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Chemical Physics Letters 427 (2006) 461-465

www.elsevier.com/locate/cplett

Production of the radicals in the ozonolysis of ethene: A chamber study by FT-IR and PERCA

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Received 24 March 2006; in final form 23 June 2006 Available online 4 July 2006

Abstract

The ozonolysis of ethene in dry synthetic air at atmospheric pressure and room temperature (298 ± 2) K was investigated in a 6065-L reaction chamber by in situ analysis of stable species by FTIR and of total peroxy radicals PO₂ (PO₂ = HO₂ + RO₂) by a chemical amplifier instrument. The yields of radical production were determined based on steady state concentrations of the peroxy radicals and the partitioning between HO₂ and RO₂ derived from model simulations. The radical yield is 0.38 ± 0.02 for HO₂ and 0.45 ± 0.03 for PO₂. © 2006 Elsevier B.V. All rights reserved.

1. Introduction

Free radicals are the crucial species in the chemistry of atmosphere both in clean and polluted environment [1-3]. The most important is OH radicals which is produced primarily from the photolysis of O_3 and the subsequent reaction of $O(^{1}D)$ with water vapor. The further reaction of OH with CO and hydrocarbons (HCs) leads to hydroperoxy radicals (HO₂) and organic peroxy radicals (RO₂). More recently, the ozonolysis of alkenes has been found to be an important light-independent source for atmospheric radicals especially in urban and rural regions where the concentration of alkenes is significantly high [4-6]. Nevertheless, despite studies for many years, the yields of radical production for the reactions are still poorly quantified, even for the simplest alkene ethene [7]. This is mainly due to the great complexity in the mechanism of the reactions. For ethene, it is believed that the ozonolysis reaction proceeds by initial 1,3 cycloaddition of O_3 to the double bond in ethene to form a primary ozonide, which then rapidly

* Corresponding author. *E-mail address:* b.qi@163.com (B. Qi). dissociates to form a carbonyl and a vibrationally exited Criegee intermediate $CH_2O_2^{\neq}$ (CI) [8]:

$$\begin{split} C_2H_4 + O_3 &\rightarrow (\text{primary ozononide}) \\ &\rightarrow \text{HCHO} + \text{CH}_2\text{O}_2^{\neq} \end{split} \tag{R1}$$

The CI is either collisionally deactivated to form stabilized intermediate CH_2O_2 (SCI) or decomposed *via* a number of channels:

$CH_2O_2^{\neq}$	$\rightarrow CH_2O_2$	(R2a)
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$$\rightarrow$$
 H₂ + CO₂ (R2b)

$$\rightarrow$$
 H₂O + CO (R2c)

$$\rightarrow CO_2 + 2H$$
 (R2d)

$$\rightarrow$$
 HCO + OH (R2e)

The recommended branching ratios are ~ 0.37 for (R2a), ~ 0.13 for (R2b), ~ 0.38 for (R2c) and ~ 0.12 for (R2d) + (R2e) [9]. At atmospheric pressure of air, the Hatoms and HCO radicals in (R2) will be titrated rapidly by O₂ to HO₂ via (R3) and (R4), so O₃-ethene reaction actually produces OH and HO₂ directly

 $H + O_2 + M \rightarrow HO_2 + M \tag{R3}$

$$HCO + O_2 \rightarrow CO + HO_2$$
 (R4)

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The previously reported radical yields were in the range 0.12-0.18 for OH [10-12], 0.12-0.26 for HO₂ [9,13] and 0.24-0.38 for PO₂ at atmospheric pressure of air [9,13]. The yields were mainly determined indirectly based on the measured stable products [9]. Recently, Mihelcic et al. [14] monitored the production of HO₂ and HOC₂H₄O₂ directly using matrix isolation and electron spin resonance (MIESR) in a flow tube and obtained OH yield of 0.20 ± 0.02 and HO₂ yield of 0.39 ± 0.03 with total radical vield of 0.59 ± 0.05 , significantly larger than the results from the indirect measurements. In this work, we investigated the reaction by observing radical production directly in a static large chamber using a chemical amplification technique (PERCA). The main object is to further determine the radical yield and test the potential of PERCA technique for chemical kinetics study.

2. Experimental

The ozonolysis of ethene occurred in dry synthetic air $([H_2O] < 10 \text{ ppmv})$ at atmospheric pressure and room temperature (298 \pm 2 K) in a 6065-L evacuable chamber. The chamber is coated with perfluoroethylene-perfluoroalkyl vinyl ether co-polymer (PFA) and equipped with an FTIR spectrometer (Nicolet, nexus 670) and a White mirror system (path length 221.5 m). The detailed description of the chamber can be found elsewhere [15-17]. Ethene (99.5%) was ordered from Takachiho Co. without further purification. Ozone was prepared from O₂ (Nippon Sanso, 99.9%) using a silent discharge ozone generator. Gas handling was accomplished with a standard all-glass vacuum system with greaseless stopcocks and MKS Baratron pressure gauge. The chamber was evacuated down to ca. 7×10^{-7} Torr prior to the experiment, then filled with synthetic air at a pressure slightly higher than one atmosphere. Ethene was added at a controlled partial pressure from a pure ethene contained in a flask. O₃/air mixture was flowed into the chamber with a flow of N₂. The initial concentration was 6.05 ppmv for ethene, and 100 ppbv for O_3 to let the ozonolysis reaction proceed in the pseudo first-order kinetics for O₃. The molecular species in the reaction system were analyzed by the FTIR spectroscopy with the resolution of 1 cm^{-1} and the peroxy radicals was monitored with a chemical amplifier instrument developed in our laboratory [18] based on the pioneered work of Cantrell and Stedman [19]. The principle for radical measurement is to convert small amount of radicals to large amount of NO2 in the presence of excess CO (10%) and NO (3 ppmv) through chain reactions. For HO₂,

 $HO_2 + NO \rightarrow NO_2 + OH$ (R5)

 $OH + CO \rightarrow H + CO_2$ (R6)

 $H + O_2 + M \rightarrow HO_2 + M \tag{R3}$

The initial concentration of HO_2 ([HO_2]₀) can be inferred from the concentration of the produced NO_2 in chemical amplifier (CA) and the chain length (CL) of the chain reactions: $[HO_2]_0 = [NO_2]/CL$. OH can be measured with same sensitivity as HO₂ since OH can be converted to HO₂ quickly in CA. RO₂ can also be detected if they are converted to HO₂ in CA,

$$RO_2 + NO \rightarrow NO_2 + RO$$
 (R7)

$$RO + O_2 \rightarrow Carbonyl \ compound + HO_2$$
 (R8)

The NO₂ from the sources other than CA should be removed which is achieved *via* a modulated technique, *i.e.*, periodically switching the addition of CO from the inlet of the reactor in which the chain reactions occur (radical mode) to a position downstream of the CA to terminate the chain reactions (baseline mode), yielding modulated NO₂ signals. In this case, the radical mixing ratio is proportional to the difference in [NO₂] measured in radical mode and baseline mode, respectively. The termination of the chain reactions is dominated *via* the following reactions:

$$OH + wall \rightarrow$$
 (R9)

$$OH + NO + M \rightarrow HONO + M$$
 (R11)

(R10)

$$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M \tag{R12}$$

The air samples were delivered continuously to the inlet of the radical detector at flow rate of 1.5 SLM *via* a Teflon tube (4.35 mm i.d. × 15.0 cm) which was extended into the chamber through a port of ~8 mm diameter. The concentration of NO₂ was measured with a commercial luminol detector (LMA-3, Scintrex/Unisearch) [20]. The CL was determined *via* the calibration of the CA instrument against a known concentration of HO₂ which originated from the photolysis of H₂O/CO/air mixture at 184.9 nm [21]. A CL of 250 ± 28 (σ) was obtained during the experiment and adopted for the quantification of HO₂. The detection limit (*S*/*N* = 3) for HO₂ measurement is 0.6– 0.8 pptv with accuracy of ±12%.

3. Results and discussion

 $HO_2 + wall \rightarrow$

The typical FTIR spectra of the reaction mixture recorded in the course of the reaction was illustrated in Fig. 1. The formation of CO, CO₂, HCHO, HCOOH and H₂O₂ was identified. The time series in the concentrations of ozone and major products were shown in Fig. 2. As expected, the decay in $[O_3]$ observed the pseudo first-order kinetics (Fig. 3). The rate constant for O₃-ethene reaction was yielded from the slope of Fig. 3 to be $k_1 = 1.44 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which is in good agreement with the previous results [9]. The production of radicals can be seen distinctly from the modulated NO_2 signals (see Fig. 4). The decline of the baseline is due to the decrease in $[O_3]$ in the chamber. As mentioned above, the ozonolysis of ethene would produce HO₂ and OH directly. However, the OH is expected to be consumed exclusively by ethene under the conditions of this experiment and converted to $HOC_2H_4O_2$ with the yield of unity.



Fig. 1. The typical FTIR spectra of the reaction mixture of the gas phase reaction of ozone with ethene.



Fig. 2. Time series of the concentrations in ozone and some products produced during the ozonolysis of ethene. The simulation lines were obtained assuming branching ratio of (R2d) of 0.08 and (R2e) of 0.04.



Fig. 3. The decay of O_3 during the ozonolysis of ethene.

 $HOC_2H_4O_2$ can be measured by PERCA instrument with the same sensitivity as HO_2 [22]. Consequently, $HOC_2H_4O_2$ measurement in the present work is really an indirect mea-



Fig. 4. The typical modulated NO_2 signal recorded during the ozonolysis of ethene.

surement of OH. Under the conditions of this experiment, the concentration of the radicals is dominated by the following reactions: $\begin{array}{ll} O_3 + \text{ethene} \rightarrow \alpha HO_2 + \beta OH & (R1) \\ OH + \text{ethene} \rightarrow \rightarrow HOC_2H_4O_2 & (R13) \\ HO_2 + HO_2 \rightarrow H_2O_2 + O_2 & (R14) \\ HO_2 - DO_2 - DO_2 & (DO_2) & (DO_2) \end{array}$

 $\mathrm{HO}_2 + \mathrm{RO}_2 \rightarrow \mathrm{ROOH} + \mathrm{O}_2 \tag{R15}$

$$\mathrm{HO}_2 + \mathrm{O}_3 \to \mathrm{OH} + 2\mathrm{O}_2 \tag{R16}$$

In (R1), α and β are radical yield for HO₂ and OH, respectively. Assuming that the production of HO₂ and HO-C₂H₄O₂ reached in a steady state, then,

$$\frac{d[\text{HO}_2]}{dt} = \alpha k_1 [\text{O}_3] [\text{C}_2\text{H}_4] - 2k_{14} [\text{HO}_2]^2 - k_{15} [\text{HO}_2] [\text{HOC}_2\text{H}_4\text{O}_2] - k_{16} [\text{HO}_2] [\text{O}_3] = 0$$
(F1)

$$\frac{d[\text{HOC}_2\text{H}_4\text{O}_2]}{\text{dt}} = \beta k_1[\text{O}_3][\text{C}_2\text{H}_4] + k_{16}[\text{HO}_2][\text{O}_3] \\ - k_{15}[\text{HO}_2][\text{HOC}_2\text{H}_4\text{O}_2] = 0$$
(F2)

From (F1) and (F2), we can get

$$\frac{d[PO_2]}{dt} = \gamma k_1 [O_3] [C_2 H_4] - 2k' [PO_2]^2 = 0$$
(F3)

where γ ($\gamma = \alpha + \beta$) denotes the total radical yield, $k' = k_{14}r^2 + k_{15}r(1 - r)$ ($r = [HO_2]/[PO_2]$) represents the composite rate constant for (R14) and (R15). γ can be obtained from the steady state expression:

$$\gamma = \frac{2k' [PO_2]^2}{k_1 [O_3] [C_2 H_4]}$$
(F4)

If the ratio *r* is known, then α , β and γ can be obtained from (F1), (F2) and (F4), respectively. In this study, the *r* value was estimated using a chemical box model which is shown

Table 1

Reaction mechanism for the simulation of the ozonolysis of ethene

Reaction	Rate constant ^a
$C_2H_4 + O_3 \rightarrow CH_2OO^{\neq} + HCHO$	1.44×10^{-18b}
$CH_2OO^{\neq} \rightarrow CH_2OO$	See text
$CH_2OO^{\neq} \rightarrow CO_2 + H_2$	1.3×10^{8}
$CH_2OO^{\neq} \rightarrow CO + H_2O$	3.8×10^{8}
$CH_2OO^{\neq} \rightarrow CO_2 + 2H$	See text
$CH_2OO^{\neq} \rightarrow HCO + OH$	See text
$\rm H + O_2 \rightarrow \rm HO_2$	1.2×10^{-12}
$H + O_3 \rightarrow OH + O_2$	2.9×10^{-11}
$HCO + O_2 \rightarrow HO_2 + CO$	5.6×10^{-12}
$OH + HCHO \rightarrow H_2O + HCO$	1.1×10^{-11}
$OH + O_3 \rightarrow HO_2 + O_2$	6.8×10^{-14}
$OH + CO \rightarrow CO_2 + H$	2.4×10^{-13}
$HO_2 + O_3 \rightarrow OH + 2O_2$	1.9×10^{-15}
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.2×10^{-12}
$OH + C_2H_4 \rightarrow HOCH_2CH_2$	8.2×10^{-12}
$HOCH_2CH_2 + O_2 \rightarrow HOCH_2CH_2O_2$	3.0×10^{-12}
$HOCH_2CH_2O_2 + HO_2 \rightarrow HOCH_2CH_2OOH + O_2$	1.2×10^{-11}
$2HOCH_2CH_2O_2 \rightarrow 2HOCH_2CH_2O + O_2$	1.0×10^{-12}
$HOCH_2CH_2O + O_2 \rightarrow HOCH_2CHO + HO_2$	5.4×10^{-20c}
$HOCH_2CH_2O \rightarrow HCHO + CH_2OH$	1 ^c
$CH_2OH + O_2 \rightarrow HCHO + HO_2$	9.6×10^{-12}

 $^{\rm a}$ Units are cm 3 molecule $^{-1}$ s $^{-1}$ for second-order reactions and s $^{-1}$ for first-order reactions.

^b This work.

^c From [29], the others from [9].

in Table 1. The calculations were conducted with the branching ratio at 0.38 for (R2b) and 0.13 for (R2c) and varying the ratios for (R2d) and (R2e) as shown in Table 2. The calculated results were also listed in Table 2. It was found that the ratio r varied from 0.5 to 1.0 with the increase in the branching ratio of (R2d) from 0 to 0.12 (low level) or from 0 to 0.24 (high level) and that the model fit the experimental data best (see Fig. 2) when the branching ratio of (R2d) was in the range 0.06–0.08 and the total branching ratio of (R2d) and (R2e) was 0.12 (see Table 2). This corresponds to the ratio r between 0.8 and 0.9. The deviation in [PO₂] between model and experiment was observed in the beginning of the reaction. This is possibly caused by the incomplete mixing of the reactants. Considering the circumstances, we selected the data recorded in the period 30-60 min for the calculations. Thus measured radical yields and their dependences on the ratio r are plotted in Fig. 5. With the range of 0.8–0.9, α and γ are not sensitive to the ratio r, but β can be changed greatly from 0.04 to 0.10. Therefore, the present method appears not to be suitable for the determination of β . Using a r value of

Table 2

The variation of the calculated $[PO_2]$ and r with the branching ratios in (R2)

Branching ratios		r	[PO ₂], model (pptv)	[PO ₂], experiment (pptv)		
(R2d)	(R2e)					
Low level ^a						
0	0.12	0.5	136.3 ± 1.5	168.4 ± 1.3		
0.02	0.10	0.6	135.6 ± 1.4			
0.04	0.08	0.7	143.5 ± 1.5			
0.06	0.06	0.8	156.8 ± 1.4			
0.08	0.04	0.9	172.2 ± 1.5			
0.10	0.02	0.9	205.3 ± 1.8			
0.12	0	1.0	203.2 ± 1.8			
High level ^b						
0	0.24	0.5	191.1 ± 2.0			
0.06	0.18	0.7	199.9 ± 2.0			
0.12	0.12	0.9	230.8 ± 2.2			
0.18	0.06	0.9	266.1 ± 2.5			
0.24	0	1.0	300.0 ± 2.9			

^a The sum of branching ratio for (R2d) and (R2e) is 0.12.

^b The sum of branching ratio for (R2d) and (R2e) is 0.24.



Fig. 5. The measured radical yields and their dependences on the ratio r.

0.85, we obtained $\alpha = 0.38 \pm 0.02$ and $\gamma = 0.45 \pm 0.03$ (σ). The uncertainties were estimated based on that of k (13%), r (10%), PO₂ (5%), O₃ (5%) and ethene (5%). The radical yields were found to be invariable within the uncertainties during the selected reaction period. The value of α and γ derived by this method is obviously larger than the results from the indirect methods, and slightly smaller than those given by MIESR. Part of the reasons for the discrepancy between PERCA and MIESR method is that they used a rate constant of k_1 smaller than the recommended one by 40%.

PERCA has been used successfully to measure the atmospheric peroxy radicals in a number of field campaigns [23,24]. However, the concentration of the reactants in this system is significantly higher than that in the atmosphere, therefore, the radical detector may be subject to interferences under the present conditions. One is the active species other than peroxy radicals formed during the ozonolysis reaction which can initiated the chain reaction in CA, hence also be detected. The SCI formed in O₃-ethene reaction is a biradical and has long lifetime to proceed bimolecular reaction with NO and CO [25]. The reaction of the SCI with NO is known to produce HCHO and NO₂ with rate constant of $\sim 2 \times 4^{-14}$ cm³ molecule⁻¹ s⁻¹ [25]. The products of the reaction SCI with CO has not been investigated experimentally and was proposed to be HCHO and CO₂, in analogous to the above reaction. Thus the SCI can not initiate the chain reactions and would not be detected by PERCA. Another is the formation of additional radicals in CA which would lead to overestimation of radical yield. One is NO3 radical formed in the reaction of the SCI with NO₂. NO₃ itself is inactive to PERCA, but it can react with ethene to generate peroxy radicals [26]. However, the reaction of NO₃ with ethene is too slow $(k = 2.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ in comparison with its competition reaction of NO₃ with NO $(k = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ to be important. Additionally, the unreacted O_3 and ethene would react continuously in CA and produce extra radicals. The radical production rate in CA is anticipated to be reduced greatly due to the lower concentration of O₃ which was titrated mostly by NO. Meanwhile the loss rate of the radicals was enhanced due to the reaction with NO_x (NO + NO₂). Model calculations indicated that the concentration of the extra radicals was ~ 1 pptv at the condition of 100 ppbv O_3 and 6.01 ppmv ethene, much lower than the measured results of ~ 168 pptv. Consequently, we concluded that the influences of the additional radical sources to the radical measurement were negligible in this experiment. This is agreement with the observation that measure radical yield was nearly constant in the course of the reaction. In addition to active species, ethene may affect radical measurement via involving in the chain relations. Ethene is known to be a more efficient chain carrier than CO for converting OH to HO₂ [27], therefore, the CL may shift in the presence of ethene. However, this effect is expected to be small because ethene concentration used in this work was much lower than its explosion limit of 2.75% at which ethene can be comparable to CO (10% in CA) as a chain carrier [28]. In conclusion, the present study of the ozonolysis of ethene in air at atmospheric pressure by combining analysis of stable species by FTIR and peroxy radicals by a chemical amplifier instrument has provided the yield of radical production from the reaction. Our work indicates that PERCA is a potential technique for the investigation of chemical kinetics issues in combination with other analytical techniques in reaction chamber with the reactant concentration in the range of ppmv levels.

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