



Development of a Structure Activity Relationship for the Gas-Phase Reactions of Ozone with Monoterpenes

A contribution to subproject CMD

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Introduction

Forests emit large amounts of complex organics into the atmosphere with isoprene and the monoterpenes being the most dominant. It is now generally accepted that these compounds may have a significant impact on the chemistry of the troposphere. For a number of terpenes, reaction with ozone is the dominant daytime loss process in the troposphere. The reactions of terpenes are known to contribute to tropospheric ozone formation and aerosol production and hence an accurate description of both rural and urban tropospheric chemistry requires a full understanding of their reactions.

Several studies have determined the room temperature rate constants for reaction of ozone with terpenes however there is considerable scatter in the data for those terpenes where more than one rate constant is reported. The main focus of this study was to determine rate constants for the gas-phase reactions of ozone with a series of dienes as these act as prototype compounds for terpenes.

Experimental

All experiments were carried out in a 50L Teflon reaction chamber which was housed in a constant temperature cabinet ($298 \pm 2\text{K}$). Reactants entered the chamber through a perforated 1/4" o.d. Teflon tube which ran the length of the chamber and ensured rapid mixing.

The diene was degassed before a known pressure was allowed into a calibrated bulb on a high vacuum line and then flushed into the chamber with air to give a final mixing ratio in the range 2–8 ppm.

Ozone (~ 0.2 ppm) was generated by passing zero-grade air through an ozone generator directly into the reaction chamber. The chamber was pummelled for 20 seconds to ensure rapid mixing and the ozone decay was then monitored over time using a chemiluminescent ozone analyser (Monitor Labs Model 8410).

Results

Room temperature rate constants were determined under pseudo first order conditions with the dienes in excess. Table 1 shows the room temperature rate constants obtained in this study together with the available literature values for the gas-phase reactions of ozone with a series of dienes.

Discussion

Room temperature rate constants for the gas-phase reactions of ozone with a series of conjugated and non-conjugated dienes determined at 298 K and 1 atm. are shown in Table 1.

For the conjugated dienes changes in reactivity towards ozone appear to be a function of the number and relative positions of the methyl substituents attached to the double bonds. Replacement of a terminal H-atom by a CH_3 group leads to a much greater increase in reactivity towards ozone than replacement of an internal H-atom.

Replacement of a second terminal H-atom on the same carbon by another CH_3 group leads to a slight decrease in reactivity in the case of 2,4-dimethyl-1,3-pentadiene and trans-2-methyl-1,3-pentadiene whereas 2,5-dimethyl-2,4-hexadiene is considerably more reactive than 2,4-hexadiene. Similar trends are observed for the monoalkenes.

The reactivity of the non-conjugated dienes can be discussed by comparison of each double bond with the corresponding monoalkenes. In all cases the reactivity per double bond towards ozone is lower than expected which suggests that an alkyl substituent containing a double bond is less activating than a saturated alkyl group.

These results were then combined with literature values for other monoalkenes and cyclic alkenes in an attempt to predict the reactivity of monoterpenes towards ozone.

Table 1: Rate constants for the gas-phase reactions of ozone with a series of dienes.

Conjugated diene	$k_{O_3}^a \times 10^{17}$	This work	Conjugated diene	$k_{O_3}^a \times 10^{17}$	This work
1,3-butadiene	0.63 ¹	0.75 ± 0.14	isoprene	1.28 ¹	1.19 ± 0.12
				1.13±0.32 ²	
2,3-dimethyl-1,3-butadiene	2.65 ± 0.08 ³	2.49 ± 0.19	cis-1,3-pentadiene	–	2.85 ± 0.29
trans-1,3-pentadiene	4.2 ⁴	4.74 ± 0.54	trans-2-methyl-1,3-pentadiene	–	8.89 ± 0.26
	4.24 ± 0.12 ³				
3-methyl-1,3-pentadiene	–	11.57 ± 0.24	2,4-dimethyl-1,3-pentadiene	8.0 ± 1.4 ³	6.44 ± 0.28
cis-2,4-hexadiene	–	16.0 ± 0.8	trans-2,4-hexadiene	–	24.0 ± 1.2
2,5-dimethyl-2,4-hexadiene	–	115.7 ± 10.6			
Non-conjugated diene			Non-conjugated diene		
1,4-pentadiene	1.45 ± 0.20 ³	1.45 ± 0.22	2-methyl-1,4-pentadiene	1.32 ± 0.20 ³	–
3-methyl-1,4-pentadiene	–	0.98 ± 0.04	1,4-hexadiene	–	10.6 ± 0.2
2,5-dimethyl-1,5-hexadiene	1.42 ± 0.20 ³	–			

^a: all rate constants reported have units of $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$

The estimated values are compared with the reported values in Table 2. In general it was found that reasonably good estimates (within a factor of 2) can be made for the acyclic and monocyclic terpenes. The accuracy of the estimated rate constants suggests that the site of O_3 addition can also be predicted with some degree of confidence.

Problems arise in predicting the rate constants for the bicyclic compounds where there is no clear pattern in reactivity. While the reactivity of β -pinene is as expected, the reactivities of camphene and sabinene are considerably different despite having similar structures. These effects are presumably a result of ring strain in the bicyclic system. Finally the reactivity of three

terpenes, citral, myrcenol and juniperol, whose rate constants have not previously been reported, were estimated.

Given the reliability of the method, particularly when predicting the reactivity of the acyclic terpenes, these values may be included in computer models in situations where experimentally determined rate constants have not been reported.

Table 2: Experimentally determined room temperature rate constants and predicted rate constants for the gas-phase reactions of ozone with a series of monoterpenes.

Terpene	Analogous structures	$k^a \times 10^{17}$	$k_{\text{expt}}^a \times 10^{17}$	$k_{\text{pred}}^a \times 10^{17}$
myrcene			1.19 ^b 39.7 ³	48.5 ⁵ 41
trans-ocimene			39.7 ³ 11.57 ^b	55.6 ⁵ 51
β -phellandrene			8.89 ^b	4.77 ⁶ 9
d-limonene			16.6 ⁷ 1.09 ³	20.9 ⁵ 18
terpinolene			16.6 ⁷ 113 ¹	141 ⁵ 188 ⁸ 130
γ -terpinene			6.39 ^{9,e}	14.3 ⁵ >6.4
α -phellandrene			197 ^{9,e}	189 ⁵ 298 ⁸ > 197
α -terpinene			197 ^{9,e}	866 ⁵ 2110 ⁸ >>197
β -pinene			1.06 ¹⁰	1.48 ⁵ 1



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Table 2: continued

Terpene		Analogous structures	$k^a \times 10^{17}$	$k_{\text{expt}}^a \times 10^{17}$	$k_{\text{pred}}^a \times 10^{17}$
2-carene			16.68 ⁷	23.2 ⁵	17
α -pinene			16.68 ⁷	8.52 ¹	17
camphene			1.06 ¹⁰	0.09 ⁵	1
Δ_3 -carene			16.68 ⁷	5.2 ⁵	17
sabinene			1.06 ¹⁰	8.07 ⁵	1
citral ^d			$\sim 4^c$	—	44
			39.7 ³	—	—
myrcenol ^d			1.19 ^b	—	1.2
			1.19 ^b	—	1.2
juniperol ^d			1.19 ^b	—	20
			18.7 ³	—	—

^a all rate constants have units of $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ ^b this work^c estimated based on structurally similar compounds^d rate constants not previously determined^e the presence of alkyl groups on the parent compound would be expected to increase the reactivity

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