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Formation of HO₂ and OH in photolytically initiated oxidation of dimethyl ether

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Abstract

Time-resolved measurements of HO₂ and OH have been conducted in 355 nm photolysis of dimethyl ether/Cl₂/O₂ mixture at elevated temperature, using near-infrared frequency modulation spectroscopy. A part of OH was found to be produced at a timescale of several microseconds by the methoxymethyl with O₂ reaction, while HO₂ is formed mainly in milliseconds with the yield increasing up to 60% between 500 and 600 K. It was rationalized that HO₂ is not a direct product of the O₂ adduct decomposition, but a secondary product through HCHO + OH reaction. Another pathway through HCO formation from the adduct is also discussed. © 2006 Elsevier B.V. All rights reserved.

1. Introduction

The reactions of alkyl radicals with molecular oxygen are important in 'low temperature combustion' region, particularly on autoignition properties. The general description for $alkyl(R) + O_2$ reactions was established by the end of last century [1,2].

In the last couple of years, Taatjes, Klippenstein and coworkers have provided further insights to the $R + O_2$ reactions using direct time-resolved measurements of HO₂ and RRKM-master equation theory for ethyl to butyl [3–8], neopentyl [9] and cyclo-propyl [10] as the alkyl radicals. Their notable results include the presence of a direct HO₂ forming channel;

$$\mathbf{R} + \mathbf{O}_2 \to \text{alkene} + \mathbf{HO}_2,\tag{1}$$

distinguished from the slow formation via decomposition of intermediates;

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 $R + O_2 \rightarrow RO_2 \rightarrow (QOOH \rightarrow) alkene + HO_2.$ (2)

It was argued that the slow HO_2 formation dominant at elevated temperature is primarily from alkylperoxy radical(RO₂) decomposition and the hydroperoxy alkyl radical(QOOH) route is of minor importance in the cases of ethyl, *n*-propyl and iso-propyl, as supported by quantumchemical calculations. Substantial contribution of the QOOH route leading to more OH formation is expected in butyl and larger alkyls as reaction (3)

$$R + O_2 \rightarrow RO_2 \rightarrow QOOH \rightarrow O - hetercycle + OH$$
 (3)

and in practice, the reduction of the HO_2 yield was recognized in their butane experiment [8].

Dimethyl ether (DME) is a diesel alternative fuel exhibiting outstanding ignitability as this size of hydrocarbon molecule. Detailed reaction mechanisms accounting for DME property have been proposed by Dagaut et al. [11] and Curran et al. [12,13], in which the methoxymethyl (CH₃OCH₂) + O₂ reaction and the following reproduction of OH constitute a growing chain reaction mechanism effective in the low temperature combustion region. With regard

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to elementary reaction studies, the $CH_3OCH_2 + O_2$ system has been investigated between 240 and 700 K, by observing species using UV absorption and mass-spectrometric sampling [14–18], through which the main pathway following the $CH_3OCH_2 + O_2$ reaction in the reduced pressure experiments is considered to be a specific case of reaction (3) as

$$CH_{3}OCH_{2} + O_{2} \rightarrow CH_{3}OCH_{2}OO$$
$$\rightarrow CH_{2}OCH_{2}OOH$$
$$\rightarrow OH + 2HCHO.$$
(4)

The dominance of this pathway has been supported by quantum chemical calculations [19–21] and is consistent with product analysis finding formaldehyde as a major product [14,15]. Ethylene oxide, which is a product corresponding to the reaction (2), was not detected between room temperature and 450 K. However, the possibility of HO₂ formation via RO₂/QOOH decomposition or other indirect pathway at higher temperature is yet to be confirmed. In this study, we examine the product formation in a DME oxidation system detecting HO₂ and OH using a near-IR modulation technique at the temperatures up to 650 K. The pathway forming HO₂ is discussed with kinetics modeling and quantum chemistry calculations.

2. Experimental

The setup of the frequency modulation spectroscopy in a Herriott type multi-pass cell has been described elsewhere [22]. Briefly, a CW diode laser (New Focus, Velocity 6327) is two-tone modulated at 600 ± 2.6 MHz using an electro-optic modulator (EOM; New Focus, 4223 M). The beam is passed through the Herriott cell, detected by a photoreceiver (New Focus, 1811MFS), and demodulated by mixing with a frequency-doubled fraction of 2.6 MHz modulation signal. The Herriott cell consists of two concave mirrors placed co-axially at a distance of 1.5 m, between which 24 reflections are established. The center region about 60 cm is the temperature controlled observation region where the probe path is overlapped with the co-axial photolysis beam from a frequency tripled Nd-YAG laser. Consequent effective path length is approximately 15 m. The temperature is measured by thermocouples placed at the center and 40 cm off-center regions in the cell. The signal is usually averaged 1000 times with a digital oscilloscope. In this study, HO₂ was detected at 7013.520 cm⁻¹ of the A-X (0'-0") ¹⁻⁰Q₂(18) transition [23] and OH was detected at 6971.291 cm^{-1} of $Q_{1e}(1.5)$ of the vibrational overtone [24]. The detection limit of HO₂ concentration with 1000 times average is estimated to be 1×10^{12} molecule cm⁻³.

The reaction is initiated by pulsed photolysis in a mixture of Cl_2 , O_2 and DME with He buffer to establish the following reaction sequence:

$$Cl_2 + h\nu \rightarrow 2Cl$$
 (5)

 $Cl + CH_3OCH_3 \rightarrow HCl + CH_3OCH_2$ (6)

$$CH_3OCH_2 + O_2 \rightarrow products$$
 (7)

High ratios of initial $[DME]/[Cl_2]$ and $[O_2]/[Cl_2]$ were maintained in order to assure prompt completion of reaction (6) and 100% yield of reaction (7) to $[Cl]_0$ by avoiding $CH_3OCH_2 + Cl$ and $CH_3OCH_2 + Cl_2$ reactions.

The quantity of HO_2 relative to that of initial radical is known by comparing with the reference reaction of $CH_3OH/Cl_2/O_2$ mixture, i.e.

$$Cl + CH_3OH \rightarrow HCl + CH_2OH$$
 (8)

$$CH_2OH + O_2 \rightarrow HO_2 + HCHO$$
 (9)

The OH reference is obtained by adding NO to the HO_2 reference, in which 100% conversion through

$$HO_2 + NO \rightarrow OH + NO_2$$
 (10)

takes place. The reference data are acquired after every DME run with the same temperature, total density and the mixture composition.

A typical condition is $[Cl_2] = 2 \times 10^{14}$, $[O_2] = 1.2 \times 10^{16}$, $[DME] = [CH_3OH] = 1 \times 10^{15}$, and a total gas density = 1.1×10^{18} all in molecule cm⁻³ with He buffer at temperature range 296–650 K in 50 K increments up to 500 K and 25 K increments over 500 K. The photolysis yield for the Cl atom was estimated as ca. 5% of the Cl₂ at a typical 355 nm fluence of about 130 mJ cm⁻² and at the typical condition. Photolysis repetition was set at 1 Hz to assure the gas replacement at the total flow rate of 5200 cm³/min.

3. Results and discussion

Fig. 1 shows typical time profiles of (a) HO_2 and (b) OH observed at 600 K in the photolysis of $Cl_2/O_2/CH_3OCH_3$ mixture and the methanol reference. The HO_2 reference



Fig. 1. Time profiles of (a) HO₂ and (b) OH FM signals at 600 K in the photolysis of $CH_3OCH_3/Cl_2/O_2$ mixture and reference mixtures. The references are $CH_3OH/Cl_2/O_2$ for HO₂ and $CH_3OH/Cl_2/O_2/NO$ for OH.

profile shows a prompt rise at the time of photolysis followed by a gradual decrease at the rate of the $HO_2 + HO_2$ self-reaction. The profile from DME shows a slower increase, which is similar to those reported for C2–C4 alkyl radicals + O_2 [4–8]. On the other hand, the OH profile from DME shows a rapid rise whose rate is equivalent to that of the reference. This rapid OH formation was also reported for ethyl, propyl and neopentane [9,25], however, the amount close to half of the reference is apparently larger than those reported.

It is necessary to correct the HO₂ profile to obtain the overall HO₂ yield relative to the initial chlorine atom amount according to the established procedure [4]. The precise rate constant of the HO₂ self-reaction necessary for the correction is obtained from the reference profile, but the rate constant of HO₂–RO₂ reaction, which should be given separately, is unknown. In this study, we set the initial radical concentration as low as possible to minimize the HO₂ consumption and corrected the HO₂ signal from DME only for the self-reaction. As shown in Fig. 2b, the extent of correction is not very significant.

As superimposed in Fig. 1b, the OH reference profile is reproduced by the reaction mechanism reported in Ref. [9], in which OH is consumed through reactions with CH_3OH , NO, OH, etc. The OH profile from DME is scaled assuming that the reference peak corresponds to the initial chlorine atom concentration.

A mechanism effective at 600 K can be extracted from the Curran et al. model [12] as:

$$CH_3OCH_2 + O_2(+M) \iff CH_3OCH_2O_2(+M)$$
 (11)

$$CH_3OCH_2O_2(+M) \iff CH_2OCH_2OOH(+M)$$
 (12)

$$CH_2OCH_2OOH(+M) \rightarrow 2HCHO + OH(+M)$$
 (13)

$$OH + HCHO \rightarrow H_2O + HCO$$
(14)

$$HCO + O_2 \rightarrow CO + HO_2 \tag{15}$$

$$CH_3OCH_3 + OH \rightarrow CH_3OCH_2 + H_2O$$
(16)

$$CH_3OCH_2(+M) \rightarrow CH_3 + HCHO(+M)$$
 (17)

The above reactions together with reactions (5) and (6)essentially represent the OH and HO₂ formations in the Curran et al. mechanism at the current experimental conditions, although we used the full Curran et al. mechanism for quantitative completeness. As drawn in Fig. 2b and c, this model with the original set of rate constants does not reproduce the amount of HO_2 and the rapid rise of OH at 600 K. Fig. 2 also shows HO₂ and OH profiles in the case of 550 K, where the HO₂ yield of the original model is in better agreement with the measurement. However, the calculated HO₂ profile resulted in considerably slower rise than that in the measurement. As well, the OH profile is in poor agreement. The Curran et al. model has been established to represent experiments of over atmospheric pressures therefore we need to revise mechanism for the reduced pressure experiments as follows:

Unimolecular reactions, for which high pressure limits have been given in the original model, were modified.



The thermal decomposition of CH₃OCH₂ (17) is most responsible to the HO₂ yield decreasing above 550 K. According to the high and low pressure limit rate constants reported by Louck et al. [26] we set the constant as $k_{17} = 5.0 \times 10^9 \times \exp(-75.8 \text{ kJ/mol/RT}) \text{ s}^{-1}$ for the current density of 1.1×10^{18} molecule/cm³, which is about 10 times lower than the original at 600 K. The O₂ addition to CH₃OCH₂ (11) was experimentally examined [15,16] and the pressure dependence was theoretically evaluated by Yamada et al. [19]. The evaluated value at the current density is close to that of the original Curran et al. model, and we used the original as it is. The reactions (12) and (13)



were also treated by Yamada et al. [19] as pressure dependent. Since the product of these series reactions is responsible for the observed time profile of HO₂, we fixed the rate constant k_{12} as $2.18 \times 10^9 \times \exp(-66.3 \text{ kJ/mol/RT}) \text{ s}^{-1}$ according to Yamada et al., which is about ten times lower than that of the original, and fit the rate constant k_{13} .

In order to reproduce the rapid rise of OH, the direct forming pathway of OH from CH_3OCH_2 is assumed, i.e.;

$$CH_3OCH_2 + O_2 \rightarrow OH + 2HCHO$$
 (18)

As shown in Fig. 2, the HO₂ and OH profiles are predicted well when the rate constants are assumed as $k_{13} = 1.25 \times 10^{13} \times \exp(-84.1 \text{ kJ/mol/RT}) \text{ s}^{-1}$, and $k_{18} = 8.3 \times 10^{-12} \times \exp(-8.8 \text{ kJ/mol/RT}) \text{ cm}^3 \text{ s}^{-1}$. These Arrhenius parameters are obtained from fitting to HO₂ and OH profiles between 500 and 600 K. The direct OH formation (18) competes with the recombination (11) and the branching ratio determines the peak OH intensity. The 550 K profiles are also predicted well by the modified model as shown in Fig. 2d for HO₂ and (e) for OH. It is noted that the estimated k_{13} is almost 10 times higher than that of Yamada et al. value, but still lower than the Curran et al. original value by a factor of 0.2. In the case of neopentane [9], which apparently has no direct HO₂ formation pathway, the reaction of OH with RO₂ was proposed to be the main pathway for the HO₂ formation. In the current case of DME, the rate constant of $OH + RO_2$ is assumed as 1.2×10^{-10} cm³ s⁻¹. Without this reaction the rise of HO₂ and the OH decay is not predicted well as shown in Fig. 3. Fig. 3 also shows the influence of k_{13} , k_{18} and k_{OH+RO} , and OH profiles. The profiles calculated from the set of estimated rate constants are compared with those from increased and decreased constants for each reaction by a factor of 2. The rate constant of the direct OH formation reaction (18) affects OH profiles strongly and the amount of OH affects that of the HO₂. The rate constant of $OH + RO_2$ has an effect on initial rise of HO₂ only and does not affect the amount of HO₂. Even at this rate of $OH + RO_2$, the OH + HCHO pathway accounts for 80% of the HO₂ formation.



Fig. 3. The HO₂ and OH profiles changing the value of k_{13} , k_{18} , k_{RO_2+OH} . The lines are present model profiles, the dash lines are twice and the dash-dot lines are half as much as the estimated value. The dot lines in (e), (f) are the profiles without the RO₂ + OH reaction.

Potential energy diagrams for the $CH_3OCH_2 + O_2$ systems are shown in Fig. 4. Our current calculations using G2M (CC1) //B3PW91/cc-pTVZ level of theory (MRMP2//CASSCF/cc-pVTZ for TS₄) are compared with those reported by Andersen et al. [20,21] using UDFT/ B3LYP and by Yamada et al. [19] using MP2(full)/6-31 G(d,p). The pathways forming OH + 2HCHO and HO₂ + c-C₂H₄O in our case and those by Yamada et al. are in good agreement, whereas the results of Anderson et al. tend to lie higher. The barrier of the direct HO₂ forming channel (TS3) is considerably above the CH₃O-CH₂ + O₂ level consistently in all cases; consequently this channel is unlikely to contribute.

We found another pathway leading to HO₂ formation via;

$$CH_2OCH_2O_2H \rightarrow HOCH_2OCH_2O \rightarrow HCHO + HCO + H_2O,$$
(19)

where HCO readily reacts with O_2 in the current experimental conditions. The energy of the final HCHO + HCO + H₂O is considerably lower than those of $C_2H_4O + HO_2$ and 2HCHO + OH. The highest barrier of this channel (TS₄) is 13 kJ/mol above that of the OH channel (TS₂) in this calculation; hence it may contribute a few percent in the CH₂OCH₂O₂H decomposition. The HO₂ profiles are also represented by giving the branching ratio of 5% for this channel with a modification of k_{13} at a factor of 0.95. Even in this case the major route to HO₂ formation is via OH + HCHO. It should be noted that the OH production further consumes DME via reaction 16 repeatedly, so that the nominal yield of HO₂ relative to initial Cl concentration is enhanced.

Fig. 5 shows temperature dependence of the HO_2 yield from DME. The HO_2 yield is reasonably predicted by this modified model through the investigated temperature



Fig. 5. Temperature dependence of HO_2 yield from DME against the initial Cl atom concentration. Solid circles are experiments. Solid lines are the result of present model and dashed lines are that of Curran et al. model.



Fig. 4. Potential energy diagrams of $CH_3OCH_2 + O_2$ system with geometry of TS4 and TS5. Thick black lines are results of present calculation, dashed lines are Andersen et al. [20] and gray lines are Yamada et al. [19].

range. It is notable that the HO₂ yield begins to rise at the temperature about 50 K lower but the maximum yield remains lower, compared with the results of ethane and propane [4,6]. As the barrier height for QOOH isomarization from RO_2 in the case of DME is lower than that of direct HO₂ formation from RO_2 in the cases of ethane and propane, the OH formation channel is favored at investigated temperature and HO₂ is formed by secondary reactions (14) and (15) as described above.

It was deduced in this study that the formation of HO₂ from methoxymethyl + O₂ is via secondary reaction of OH + HCHO. It is contrasted from the cases of C₂-C₄ alkyl radicals, where HO₂ is formed directly from RO₂ species. Neopentyl radical also forms HO₂ secondarily via OH + RO₂. Despite the different pathways, all these reactions show remarkably similar behavior of HO₂ formation, such as the slower rise than the rate of R + O₂ reaction and the dramatic increase of yield with increasing temperature. It is because the overall rate is governed by the unimolecular decomposition of RO₂/QOOH species whichever it directly produces HO₂ or OH.

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