, W., Kubo, K., Blake, J., Smith, T.W., Blake, D.R., Rowland, F.S., *Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl , atomic chlorine , and vertical mixing obtained during Lagrangian flights*, Geophysical Research Letters, 101, 4331–4340, **1996**
- Zhang, Q.H., Schlyter, F., Birgersson, G., *2-methyl-3-buten-2-ol: A pheromone component of conifer bark beetles found in the bark of nonhost deciduous trees*, Psyche, 2012, 7 pages, **2012**

PERSONAL CONTRIBUTIONS LIST

Scientific articles published *in extenso* in journals rated Web of Science with impact factor

1. Rusu (Vasilache), A.-M., Roman, C., Bejan, I.G., Arsene, C., Olariu, R.I., Gas-Phase Reaction Kinetic Study of a Series of Methyl-Butenols with Ozone under Atmospherically Relevant Conditions, ***Journal of Physical Chemistry A***, 128, 6745-6756, **2024**.
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2. Rusu (Vasilache), A.-M., Roman, C., Bejan, I.G., Arsene, C., Olariu, R.I., Gas-Phase Kinetic Investigation of the OH-Initiated Oxidation of a Series of Methyl-Butenols under Simulated Atmospheric Conditions, ***Journal of Physical Chemistry A***, 128, 4838-4849, **2024**.
   https://doi.org/10.1021/acs.jpca.4c02287
   Factor de impact: **2,70** – cvartila Q2 (zona galbenă).

Conferences and scientific events

Oral communications

1. Rusu-Vasilache, A.M., Roman, C., Arsene, C., Bejan, G.I., Olariu, R.I., OH radicals and ozone kinetic studies with some methyl-butenols undesimulated atmospheric conditions / Cinetica în fază gazoasă cu radicali OH şi ozon a unei serii de methylbutenoli în condiţii de atmosferă simulate, Scientific Session of Undergraduate, Master and PhD Students, XIIth Edition, 11-12 November 2021 Iasi, Romania,
2. Rusu (Vasilache), A. M., Roman, C., Arsene, C., Bejan, I. G., Olariu, R. I.: OH-tracer versus OH-scavenger use in the gas-phase kinetic study of the methyl-butenols ozone-initiated reactions, Scientific Communication Session for Undergraduate, Master and PhD Students (SCSSMD) XIII ed., pp. 14, 28 October 2022, Iași, Romania.

Posters

1. Rusu (Vasilache), A. M., Roman, C., Bejan, I. G., Arsene, C., Olariu, R. I.: Ozonolysis of selected methyl-butenols under atmospheric relevant simulated conditions, CNChim2022 XXXVI ed., pp. 86, 04-07 October 2022, Călimănești-Căciulata, Romania.