



# Rate Constants for the Reactions of Methylvinyl Ketone, Methacrolein, Methacrylic Acid and Acrylic Acid with Ozone

A contribution to subproject CMD

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## Introduction

In recent years rate constants for a large number of hydrocarbons and oxygenated hydrocarbons with OH, O<sub>3</sub> and NO<sub>3</sub> have been reported in the literature (Atkinson, 1997). These data provide valuable information to assess the tropospheric lifetimes and the relative importance of the various degradation pathways of these compounds. Since isoprene is the most important emitted non-methan-hydrocarbon (Guenther *et al.*, 1995), investigations have focused on the tropospheric degradation of isoprene and its oxidation products. While rate constants for the various degradation pathways of isoprene, methylvinyl ketone (MVK) and methacrolein (MAC) are known, no rate constant has been reported for methacrylic acid (MAA) which has been proposed as a reaction product of the isoprene oxidation (Jacob and Wofsy, 1988, Grosjean *et al.*, 1993). The aim of this study was therefore to determine the rate constants for the gas-phase reactions of MVK, MAC, MAA and the analogous organic compound acrylic acid (ACA) with ozone.

## Experimental

Experiments were carried out in synthetic air at  $296 \pm 2$  K and  $730 \pm 5$  torr in a 570 L spherical glass vessel. Details on the experimental design of the reactor have been given elsewhere (Neeb *et al.*, 1996, Horie *et al.*, 1997). Previous studies have shown that OH radicals are generally formed in the O<sub>3</sub> reaction with alkenes (Atkinson, 1997), therefore all experiments were performed in the presence of 54–65 ppm (1 ppm =  $2.38 \times 10^{13}$  molecule cm<sup>-3</sup> at the above temperature and pressure) cyclohexane to minimize alkene consumption through the OH reaction. The initial mixing ratios of the organic acids and carbonyl compounds were 0.8–1.2 ppm as determined by standard volumetric methods and

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0.5 cm<sup>-1</sup>. To evaluate the absorbance-time profiles only the first 8–10 datapoints, corresponding to an alkene consumption of 20–80 %, were used for the linear regression (Fig. 1).

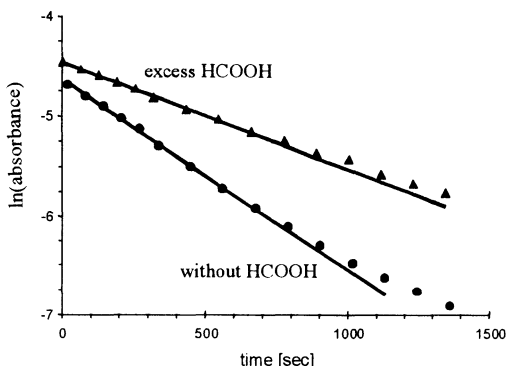
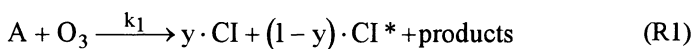


Fig. 1: Semi-logarithmic plot of the decrease of the characteristic absorbance of MAA at 1124 cm<sup>-1</sup> in pseudo-first-order experiments. Circles represent the data in the absence of HCOOH and triangles those in the presence of 19 ppm HCOOH. Solid lines are linear regressions, considering the first eight data points.

## Results and Discussion

Criegee intermediates formed in the gas phase ozonolysis of unsaturated compounds are reported to react among others with hydroxylic and carbonyl compounds (Neeb *et al.*, 1996, Neeb *et al.*, 1995, Niki *et al.*, 1977). Therefore, the organic acids and carbonyl compounds investigated (abbreviated as A) are expected not only to be removed by ozone (reaction R1), but also by the thermalised Criegee intermediates (CI) (reaction R2). The degree of stabilised Criegee intermediates is defined as  $y$ .



This alternative degradation pathway for the unsaturated organic compounds would lead to an overestimation of the observed rate constants for the reaction with ozone. As formic acid is known to react efficiently with thermalised Criegee intermediates (Neeb *et al.*, 1996), it should scavenge the Criegee intermediates (reaction R3) and therefore influence the degradation rates of the unsaturated compounds.



Varying amounts of formic acid were added to the investigated ozone-alkene-systems and the corresponding rate constants were determined. The dependence of the effective rate constant on the amount of added formic acid is analysed using a pseudo-first-order approach and the assumption of steady state conditions for the thermalised Criegee intermediates, that are treated as one species (reaction R4).

$$\frac{d[A]}{dt} = -k_1[O_3][A] - \frac{k_1k_2y[O_3][A]^2}{k_2[A] + k_3[HCOOH]} \quad (R4)$$

The experimentally observed rates of the reactions of ozone with MAA and ACA were strongly influenced by HCOOH (Figs. 2a and 2b). In the absence of a scavenger, the thermalized Criegee intermediates react with the unsaturated organic compound, resulting in an overestimation of the rate constant with ozone. Under conditions where HCOOH was added in excess, the thermalized Criegee intermediates are scavenged by HCOOH. The loss of MAA and ACA due to reaction R2 can than be neglected and the effective rate constants obtained (Table 1) are therefore suggested to represent the rate constant of reaction R1.

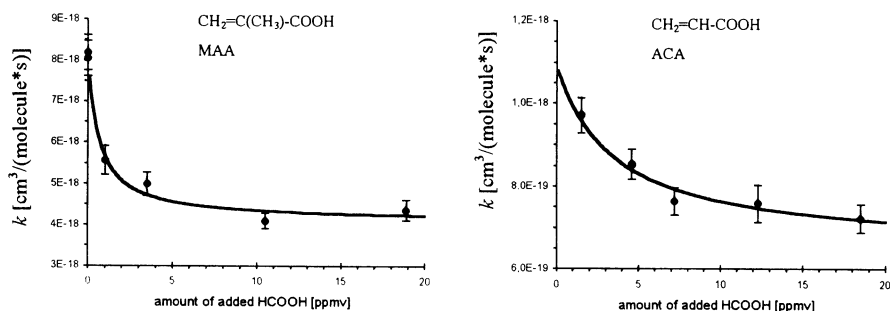


Fig. 2: Dependence of the effective rate constants  $k$  of the reaction of a) MAA and b) ACA with ozone on the amount of added HCOOH. Symbols represent the individual experiments and the line shows a fit. Error bars ( $\pm 2\sigma$ ) describe the statistical uncertainties from the linear regression of the absorbance-time-profiles.

No such dependency on HCOOH of the effective rate constants of ozone with MVK and MAC was observed (Fig. 3) and the results of this work are in good agreement with data from literature (Atkinson *et al.*, 1981, Treacy *et al.*, 1992, Grosjean and Grosjean, 1998). Values of the rate constants for the reaction of ozone with the unsaturated organic compounds investigated in this study are given in Table 1. For comparison also data for acrolein are included.

Table 1: Rate constants for the reaction of  $O_3$  with methacrylic acid, acrylic acid, methylvinyl ketone, methacrolein and acrolein

	$k_{O_3} \times 10^{-18} \text{ (cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\text{)}$			
	this work	(Atkinson <i>et al.</i> , 1981)	(Treacy <i>et al.</i> , 1992)	(Grosjean and Grosjean, 1998)
Methacrylic acid	$4.1 \pm 0.4$			
Methacrolein	$1.3 \pm 0.14$	$1.12 \pm 0.2$	$1.1 \pm 0.2$	$1.08 \pm 0.2$
Acrylic acid	$0.65 \pm 0.13$			
Acrolein		$0.28 \pm 0.05$	$0.30 \pm 0.04$	
Methylvinyl ketone	$5.4 \pm 0.6$	$4.77 \pm 0.59$	$4.2 \pm 0.4$	$5.84 \pm 0.39$

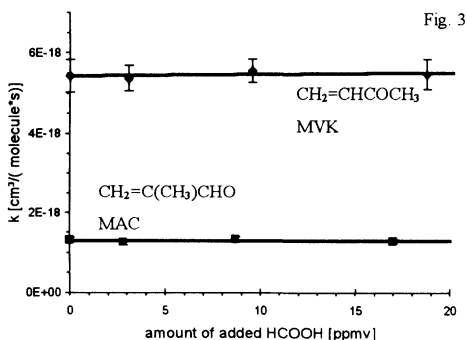


Fig. 3: Determined rate constants of the reaction of MVK and MAC with ozone. Symbols represent experiments performed in the presence of various amounts of added HCOOH, lines are obtained by linear regressions of the data. Error bars ( $\pm 2\sigma$ ) include only the statistical uncertainties from linear regression of the data.

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