Effect of CH_3OOH on the atmospheric concentration of OH radicals*

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Received January 18, 2006

Abstract Methyl hydroperoxide (CH_3OOH, MHP) is known to be a significant sink and reservoir of HO_x and RO_x radicals in the atmosphere. In order to investigate the impact of MHP on the concentration of atmospheric OH radicals, two key gas-phase reactions of MHP, i.e. the reactions with OH radicals and with UV photolysis, have been simulated at temperature of 293 ± 2 K and total pressure of 1.01×10^5 Pa, using the long path Fourier transform infrared (LP-FTIR) spectrometry. OH radicals are generated by the photolysis of O_3 in the presence of water vapor. Combined with the relative rate method, the reaction rate constant of MHP with OH radicals is determined to be $(3.99 \pm 0.15) \times 10^{-12}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, and thus the atmospheric lifetime of MHP is estimated at 2.9 days. Furthermore, from detailed analysis of the UV photolysis of MHP, the yield of OH radicals is obtained to be 0.91 ± 0.04. Based on the MHP atmospheric lifetime and the yield of OH radicals, it is concluded that MHP plays an essential role in the redistribution of OH radicals in the troposphere.

Keywords: **OH radicals, methyl hydroperoxide, rate coefficient, UV photolysis, gas-phase reaction, LP-FTIR.**

Peroxides play an important role in atmospheric chemistry, because they are not only among the principle oxidants in the chemical conversion of O_3 and SO_2, but also act as an atmospheric sink and temporary reservoir for important oxidizing radicals such as OH, HO_2 and RO_2[1,2]. With the development of measurement techniques, several organic peroxides were identified in the atmosphere in addition to hydrogen peroxide (H_2O_2)[3—5]. And among these organic peroxides, methyl hydroperoxide (MHP, CH_3OOH) has been detected as a main one with a maximum concentration approaching that of H_2O_2, i.e. at 10^{-9} levels by volume under strong photochemical conditions[6—8]. Recent studies also revealed that MHP has multiple sources, including its production in the oxidizing processes of methane (CH_4)[9,10] as well as other alkanes[11,12] and alkenes[13,14]. Moreover, biomass burning is also an important source of MHP. According to the global biomass burning emissions for the year 2000, Ito et al.[15] estimated that the total emission of MHP is as high as 21.7 $Tg \cdot yr^{-1}$.

The results from atmospheric chemistry model revealed that MHP may be of great importance in the redistribution of OH radicals along with the driving force of atmospheric chemistry[16—18]. MHP is formed mainly through the reactions of hydrocarbons with OH radicals. This process will consume OH radicals. On the other hand, the photolysis of MHP will lead to the regeneration of OH radicals. Namely, MHP acts as a reservoir of OH radicals. Thus the transportation of MHP will result in the transportation of OH radicals. Moreover, on account of the low solubility of MHP in water[19,20], little will be removed through liquid phases. Under deep convective conditions, MHP at an area can be transported to other areas and to the upper troposphere without scavenging[18], and this process will probably lead to the redistribution of OH radicals in different regions and altitudes. Therefore, it is critical to find out the clear formation and removal mechanisms of MHP in the atmosphere. However, previous work has been focused mainly on measurements, sources, and concentration levels of MHP. The experimental information on its atmospheric chemical reactions can only be found in a few studies[4,21]. In the atmosphere, MHP mainly undergoes photolysis and its reactions with OH radicals and other oxidants. And these reactions will have impact on the concentration level of OH radicals and change the oxidizing capacity of the atmosphere.

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* Supported by National Natural Science Foundation of China (Grant No. 20107001), the Major State Basic Research Development Program of China (Grant No. 2002CB410802), and the Excellent Yong Teachers Program of MOE, China

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OH radicals are the most important oxidant in the atmosphere. They provide a predominant sink for the majority of natural and anthropogenic pollutants[22,23] and thus are called the "detergent" of the atmosphere. The abundance of OH radicals, which is controlled by its formation and removal paths, is a critical factor in the processes of atmospheric chemistry. Recent studies have proposed that the photodissociation of MHP under near UV may provide an important source of OH radicals[24]. At the same time, the OH-initiated oxidation of MHP is also an important removal mechanism for OH radicals in the troposphere[18]. Therefore, the impact of MHP on the concentration level of tropospheric OH radicals is noticeable. In order to provide an accurate description of the relationship between MHP and OH radicals, it is critical for the exact determination of the reaction rate constant of MHP with OH radicals and the yield of OH radicals formed in the photolysis of MHP. Up to now, there are only a few studies about this issue[25—28], and these results differ from each other because of the difference in experimental methods. Moreover, none of the studies reported have taken the interrelationship between the photolysis and the oxidation reaction into account. Hence, further investigations are required to clarify these unresolved aspects. In this paper, we report the investigation of the reaction kinetics of the MHP oxidation by OH radicals and its photolysis. The long-path Fourier transform infrared (LP-FTIR) spectrometry was used for an *in situ* observation of the reaction process. Combined with the relative rate method, the reaction rate constant of MHP with OH radicals and the yield of OH radicals in the UV photolysis of MHP were determined.

1 Experimental section

1.1 Reagents and instruments

Cyclohexane (≥ 99.5%, Beijing Chemical Plant, analytically pure), meta-xylene (≥99%, Beijing Jinlong Chemical Reagent Company Ltd., analytically pure), mesitylene (≥99.9%, Nankai University Fine Chemical Experiment Plant, chromatogram pure), MHP (≥ 95%, synthesized by methylation of hydrogen peroxide according to procedures described by Vaghjiani and Ravishankara[25]), N_2 (≥99.999%, Beijing Pryx Applied Gas Company Ltd.) and O_2 (≥99.999 %, Beijing Analytical Instrument Factory) were used in this study.

The simulation experiments were carried out in a 28.5 L quartz reaction chamber (Infrared Analysis Inc., USA). FTIR spectrometer (Nexus, Thermo Nicolet, USA) was used to observe the concentration alteration of reactants and products. The reaction chamber was equipped with a digital thermometer, a piezometer, a vacuum system and a White-mirror system. The infrared light could undergo multiple reflections through the White-mirror system. Thus the long-path *in situ* detection could be achieved. There were five UV lamps ($\lambda_{max} = 254$ nm, 40 W) and a stainless encloser around the reactor. The FTIR facility was mounted with 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—4000 cm^{-1}. And the temperature was controlled at (293±2) K, while the total pressure of gas mixture was controlled at 1.01×10^5 Pa. The instrument was described in detail in our previous work[14].

1.2 Investigation of wall effect

The reaction chamber is made of quartz and its wall effect is much smaller compared with common glass. In order to reduce the interference of wall effect, the reaction chamber was deactivated with OH radicals (the generation method of OH radicals will be discussed in Section 1.3) for more than 12 h beforehand. And the attenuation experiment of MHP in pure N_2 was carried out for further study of the wall effect. MHP was introduced into the evacuated reactor with a microinjector. Then N_2 was added to reach the pressure of 1.01×10^5 Pa. The initial concentration of MHP is 80×10^{-6} (V/V). The reaction chamber was kept in darkness for 5 h and *in situ* IR spectra were recorded for determination of the concentration alteration of MHP.

1.3 Determination of the reaction rate constant of MHP with OH radicals

The relative rate method was used to determine the reaction rate constant of MHP with OH radicals. OH radicals were generated by UV photolysis of O_3 in the presence of water vapor:

$$O_3 + UV \rightarrow O(^1D) + O_2, \quad (1)$$

$$O(^1D) + H_2O \rightarrow 2OH. \quad (2)$$

In addition to what mentioned above there are usually three other methods to produce OH radicals. The first is the photolysis of nitrous acid (HONO):

$$HONO + h\nu \rightarrow OH + NO. \quad (3)$$

HONO has the largest absorption cross-section in the solar spectral region and serves as an efficient OH source for the LP-FTIR studies. However, there is a drawback for using HONO due to its chemical instability. Namely, it undergoes a reversible reaction heterogeneously:

$$2HONO \leftrightarrow NO + NO_2 + H_2O, \quad (4)$$

therefore, it is difficult to be well controlled in practice[29, 30]. The second method involves the photodissociation of alkyl nitrites (RONO) and the reactions with NO. CH_3ONO and C_2H_5ONO are usually used[31].

$$RONO + h\nu \rightarrow RO + NO, \quad (5)$$

$$RO + O_2 \rightarrow \text{carbonyl} + HO_2, \quad (6)$$

$$HO_2 + NO \rightarrow OH + NO_2. \quad (7)$$

This way is also unsuitable for our experiment because of the formation of NO_x (where $NO_x = NO + NO_2$), which will react with the radicals formed during the oxidation of MHP. The third one is the photolysis of H_2O_2:

$$H_2O_2 + h\nu \rightarrow 2OH. \quad (8)$$

This seems a “clean” method for the generation of OH radicals. But H_2O_2 is not steady enough to produce high concentration of OH radicals. Moreover, the photolysis of H_2O_2 also results in the formation of H_2O and O_2, which will complicate the reactions. In order to avoid the disturbance of NO_x to the photochemical system of MHP and to obtain a higher concentration of OH radicals, the UV photodissociation of O_3 in the presence of water vapor was chosen as the OH source in this work. This is actually the primary source of OH radicals in the troposphere[32, 33]. The only drawback of this method is disturbance of UV radiation and $O(^1D)$. Hence the experiment of the UV photolysis of MHP was carried out in pure N_2 and the contribution of photolysis reaction was deducted when the reaction rate constant of MHP with OH radicals was calculated.

In this study, the relative rate method was employed to determine the reaction rate constant of MHP with OH radicals. Cyclohexane, meta-xylene and mesitylene were respectively selected as the competitive reactants, i.e. the references. These references do not photolyze and their oxidation by OH radicals will not produce MHP. Furthermore, the reaction rate constants of these references with OH radicals have been well studied[34—39] and the results from different groups are almost identical.

In the reactor, MHP will compete with the reference (denoted by Ref) to react with OH radicals:

$$MHP + OH \rightarrow \text{products}, \quad (9)$$

$$Ref + OH \rightarrow \text{products}. \quad (10)$$

The reaction rate equation can be expressed as:

$$-\frac{d[MHP]}{dt} = k_{MHP\text{-}OH}[MHP][OH], \quad (11)$$

$$-\frac{d[Ref]}{dt} = k_{Ref\text{-}OH}[Ref][OH], \quad (12)$$

where [MHP], [Ref] and [OH] are the concentration of MHP, reference and OH radicals, respectively. $k_{MHP\text{-}OH}$ and $k_{Ref\text{-}OH}$ are the corresponding second-order rate constants.

From Eqs. (11) and (12), the following equation can be obtained:

$$\ln\frac{[MHP]_{t0}}{[MHP]_t} = \frac{k_{MHP\text{-}OH}}{k_{Ref\text{-}OH}}\ln\frac{[Ref]_{t0}}{[Ref]_t}, \quad (13)$$

where $[MHP]_{t0}$ and $[Ref]_{t0}$ are the initial concentration of MHP and reference, $[MHP]_t$ and $[Ref]_t$ are concentration of MHP and reference at the reaction time t. Using FTIR for the *in situ* investigation of the decrease of MHP and references, and combined with the reaction rate constants of references with OH radicals, we can calculate the reaction rate constant of MHP with OH radicals from Eq. (13).

Water, MHP and reference were introduced into the evacuated reactor in turn. After these three compounds had been evaporated completely, O_3, which was generated beforehand, was added, and followed by O_2 and N_2 ($O_2 : N_2 = 1 : 4$, i.e. the experiments were carried out under simulated atmospheric conditions) to reach the pressure of 1.01×10^5 Pa. After the gases were mixed homogenously, the UV lamps were turned on and the *in situ* IR spectra were recorded to determine the concentration alteration of MHP and references.

1.4 Determination of the yield of OH radicals in the UV photolysis of MHP

For the purpose of measurement of the OH radicals yield in the photolysis of MHP, we added scavenger of OH radicals into the reaction system to rapidly eliminate the formed OH radicals. The reaction rate constant of scavenger with OH radicals is known. Combined with the reduction rates of MHP and the scavenger identified through the *in situ* detection by FTIR, the OH radicals yield in the UV photolysis of MHP can be achieved. The detailed calculation process will be discussed in Section 2.3.

Hydrocarbons are commonly used as the scavenger of OH radicals. But it is necessary to select an appropriate scavenger for the system of the photolysis of MHP. In this reaction system, the scavenger should not produce MHP and can eliminate OH radicals effectively in time. In this study, cyclohexane, meta-xylene and mesitylene were selected as the scavenger.

Water, MHP and the scavenger were introduced into the evacuated reactor in turn. Then pure N_2 was added to reach the pressure of 1.01×10^5 Pa. After the reactants were mixed homogenously, the UV lamps were turned on and *in situ* IR spectra were recorded to probe the concentration of MHP and the scavenger. The OH radicals produced from the UV photolysis of MHP would react with the scavenger and then the concentration of OH radicals could be calculated by the reaction rate constant and the decrease of the scavenger. Finally, the yield of OH radicals could be calculated based on the experimental results.

2 Results and discussion

2.1 Wall effect

The results of the attenuation experiment of MHP in pure N_2 indicate that the change rate of MHP is less than $0.04\times 10^{-6}\ \mathrm{min}^{-1}$ and the decrease of MHP is less than 3% in 1 h. Besides, as mentioned in Section 1.2, the quartz reaction chamber had a smaller wall effect and was deactivated with OH radicals beforehand. Therefore, the consumption of MHP due to wall effect was negligible.

In addition, the reaction chamber is columniform with the cubage of 28.5 L and diameter of 16 cm. In this study, FTIR spectrometry was performed for *in situ* observation of the reaction process and the infrared light beam went through where close to the one-third of the chamber center. Hence such an *in situ* detection method further reduced the influence of wall effect.

2.2 Reaction rate constant of MHP with OH radicals

According to Niki et al.[26], the reaction of MHP with OH radicals has two possible H-abstraction channels:

$$CH_3OOH + OH \rightarrow CH_2OOH + H_2O, \quad (14a)$$

$$CH_3OOH + OH \rightarrow CH_3OO + H_2O. \quad (14b)$$

The proportion of the two channels was assumed to be $k_{14a}/k_{14b}=0.77$.

In this study, the competitive reaction was employed to determine the reaction rate constant of MHP with OH radicals. Cyclohexane, meta-xylene and mesitylene were selected as the references. First, the kinetic curves of the concentration variation were determined for the simultaneous reaction of MHP and reference with OH radicals (reaction system I). At the meantime, the UV photolysis of MHP also contributes to the reduction of MHP because of the existence of UV radiation in the reaction system. It is necessary to take the UV photolysis reaction into account. Therefore, we measured the kinetic curves for the UV photolysis reaction of MHP in N_2 (reaction system II). The fractional variation of MHP at different time in reaction system II was calculated and this value was added to the MHP concentration detected in reaction system I to get the actual concentration of MHP at the corresponding time without the disturbance of the photolysis reaction. Thus the kinetic curve of concentration variation of MHP was drawn. The relationship between $\ln([MHP]_{t0}/[MHP]_t)$ and $\ln([Ref]_{t0}/[Ref]_t)$ is illustrated in Fig. 1. All the correlation coefficients (R^2) from several times of experiments are larger than 0.99.

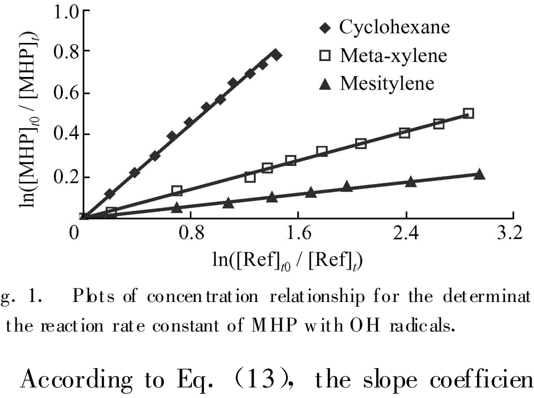

Fig. 1. Plots of concentration relationship for the determination of the reaction rate constant of MHP with OH radicals.

According to Eq. (13), the slope coefficient in Fig. 1 is the value of $k_{\text{MHP-OH}}/k_{\text{Ref-OH}}$. Combined with the reaction rate constants of the references with OH radicals (Table 1), the reaction rate constant of MHP with OH radicals can be obtained. The results with different references are listed in Table 1. And the average value was taken as the rate constant of MHP with OH radicals, which is $(3.99\pm 0.15)\times 10^{-12}\ \mathrm{cm^3\cdot molecule^{-1}\cdot s^{-1}}$. The random errors are 2σ.

Table 1. Reaction rate constant of MHP with OH radicals

Reference	[Ref]$_{t0}$ (10^{-6})	[MHP]$_{t0}$ (10^{-6})	$k_{\text{Ref-OH}}$ (10^{-12} cm^3·molecule^{-1}·s^{-1})	$k_{\text{MHP-OH}}/k_{\text{Ref-OH}}$	$k_{\text{MHP-OH}}$ (10^{-12} cm^3·molecule^{-1}·s^{-1})
Cyclohexane	80	80	6.97	0.56±0.01	3.90±0.07
Meta-xylene	64	80	23.1	0.17±0.01	3.93±0.15
Mesitylene	56	80	56.7	0.073±0.002	4.14±0.11
Average value					3.99±0.15

In addition, the UV photolysis of O_3 will result in the formation of $O(^1D)$. However, due to the high H_2O concentration of 4000×10^{-6}(V/V), $O(^1D)$ reacts mainly with H_2O to produce OH radicals[40]. Thus the dynamic concentration of $O(^1D)$ is very low and its reaction with MHP is negligible.

The result of this study and its comparison with the reported ones are summarized in Table 2. It can be seen from the table that there is of great difference between the reported values of the reaction rate constant of MHP with OH radicals. This is possibly due to the different experimental methods and analytical techniques used. In the study carried out by Niki et al.[26], OH radicals were generated from the photolysis of CH_3ONO and C_2H_5ONO. However, NO_x, which formed during the photolysis process of RONO, could react with CH_3OO radicals. This process will accelerate the consumption of MHP and result in the higher determined reaction rate constant. Moreover, the suggested value in the overview of IUPAC by Atkinson et al.[41] is what Vaghjiani and Ravishankara[25] have reported, while DeMore et al.[42] consider the average (7.52×10^{-12} cm^3·molecule^{-1}·s^{-1}) of what reported by Niki et al.[26] and by Vaghjiani and Ravishankara[25] is more reasonable. Our experimental result is close to that of Vaghjiani and Ravishankara[25] who employed an absolute rate method.

Table 2. Reaction rate constant of MHP with OH and its comparison with the data in the literature

$k_{\text{MHP-OH}}/10^{-12}$ cm^3·molecule^{-1}·s^{-1}	Experimental method	Generation of OH radicals	Analytical technique	Reference
3.99	Relative rate	Photolysis of O_3 in the presence of H_2O	FTIR	This work
5.54	Absolute rate	Pulsed laser photolysis of H_2O or O_3-H_2O	Laser induced fluorescence	25
10.20	Relative rate	Photolysis of CH_3ONO and C_2H_5ONO	FTIR	26

2.3 Determination of the yield of OH radicals in the MHP photolysis

Cyclohexane, meta-xylene and mesitylene were selected as the scavenger of OH radicals in the measurement of the yield of OH radicals in the MHP photolysis. On the basis of analysis and calculation from the IR spectra during the reactions, the yield of OH radicals was obtained.

In the photolysis system of MHP, the main reactions are as follows:

$$\text{MHP} + h\nu \rightarrow \text{OH} + \text{other products}, \quad (15)$$

$$\text{MHP} + \text{OH} \rightarrow \text{products}, \quad (16)$$

$$\text{Sca} + \text{OH} \rightarrow \text{products}, \quad (17)$$

where Sca denotes the scavenger of OH radicals. The yield of OH radicals (γ) is the ratio of the amount of OH radicals formed vs. the amount of MHP consumed through the photolysis reaction during the reaction time. And because this is a constant volume reaction system, the yield is also the ratio of the concentration variation of OH radicals to MHP, i.e.

$$\gamma = \frac{\Delta[\text{OH}]}{\Delta[\text{MHP}]_{\text{UV}}}, \quad (18)$$

where $\Delta[\text{OH}]$ is the concentration of OH radicals formed during the reaction time; $\Delta[\text{MHP}]_{\text{UV}}$ the concentration reduction of MHP induced by the photolysis reaction in the same period. According to reactions (15)—(17), the consumption of MHP includes the UV photolysis of MHP and its oxidation by OH radicals. Hence $\Delta[\text{MHP}]_{\text{UV}}$ can be expressed as:

$$\Delta[\text{MHP}]_{\text{UV}} = \Delta[\text{MHP}] - \Delta[\text{MHP}]_{\text{OH}}, \quad (19)$$

where $\Delta[\text{MHP}]$ is the reduction of MHP which was observed in the experiments and $\Delta[\mathrm{MHP}]_{\mathrm{OH}}$ is reduction of MHP due to reaction (16). Moreover, the lifetime of OH radicals was estimated to be the magnitude order of 10^{-5} s under our experimental conditions according to the concentration of OH scavengers and the reaction rate constants of these scavengers with OH radicals. This indicates that OH radicals formed through the photolysis of MHP is consumed rapidly by the scavenger and MHP. Therefore, the concentration of OH radicals formed in a reaction period is equal to the sum of concentration reduction of the scavenger ($\Delta[\mathrm{Sca}]$) and $\Delta[\mathrm{MHP}]_{\mathrm{OH}}$.

$$\Delta[\mathrm{OH}] = \Delta[\mathrm{Sca}] + \Delta[\mathrm{MHP}]_{\mathrm{OH}}. \tag{20}$$

According to Eqs. (18)—(20), we have

$$\gamma = \frac{\Delta[\mathrm{OH}]}{\Delta[\mathrm{MHP}]_{\mathrm{UV}}} = \frac{\Delta[\mathrm{Sca}] + \Delta[\mathrm{MHP}]_{\mathrm{OH}}}{\Delta[\mathrm{MHP}] - \Delta[\mathrm{MHP}]_{\mathrm{OH}}}. \tag{21}$$

The value of $\Delta[\mathrm{Sca}]$ and $\Delta[\mathrm{MHP}]$ for different reaction time can be calculated directly from the IR spectra. Thus the values of $\Delta[\mathrm{OH}]$ and $\Delta[\mathrm{MHP}]_{\mathrm{UV}}$ can be obtained if the corresponding value of $\Delta[\mathrm{MHP}]_{\mathrm{OH}}$ is derived.

The kinetic equation of reaction (16) can be expressed as follows:

$$\frac{\Delta[\mathrm{MHP}]_{\mathrm{OH}}}{\Delta t} \approx \frac{\mathrm{d}[\mathrm{MHP}]_{\mathrm{OH}}}{\mathrm{d}t} = k_{\mathrm{MHP\text{-}OH}}[\mathrm{MHP}][\mathrm{OH}]. \tag{22}$$

If the values of [MHP] and [OH] are replaced by the average concentration of MHP and OH radicals, then the following equation is reasonable:

$$\Delta[\mathrm{MHP}]_{\mathrm{OH}} = k_{\mathrm{MHP\text{-}OH}} \frac{[\mathrm{MHP}]_{t0} + [\mathrm{MHP}]_{t}}{2}[\mathrm{OH}]\Delta t, \tag{23}$$

where $[\mathrm{MHP}]_{t0}$ and $[\mathrm{MHP}]_{t}$ are the MHP concentrations at the beginning of and time t of the reaction, respectively. Now, it is needed to obtain the value of [OH]. From the IR spectra, the concentration alteration of OH scavenger was calculated. The plots of $\ln([\mathrm{Sca}]_{t0}/[\mathrm{Sca}]_{t})$ against the reaction time were drawn and linear fitting was made. The ratio of the slope coefficient with $k_{\mathrm{Sca\text{-}OH}}$ is the steady state concentration of OH radicals. Then the value of $\Delta[\mathrm{MHP}]_{\mathrm{OH}}$ can be calculated from Eq. (23). Finally, the values of $\Delta[\mathrm{OH}]$ and $\Delta[\mathrm{MHP}]_{\mathrm{UV}}$ can be obtained and the plots of $\Delta[\mathrm{OH}]$ against $\Delta[\mathrm{MHP}]_{\mathrm{UV}}$ are presented in Fig. 2 (a)—(c). From the slope coefficient, we can get the yield of OH radicals formed in the photolysis of MHP.

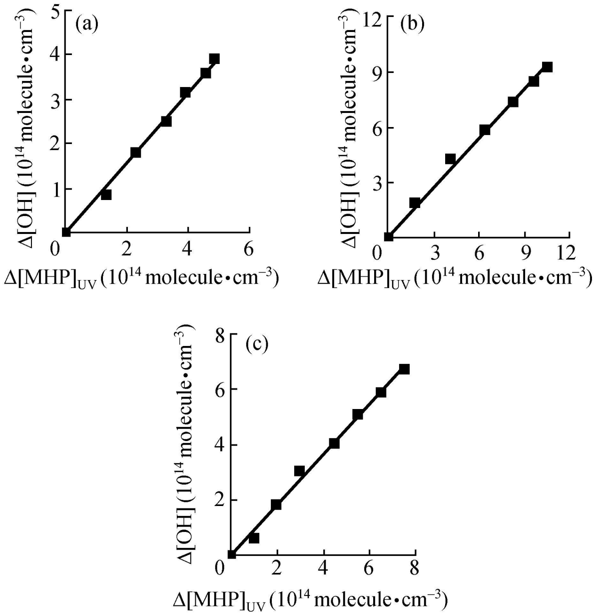

Fig. 2. Plots of the formation of OH radicals *vs*. the consumption of MHP via UV photolysis with different OH scavengers. (a) Cyclohexane; (b) meta-xylene; (c) mesitylene.

Table 3 shows the yield of OH radicals with different OH scavengers. It can be seen that the OH yield based on cyclohexane as the OH scavenger is obviously less than those based on other two OH scavengers. Whereas the experimental results with meta-xylene and mesitylene as scavengers are in great correspondence. The clearance efficiency of the scavengers is probably a critical factor for the determination of OH yield. The reaction rate constant of cyclohexane with OH radicals is close to that of MHP with OH radicals. Therefore, cyclohexane cannot scavenge OH radicals efficiently, thus gives a large inaccuracy. Moreover, in terms of reaction with OH radicals, meta-xylene and mesitylene are much faster than MHP, so that they can scavenge OH radicals rapidly and restrain the reaction of MHP with OH radicals. According to the concentration of mesitylene and meta-xylene and the rate constants for their reactions with OH radicals, it can be estimated that the scavenging efficiency of the former is 2.2 times of the latter, but the yields of OH radicals calculated from these two scavengers are consistent with each other. Hence it can be concluded that each of these two compounds has a enough capability to scavenge OH radicals efficiently. Summing up what mentioned above, we decided to use the average value, based on mesitylene and meta-xylene scavengers, as the yield of OH radicals in the UV photolysis of MHP, i.e. 0.91 ± 0.04.

Table 3. Yield of OH radicals formed in the UV photolysis of MHP

OH scavenger	$[\mathrm{Sca}]_{t0}$ (10^{-6})	$[\mathrm{MHP}]_{t0}$ (10^{-6})	$k_{\mathrm{Ref\text{-}OH}}$ (10^{-12} $\mathrm{cm^3 \cdot molecule^{-1} \cdot s^{-1}}$)	γ
Cyclohexane	160	80	6.97	0.79 ± 0.07
Meta-xylene	128	80	23.1	0.90 ± 0.04
Mesitylene	112	80	56.7	0.92 ± 0.02

3 Conclusions

Using the technique of *in situ* long path FTIR spectrometry, with cyclohexane, meta-xylene and mesitylene as the references individually, the reaction rate constant of MHP with OH radicals was determined to be $(3.99 \pm 0.15) \times 10^{-12}\ \mathrm{cm^3 \cdot molecule^{-1} \cdot s^{-1}}$. At the meantime, the UV photolysis system of MHP was investigated and the yield of OH radicals in this system was measured to be 0.91 ± 0.04. The main mechanisms for the photolysis of MHP can be deduced as follows:

$$CH_3OOH + h\nu \rightarrow CH_3OO + H, \quad (24a)$$

$$CH_3OOH + h\nu \rightarrow CH_3O + OH, \quad (24b)$$

$$2CH_3OO \rightarrow 2CH_3O + O_2, \quad (25a)$$

$$2CH_3OO \rightarrow HCHO + CH_3OH + O_2, \quad (25b)$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2. \quad (26)$$

According to our experimental results, for the two channels of MHP photolysis, path (24a) accounts for 9% and path (24b) accounts for 91%.

From the reaction mechanism mentioned above, it can be seen that the photolysis process of MHP involves formation of formaldehyde. In the atmosphere, where NO and O_3 always present, formaldehyde can undergo the following photochemical reactions to produce OH radicals:

$$HCHO + h\nu \rightarrow HCO + H, \quad (27a)$$

$$HCHO + h\nu \rightarrow CO + H_2, \quad (27b)$$

$$HCO + O_2 \rightarrow HO_2 + CO, \quad (28)$$

$$H + O_2 \rightarrow HO_2, \quad (29)$$

$$HO_2 + NO \rightarrow NO_2 + OH, \quad (30)$$

$$HO_2 + O_3 \rightarrow 2O_2 + OH. \quad (31)$$

It is obvious that MHP can produce OH radicals not only through its direct photolysis but also through the indirect process, i.e. the photochemical reactions of its product HCHO. Therefore, the yield of OH radicals in the atmospheric photolysis of MHP should be larger than 91%. In the future, further efforts are needed to obtain how much OH radicals comes from the contribution of HCHO which formed in the photolysis of MHP in the atmosphere.

In the lower troposphere, the primary source of OH radicals is the reaction of ground state oxygen atoms which generate from the photodissociation of O_3 by solar UV, with H_2O[32, 33] (Reactions (1) and (2)). In the troposphere, MHP can reach a certain concentration level of parts per billion levels by volume[8, 43]. According to the reaction rate constant of MHP with OH radicals determined in this study and the daytime means concentration of OH in the troposphere (2.0×10^6 molecule·$\mathrm{cm^{-3}}$), the atmospheric lifetime of MHP can be estimated to be 2.9 days. Hence MHP can be transported to the upper troposphere under strong convective weather conditions. This point of view is also confirmed by the results of the recent atmospheric observation[19, 44]. Furthermore, the yield of OH radicals formed in the photolysis of MHP (including the contribution of HCHO) is larger than 91%. On the other side, on account of the higher UV light intensity in the upper troposphere, the photolysis reaction of MHP is more important. Hence this provides probably a main source of OH radicals in the upper troposphere and leads to the redistribution of OH radicals from lower troposphere to upper troposphere. Recent atmosphere observations and modeling calculations indicate that the photolysis of MHP and other organic peroxides transported from the lower troposphere is a “new” important source of HO_x (where $HO_x = OH + HO_2$) in the upper troposphere[17, 18, 44—47]. The results of our laboratory simulation further verified this presumption.

OH radicals react with the vast majority of atmospheric trace gases, in most cases as the first and rate-determining step of a reaction chain. These chains often lead to formation of HO_2 radicals, which then react with O_3 or NO to recycle back to OH, i.e. the circulation of HO_x radicals. Moreover, in the troposphere, important greenhouse gases such as CH_4 and hydrogen-containing chlorofluorocarbons (HCFCs and HFCs) are removed mainly through their reactions with OH radicals[48], which restrain their atmospheric concentration level. Accordingly, it is positive to slow down the greenhouse effect. But there is not yet any quantitative experimental data about this. Therefore, for the modeling of the concentration variation of atmospheric trace gases, both the oxidation of MHP by OH radicals and the UV photolysis should be added into the modeling calculations so that the indirect influence of MHP is taken into account.

In this study, our experiments provide quantitative parameters for atmospheric chemistry and climate models. It will contribute to estimating the source and concentration level of atmospheric OH radicals exactly，thus helping to forecast atmospheric oxidation capacity and global climate change.

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