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# Formation of hydroxyl and hydroperoxy radicals in the gas-phase ozonolysis of ethene

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### Abstract

Ozonolysis of alkenes is thought be a significant source of free radicals (OH and HO<sub>2</sub>) in the atmosphere. Although studied for many years, the reaction mechanism and the product yields are still very much under discussion. We report measurements of the production of HO<sub>2</sub> radicals from the reaction of O<sub>3</sub> with ethene using matrix isolation and electron-spin-resonance spectroscopy (MIESR). Formation of OH radicals was established by conversion of OH to HO<sub>2</sub> via reaction with CO. The OH yield is  $20 \pm 2\%$ , the HO<sub>2</sub> yield is  $39 \pm 3\%$ . Our measurements suggest that the Criegee intermediate in the ground state is not a radical. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The formation of free radicals in the ozonolysis of olefinic hydrocarbons, which are emitted in large quantities from both anthropogenic and biogenic sources [1,2], is of considerable interest to atmospheric chemists, as it may significantly influence the radical budgets in rural and urban environments [3]. Although the mechanism of gas-phase ozonolysis has been intensively studied, there is still considerable uncertainty about the exact mechanism of ozonolysis and in particular the radical yields, even for the simplest alkene,  $C_2H_4$ , which has been most widely studied. Reaction of  $O_3$  with  $C_2H_4$  in the gas phase is believed to occur, in analogy to the Criegee mechanism in the liquid phase [4], by addition of  $O_3$  to the double bond (R1). The five-membered ring intermediate with an excess energy of up to 60 kcal/mol [5–7] is believed to decompose into formaldehyde and an excited carbonyl oxide, often referred to as Criegee bi-radical ( $H_2C'OO'$ ):



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The excited bi-radical is thought to be either stabilized by collision with  $O_2$  and  $N_2$  (R2a) or to undergo further decomposition (R2b-f), thereby producing free radicals (H, OH and HCO) and stable molecules, such as  $H_2O$ , CO,  $CO_2$ ,  $H_2$  and HC(O)OH [7–10]. The postulated reactions are listed below, together with the measured branching ratios [10].

R2a	$[H_2COO]^* + M \rightarrow H_2COO + M$	<b>~</b> 40%
R2b	$[H_2COO]^* \rightarrow HCO + OHr$	12-40%
R2c	$[H_2COO]^* \rightarrow CO_2 + 2H$	3-5%
R2d	$[H_2COO]^* \rightarrow CO + H_2O$	31-58%
R2e	$[\mathrm{H}_{2}\mathrm{COO}]^{*} \rightarrow \mathrm{CO}_{2} + \mathrm{H}_{2}$	<b>~</b> 13%
R2f	$[H_2COO]^* \rightarrow HC(O)OH$	~ 7%

The H-atoms and HCO radicals are instantaneously converted to  $HO_2$  in the presence of  $O_2$  at atmospheric conditions (R3 and R4).

- R3 HCO +  $O_2 \rightarrow HO_2 + CO$
- R4  $H + O_2 + M \rightarrow HO_2 + M$
- R5  $OH + C_2H_4 + O_2 \rightarrow HOCH_2CH_2O_2$
- R6  $OH + CO + O_2 \rightarrow HO_2 + CO_2$

There is little direct spectroscopic evidence for the proposed mechanism. In most studies, the branching ratios and radical yields were estimated from the observed stable products [10]. The yield of OH radicals was inferred from the observed excess consumption of  $C_2H_4$  due to R5 as compared to that of ozone or from the decay of OH scavengers which were added to the  $O_3-C_2H_4$  mixture or from the products of the reaction of OH with the scavenger [10–13]. The only direct measurement of OH formation [7] was done at low pressure (5–8 hPa). While OH was detected in these experiments, the yields were much larger than those determined from indirect measurements. Recently, the formation of OH was called into question since the relative decay rates of two different OH scavengers which were added to  $O_3/alkene$  mixtures were inconsistent with OH kinetics [14].

Peroxy radicals have been identified by ESR spectroscopy in Ar-matrices [9], however, without sufficient spectral resolution to allow the distinction between HO<sub>2</sub> from R2b and R2c and the HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> radicals formed in R5. No spectroscopic evidence exists for the stabilized Criegee bi-radical.

#### 2. Experimental

We have used matrix isolation and electron spin resonance (MIESR, [15]) to study the radical products that emerge from the ozonolysis of ethene. The experiments were performed at 1000 hPa and 295 K in a flow reactor with a movable injector. The flow reactor consisted of a pyrex glass tube with an internal diameter of 1.8 cm (Fig. 1). Ozone was generated in an O<sub>3</sub> Calibrator (Thermo. Instr., Model TE 49) by irradiation of pure O<sub>2</sub> (Linde, purity 99.999%) with a low-pressure mercury lamp. Pure ethene (Linde, purity 99.95%) was metered with quartz capillaries into a flow of synthetic air (Messer–Griesheim, purity 99.998%). The flow rates of ethene (1–3 ml/min), synthetic air (3 1/min) and the O<sub>3</sub>/O<sub>2</sub> mixture (3 1/min) were determined volumetrically with an automated soap-film flow meter (Gillibrator). The C<sub>2</sub>H<sub>4</sub>/air mixture was introduced into the flow of O<sub>3</sub>/O<sub>2</sub> through an 8 mm long tubular glass frit at the tip of a movable injector (Fig. 1). In order to achieve efficient mixing of the reagent gases, the total gas flow rate was divided evenly between the injector and the surrounding tube. The injector could be moved about 12 cm, corresponding to a maximum reaction time of



Fig. 1. Schematic diagram of the flow system and the MIESR cryosampler used for the experiments.

0.4 s. The end of the flow tube was attached to the MIESR sampling nozzle, which sampled about 3% of the total gas flow. The rest was vented through a coaxial slit around the nozzle.

The initial concentrations of  $C_2H_4$  and  $O_3$  and the maximum reaction time (see Table 1) were chosen such that less than 0.5% of the reactants was consumed in the flow tube. Under these conditions, reactions of the radicals with themselves or with  $O_3$  were negligible (< 1% of the primary reaction rate), and the OH radicals produced in R2b reacted exclusively with  $C_2H_4$  (R5), thereby producing hydroxyethylperoxy radicals (HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>). In separate experiments, carbon monoxide (purity 99.997%, further purified by passage over iodine/activated charcoal) was supplied together with the  $C_2H_4$  through the movable injector at sufficiently large concentrations to convert > 99% of the OH radicals to HO<sub>2</sub>.

Samples for the MIESR are collected under vacuum (p < 10 - 2 hPa) and at 77 K on a gold-plated cold finger in a polycrystalline matrix formed by the controlled addition of D<sub>2</sub>O. The sample flow (0.2 1/min) is controlled by a critical orifice. Total sample volume is 5 1 (STP). The sampling efficiency as determined for NO<sub>2</sub>, NO<sub>3</sub>, HO<sub>2</sub>, HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> and several other RO<sub>2</sub> is > 95% [15]. The samples are transferred under vacuum and at 77 K into the cavity of a Bruker, Model ESP 300E, ESR spectrometer. The method allows the speciation of NO<sub>2</sub>, NO<sub>3</sub>, HO<sub>2</sub>, CH<sub>3</sub>COO<sub>2</sub>, and the sum of organic peroxy radicals ( $\Sigma$  RO<sub>2</sub>) with a detection limit of 2–3 ppt and an accuracy of ±5%. For further details of the method see Ref. [15]. The radicals are trapped in a D<sub>2</sub>O matrix, which provides sufficient spectral resolution to discriminate between HO<sub>2</sub> and HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> [16].

Table 1 Experimental conditions and measured radical concentrations

Sample No.	$O_3$ (molecules cm <sup>-3</sup> )	Ethene (molecules cm <sup>-3</sup> )	$\Delta t$ (s)	CO (molecules cm <sup>-3</sup> )	O <sub>3</sub> consumption (% of O <sub>3</sub> )	$HO_2$ (molecules cm <sup>-3</sup> )	$RO_2$ (molecules cm <sup>-3</sup> )
1	$6.1 \times 10^{12}$	$8.3 \times 10^{15}$	0.28	0.0	0.3	$7.5 \times 10^{9}$	$3.4 \times 10^{9}$
2	$6.1 \times 10^{12}$	$8.3 \times 10^{15}$	0.15	0.0	0.2	$3.9 \times 10^{9}$	$2.0 \times 10^{9}$
3	$6.0 \times 10^{12}$	$3.3 \times 10^{15}$	0.15	0.0	0.1	$2.2 \times 10^{9}$	$1.0 \times 10^{9}$
4	$5.7 \times 10^{12}$	$3.1 \times 10^{15}$	0.15	$1.4 \times 10^{18}$	0.1	$2.7 \times 10^{9}$	0.0
5	$5.7 \times 10^{12}$	$3.1 \times 10^{15}$	0.28	$1.4 \times 10^{18}$	0.1	$4.9 \times 10^{9}$	0.0
6	$6.0 \times 10^{12}$	$3.3 \times 10^{15}$	0.29	0.0	0.1	$3.5 \times 10^{9}$	$1.7 \times 10^{9}$
7	$6.0 \times 10^{12}$	$3.3 \times 10^{15}$	0.42	0.0	0.2	$5.0 \times 10^{9}$	$2.5 \times 10^{9}$
8	$5.7 \times 10^{12}$	$3.1 \times 10^{15}$	0.40	$1.4 \times 10^{18}$	0.2	$5.9 \times 10^{9}$	0.0
9	$6.3 \times 10^{12}$	$8.8 \times 10^{15}$	0.43	0.0	0.5	$1.1 \times 10^{10}$	$6.3 \times 10^{9}$

## 3. Results and discussion

Fig. 2 shows two typical examples of the ESR-spectra recorded from samples collected in the experiments. In the presence of CO, the ESR spectrum is exclusively due to HO<sub>2</sub> (Fig. 2A). In the samples collected from experiments without the addition of CO (Fig. 2B), the HO<sub>2</sub> signal is reduced and the spectra contain a strong signature from hydroxyethylperoxy radicals HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>. After normalizing to identical reaction conditions, the total peroxy radical concentration (HO<sub>2</sub> and HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>) obtained in the absence of CO agrees within 5% with the HO<sub>2</sub> concentration when CO is present. The hydroxyethylperoxy radicals must have been produced, therefore, by reaction of C<sub>2</sub>H<sub>4</sub> with the OH radicals formed in reaction R2b.

The measured HO<sub>2</sub> and HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> concentrations are plotted in Fig. 3 versus the ozone consumption due to R1. Since the initial concentrations of O<sub>3</sub> and C<sub>2</sub>H<sub>4</sub> changed by less than 0.5% in our experiments, the ozone consumption was not measured but calculated from the reaction time and the initial reaction rate, i.e.  $\int [O_3][C_2H_4]k_1 dt$ . For the rate coefficient  $k_1$ , we adopted the value obtained from Ref. [17], where cyclohexane was added as a scavenger for OH and which is 40% smaller than the currently recommended value. Since the free radicals formed in R1 can react further with the reactants, experiments in which only the disappearance of the educts is monitored tend to overestimate the rate coefficient for R1, if no measures are taken to scavenge the OH radicals.

In the absence of CO, the slopes of the regressions correspond to stoichiometric radical yields of  $39 \pm 3\%$  for HO<sub>2</sub> and  $20 \pm 2\%$  for HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>, which corresponds to the OH yield from R2b. Since one HO<sub>2</sub> molecule is formed in R2b, the branching ratio for R2c is calculated to  $10 \pm 4\%$ , about 2–3 times larger than what was



Fig. 2. (A) ESR spectrum of a sample collected from the reaction of  $C_2H_4 + O_3$  in the presence of excess CO. The sample was measured at 77 K (2 gauss modulation amplitude, 200 gauss scan range, 50 scans averaged). The middle trace shows the HO<sub>2</sub> reference spectrum produced by the reaction of H-atoms with O<sub>2</sub>. Comparison of the two spectra gave a concentration of  $5.9 \times 10^9$  molecules cm<sup>-3</sup>. The lowest trace shows the residuals after subtraction of the reference spectrum from the original spectrum magnified by 100. (B) ESR spectrum of a sample collected from the reaction of  $C_2H_4 + O_3$ . The HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> reference spectrum was produced by the reaction of OH radicals with ethene. The lowest trace shows the residuals after subtraction of the right subtraction of the fitted reference spectra from the original spectrum, magnified by 100. No spectroscopic evidence for biradicals was found in any of the samples.



Fig. 3.  $HO_2$  and  $HOCH_2CH_2O_2$  radical concentrations measured by MIESR during the ozonolysis of ethene plotted versus the time integrated reaction rate of R1 (ozone consumption). Filled and open circles denote the  $HO_2$  concentrations from experiments with and without addition of CO, respectively. Crosses give the  $HOCH_2CH_2O_2$  concentrations from experiments without CO. Error bars include the uncertainties from the determination of the concentrations of  $O_3$  (5%) and  $C_2H_4$  (5–8%) and the residence time in the reactor (5–8%), as well as the measurement accuracy of the MIESR (5%). The regression lines are calculated by minimizing errors in both coordinates. The offsets reflect the uncertainty about the time which is required for complete mixing of the reagents (20 ms).

suggested from indirect experiments [18]. The experiments with CO give an HO<sub>2</sub> yield of  $66 \pm 9\%$ , which confirms the total radical yield of  $59 \pm 5\%$  (HO<sub>2</sub> + OH) from the experiments without CO within the experimental uncertainties.

Because of the increased spectral resolution that is obtained in a  $D_2O$ -matrix, our results unequivocally confirm the formation of HO<sub>2</sub> during the ozonolysis of ethene. The HO<sub>2</sub> yield is significantly larger than that estimated from stable product analysis [10,18]. Part of the difference is due to the fact that we adopt a smaller rate coefficient for R1 in our calculations [17]. With the currently accepted value for  $k_1$ , the radical yields would come out 40% smaller. Loss of radicals to the walls of the flow tube would lead to an underestimate of the radical yields. However, since experiments conducted at different reaction times but comparable O<sub>3</sub> consumption (due to higher [C<sub>2</sub>H<sub>4</sub>]) yield nearly identical results (see Table 1, samples #2 and #6), we conclude that wall losses are negligible.

The formation of OH is strongly implied by the formation of HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> in the experiments without CO and is confirmed by the additional production of HO<sub>2</sub> in the experiments with excess CO. Donahue et al. [7] measured a larger OH yield of  $40 \pm 20\%$ . The large uncertainty in the latter experiment makes it difficult to claim a significant difference to our  $20 \pm 2\%$ . A possible explanation for the difference is that those experiments were conducted at reduced pressure, at which the decomposition of the excited carbonyl oxide is favored because of the less efficient thermalisation [19].

The ESR spectra also provide important information on the structure of the thermalized Criegee intermediate formed in R2a, for which three possible mesomeric structures exist, with the peroxymethylene having the highest and the dioxirane the lowest internal energy.



Only the dioxirane has been identified spectroscopically as a reaction product in the reaction of  $O_3$  with ethene [20], whereas the existence of the peroxy form is suggested from the observed formation of  $H_2O_2$  and

organic peroxides when  $H_2O$  or alcohols are added to the ozonolysis mixture [21–23]. Hatakeyama et al. [19] determined the yield of the thermalized Criegee intermediate at 1013 mbar via reaction with SO<sub>2</sub> (forming  $H_2SO_4$ ) to  $39 \pm 5\%$ .

The ESR spectra (Fig. 2) contain no significant signature besides those from HO<sub>2</sub> and HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>. This rules out the presence of peroxymethylene and methylene bis oxy, which should have a significantly different spectrum. Most important is the absence of a spectral signature at half of the magnetic field. For a bi-radical, as the postulated Criegee intermediate, we expect a forbidden transition ( $\Delta M_s = 2$ ) at half of the magnetic field of the allowed transition [24]. From the absence of such a spectroscopic signature and the estimated relative signal intensities (0.19 because of the higher microwave power that can be used for the forbidden transition), we obtain an upper limit for the possible concentration of the stabilized bi-radical intermediate of 4% of the HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> concentration, which corresponds to <1% of R1. Isomerisation of the thermalized methylene bis oxy to dioxirane in the D<sub>2</sub>O matrix is unlikely due to the low temperature (77 K) and the required energy [6,7].

Theoretical calculations [6,7] have shown that the most likely reaction of the excited intermediate is isomerisation to the vibrationally excited dioxirane, followed by rearrangement to methylene bis oxy, which further decomposes into molecular products such as formic acid,  $H_2$ ,  $H_2O$ , CO and  $CO_2$ . Complete decomposition of the intermediate, however, would be in conflict with the observed formation of  $H_2O_2$  in the presence of water vapor [21–23] and also the formation of  $H_2SO_4$  in the presence of  $SO_2$  [19]. We hence conclude that the most likely form for the stabilized Criegee intermediate is the dioxirane, which was first observed by Ref. [20].

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