Gas-Phase Ozonolysis: Rate Coefficients for a Series of Terpenes and Rate Coefficients and OH Yields for 2-Methyl-2-butene and 2,3-Dimethyl-2-butene

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ABSTRACT: The kinetics of the gas-phase reactions of O_3 with a series of selected terpenes has been investigated under flow-tube conditions at a pressure of 100 mbar synthetic air at 295 ± 0.5 K. In the presence of a large excess of *m*-xylene as an OH radical scavenger, rate coefficients $k(O_3+\text{terpene})$ were obtained with a relative rate technique, (unit: cm^3 $molecule^{-1}$ s^{-1}, errors represent 2σ): α-pinene: $(1.1 \pm 0.2) \times 10^{-16}$, $^3\Delta$-carene: $(5.9 \pm 1.0) \times 10^{-17}$, limonene: $(2.5 \pm 0.3) \times 10^{-16}$, myrcene: $(4.8 \pm 0.6) \times 10^{-16}$, *trans*-ocimene: $(5.5 \pm 0.8) \times 10^{-16}$, terpinolene: $(1.6 \pm 0.4) \times 10^{-15}$ and α-terpinene: $(1.5 \pm 0.4) \times 10^{-14}$. Absolute rate coefficients for the reaction of O_3 with the used reference substances (2-methyl-2-butene and 2,3-dimethyl-2-butene) were measured in a stopped-flow system at a pressure of 500 mbar synthetic air at 295 ± 2 K using FT-IR spectroscopy, (unit: cm^3 $molecule^{-1}$ s^{-1}, errors represent 2σ): 2-methyl-2-butene: $(4.1 \pm 0.5) \times 10^{-16}$ and 2,3-dimethyl-2-butene: $(1.0 \pm 0.2) \times 10^{-15}$. In addition, OH radical yields were found to be 0.47 ± 0.04 for 2-methyl-2-butene and 0.77 ± 0.04 for 2,3-dimethyl-2-butene.
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INTRODUCTION

Terpenes are released into the atmosphere from vegetation with an estimated global emission rate in the order of 10^{14} g yr^{-1} [1,2]. α-Pinene (35%), β-pinene (23%), and limonene (23%) are the most important compounds in this process accounting for ca. 80% of the emitted terpenes [1]. Their atmospheric degradation process in the gas phase is initiated either by the attack of OH or NO_3 radicals or O_3. The contribution of the three different oxidants to the overall removal process is spatially and temporally variable and depends on NO_x availability, meteorological parameters, and the local terpene emission itself. In the past two decades laboratory studies have been performed concerning the kinetics and the product distribution of terpenes oxidation [3,4]. Especially in the last few years, interest has been focused

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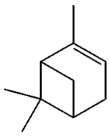
on the contribution of terpene oxidation products to the formation and growth of particles [5]. This idea was hypothesized first in the sixties [6]. Furthermore, the ozonolysis of alkenes including terpenes represents a significant OH radical source [3]. For a rural area in the southeast of the United States, 10–15% of the total radical production was attributed to the ozonolysis of alkenes [7]. Generally, for the modeling of atmospheric processes concerning terpene degradation as well as for laboratory studies a high quality data set of kinetic parameters for the reaction of O_3 with terpenes is desired.

The aim of the present study was kinetic investigations for the reaction of O_3 with a series of terpenes (α-pinene, $^3\Delta$-carene, limonene, myrcene, *trans*-ocimene, terpinolene, and α-terpinene) under flow-tube conditions using a relative rate technique.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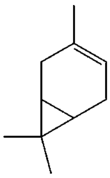
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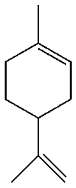
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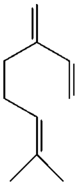
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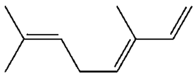
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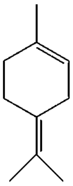
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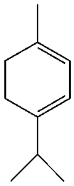

α-terpinene

For the kinetic parameters, several investigations exist in the literature [8–15]. The reported room temperature rate coefficients show a high variability and differ by a factor of three ($^3\Delta$-carene and limonene) up to an order of magnitude (terpinolene and α-terpinene) making a reinvestigation necessary. So as to set the relative rate coefficients on an absolute scale, the absolute rate coefficients of the reference substances have to be known with high accuracy. Therefore, for the reference substances, 2-methyl-2-butene and 2,3-dimethyl-2-butene, used in the present study, the absolute rate coefficients were also measured. As a by-result of the experimental evaluation the yield of OH radicals was determined for both reference substances. It has to be noted that the formation pathways of OH radicals from the gas-phase ozonolysis of alkenes and the resulting OH radical yields, applicable under atmospheric conditions, are still subject of intensive research [16,17].

EXPERIMENTAL

The experiments have been performed using two different approaches: (i) a stopped-flow system for measuring absolute rate coefficients for the reaction of O_3 with 2-methyl-2-butene and 2,3-dimethyl-2-butene as well as the corresponding OH radical yields and (ii) a quartz flow-tube (*IfT*-LFT: *Institute for Tropospheric Research*–Laminar Flow Tube) for the determination of relative rate coefficients for the reaction of O_3 with a series of terpenes.

Stopped-Flow System

The schematic diagram of the stopped-flow system is shown in Fig. 1a. These experiments have been performed at a pressure of 500 mbar at 295 ± 2 K. The temperature of the whole laboratory and hence for the equipment was controlled by an air conditioning system. O_3 was produced by means of a low pressure Hg-lamp using pure O_2 and analyzed downstream flushing the resulting O_3/O_2 mixture through a gas cell for UV-absorption measurements (path length: 10 cm, Lambda 2, Perkin-Elmer). The O_3 concentration was determined at $\lambda = 254$ nm with a cross section of $\sigma = 1.16 \times 10^{-17}$ cm^2 molecule^{-1} (base e) [18]. After further dilution of the O_3/O_2 mixture with O_2, just before the entrance to the reaction cell the organics

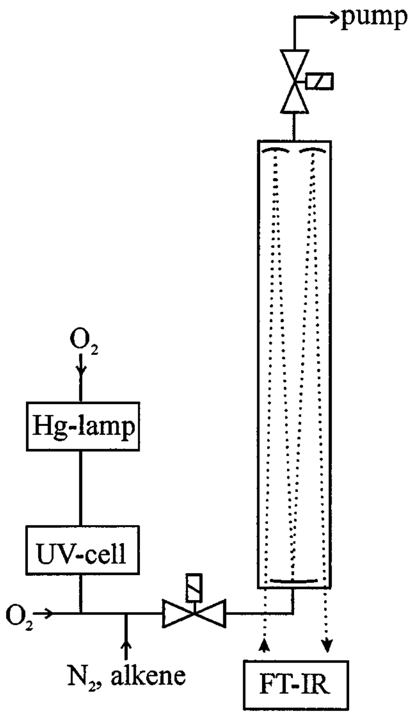


Figure 1a Scheme of the experimental set-up of the stopped-flow system.

(2-methyl-2-butene or 2,3-dimethyl-2-butene) premixed in N_2 were added to the O_3/O_2 mixture. The several flows were set in a way that in the final gas mixture the carrier gas consisted of 20% O_2 and 80% N_2. The total gas flow was 10.8 l min^{-1} and the bulk residence time of the final gas mixture before the entrance to the reaction cell was approximately 0.3 s. The reaction cell (volume: 2.05 l, quartz glass) was equipped with a White mirror system (path length: 10 m) allowing FT-IR analysis of the reaction gas (Magna 750, Nicolet). The O_3 decay was followed by the absorption centered at 1055 cm^{-1}. For starting the experiment the reaction cell was closed with the help of solenoid valves. The pressure was controlled by a capacitive manometer (Baratron) and all flow rates were set by mass flow controllers (MKS 1259). The initial concentrations of O_3 and the organics were kept nearly constant with 2.78×10^{13} molecule cm^{-3}.

Absolute Rate Coefficients

Using the described stopped-flow system absolute rate coefficients were determined for 2-methyl-2-butene and 2,3-dimethyl-2-butene. Because of the low time resolution of the FT-IR measurements, the insufficient detection limit for O_3 and a distinct wall loss of O_3, experiments under pseudo-first-order conditions (initial [organic]/$[O_3] > 20$) were impossible. Under second-order conditions (here initial [organic]/$[O_3] = 1$) the disappearance rate of the organics was influenced by produced OH radicals [19]. Because the O_3 absorption was influenced by absorptions arising from products of the OH radical scavenger, experiments in the presence of OH radical scavenger gave no useful results. Therefore, the following generalized reaction sequence has to be considered:

$$O_3 + \text{organic} \rightarrow x\text{OH} + y \text{ product} + \text{other products} \tag{1}$$

$$\text{OH} + \text{organic} \rightarrow \text{other products} \tag{2}$$

$$\text{OH} + \text{product} \rightarrow \text{other products} \tag{3}$$

$$O_3 \rightarrow \text{wall} \tag{4}$$

For a better description of the OH radical balance, besides the reaction of OH radicals with the parent organic, the reaction of OH radicals with the "main" product from the ozonolysis (acetaldehyde from 2-methyl-2-butene and acetone from 2,3-dimethyl-2-butene) was also included. The formation yield y and the rate coefficients k_2 and k_3 were taken from literature. The rate coefficient of the first-order wall loss for O_3 (k_4) was obtained experimentally. For the determination of the free parameters k_1 and the OH radical yield x, the resulting differential equations derived from pathway (1)–(4) were solved numerically by an extrapolation method connected with a Newton-technique for parameter estimation [20].

Flow-Tube

The experiments under flow conditions were performed at a pressure of 100 mbar synthetic air at 295 K using a quartz flow-tube (*IfT*-LFT) with a length of 505 cm and an inner diameter of 8.0 cm, cf. Fig. 1b. The *IfT*-LFT is surrounded with a thermo-jacket controlling the temperature with a precision of ±0.5 K. O_3 was produced in pure O_2 outside the *IfT*-LFT using a low pressure Hg-lamp. After dilution with the carrier gas, the mixture was introduced into the flow tube through an inlet. Three symmetrically distributed ports on the top served as the entrance for the organics (terpene and reference substance) which were also diluted in the carrier gas. At the outlet of the *IfT*-LFT a small gas stream was pumped continuously through a GC loop for on-line GC-FID analysis (HP 5890) of the organics. To reduce wall effects, the GC-loop and the transfer line were

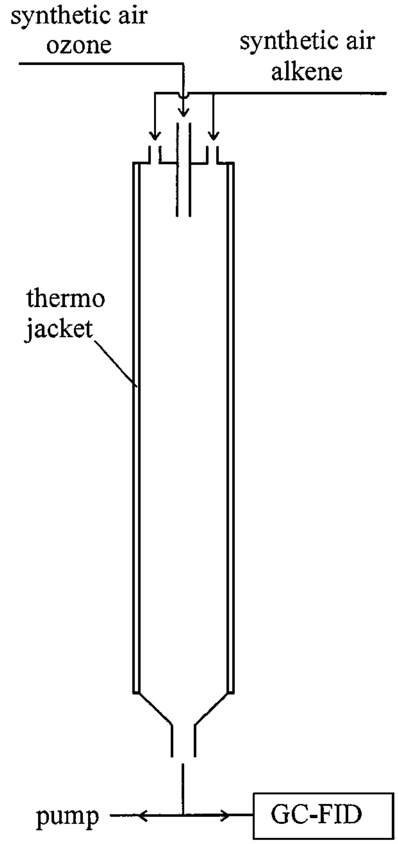


Figure 1b Scheme of the experimental set-up of the flow tube (*IfT*-LFT: *Institute for Tropospheric Research*–Laminar Flow Tube).

heated to approximately 373 K. All flows were set by mass flow controllers (MKS 1259) and the pressure in the tube was measured by a capacitive manometer (Baratron). The residence time in the flow tube varied in the range 140–280 s assuming an ideal plug flow (bulk velocity: 0.018–0.036 m s^{-1}). *m*-Xylene was used as the OH radical scavenger and the amount of added *m*-xylene was adjusted so that more than 90% of produced OH radicals reacted with this substance. The initial concentrations of the terpenes and the reference substances were $(1.9–4.1) \times 10^{12}$ molecule cm^{-3}, of *m*-xylene $(3.1–5.3) \times 10^{14}$ molecule cm^{-3}, and of O_3 $(3.0–46) \times 10^{12}$ molecule cm^{-3}.

Relative Rate Technique

Using the *IfT*-LFT rate coefficients were obtained with a relative rate technique, i.e. the consumption of a terpene relative to that of a reference substance with a well known rate coefficient was measured.

$$\mathrm{O_3} + \text{terpene (2,3-dimethyl-2-butene)} \rightarrow \text{products} \tag{5}$$

$$\mathrm{O_3} + \text{reference} \rightarrow \text{products} \tag{6}$$

For the concentrations in the absence of O_3 (index "0") and in the presence of O_3 (index "*t*") the following expression is valid:

$$\ln\left(\frac{[\text{terpene}]_0}{[\text{terpene}]_t}\right) = \frac{k_5}{k_6}\ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) \tag{I}$$

The consumption of the organics was varied by changing the light intensity of the Hg-lamp for O_3 formation by means of an aperture. As the reference substance, 2-methyl-2-butene was applied for the reaction of α-pinene, $^3\Delta$-carene, limonene, myrcene, and *trans*-ocimene. Because terpinolene and α-terpinene are more reactive towards O_3, the usage of 2-methyl-2-butene was found to be inappropriate and 2,3-dimethyl-2-butene (TME) was chosen as the reference substance for these experiments. To check the accuracy of the measured absolute rate coefficients of the reference substances, the relative rate coefficient of 2,3-dimethyl-2-butene (TME) with respect to 2-methyl-2-butene was investigated additionally. The given errors in this study take into consideration the experimental errors $\Delta(k_5/k_6)$ and the errors of the reference rate coefficient Δk_6 according to Eq. (II) (2σ limits).

$$\frac{\Delta k_5}{k_5} = \sqrt{\left\{\frac{\Delta(k_5/k_6)}{k_5/k_6}\right\}^2 + \left\{\frac{\Delta k_6}{k_6}\right\}^2} \tag{II}$$

Chemicals

The gases used had stated purities as follows: synthetic air (99.999%), N_2 (99.999%) and O_2 (99.9996%) (Linde). The organics were used as purchased: *m*-xylene (>99.5%), 2-methyl-2-butene (>99.5%), α-pinene (≥99.5%), $^3\Delta$-carene (99%), limonene (>99%), myrcene (90%), *trans*-ocimene (ca.70%, main impurity: limonene), terpinolene (>97%), α-terpinene (97%) (Fluka), and 2,3-dimethyl-2-butene (≥99%) (Aldrich). Purities were checked by GC-MS/FID.

RESULTS AND DISCUSSION

O_3 + 2-Methyl-2-butene/2,3-Dimethyl-2-butene

First, in separate experiments the disappearance of the individual reactants in the reaction cell of the stopped-flow system was measured. For O_3, the observed disappearance was described with first-order kinetics, $k_4 = (5.65 \pm 0.16) \times 10^{-4}\ s^{-1}$. In Fig. 2 the measured data (open triangles) and the modeling curve are given. In a further experiment at 950 mbar k_4 was obtained to be $(2.89 \pm 0.18) \times 10^{-4}\ s^{-1}$ indicating clearly a diffusion controlled O_3 disappearance to the walls and not a reaction of O_3 with possible impurities from the

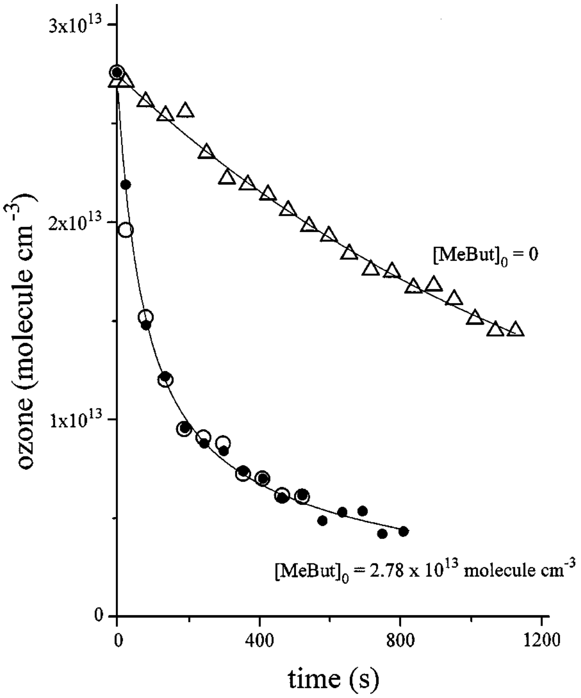


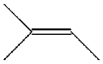
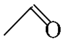
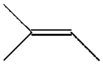
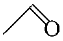
Figure 2 Measured O_3 profiles in the absence and presence of 2-methyl-2-butene (MeBut). The curves result from the reaction scheme given in Table I.

carrier gas. For 2-methyl-2-butene and 2,3-dimethyl-2-butene no significant loss was found in a time period of 1200 s.

In Fig. 2 the experimental findings of the O_3 profile in the absence and presence of 2-methyl-2-butene (MeBut) are shown, $[O_3]_0 = [\text{MeBut}]_0 = 2.78 \times 10^{13}$ molecule cm^{-3}. Open and filled circles represent two series of measurements. The considered pathways for the description of the measured O_3 profile from the reaction of O_3 with 2-methyl-2-butene are compiled in Table I. The formation yield of acetaldehyde in pathway (1a) was taken from the literature [22]. Because of the relatively low reactivity towards OH radicals, acetone formed from pathway (1a) with a yield of 0.3 was disregarded for the consumption of OH radicals. The parameter estimation yielded $k_{1a} = (4.1 \pm 0.5) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} and an OH radical yield of 0.47 ± 0.04, error limit: 2σ. The line in Fig. 2 represents the calculated O_3 profile using the estimated values for k_{1a} and the OH radical yield. For a time period of 820 s, it was calculated that 85% of the produced OH radicals were consumed in the reaction with 2-methyl-2-butene via pathway (2a).

In Fig. 3 the obtained O_3 profiles from two series of measurements (open and filled circles) of the reaction of O_3 with 2,3-dimethyl-2-butene (TME) are plotted, $[O_3]_0 = 2.77 \times 10^{13}$ molecule cm^{-3}, $[\text{TME}]_0 = 2.78 \times 10^{13}$ molecule cm^{-3}. The corresponding pathways for this reaction system are given in Table II. The acetone formation yield of 1.0 in pathway (1b) was taken from Ref. [24]. As a result of the parameter estimation $k_{1b} = (1.0 \pm 0.2) \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} and an OH radical yield of 0.77 ± 0.04 were obtained, error limit: 2σ. For a time period of 375 s, it was calculated that more than 99% of the produced OH radicals reacted with 2,3-dimethyl-2-butene via pathway (2b) reflecting the low reactivity of the main product acetone towards OH radicals.

Table I Pathways Describing the Reaction of O_3 with 2-Methyl-2-butene

Reaction	$k_{295\,K}$ (cm^3 $molecule^{-1}$ s^{-1})	
O_3 + 	estimated	(1a)
→ x OH + 0.685  + ..		
OH +  → ..	8.8×10^{-11}[a]	(2a)
OH +  → ..	1.6×10^{-11}[a]	(3a)
O_3 → wall	5.65×10^{-4}[b]	(4)

[a] Ref. [21].
[b] This study.

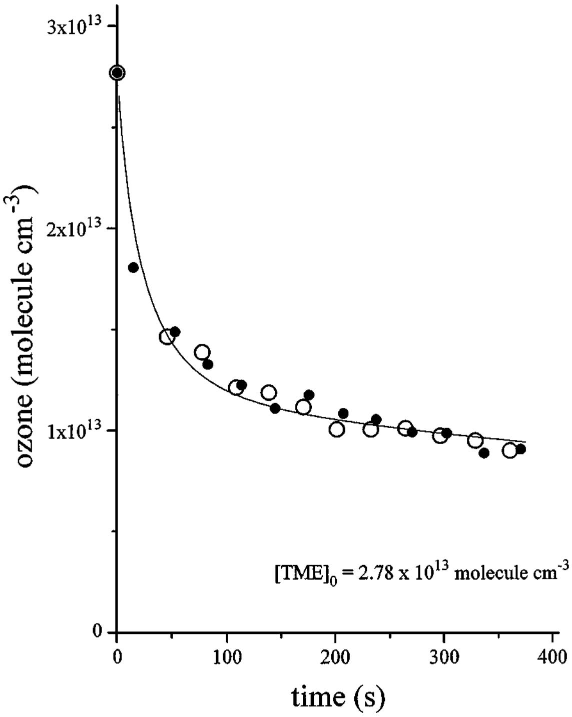
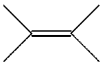
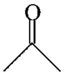
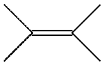
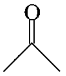


Figure 3 Measured O_3 profiles in the presence of 2,3-dimethyl-2-butene. The curve results from the reaction scheme given in Table II.

To check the accuracy of the obtained absolute rate coefficients, the relative rate coefficient of 2,3-dimethyl-2-butene (TME) with respect to 2-methyl-2-butene (MeBut) was measured in the *IfT*-LFT; $p = 100$ mbar, $[\text{TME}]_0 = [\text{MeBut}]_0 = (2.8\text{–}4.1) \times 10^{12}$ molecule cm^{-3}, $[m\text{-xylene}]_0 = 4.7 \times 10^{14}$ molecule cm^{-3}. In Fig. 4 the experimental findings are plotted according to Eq. (II). The intercept was found to be insignificant with 0.022 ± 0.041. The relative rate

Table II Pathways Describing the Reaction of O_3 with 2,3-Dimethyl-2-butene

Reaction	$k_{295\,K}$ (cm^3 $molecule^{-1}$ s^{-1})	
O_3 + 	estimated	(1b)
→ x OH +  + ..		
OH +  → ..	1.1×10^{-10}[a]	(2b)
OH +  → ..	2.1×10^{-13}[b]	(3b)
O_3 → wall	5.65×10^{-4}[c]	(4)

[a] Ref. [21].
[b] Ref. [23].
[c] This study.

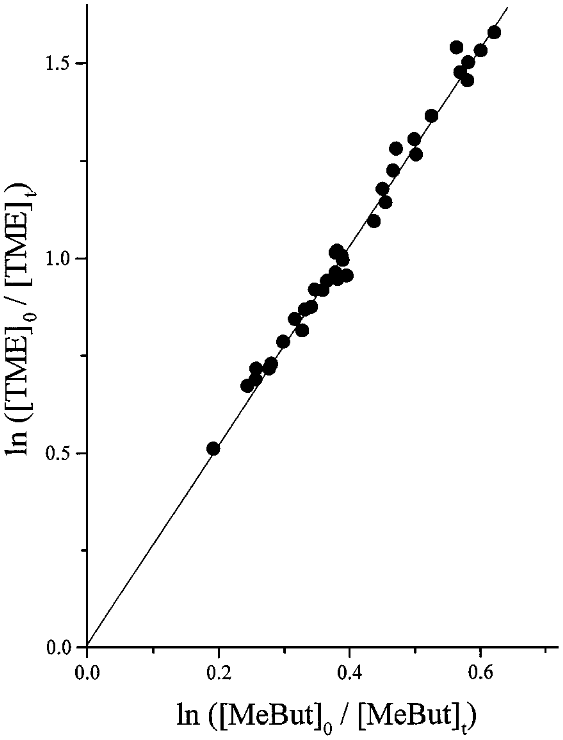


Figure 4 Experimental data for the kinetics of the reaction of O_3 with 2,3-dimethyl-2-butene (TME) by using 2-methyl-2-butene (MeBut) as the reference substance.

coefficient was $k_5/k_6 = 2.53 \pm 0.10$ (here 2-methyl-2-butene was used as the reference substance) to be in excellent agreement with the ratio of the absolute rate coefficients from the present study, $k_{1b}/k_{1a} = 2.4 \pm 0.6$. This fact indicates the usefulness of the obtained absolute rate coefficients and the consistence of the results by using different experimental approaches.

In Table III, absolute rate coefficients for the reaction of O_3 with 2-methyl-2-butene and 2,3-dimethyl-2-butene available from the literature are compared with the data from the present study. For 2-methyl-2-butene, the reported rate coefficients by Bufalini and Altschuler [25] and Cox and Penkett [26] are approximately twice as high as the value from the present study. An explanation for this discrepancy cannot be given. The rate coefficient from Japar et al. [27] is 20% higher than that of this study. Although the given error limit indicates a significant difference there is a reasonable agreement. The rate coefficients for 295 K derived from the Arrhenius equations given by Huie and Herron [28] and Treacy et al. [29] are in excellent agreement with the value reported in this study.

For 2,3-dimethyl-2-butene, only two experimental studies exist in the literature so far. The reported value from Japar et al. [27] is again higher as pointed out for 2-methyl-2-butene. The derived rate coefficient from the Arrhenius equations reported by Huie and Herron [28] is full in line with the value of this study.

Because the OH radical yield from the reaction of O_3 with alkenes is not the main topic of this work, only a brief discussion is given here. For 2-methyl-2-butene, the OH radical yield of 0.47 ± 0.04 from the present study is significantly lower compared to values reported in the literature (yields: 0.81–0.93) [30–32]. The data from the literature were obtained using the OH radical scavenger technique measuring the products from the OH attack on the scavenger (*cyclo*-hexane [30] or 2-butanol [31]) or measuring the disappearance of the scavenger (mesitylene [32]). In the present study, no scavenger was added and the produced OH radicals reacted with the parent organic (85%) and the main product acetaldehyde (15%). If other products are formed in considerable amounts and these products are very reactive towards OH radicals, the OH radical yield can be underestimated using the reaction scheme from Table I. But, there is no experimental evidence in the literature for the occurrence of such reactive products.

For 2,3-dimethyl-2-butene, the OH radical yield of 0.77 ± 0.04 from the present study is on the lower end of the reported literature data (yields: 0.7–1.0) [24,30,31]. There is an excellent agreement with the

Table III Absolute Rate Coefficients for the Reaction of O_3 with 2-Methyl-2-butene and 2,3-Dimethyl-2-butene

Reactant	Temperature (K)	k (cm^3 molecule^{-1} s^{-1})	Ref.
2-Methyl-2-butene	303	7.47×10^{-16a}	[25]
	295 ± 2	7.97×10^{-16a}	[26]
	299 ± 2	$(4.93 \pm 0.16) \times 10^{-16}$	[27]
	295	3.86×10^{-16b}	[28]
	295	3.89×10^{-16b}	[29]
	295 ± 2	$(4.1 \pm 0.5) \times 10^{-16}$	This study
2,3-Dimethyl-2-butene	299 ± 2	$(1.51 \pm 0.08) \times 10^{-15}$	[27]
	295	1.04×10^{-15b}	[28]
	295 ± 2	$(1.0 \pm 0.2) \times 10^{-15}$	This study

[a] No errors given in the original work.

[b] Value taken from Arrhenius plot.

values of 0.7 ± 0.1 derived from the stoichiometry Δ[TME]/[O_3] from Niki et al. [24] and 0.80 ± 0.12 from Chew and Atkinson [31] using the scavenger technique with 2-butanol. The reported yield of 1.0 from experiments with *cyclo*-hexane [30] is significantly higher.

Furthermore, using a modeling study, it was tested whether or not the wall loss of OH radicals was important for the OH radical balance under the experimental conditions. To account properly for gas losses to all walls of the cell (top, bottom, side) 3-D simulations were performed using the software package FLUENT 5.4 [33]. Input parameters for the calculations were the actual cell geometry, the gas diffusion coefficient for OH radicals ($D(\mathrm{OH}) = 0.6\ \mathrm{cm}^2\ \mathrm{s}^{-1}$, $p = 500$ mbar, $T = 295$ K [34]), a constant initial OH radical concentration for the whole gas volume, and a zero OH radical concentration on the walls as the boundary condition. From the calculated OH time profile in the actual measurement volume (volume of the FT-IR paths) a first-order rate coefficient for the diffusion limited wall loss of OH radicals of $0.41\ \mathrm{s}^{-1}$ was derived. Even, assuming a 90% conversion of 2-methyl-2-butene (2,3-dimethyl-2-butene) in the present experiments, at this concentration the OH radical life time with respect to reaction (2a) from Table I (reaction (2b) from Table II) is 0.004 s (0.003 s) to be more than two orders of magnitude shorter compared to the diffusion limited wall loss (life time: 2.4 s) making the wall loss of OH radicals negligible.

The same considerations, as pointed out for OH radicals, were performed for O_3, 2-methyl-2-butene (MeBut), 2,3-dimethyl-2-butene (TME) and additionally for α-pinene. This was needed to estimate wall loss processes in the flow tube. For O_3 a diffusion limited first-order rate coefficient of $0.24\ \mathrm{s}^{-1}$ ($D(O_3) = 0.36\ \mathrm{cm}^2\ \mathrm{s}^{-1}$, $p = 500$ mbar, $T = 295$ K [34]) was calculated. Using the experimental rate coefficient $k_4 = (5.65 \pm 0.16) \times 10^{-4}\ \mathrm{s}^{-1}$ it was found that the effective first-order rate coefficient for the O_3 wall loss is 1/425 of the diffusion limited value. For MeBut, TME, and α-pinene the diffusion limited first-order rate coefficients at $p = 500$ mbar and $T = 295$ K were calculated to be $0.13\ \mathrm{s}^{-1}$ ($D(\mathrm{MeBut}) = 0.19\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ [34]), $0.11\ \mathrm{s}^{-1}$ ($D(\mathrm{TME}) = 0.16\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ [34]), and $0.08\ \mathrm{s}^{-1}$ ($D(\alpha\text{-pinene}) = 0.12\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ [34]), respectively. As mentioned earlier, in a time period of 1200 s for 2-methyl-2-butene and 2,3-dimethyl-2-butene no significant loss was found. The same behavior was observed for α-pinene. Assuming a decay of the organics $\leq 2\%$ after 1200 s an "experimental" first-order rate coefficient $\leq 1.7 \times 10^{-5}\ \mathrm{s}^{-1}$ follows and the effective first-order rate coefficients for the wall loss of the organics is $\leq 1/5000$ of the diffusion limited rate coefficients.

O_3+ Terpenes

All these experiments were performed with a large excess of *m*-xylene scavenging more than 90% of produced OH radicals. The room-temperature rate coefficient for the reaction of O_3 with *m*-xylene is reported to be $\leq 2.9 \times 10^{-21}\mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$ [35] making a conversion of *m*-xylene by O_3 negligible under the conditions used. 2-Methyl-2-butene was used as the reference substance for α-pinene, $^3\Delta$-carene, limonene, myrcene, and *trans*-ocimene. For the more reactive substances terpinolene and α-terpinene the more reactive 2,3-dimethyl-2-butene was chosen as the reference substance. To set the relative rate coefficients on an absolute scale, the absolute rate coefficients for 2-methyl-2-butene and 2,3-dimethyl-2-butene measured in the present study were used.

An assessment of the wall loss processes of O_3 for the different reactants was carried out in the following way. The diffusion limited wall loss with a first-order rate coefficient $k_{\mathrm{wall}} \approx 4\ D/r^2$ (D: diffusion coefficient, r: tube radius [36]) was calculated to be $k_{\mathrm{wall}}(O_3) \approx 0.45\ \mathrm{s}^{-1}$ ($D(O_3) = 1.8\ \mathrm{cm}^2\ \mathrm{s}^{-1}$, $p = 100$ mbar, $T = 295$ K [34]; $r = 4$ cm). Because both of the reaction cell of the stopped-flow system and the flow tube were manufactured from quartz glass, it was assumed that the effective wall loss for O_3 in the flow tube was also 1/425 of the diffusion limited value as pointed out for the reaction cell of the stopped-flow system. This assumption leads to an effective first-order rate coefficient for the O_3 wall loss of $1 \times 10^{-3}\ \mathrm{s}^{-1}$ (life time with respect to wall loss: 10^3 s). The initial concentrations of the added terpenes and the reference substances were in the order of $(2\text{–}4) \times 10^{12}\ \mathrm{molecule\ cm}^{-3}$ and the corresponding rate coefficients of the ozonolysis ranged from 5×10^{-17} to $10^{-14}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$ resulting in initial life times of O_3 with respect to the ozonolysis in the range of 25–10^4 s. This indicates that for the less reactive terpenes the wall loss of O_3 represented an important process. Using the same approach as discussed for O_3, diffusion limited first-order rate coefficient for the wall loss of 2-methyl-2-butene (MeBut), 2,3-dimethyl-2-butene (TME), and terpenes (α-pinene) were found to be $k_{\mathrm{wall}}(\mathrm{MeBut}) \approx 0.24\ \mathrm{s}^{-1}$, $k_{\mathrm{wall}}(\mathrm{TME}) \approx 0.2\ \mathrm{s}^{-1}$ and $k_{\mathrm{wall}}(\alpha\text{-pinene}) \approx 0.15\ \mathrm{s}^{-1}$. Taking into account that the effective rate coefficients are lower than 1/5000 of the diffusion limited values (as derived from the stopped-flow system), for a residence time of 140 s less than 0.7% of the injected organics were deposited on the walls. Therefore, the wall loss of the organics was negligible under the experimental conditions used.

The experimental findings for the relative rate coefficients of the terpenes are plotted for the two reference

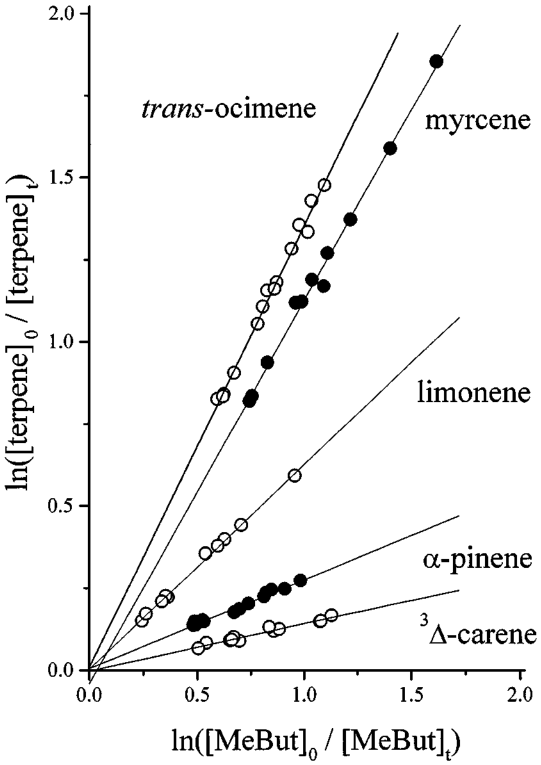


Figure 5 Experimental data for the kinetics of the reaction of O_3 with selected terpenes by using 2-methyl-2-butene (MeBut) as the reference substance.

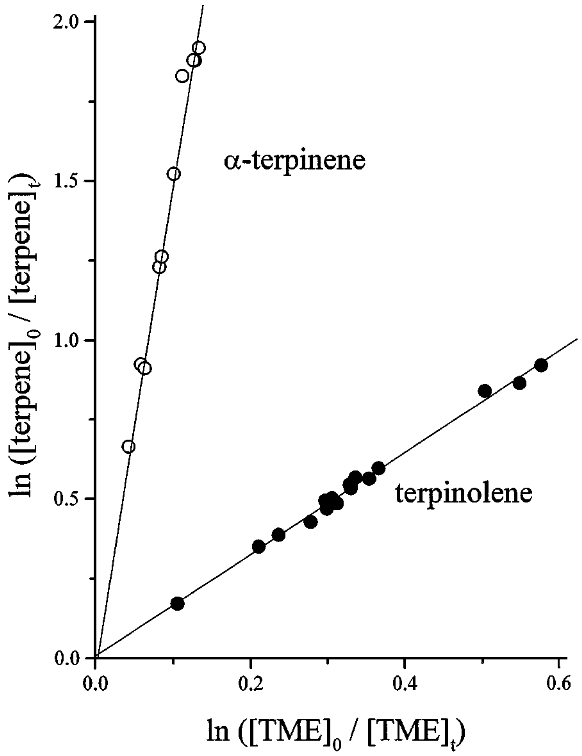


Figure 6 Experimental data for the kinetics of the reaction of O_3 with α-terpinene and terpinolene by using 2,3-dimethyl-2-butene (TME) as the reference substance.

substances 2-methyl-2-butene (MeBut) and 2,3-dimethyl-2-butene (TME) in Figs. 5 and 6, respectively. The results from the linear regression analyses are summarized in Table IV. In all cases, the plots according to Eq. (I) showed a straight line and the intercepts were insignificant. In Table V the derived rate coefficients of the present study are given together with literature data for comparison.

Generally, the values from the present study are in reasonable agreement with those from the Atkinson group [11,13,14] and in the case of α-pinene with those from Ripperton et al. [8], Nolting et al. [12], and Khamaganov and Hites [15]. The reported absolute rate coefficients from Grimsrud et al. [10] are all higher by a factor of 1.3 for α-pinene up to 6.4 for terpinolene. This overestimation is probably caused by systematic experimental problems as pointed out earlier [13]. The absolute rate coefficient from Japar et al. [9] for α-pinene is higher compared to the value of the present study by a factor of three. On the other hand, for terpinolene the reported value from Japar et al. [9] is somewhat lower compared to the other rate coefficients published to date indicating no systematic errors in the measurements of Japar et al. [9]. Neglecting the rate coefficients from Grimsrud et al. [10], for $^3\Delta$-carene and limonene the relative rate coefficients from the

Table IV Obtained Data from the Gas-Phase Reaction of O_3 with a Series of Terpenes in the Presence of an OH Radical Scavenger, $T = 295$ K, $p = 100$ mbar Synthetic Air

Reactant	Reference Substance	Intercept	k_5/k_6	k_5 (cm^3 molecule^{-1} s^{-1})
α-Pinene	2-Methyl-2-butene	0.005 ± 0.016	0.270 ± 0.022	$(1.1 \pm 0.2) \times 10^{-16}$
$^3\Delta$-Carene	2-Methyl-2-butene	−0.002 ± 0.015	0.143 ± 0.018	$(5.9 \pm 1.0) \times 10^{-17}$
Limonene	2-Methyl-2-butene	0.003 ± 0.012	0.622 ± 0.024	$(2.5 \pm 0.3) \times 10^{-16}$
Myrcene	2-Methyl-2-butene	−0.041 ± 0.071	1.17 ± 0.06	$(4.8 \pm 0.6) \times 10^{-16}$
trans-Ocimene	2-Methyl-2-butene	0.008 ± 0.062	1.35 ± 0.08	$(5.5 \pm 0.8) \times 10^{-16}$
Terpinolene	2,3-Dimethyl-2-butene	0.008 ± 0.024	1.60 ± 0.06	$(1.6 \pm 0.4) \times 10^{-15}$
α-Terpinene	2,3-Dimethyl-2-butene	0.012 ± 0.014	14.7 ± 1.7	$(1.5 \pm 0.4) \times 10^{-14}$

Table V Rate Coefficients for the Reaction of O_3 with a Series of Terpenes

Reactant	Method	$k_{295\ \mathrm{K}}$ ($\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$)	Ref.
α-Pinene	A	1.69×10^{-16a} (294 K)	[8]
	A	$(3.3 \pm 0.3) \times 10^{-16}$ (298 K)	[9]
	A	1.46×10^{-16a}	[10]
	A	$(8.3 \pm 1.3) \times 10^{-17}$	[11]
	RR (*cis*-2-butene)	$(8.6 \pm 1.3) \times 10^{-17}$ (297 K)	[12]
	A	$(9.71 \pm 1.06) \times 10^{-17}$ (296 K)	[13]
	RR (1-butene and 2-methyl-propene)	$(8.41 \pm 0.74) \times 10^{-17}$ (298 K)	[15]
	RR (2-methyl-2-butene)	$(1.1 \pm 0.2) \times 10^{-16}$	This study
$^3\Delta$-Carene	A	1.22×10^{-16a}	[10]
	A	$(5.20 \pm 0.56) \times 10^{-17}$ (296 K)	[13]
	RR (α-pinene)	$(3.87 \pm 0.40) \times 10^{-17}$ (296 K)	[13]
	RR (2-methyl-2-butene)	$(5.9 \pm 1.0) \times 10^{-17}$	This study
Limonene	A	6.49×10^{-16a}	[10]
	RR (α-pinene)	$(2.09 \pm 0.22) \times 10^{-16}$ (296 K)	[13]
	RR (*cis*-2-butene)	$(2.01 \pm 0.07) \times 10^{-16}$ (296 K)	[14]
	RR (*cis*-2-butene, 2-methyl-propene and 1-butene)	$(2.13 \pm 0.15) \times 10^{-16}$ (298 K)	[15]
	RR (2-methyl-2-butene)	$(2.5 \pm 0.3) \times 10^{-16}$	This study
Myrcene	A	1.26×10^{-15a}	[10]
	RR (limonene)	$(4.85 \pm 0.78) \times 10^{-16}$ (296 K)	[13]
	RR (2-methyl-2-butene)	$(4.8 \pm 0.6) \times 10^{-16}$	This study
trans-Ocimene	RR (limonene)	$(5.56 \pm 0.85) \times 10^{-16}$ (296 K)	[13]
	RR (2-methyl-2-butene)	$(5.5 \pm 0.8) \times 10^{-16}$	This study
Terpinolene	A	$(7.3 \pm 1.1) \times 10^{-16}$ (298 K)	[9]
	A	1.02×10^{-14a}	[10]
	RR (limonene)	$(1.41 \pm 0.25) \times 10^{-15}$ (296 K)	[13]
	RR (2,3-dimethyl-2-butene)	$(1.88 \pm 0.08) \times 10^{-15}$ (296 K)	[14]
	RR (2,3-dimethyl-2-butene)	$(1.6 \pm 0.4) \times 10^{-15}$	This study
α-Terpinene	A	8.94×10^{-14a}	[10]
	RR (terpinolene)	$(8.66 \pm 2.33) \times 10^{-15}$ (296 K)	[13]
	RR (2,3-dimethyl-2-butene)	$(2.69 \pm 0.90) \times 10^{-14}$ (296 K)	[14]
	RR (β-caryophyllene)	$(2.11 \pm 0.22) \times 10^{-14}$ (296 K)	[14]
	RR (2,3-dimethyl-2-butene)	$(1.5 \pm 0.4) \times 10^{-14}$	This study

A: absolute method; RR: relative rate technique, reference substance is given in parentheses.

[a] No errors given in the original work.

present study are on the upper end of the range of the reported data. In most cases, however, the differences are not significant. For myrcene and *trans*-ocimene the agreement of the relative rate coefficients from the present study with those reported from Atkinson et al. [13] is excellent. Disregarding again the Grimsrud et al. data [10] as well as the given value for terpinolene from Japar et al. [9], for terpinolene and α-terpinene the existing rate coefficients in the literature from Atkinson et al. [13] and Shu et al. [14] were confirmed by rate coefficients from the present study.

SUMMARY

In the present work, kinetic investigations concerning the gas-phase reactions of O_3 with unsaturated compounds are reported using two different approaches: (i) a stopped-flow system and (ii) a flow tube. As a result of the stopped-flow experiments absolute rate coefficients at 295 ± 2 K for the reaction of O_3 with 2-methyl-2-butene, $k_{1a} = (4.1 \pm 0.5) \times 10^{-16}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$, and 2,3-dimethyl-2-butene, $k_{1b} = (1.0 \pm 0.2) \times 10^{-15}\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$, were determined. The OH radical yields were found to be 0.47 ± 0.04 for 2-methyl-2-butene and 0.77 ± 0.04 for 2,3-dimethyl-2-butene. The determination of relative rate coefficients for the reaction of O_3 with a series of terpenes was performed under flow-tube conditions using 2-methyl-2-butene and 2,3-dimethyl-2-butene as the reference substances. *m*-Xylene was used for OH radical scavenging. To set the relative rate coefficients on an absolute scale, the determined data for the reference substances resulting from the stopped-flow experiments were chosen. The resulting rate coefficients are ($T = 295 \pm 0.5$ K, unit: $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$): α-pinene: $(1.1 \pm 0.2) \times 10^{-16}$, $^3\Delta$-carene: $(5.9 \pm 1.0) \times 10^{-17}$, limonene: $(2.5 \pm 0.3) \times 10^{-16}$, myrcene: $(4.8 \pm 0.6) \times 10^{-16}$, *trans*-ocimene: $(5.5 \pm 0.8) \times 10^{-16}$, terpinolene: $(1.6 \pm 0.4) \times 10^{-15}$, and α-terpinene: $(1.5 \pm 0.4) \times 10^{-14}$. Generally, the presented set of rate coefficients for a series of terpenes can help to evaluate existing data and improve the reliability of recommended data.

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