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

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ABSTRACT: Rate constants for the reaction of ozone with methylvinyl ketone ($H_2C{=}CHC(O)CH_3$), methacrolein ($H_2C{=}C(CH_3)CHO$), methacrylic acid ($H_2C{=}C(CH_3)C(O)OH$), and acrylic acid ($H_2C{=}CHC(O)OH$) were measured at room temperature (296 ± 2 K) in the presence of a sufficient amount of cyclohexane to scavenge OH-radicals. Results from pseudo-first-order experiments in the presence of excess ozone were found not to be consistent with relative rate measurements. It appeared that the formation of the so-called Criegee-intermediates leads to an enhanced decrease in the concentration of the two organic acids investigated. It is shown that the presence of formic acid, which is known to react efficiently with Criegee-intermediates, diminishes the observed removal rate of the organic acids. The rate constant for the reaction of ozone with the unsaturated carbonyl compounds methylvinyl ketone and methacrolein was found not to be influenced by the addition of formic acid. Rate constants for the reaction of ozone determined in the presence of excess formic acid are (in cm^3 $molecule^{-1}$ s^{-1}): methylvinyl ketone $(5.4 \pm 0.6) \times 10^{-18}$; methacrolein $(1.3 \pm 0.14) \times 10^{-18}$; methacrylic acid $(4.1 \pm 0.4) \times 10^{-18}$; and acrylic acid $(0.65 \pm 0.13) \times 10^{-18}$. Results are found to be consistent with the Criegee mechanism of the gas-phase ozonolysis. © 1998 John Wiley & Sons, Inc. Int J Chem Kinet 30: 769–776, 1998

INTRODUCTION

In recent years rate constants for a large number of hydrocarbons and oxygenated hydrocarbons with OH, O_3, and NO_3 have been reported in the literature. These data provide valuable information to assess the tropospheric lifetimes and the relative importance of the various degradation pathways of these compounds which are emitted either by vegetation or by anthroprogenic activities into the atmosphere. The kinetics of the gas-phase reactions of organic compounds have recently been comprehensively reviewed by Atkinson [1].

Among the various species known to be constituents of the troposphere, isoprene, and monoterpenes emitted from plants are thought to represent the most important contributors to nonmethane-hydrocarbon (NMHC) emissions [2]. These compounds, containing one or more double bonds, are rapidly oxidized in the troposphere and serve as an important source of partially oxidized compounds such as CO, aldehydes, ketones, and organic acids.

Since isoprene is the most important emitted com-

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pound, investigations have focused on the tropospheric degradation of isoprene and its oxidation products. 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 [3,4] but has not been reported in field measurements [5]. Since MAA contains a double bond it is expected to have a short tropospheric lifetime yielding presumably pyruvic acid as a major oxidation product [4,6].

In this work we have determined the rate constants for the gas-phase reactions of MVK, MAC, MAA, and acrylic acid (ACA) with O_3. To the best of our knowledge this is the first time that rate constants for the reaction of unsaturated organic acids with ozone are reported. Because previous studies have shown that OH radicals are generally formed in the O_3 reaction with alkenes [1], experiments were carried out in the presence of cyclohexane to minimize alkene consumption through the alkene-OH reaction. In pseudo-first-order experiments with excess ozone concentration the observed decay rates for MAA and ACA were found to be influenced by the presence of HCOOH. The experimental results of this study are explained by the reaction of the Criegee-intermediates formed in the ozonolysis of MAA and ACA.

EXPERIMENTAL

Experiments were carried out in an evacuable, 570 l spherical glass reactor in 730 ± 5 torr (1 torr = 133.3224 Pa) synthetic air. The reaction temperature was kept constant at 296 ± 2 K by the laboratory air conditioner. Details on the experimental design of the reactor have been given elsewhere [7,8] and only a brief description will be given here.

The initial mixing ratios of the organic acids and carbonyl compounds were 0.8–1.2 ppmv (1 ppmv = 2.38×10^{13} molecule cm^{-3} at the above temperature and pressure) as determined by standard volumetric methods. The IR-absorption coefficient of ozone at 1034 cm^{-1} was determined by comparison with the known UV-absorbance at 253 nm [9]. MAC, MVK, and cyclohexane were calibrated using standard volumetric methods. Due to the formation of organic acid dimers [10] in the gas-phase, calibrations of organic acids based on volumetric methods inherently underestimate their concentrations. Formic acid was therefore calibrated using an in situ pyrolytic method [11]. No attempts have been made to avoid possible uncertainties due to the formation of MAA- and ACA-dimers in the gas-phase. Calibration factors obtained for MAA and ACA by volumetric methods were merely used to determine the amount of ozone needed to obtain pseudo-first-order conditions and the evaluation of the data was therefore not affected by the accuracy of the calibration factors.

After filling the reactor to about 670 Torr with synthetic air, ozone was produced by the photolysis of oxygen at 185 nm using a Penray UV-lamp mounted inside the reactor as source of light. After approximately 10 ppmv O_3 was admitted to the reactor, cyclohexane was added as an OH scavenger in all experiments. A mixing ratio of 54–65 ppmv cyclohexane was sufficient to scavenge more than 90% of the OH-radicals formed during the ozonolysis [12]. In some experiments HCOOH was added as a scavenger for the Criegee-intermediates. Prior to the addition of the alkene, FTIR spectra were recorded to determine the exact amount of ozone, $c\text{-}C_6H_{12}$, and HCOOH, if present, in the reaction chamber.

The decrease of the alkene concentration was monitored by FTIR spectroscopy using an MCT detector at the spectral resolution of 0.5 cm^{-1}. 64 or 128 individual scans were coadded for each spectrum resulting in a temporal resolution of 65 or 120 s, respectively. 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. The systematic error due to the assumption of first-order-conditions and the formation of OH-radicals during ozonolysis were estimated by numerical simulation of a simplified reaction scheme using the FACSIMILE program [13]. Treating the simulated absorbance-time profiles in similar manner as the experimental data, the evaluated rate constant showed a deviation of less than 2% compared to the rate constant used in the simulation.

Chemicals were used as purchased commercially: MVK (Aldrich 99.5%), MAC (Aldrich 99%), ACA (Aldrich 99%) and MAA (Fluka 99.5%).

RESULTS AND DISCUSSION

Methacrylic Acid

Rate constants for the alkene-ozone reactions were determined by employing the pseudo-first-order technique, namely by measuring the decay of the alkene absorbance in the presence of excess ozone. With an ozone concentration in excess of the concentration of MAA, the decay rate of MAA should obey the pseudo-first-order expression:

$$-\frac{d\ln[\mathrm{MAA}]}{dt} = k_{2\mathrm{eff}}[\mathrm{O}_3] = k_{\mathrm{obs}} \qquad (1)$$

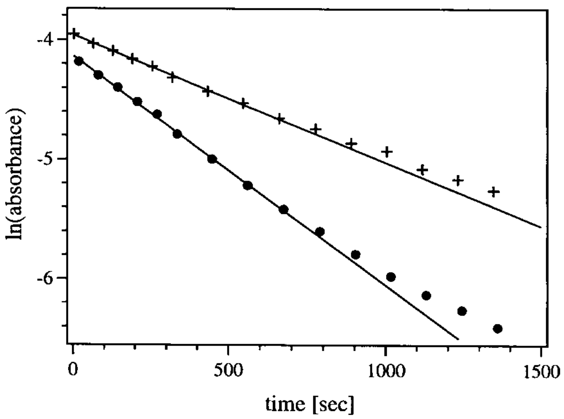


Figure 1 Semilogarithmic plot of the decrease of the characteristic absorbance of MAA at 1124 cm^{-1} in pseudo-first-order experiments. Initial concentration of the reactants were $[O_3]_0 = 10$ ppmv, $[MAA]_0 \approx 1$ ppmv and $[C_6H_{12}]_0 = 54$ ppmv. Filled circles represent the data in the absence of HCOOH and crosses those in the presence of 19 ppmv HCOOH. Solid lines are linear regressions, considering the first eight data points.

where k_{2eff} is the effective second-order rate constant for the reaction of O_3 with MAA.

Figure 1 shows a semilogarithmic plot of the IR-absorbance of MAA, which decayed exponentially in accordance with eq. (1). From the slope of the semilogarithmic plot, the observed decay rate k_{obs} was determined to be $(2.03 \pm 0.04) \times 10^{-3}$ s^{-1}, with the error limit being twice the standard deviation obtained in the least-squares fitting procedure.

According to the Criegee mechanism the ozonolysis of MAA yields two carbonyl compounds (HCHO and pyruvic acid) and two Criegee-intermediates [4]:

$$H_2C{=}C(CH_3)COOH + O_3 \longrightarrow [H_2COO]^* + CH_3C(O)COOH \qquad (2a)$$

$$\longrightarrow HCHO + [CH_3C(OO)COOH]^* \qquad (2b)$$

It was recently shown that the collisionally thermalized Criegee-intermediate CH_2OO reacts with hydroxylic compounds to form hydroperoxides [7]:

$$[H_2COO]^* + M \longrightarrow H_2COO + M \qquad (3)$$

$$H_2COO + ROH \longrightarrow H_2C(OOH){-}O{-}R \qquad (4)$$

To test whether MAA is consumed in a reaction analogous to reaction (4), pseudo-first-order experiments were repeated in the presence of varying amounts of HCOOH. In Figure 1 the semilogarithmic plot of the MAA absorbance in an experiment with 19 ppmv HCOOH added is shown. The addition of HCOOH resulted in a clearly noticeable decrease in the observed removal rate.

The formation of hydroperoxymethyl formate which is known to be formed in the reaction of the CH_2OO intermediate (reaction 5) with HCOOH [14] was also observed together with a decrease in the HCOOH concentration.

$$H_2COO + HCOOH \longrightarrow H_2C(OOH){-}O{-}CHO \qquad (5)$$

To further investigate the influence of HCOOH on k_{obs}, a series of experiments with constant initial concentrations of MAA and ozone and varying amounts of added HCOOH were performed. Rate constants k_{2eff} obtained from the individual experiments are plotted against the HCOOH initial concentration in Figure 2. It appears that the effective rate constants are constant under conditions where HCOOH was added in excess. Under these conditions it can be assumed that all the thermalized Criegee-intermediates have reacted with HCOOH and hence the loss of MAA due to reaction (4) can be neglected. At sufficient high HCOOH concentrations the value of $k_{2eff} \approx k_2 \approx (4.2 \pm 0.2) \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} obtained is therefore suggested to represent the rate constant of reaction (2).

Acrylic Acid

From the results of the experiments with MAA, it was expected that the decay rates of the reaction of ACA with ozone exhibit a similar behaviour towards ad-

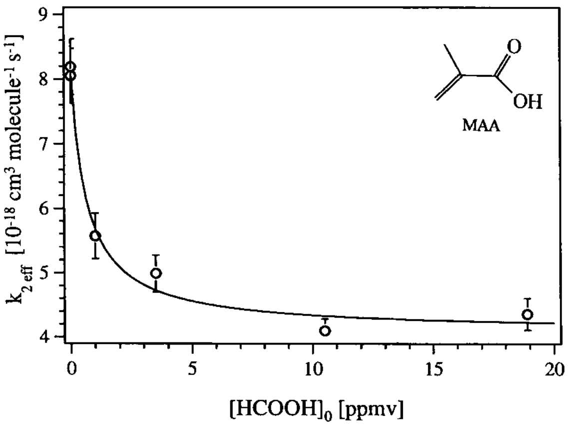


Figure 2 Dependence of the effective rate constant k_{2eff} of the reaction of MAA with ozone on the amount of added HCOOH. Initial concentration of the reactants were $[O_3]_0 = 10$ ppmv, $[MAA]_0 \approx 1$ ppmv and $[C_6H_{12}]_0 = 54$ ppmv. Symbols represent individual experiments and the line shows the the fit according to equation 16 (see text). Error bars ($\pm 2\sigma$) describe the statistical uncertainties from the linear regressions of the absorbance-time profiles.

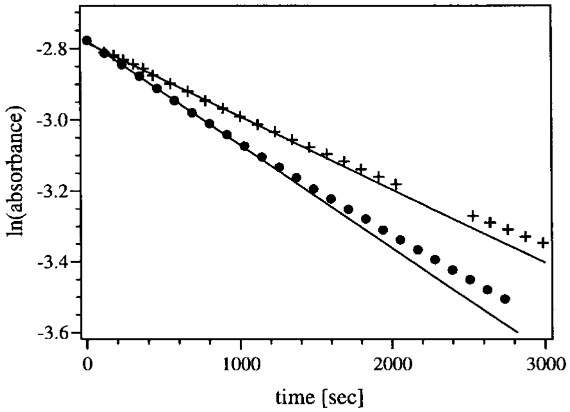


Figure 3 Semilogarithmic plot of the decrease of the characteristic absorbance of ACA at 1139 cm^{-1} in pseudo-first-order experiments. Initial concentration of the reactants were $[O_3]_0 = 10$ ppmv, $[ACA]_0 \approx 1$ ppmv and $[C_6H_{12}]_0 = 54$ ppmv. Filled circles represent the data in the absence of HCOOH and crosses those in the presence of 19 ppmv HCOOH. Solid lines are linear regressions, considering the first ten data points.

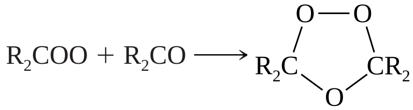
dition of HCOOH. Expected primary products from the ozonolysis are HCHO and 2-oxoacetic acid (glyoxylic acid, HC(O)C(O)OH) and two Criegee-intermediates.

$$H_2C{=}CHCOOH + O_3$$
$$\longrightarrow [H_2COO]^* + HC(O)COOH \qquad (6a)$$
$$\longrightarrow HCHO + [HC(OO)COOH]^* \qquad (6b)$$

Figure 3 shows semilogarithmic plots of the IR-absorbance of ACA at 1139 cm^{-1} in pseudo-first-order experiments in the absence and presence of HCOOH. As in the case of the MAA-O_3 system, the observed removal rate decreases upon addition of HCOOH. The dependence of k_{6eff} in the reaction of ACA with ozone on the initial HCOOH concentration is shown in Figure 4. The first-order rates k_{obs} showed the same behavior as in the case of MAA, although the decrease was less pronounced. Hence, the experimentally obtained absorbance-time profiles were treated in the same way as discussed above in order to determine k_6. From the results shown in Figure 4, the value of k_6 was estimated to be $(0.73 \pm 0.05) \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}.

MVK and MAC

Criegee-intermediates are reported not only to react with hydroxylic compounds but also with carbonyl compounds in the gas phase [15,16]. This reaction has been thoroughly investigated in the liquid phase where in inert solvents the secondary ozonides are the main products [17]:



(7)

In the gas phase, under experimental conditions where carbonyl compounds are in large excess and in the absence of alternative reaction partners (e.g., H_2O), it is expected that the Criegee-intermediate reacts with carbonyl compounds. With respect to the systematic errors of the determination of rate constants which may result from neglecting an additional sink reaction for one of the reactants, effective rate constants for the reaction of MVK and MAC with ozone were determined in the presence of HCOOH.

$$H_2C{=}CHC(O)CH_3 + O_3$$
$$\longrightarrow [H_2COO]^* + HC(O)C(O)CH_3 \qquad (8a)$$
$$\longrightarrow HCHO + [CH_3C(O)CHOO]^* \qquad (8b)$$

$$H_2C{=}C(CH_3)CHO + O_3$$
$$\longrightarrow [H_2COO]^* + CH_3C(O)CHO \qquad (9a)$$
$$\longrightarrow HCHO + [HC(O)C(CH_3)OO]^* \qquad (9b)$$

The semilogarithmic plots of the IR-absorbances of MVK and MAC (at 953 cm^{-1} and 933 cm^{-1} respectively) are shown in Figure 5. In experiments with added HCOOH, no change in the determined removal rates was observed (Figs. 5 and 6). From the data shown in Figure 6 the rate constants $k_8 = (5.4 \pm$

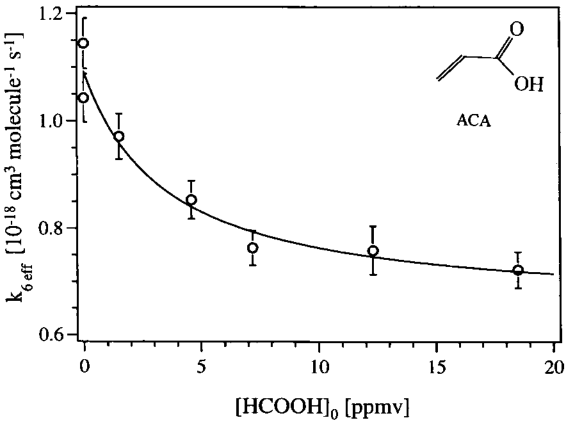


Figure 4 Dependence of the effective rate constant k_{6eff} of the reaction of ACA with ozone on the amount of added HCOOH. Initial concentration of the reactants were $[O_3]_0 = 10$ ppmv, $[ACA]_0 \approx 1$ ppmv and $[C_6H_{12}]_0 = 54$ ppmv. Symbols represent individual experiments and the line shows the fit according to equation 16 (see text). Error bars ($\pm 2\sigma$) describe the statistical uncertainties from the linear regression only.

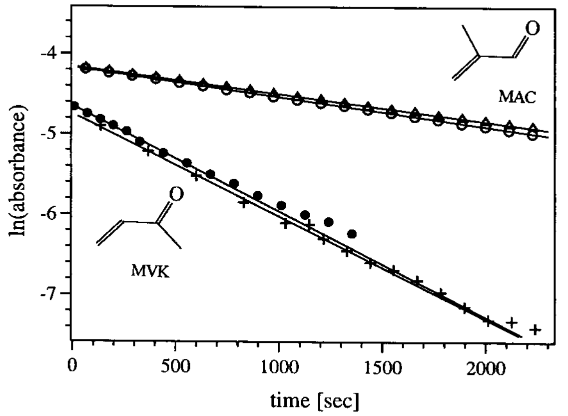


Figure 5 Semilogarithmic plot of the decrease of the characteristic absorbance of MVK at 953 cm^{-1} and of MAC at 933 cm^{-1} in pseudo-first-order experiments. Initial concentration of the reactants were $[O_3]_0 = 10$ ppmv, $[\text{carbonyl compound}]_0 = 1$ ppmv and $[C_6H_{12}]_0 = 54–65$ ppmv. For both MAC and MVK the data of experiments in the absence of HCOOH (triangles and crosses) and with $[HCOOH]_0 = 19$ ppmv (filled and open circles) are shown. Solid lines are the linear regressions lines considering the first eight data points.

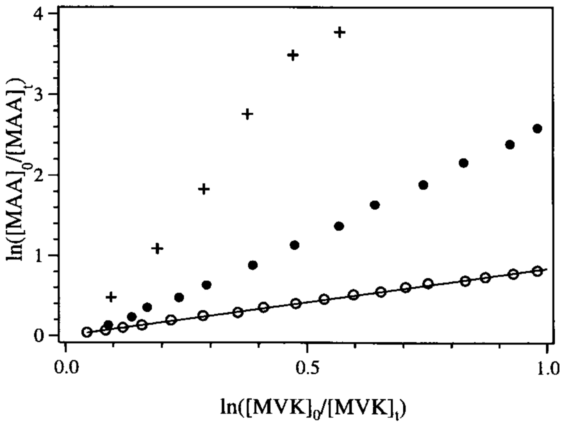


Figure 7 Relative rate experiments of MVK and MAA. Open circles show results obtained from an experiment in the presence of 19 ppmv HCOOH and filled circles were obtained under identical conditions but without addition of HCOOH. The solid line corresponds to the slope which can be expected based on the absolute rate constants k_2 and k_8 for the reactions of MAA and MVK with ozone, respectively. Crosses are from an experiment without HCOOH, where the initial concentration of MVK exceeds that of MAA by a factor of three.

$0.6) \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} and $k_9 = (1.3 \pm 0.14) \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} were determined. It was found that the ratio of the consumption of the unsaturated organic compounds to the consumption of ozone is unity, indicating that MVK and MAC react exclusively with ozone in the presence of an OH-scavenger. From these results it appears that the Criegee-intermediates formed in the MAC/MVK-ozone systems do not react with MAC or MVK, respectively, although a decrease of the HCOOH mixing ratio was observed. To our knowledge there are no comprehensive product studies of the ozonolysis of MVK or MAC, so little information concerning possible reactions of the Criegee-intermediates is available. However, it is known that HCOOH is a product of the isomerisation of the H_2COO Criegee-intermediate [18, 19] and may react according to reaction (4). The formation of hydroperoxymethyl formate (HPMF, $CH_2(OOH)$-O-CHO was observed in all experiments, although no attempts were made to quantify this product. It was noticed, that more HPMF was formed in the presence of HCOOH.

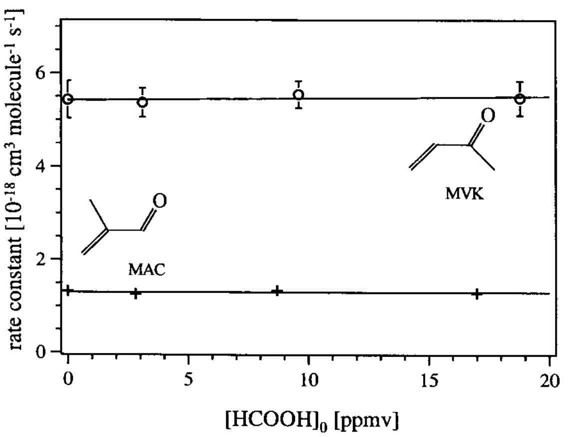


Figure 6 Determined rate constants of the reaction of MVK and MAC with ozone. Symbols represent experiments performed in the presence of various amounts of added HCOOH, lines are obtained by linear regression of the data. Error bars shown ($\pm 2\sigma$) include only the statistical uncertainties from linear regression of the data.

Relative Rate Measurements

To test the consistency of the rate constants for MVK and MAA obtained in pseudo-first-order experiments, also relative rate measurements were performed. It was expected that the decrease of MAA would not only be caused by the reaction with ozone but also with the thermalized Criegee-intermediate. Relative rate measurements were therefore repeated in the presence of HCOOH and with varying ratios of $[MVK]_0/[MAA]_0$. The results of these experiments are shown in Figure 7. The expression for evaluating relative rate constants

$$\ln\left\{\frac{[\mathrm{MAA}]_0}{[\mathrm{MAA}]_t}\right\} = \left(\frac{k_2}{k_8}\right)_{\mathrm{eff}}\left[\ln\left\{\frac{[\mathrm{MVK}]_0}{[\mathrm{MVK}]_t}\right\}\right]$$

yields in the presence of 19 ppmv HCOOH a ratio of 0.84 ± 0.01 for $(k_2/k_8)_{\mathrm{eff}}$, which is in good agreement with the value of 0.76 ± 0.09 (1σ) calculated from the pseudo-first-order experiments in the presence of HCOOH. In the absence of HCOOH the ratio of $(k_2/k_8)_{\mathrm{eff}}$ was found to be 2.67. From the comparison of the decrease of MVK in the two relative rate experiments, it can be stated that the strong increase in the ratio $(k_2/k_8)_{\mathrm{eff}}$ in the absence of HCOOH is solely due to an enhanced removal of MAA. Since the Criegee-intermediates formed in the ozonolysis of MVK are also expected to react with MAA, the removal rate of MAA is not only dependent on the degree of stabilization of the Criegee-intermediate but also on the ratio of the initial concentrations of the two alkenes. Figure 7 also shows data from an experiment where the initial MVK concentration was in excess of the concentration of MAA. In this experiment more than 95% of the MAA was consumed while less than 38% of the initially present MVK has reacted.

Kinetic Analysis

The apparent decrease of the effective rate constants for reactions (2) and (6) in the presence of HCOOH enables us to determine the degree of stabilization of the Criegee-intermediates formed. The kinetic description of the decrease in organic acid can be expressed as follows, where no distinction is made between the different Criegee-intermediates formed (see eg., reaction (2) and (6)).

$$\mathrm{R_1R_2C{=}CRCOOH} + \mathrm{O_3} \longrightarrow [\mathrm{R_1R_2COO}]^* + \mathrm{RC(O)COOH} \qquad (10)$$

$$[\mathrm{R_1R_2COO}]^* \longrightarrow \text{decomposition} \qquad (a)$$

$$[\mathrm{R_1R_2COO}]^* + \mathrm{M} \longrightarrow \mathrm{R_1R_2COO} + \mathrm{M} \qquad (b)$$

Defining the degree of stabilization as $\mathrm{Y} = (k_b \times [\mathrm{M}])/(k_a + k_b \times [\mathrm{M}])$, the net reaction can be written as:

$$\mathrm{R_1R_2C{=}CRCOOH} + \mathrm{O_3} \longrightarrow \mathrm{Y} \times \mathrm{R_1R_2COO} + (1-\mathrm{Y}) \times [\mathrm{R_1R_2COO}]^* + \mathrm{RC(O)COOH}$$

At initial stages of the reaction (10), where the concentration of any product is negligible, the reactions of the Criegee-intermediate $\mathrm{R_1R_2COO}$ can be formulated according to reaction (4):

$$\mathrm{R_1R_2COO} + \mathrm{R_1R_2C{=}CRCOOH} \longrightarrow \text{products} \qquad (11)$$

$$\mathrm{R_1R_2COO} + \mathrm{HCOOH} \longrightarrow \text{products} \qquad (12)$$

The temporal decrease of the organic acid $\mathrm{R_1R_2C{=}CRCOOH}$ (hereafter abbrievated as A) can therefore be described by using reactions (10–12) and the parameter Y for the extent of stabilization:

$$\frac{d[A]}{dt} = -k_{10}[\mathrm{O_3}][A] - k_{11}[\mathrm{R_1R_2COO}][A] \qquad (13)$$

it follows under the assumption of steady-state conditions for the Criegee-intermediate ($d[\mathrm{R_1R_2COO}]/0$:

$$\frac{d[\mathrm{A}]}{dt} = -k_{10}[\mathrm{O_3}][\mathrm{A}] - \frac{k_{10}k_{11}\mathrm{Y}[\mathrm{O_3}][\mathrm{A}]^2}{k_{11}[A] + k_{12}[\mathrm{HCOOH}]} \qquad (14)$$

In experiments without addition of HCOOH one can assume [HCOOH] = 0 and the equation (14) can be simplified to:

$$\frac{d[A]}{dt} = -k_{10}(1+\mathrm{Y})[\mathrm{O_3}][A] = -k_{10\mathrm{eff}}[\mathrm{O_3}][A] \qquad (15)$$

In the presence of excess HCOOH the second part of eq. (14) can be set to zero and under pseudo-first-order conditions $[A] = [A]_0 \exp(-k_{\mathrm{obs}} \times t)$ with $k_{\mathrm{obs}} = k_{10}[\mathrm{O_3}]$. For the reaction of MAA with ozone, k_{obs} was constant within the experimental errors if more than 10 ppmv HCOOH were present (Fig. 3). For the corresponding reaction of ACA it appeared that $k_{6\mathrm{eff}}$ has not yet reached the limit of k_6 even at the highest HCOOH concentration employed, resulting in an overestimation of the rate constant for the reaction with ozone under these conditions.

A more detailed kinetic analysis is available by extrapolating eq. (14) to $t \rightarrow 0$.

$$\left(\frac{d[A]}{dt}\right)_{t\rightarrow 0} = -k_{10}[\mathrm{O_3}][A]_0\left(1 + \frac{\mathrm{Y}}{1 + \dfrac{k_{12}[\mathrm{HCOOH}]_0}{k_{11}[A]_0}}\right) \qquad (16)$$

This procedure enables us to determine k_{10}, and the degree of stabilization Y of the Criegee intermediates

R_1R_2COO from the experimentally observed rates as a function of HCOOH by least-square fitting to eq. (16).

The parameters derived from the fitting procedure were $k_2 = (4.1 \pm 0.4) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} and $k_6 = (0.65 \pm 0.13) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} for the reaction of MAA and ACA with ozone, respectively. The value obtained for k_2 is in good agreement with the value derived directly from experiments in the presence of more than 10 ppmv HCOOH. For ACA the resulting value for k_6 is about 12% lower than the experimental value in the presence of 19 ppmv HCOOH, indicating that the Criegee-intermediate formed in the gas-phase reaction does not solely react with HCOOH.

Values for the degree of stabilization Y as determined from eq. (16) are 0.98 ± 0.12 for MAA and 0.69 ± 0.16 for ACA. Compared to results of other, more direct methods for the determination of the degree of stabilization that were performed for various alkenes, these values seem to be too high [20]. Especially the calculated degree of stabilization for the Criegee-intermediate of nearly unity for MAA seems unrealistic. This discrepancy cannot be explained at present. Although wall effects cannot be ruled out, an overestimation of the degree of stabilization may also result from an additional reaction consuming organic acids which are not taken into account in the kinetic analysis given before.

It is unlikely that the OH-radical formed in the ozonolysis [12] may account for the observed effect. The rate constants for the reactions of the OH-radical with the unsaturated organic acids as well as the OH-yield in the ozonolysis of these compounds have not been reported, and, therefore, experimental conditions (eg., amount of cyclohexane) were adjusted on the basis of the corresponding values of MVK. However losses of MAA and ACA due to reaction with OH-radicals would result in an additional increase of k_{eff} without affecting the degree of stabilization Y . There are some analogous findings from experiments in the ethene-ozone system in the presence of HCOOH [14]. In these experiments it was observed that the amount of HCOOH consumed exceeds the expected conversion of HCOOH due to reaction (5), hence, implying an additional sink of HCOOH.

CONCLUSION

To date no rate constants have been reported for the gas-phase reactions of ozone with an unsaturated organic acid. It was shown that the experimentally observed rates of the reactions of ozone with MAA and ACA were strongly influenced by HCOOH, a result which can be explained on the basis of the Criegee mechanism.

No such dependency of the effective rate constants of ozone with MVK and MAC was observed and the results of this work are in good agreement with data from the literature [21–23]. Values of the rate constants for the reaction of ozone with the unsaturated compounds investigated in this study are given in Table I. For comparison also data from acrolein are included.

In the absence of a scavenger, the thermalized Criegee-intermediate reacts with the unsaturated organic acid, resulting in an overestimation of the rate constant with ozone. Together with the recently reported reaction of HCOOH and CH_3COOH with the Criegee-intermediate CH_2OO [7], it can be concluded that the Criegee-intermediates generally react with organic acids. Although no products were identified in this study, it is expected that these reactions lead to the formation of oxygenated hydroperoxides in analogy to reaction (5):

$$R_1R_2COO + R_3COOH \longrightarrow R_1R_2C(OOH){-}O{-}C(O)R_3 \quad (17)$$

From an analysis of the dependence of the effective rate constants on the HCOOH concentrations, an estimation of the degree of stabilization was obtained which seems too high to be realistic. The most likely

Table I Rate Constants for the Reaction of O_3 with Methacrylic Acid, Acrylic Acid, Methylvinyl Ketone, Methacrolein, and Acrolein

	k_{O3} [$\times 10^{-18}$ cm^3 molecule^{-1} s^{-1}]	Ref.
Methacrylic acid	4.1 ± 0.4	this work[a]
Methacrolein	1.3 ± 0.14	this work[a]
	1.12 ± 0.2	[21]
	1.1 ± 0.2	[22]
	1.08 ± 0.2	[23]
Acrylic acid	0.65 ± 0.13	this work[a]
Acrolein	0.28 ± 0.05	[21]
	0.30 ± 0.04	[22]
Methylvinyl ketone	5.4 ± 0.6	this work[a]
	4.77 ± 0.59	[21]
	4.2 ± 0.4	[22]
	5.84 ± 0.39	[23]

[a] Error limits for the rate constants determined in this study include a 10% uncertainty in the absolute calibration factor used to quantify ozone concentrations.

reason for this behavior is the neglect of an additional sink process for organic acids in the simple kinetic scheme used to derive the degree of stabilization.

Comparing the rate constants in Table I reveals that the substitution of a carbonyl group by a carboxylic acid group leads to an increase of the rate constant by roughly a factor of three. This is in accordance with the basic concept of the Criegee-mechanism that the ozonolysis is initiated by an electrophilic cycloaddition.

BIBLIOGRAPHY

1. R. Atkinson, *J. Phys. Chem. Ref. Data,* **26,** 215 (1997).
2. A. Guenther, N. C. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W. A. McKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor, and P. Zimmerman, *J. Geophys. Res.,* **100,** 8873 (1995).
3. D. J. Jacob and S. C. Wofsy, *J. Geophys. Res.,* **93,** 1477 (1988).
4. D. Grosjean, E. L. Williams, II, and E. Grosjean, *Environ. Sci. Technol.,* **27,** 830 (1993).
5. R. W. Talbot, B. W. Mosher, B. G. Heikes, D. J. Jacob, J. W. Munger, B. C. Daube, W. C. Keene, J. R. Maben, and R. S. Artz, *J. Geophys. Res.,* **100,** 9335 (1995).
6. Y. N. Lee, X. L. Zhou, and K. Hallock, *J. Geophys. Res.,* **100,** 25933 (1995).
7. P. Neeb, O. Horie, and G. K. Moortgat, *Int. J. Chem. Kin.,* **28,** 721 (1996).
8. O. Horie, P. Neeb, and G. K. Moortgat, *Int. J. Chem. Kin.,* **29,** 461 (1997).
9. W. B. DeMore, S. P. Sander, C. J. Howard, A. R. Ravishankara, D. M. Golden, C. E. Kolb, R. F. Hampson, M. J. Kurylo, and M. J. Molina, *JPL Publication 97-4,* 1997.
10. R. Büttner and G. Maurer, *Ber. Bunsenges. Phys. Chem.,* **87,** 877 (1983).
11. M. Finkbeiner, P. Neeb, O. Horie, and G. K. Moortgat, *Fresenius J. Anal. Chem.,* **351,** 521 (1995).
12. R. Atkinson, S. M. Aschmann, J. Arey, and B. Shorees, *J. Geophys. Res.,* **97,** 6065 (1992).
13. A. M. Malleson, H. M. Kellett, R. G. Myhill, and W. P. Sweetenham, *FACSIMILE User Guide,* Oxfordshire, Harwell Laboratory, 1990.
14. P. Neeb, O. Horie, and G. K. Moortgat, *Chem. Phys. Lett.,* **246,** 150 (1995).
15. H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *Chem. Phys. Lett.,* **46,** 327 (1977).
16. P. Neeb, O. Horie, and G. K. Moortgat, *Tetrahedron Lett.,* **37,** 9297 (1996).
17. K. Griesbaum, M. Hilß, and J. Bosch, *Tetrahedron,* **52,** 14813 (1996).
18. J. T. Herron and R. E. Huie, *J. Am. Chem. Soc.,* **99,** 5430 (1977).
19. F. Su, J. G. Calvert, and J. H. Shaw, *J. Phys. Chem.,* **84,** 239 (1980).
20. S. Hatakeyama, H. Kobayashi, and H. Akimoto, *J. Phys. Chem.,* **88,** 4736 (1984).
21. R. Atkinson, S. M. Aschmann, A. M. Winer, and J. N. Pitts Jr., *Int. J. Chem. Kinet,* **13,** 1133 (1981).
22. J. Treacy, M. El Hag, D. O'Farrell, and H. Sidebottom, *Ber. Bunsenges. Phys. Chem.,* **96,** 422 (1992).
23. E. Grosjean and D. Grosjean, *Int. J. Chem. Kin.,* **30,** 21 (1998).