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Rate constants of the gas-phase reactions of CH₃OOH with O₃ and NO_x at 293 K

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Received 24 October 2005; in final form 26 January 2006
Available online 26 April 2006

Abstract

Using the long-path technique of Fourier transform infrared (LP FTIR) spectrometry, the rate coefficients of methyl hydroperoxide (MHP, CH₃OOH) reactions with O₃, NO₂ and NO at (293 ± 2) K have been determined. The coefficients are $k_{\text{MHP}+\text{O}_3} = (7.3 \pm 0.1) \times 10^{-21}$, $k_{\text{MHP}+\text{NO}_2} = (9.6 \pm 1.3) \times 10^{-21}$ and $k_{\text{MHP}+\text{NO}} < 8.6 \times 10^{-22}$ cm³ molecule⁻¹ s⁻¹. Random errors are ±2σ. The atmospheric lifetimes of MHP with respect to reactions with O₃ and NO₂ were estimated at 3.5 and 2.6 years, respectively. Finally, the results are discussed within the context of the atmospheric decay chemistry of MHP and its environmental impact.

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1. Introduction

An accurate knowledge of the total chemistry of VOC (volatile organic compound)/OH/O₃/NO_x is the most critical problem involved in photochemical processes in the atmosphere. Recent studies revealed that organic peroxides may play important roles in the VOC/OH/O₃/NO_x reaction system, because they serve as sinks and temporary reservoirs for important oxidants such as HO_x (OH and HO₂) radicals and O₃ [1,2]. For example, it has been suggested that the photolysis of methyl hydroperoxide (MHP, CH₃OOH) from the lower troposphere can provide a significant source of HO_x in the upper troposphere [3–6]. MHP has multiple sources, including its production in the oxidizing processes of VOC [7–15] and in biomass burning [16]. It has been detected as a major organic peroxide with a maximum concentration approaching that of hydrogen peroxide, i.e., at parts per billion levels by volume under heavy photochemical conditions [17–19]. Previous researches on MHP have focused mainly on its measurements and sources, however, experimental information about its atmospheric decay reactions can only be found in a few studies

[20–24]. The atmospheric fate of MHP probably includes its photolysis and its reactions with oxidants, such as OH radicals, O₃ and NO_x (NO₂ and NO). Its atmospheric lifetime depends on the rates of these reactions and the concentration levels of the oxidants. Although the rate constant of its reaction with the OH radicals has been reported [20,21], we are unaware of any published data about the rate constants for the reactions of MHP with O₃ and NO_x. In order to further understand the atmospheric loss pathways, it is necessary to have a quantitative description of the kinetics of the MHP reactions with O₃ and NO_x, although it may be expected from the lack of C=C bonds in MHP that the gas-phase reactions of MHP with O₃ or NO_x are slow.

In the present Letter, we report the first investigation of the kinetics of the MHP reactions with O₃ and NO_x at (293 ± 2) K. The rate constants were obtained by monitoring the time-resolved concentration of MHP using in situ long-path FTIR spectroscopy. Finally, the relative importance of these loss processes of MHP in the troposphere is discussed.

2. Experimental

N₂ (≥99.999%, Beijing Pryx Applied Gas Company Limited), O₂ (≥99.999%, Beijing Analytical Instrument

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Factory), cyclohexane ($\geq 99.5\%$, Beijing Chemical Plant), NO_2 and NO (China Research Center for Standard Compounds) were used. Methyl hydroperoxide is not commercially available. It was synthesized by methylation of hydrogen peroxide according to procedures described by Vaghjani and Ravishankara [21]. The purity of MHP was confirmed to be $\geq 95\%$ by FTIR spectroscopy.

The simulation experiments were carried out in a 28.5 L quartz reaction chamber (Infrared Analysis Inc., USA) equipped with a FTIR spectrometer (Nexus model, Thermo Nicolet, USA), a white-mirror system, a digital thermometer, a piezometer, and a vacuum system, which is described in detail in our previous work [9,14,15]. The pure MHP liquid was first introduced into the evacuated reactor without light. After it had evaporated completely, gaseous O_3 (which was generated in 2.8 L quartz chamber beforehand) or NO_x , was added, followed by pure N_2 or synthesized air (mixture of N_2 and O_2 in a volume ratio of 1:4) to reach atmospheric pressure. The initial gaseous concentration of MHP was 80 ppm by volume.

In order to reduce the interference by the chamber wall, the reaction chamber was deactivated with OH radicals for more than 12 h beforehand. The attenuation experiments of reactants (MHP, O_3 , NO_2 and NO) in pure N_2 was performed separately for further study of the wall effect. Impurities and heterogeneous reactions can lead to the formation of OH radicals that will impact the accuracy of the kinetic measurements. Therefore, cyclohexane was added to the reactant/ N_2 system to probe OH radicals (the reactant represents MHP or O_3 or NO_x). Finally, the reaction chamber was kept in darkness for 5 h to observe the change in the mixture system.

The loss of reactants and the formation of products were monitored with an FTIR spectrometer. An optical path length of 8.2 m was used in this work. The FTIR facility was mounted with a KBr beam splitter and a liquid nitrogen-cooled mercury–cadmium–telluride (MCT) detector. IR spectra were recorded by co-adding 64 scans at 1 cm^{-1} spectral resolution throughout the frequency region of $500\text{--}4000\text{ cm}^{-1}$. IR spectra were recorded for in situ monitoring of the concentration alteration of reactants and products. All experiments have been performed at $(293 \pm 2)\text{ K}$ and 760 Torr total pressure.

3. Results and discussion

3.1. Determination of rate constant

The reaction between MHP and O_3 or NO_x can be described as



where XO represents O_3 or NO_x . Assuming the reaction orders for MHP and XO to be m and n , respectively, the rate of the reaction can be written as

$$-\frac{d[\text{MHP}]}{dt} = k[\text{MHP}]^m[\text{XO}]^n \quad (2)$$

where k is a rate constant, and $[\text{MHP}]$ and $[\text{XO}]$ are the concentrations of MHP and XO.

If the concentration of XO is in excess of MHP or the percent conversion of XO is less than 15%, the concentration of XO can be assumed to be constant during the reaction. Then Eq. (2) can be rewritten as

$$-\frac{d[\text{MHP}]}{dt} = k'[\text{MHP}]^m \quad (3)$$

where $k' = k[\text{XO}]^n$. If $m = 1$, then we have

$$\ln \frac{[\text{MHP}]_t}{[\text{MHP}]_{t_0}} = -k^{1st}t \quad (4)$$

where

$$k^{1st} = k' = k[\text{XO}]^n \quad (5)$$

k^{1st} is a pseudo-first-order rate constant which is independent of the MHP concentration, t is the reaction time and $[\text{MHP}]_{t_0}$ and $[\text{MHP}]_t$ are the concentration of MHP at the beginning and at the reaction time of t , respectively. Under these conditions, the natural logarithm (\ln) of $([\text{MHP}]_{t_0}/[\text{MHP}]_t)$ was plotted against the reaction time, and the pseudo-first-order rate coefficient, k^{1st} , was the slope of the straight line fitted to experimental data. In addition, one can measure k^{1st} at different concentrations of XO and k^{1st} against the corresponding concentration of the excess compound. If the plot is a straight line, then it suggests that $n = 1$ according to Eq. (5), and the second-order rate constant, k^{2nd} , can be obtained from the slope of the plot.

3.2. Wall effect

The results of the attenuation experiment indicate that the reduction rates of MHP, O_3 , NO_2 and NO are about $1\% \text{ h}^{-1}$ of their initial concentrations. In the reactant/cyclohexane/ N_2 system, cyclohexane is a tracer for OH radicals. There was no obvious variation in the concentration of cyclohexane which suggests that no OH radicals were formed. Besides, no new products were detected according to the IR spectra. Therefore, the impact of impurities and heterogeneous reactions is negligible.

3.3. O_3 reaction with MHP

Fig. 1a shows the initial FTIR absorption spectrum of MHP and O_3 from which we can identify the major absorption bands of MHP at 2963, 1344, 1333 and 1320 cm^{-1} . The 1320 cm^{-1} absorption band was used for quantitative measurement of MHP. Fig. 1b shows a FTIR absorption spectrum of the mixture after a reaction period. From the subtraction analysis of the FTIR absorption spectra, CH_3OH and HCHO were defined as the main products.

In the reaction time allowed, the percent conversion of O_3 was less than 15%, thus the concentration variation of MHP was treated as pseudo-first-order reaction. The relationship between $\ln([\text{MHP}]_{t_0}/[\text{MHP}]_t)$ and the reaction time is shown in Fig. 2. As for the first-order reaction, the rate

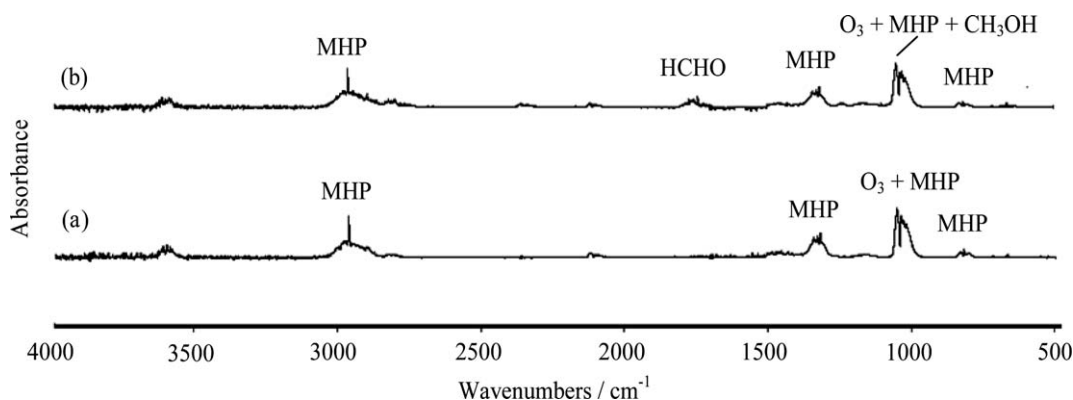


Fig. 1. IR spectra obtained before and after reaction of the mixture of MHP and O₃: (a) $t = 0$ min, (b) $t = 250$ min.

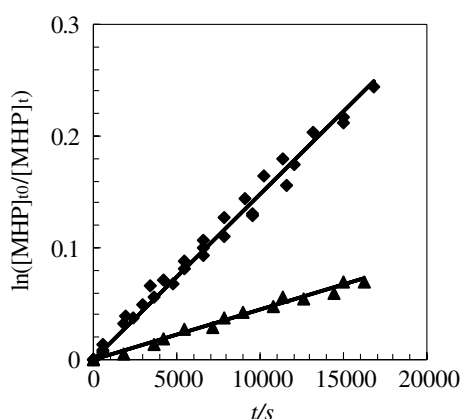


Fig. 2. Plots of $\ln([MHP]_0/[MHP]_t)$ vs. time: (▲) MHP–Air and (■) MHP–O₃–Air.

constant can be obtained from Eq. (4). Values of the first-order loss rate coefficients of MHP in the absence and presence of O₃, i.e., k_1^{1st} (MHP + Air) and k_2^{1st} (MHP + O₃ + Air), thus determined were $(4.6 \pm 0.2) \times 10^{-6} \text{ s}^{-1}$ and $(1.48 \pm 0.03) \times 10^{-5} \text{ s}^{-1}$, respectively. Taking the k_1^{1st} (MHP + Air) into account, the first-order rate coefficient of MHP with O₃ (k^{1st}) is $(1.02 \pm 0.02) \times 10^{-5} \text{ s}^{-1}$. From this, a differential analysis was made and an absolute value of second-order rate constant $k^{2nd} = k^{1st}/[O_3] = (7.3 \pm 0.1) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived, where $[O_3]$ represents the average concentration of O₃ (57 ppm) during the reaction period. There are no previous studies of this reaction reported as far as we know, but it is consistent with the reaction rate constant of H₂O₂ with O₃ ($k^{2nd} < 4.0 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) reported by Wallington, et al. [25].

According to the background concentration of O₃ which is reported to range from 5×10^{11} to $2.5 \times 10^{12} \text{ molecule cm}^{-3}$ in the troposphere and the second-order rate constant determined in this work, the rate of MHP decay by O₃ is less than $1.8 \times 10^{-8} \text{ s}^{-1}$.

3.4. NO₂ reaction with MHP

Fig. 3a, and b show typical FTIR spectra of the MHP/NO₂/N₂ mixture before and after the reaction, respectively.

CH₃ONO₂ is identified as the major product. A decrease of both MHP and NO₂ was observed and an analysis of the FTIR spectra shows no evidence of other organic nitrates.

On the basis of the absorbance of MHP at different reaction times, straight lines were obtained for plots of $\ln([MHP]_0/[MHP]_t)$ and the reaction time. Different symbols indicate that the initial concentrations of NO₂ were 2.30×10^{15} , 3.43×10^{15} , 5.59×10^{15} , 9.74×10^{15} and $1.89 \times 10^{16} \text{ molecule cm}^{-3}$, respectively. The pseudo-first-order rate constant, k^{1st} , can be calculated from Eq. (4) as the slope of the plot and is illustrated in Fig. 4. The solid squares in Fig. 4 describe the loss of MHP on the wall of the quartz reactor in the absence of NO₂. The wall loss of MHP is very small ($k_w = 3.8 \times 10^{-6} \text{ s}^{-1}$) compared with k^{1st} ($k^{1st} \geq 1.8 \times 10^{-5} \text{ s}^{-1}$). The straight lines between $\ln([MHP]_0/[MHP]_t)$ and reaction time at different concentrations of NO₂ clearly indicate that the reaction order with respect to MHP is unity, i.e., $m = 1$.

A plot of k^{1st} vs. the NO₂ concentration is shown in Fig. 5. The measurement was repeated three or four times at each concentration of NO₂. The mean k^{1st} values were used in the plot. The solid line in Fig. 5 is a linear least-square fit to the experimental data. The correlation coefficient, R^2 , is 0.95. The linear relationship between k^{1st} and the concentration of NO₂ suggests that the reaction order with respect to NO₂ is unity, i.e., $n = 1$ according to Eq. (5). The slope of this plot is the second-order rate constant, k^{2nd} . The intercept of the plot ought to be zero, from Eq. (5). However, Fig. 5 showed a finite intercept of $4.8 \times 10^{-6} \text{ s}^{-1}$, which may be attributed to a heterogeneous reaction loss of MHP on the reactor wall. This value is in accord with the experimental value of k_w , i.e., $3.8 \times 10^{-6} \text{ s}^{-1}$. After taking the heterogeneous reaction loss into consideration, the pseudo-first-order rate constant can be expressed as follows:

$$k^{1st} = k^{2nd}[NO]_2 + k_w \quad (6)$$

where k_w is the heterogeneous surface loss rate constant that depends on the surface property of the reactor, and k^{2nd} is the second-order rate constant for the MHP + NO₂ reaction. According to Fig. 5 and Eq. (6), k^{2nd} was determined to be $(9.6 \pm 1.3) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

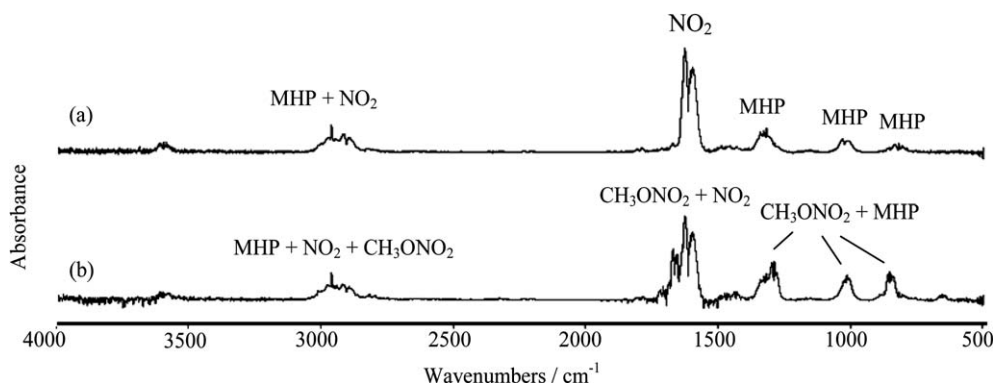


Fig. 3. IR spectra of the MHP/NO₂/N₂ mixture obtained before and after reaction: (a) $t = 0$ min, (b) $t = 70$ min.

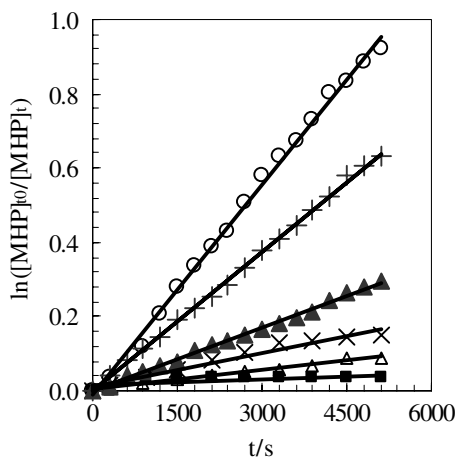


Fig. 4. A plot of $\ln([MHP]_0/[MHP]_t)$ vs. the reaction time. The initial concentration of NO₂ was: (Δ) 2.30×10^{15} molecule cm⁻³, (\times) 3.43×10^{15} molecule cm⁻³, (\blacktriangle) 5.59×10^{15} molecule cm⁻³, ($+$) 9.74×10^{15} molecule cm⁻³, and (\circ) 1.89×10^{16} molecule cm⁻³. (\blacksquare) was the wall loss of pure MHP. The pseudo-first-order rate constant k^{1st} was determined to be 1.8×10^{-5} , 3.4×10^{-5} , 5.7×10^{-5} , 1.2×10^{-4} and 1.8×10^{-4} s⁻¹, respectively.

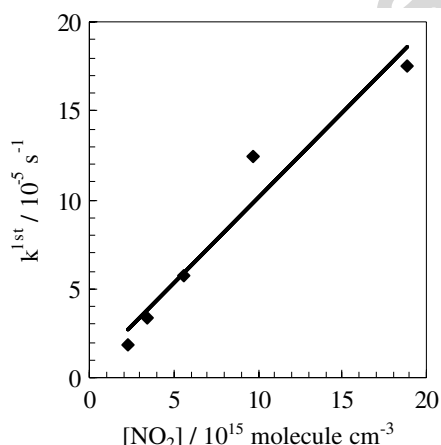
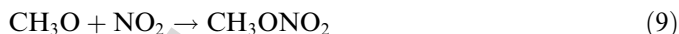


Fig. 5. A relationship between the pseudo-first-order rate constants and NO₂ concentrations.

To our surprise, CH₃ONO₂ is identified as the major product of the dark reaction, indicating that MHP can react directly with NO₂ or it can undergo a decomposition reaction to form CH₃O[•] radicals:



So far, reactions (7) and (8) have not been confirmed and a further study is required to validate these two possible pathways. In addition, from the ratio of $\Delta[CH_3ONO_2]$ vs. $\Delta[MHP]$ at different reaction times, the molar yield of CH₃ONO₂ is determined to be 0.92 ± 0.01 . Here, $\Delta[CH_3ONO_2]$ is the formation concentration of CH₃ONO₂ and $\Delta[MHP]$ is the conversion concentration of MHP at a certain reaction time. The detailed reaction mechanism needs a further study and will be discussed in another article that is in preparation.

3.5. NO reaction with MHP

In order to further elucidate the loss mechanism of MHP with special regard to NO_x, the reaction of MHP with NO was also investigated in the dark. This reaction experiment lasted for 70 min and the result revealed that there was no distinct variation for MHP and no products were found. Based on the value of k_w and the concentration of NO, the second-order rate constant of the reaction of MHP with NO can be derived as $k^{2nd} < k_w/[NO] = 8.6 \times 10^{-22}$ cm³ molecule⁻¹ s⁻¹.

4. Atmospheric implications

The chemical processes that remove MHP from the atmosphere are possibly its photolysis, and its reactions with OH, Cl, O₃ and NO_x. Therefore, the MHP concentration is controlled by the mixing ratios of these trace gases and the radiation intensity. The atmospheric lifetimes of MHP have been calculated with respect to these loss reactions using the corresponding rate constants, coupled with estimated ambient tropospheric concentrations of these reactive species, according to the following equation:

$$\tau_{MHP-XO} = \frac{1}{k_{MHP+XO}[XO]} \quad (10)$$

The rate constants measured in the present work have been used as k_{MHP+XO} for the reactions of MHP with O₃ and

Table 1

Calculated lifetimes of MHP with respect to photolysis, OH radicals, Cl atoms, O₃ and NO₂

Reactants	Concentration (molecule cm ⁻³)		<i>k</i> (cm ³ molecule ⁻¹ s ⁻¹)	τ (days) ^e	
	Day-time	Night-time		Day-time	Night-time
OH	1.6 × 10 ⁶	~0	5.54 × 10 ^{-12a}	2.6	~∞
Photolysis	—	—	2.6 × 10 ⁻⁶ s ^{-1b}	8.9	~∞
Cl	3.0 × 10 ⁵	3.0 × 10 ³	5.9 × 10 ^{-11c}	1.3	1.3 × 10 ²
O ₃	2.5 × 10 ¹²	2.5 × 10 ¹¹	7.3 × 10 ^{-21d}	1.3 × 10 ³	1.3 × 10 ⁴
NO ₂	2.5 × 10 ¹²	1.0 × 10 ¹¹	9.6 × 10 ^{-21d}	9.6 × 10 ²	2.4 × 10 ⁴

^a Ref. [26].^b Ref. [27].^c Ref. [28].^d This work.^e The lifetimes are calculated based on the 12 h daytime or nighttime average concentrations of the relative compounds.

NO₂, while the rate constants corresponding to the OH radicals, Cl atoms and photolysis reactions were obtained from Refs. [26–28].

As illustrated in Table 1, the atmospheric lifetimes of MHP with respect to reactions with O₃ and NO₂ were estimated at 3.5 and 2.6 years, respectively. The NO₂ + MHP reaction is about 370-fold slower than the OH + MHP reaction during daytime. While the O₃ + MHP reaction more slower. At night, the OH concentration is near zero and the rate for the OH + MHP reaction can be ignored. But, the rate of the Cl + MHP reaction is a factor of 184-fold faster than the NO₂ + MHP reaction. Thus, the removal of MHP by NO₂ and O₃ accounts for a few percent of the total MHP loss under typical tropospheric conditions. The overall atmospheric lifetime of MHP is mainly determined by its reaction with OH radicals and its photolysis, and is likely to be about 2.6 days in most environments. The direct reaction with NO₂ and O₃ is, therefore, a negligible sink for MHP under the vast majority of ambient conditions.

However, a few of studies have indicated that the CH₃O and CH₃O₂ radicals, which are the main intermediates of MHP during its photolysis or its reaction with OH radicals and other oxidants, can rapidly react with both O₃ and NO_x [29–33]. The reaction of CH₃O with NO₂ has recently been identified as an important source of CH₃ONO₂ in the lower stratosphere [31]. These reactions will accelerate the consumption of MHP, thus providing an indirect sink of MHP. In this way, our experimental simulations yield an overview of the role of O₃ and NO_x in controlling the MHP level in the atmosphere.

In addition, for the experimental simulation of the VOC/OH/O₃/NO_x reaction system in the atmosphere, higher concentrations of NO_x and/or O₃ are usually employed. Based on the values of *k*_{MHP+O₃}, *k*_{MHP+NO₂} and *k*_{MHP+NO} obtained in this study, the contribution of NO_x and/or O₃ to the conversion of organic peroxides in this system should be taken into account if the concentration ratio of NO_x and/or O₃ vs. OH radicals is more than 6 × 10⁷.

Acknowledgements

The author gratefully thanks the National Natural Science Foundation of China (Grant No. 20107001), the Project

of Development Plan of the State Key Fundamental Research (Grant No. 2002CB410802), and the Excellent Young Teachers Program of MOE, for support of this work.

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