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Product study of the $C_2H_5O_2 + HO_2$ reaction in 760 Torr of air at 284–312 K

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Abstract

The title reaction was studied in 1 atmosphere pressure of synthetic air at 284, 298, and 312 K. FTIR spectroscopy was used to identify two products; ethyl hydroperoxide and acetaldehyde. Acetaldehyde was a minor product formed in a yield consistent with that expected from unwanted secondary reactions. In 1 atmosphere pressure of air at 284–312 K the title reaction produces ethyl hydroperoxide in a yield of $(104 \pm 5)\%$ and acetaldehyde in a yield of $(2 \pm 4)\%$. We recommend that in atmospheric models the reaction of $C_2H_5O_2$ with HO₂ radicals be represented by a single-reaction pathway giving C_2H_5OOH . © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Peroxy radicals play a key role in atmospheric chemistry. They are intimately involved in the formation and destruction of ozone and in the photo-oxidation of all organic compounds in the atmosphere. In urban areas organic peroxy radicals, RO_2 , and HO_2 radicals react with NO_x and are part of the chemical cycles that produce unwanted photochemical air pollution, 'smog'. Recognition of the key role of peroxy radical chemistry in the formation of 'smog' has led to many kinetic and mechanistic studies of the reactions of peroxy radicals with NO_x – the gross features of which are now reasonably well understood [1]. At the present time the environ-

mental focus is shifting from local air quality issues to a consideration of impacts on wider geographic scales (regional, national, and global). Global atmospheric chemistry models are under development to assess the impact of man-made emissions on the global atmospheric environment. To provide reliable results, such models must incorporate an accurate description of peroxy radical chemistry. On local scales near to NO_x sources such as large urban areas, the fate of organic peroxy radicals is reaction with NO_{r} . On regional and global scales where the NO_{r} concentrations are lower the chemistry of organic peroxy radicals is no longer dominated by reaction with NO_x. Loss of organic peroxy radicals via reaction with HO₂ radicals become important in air masses remote from pollution sources. Unfortunately, our understanding of the reactions of organic peroxy, RO₂, with HO₂ radicals is far from complete, and incorporation of these reactions into com-

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puter models introduces a significant degree of uncertainty into the model results.

Mechanistic information for reactions of RO_2 with HO_2 radicals is largely confined to room temperature. Such reactions can proceed via two reaction channels giving either hydroperoxide or carbonyl products. The hydroperoxide channel is dominant for reactions of unsubstituted peroxy radicals (e.g., CH_3O_2 [2], CD_3O_2 [3], $C_2H_5O_2$ [4], cyclo- $C_5H_9O_2$ [5], cyclo- $C_6H_{11}O_2$ [5], and $(CH_3)_3CCH_2O_2$ [6]) with HO_2 . The carbonyl channel is generally important, and can be dominant, for peroxy radicals carrying electron withdrawing substituents (e.g., CH_2FO_2 [7], CH_2CIO_2 [8], $CHCI_2O_2$ [9], $CH_3OCH_2O_2$ [10]). There is no information concerning the effect of temperature on the branching ratio of such reactions.

The kinetics of the reaction of $C_2H_5O_2$ with HO₂ radicals have been the subject of 4 separate studies [11–14] and are reasonably well established. The overall reaction proceeds with a rate constant of approximately 8×10^{-12} cm³ molecule⁻¹ s⁻¹ at room temperature. Measurements between 210 and 480 K show that the reaction has a negative temperature dependence with reported E_a/R values of between -650 K and -1260 K. The kinetic studies suggest, but do not prove, that the reaction occurs by a single mechanism over the range of atmospherically relevant temperatures (200–300 K). The two possible products of reaction (1) are ethylhydroperoxide and acetaldehyde:

$$C_2H_5O_2 + HO_2 \rightarrow C_2H_5OOH + O_2$$
(1a)

$$C_2H_5O_2 + HO_2 \rightarrow CH_3CHO + H_2O + O_2 \qquad (1b)$$

In 20 – 700 Torr of air at 295 K it has been reported that the reaction of $C_2H_5O_2 + HO_2$ produces ethylhydroperoxide in a yield of $102 \pm 6\%$ [4] indicating that under these conditions reaction (1) proceeds predominately, if not exclusively, via pathway (1a). To study the effect of temperature we have used FTIR – smog chamber techniques to measure the products of reaction (1) at 284–312 K in 1000 mbar of air. Results are reported herein.

2. Experimental

Experiments were performed in Wuppertal using a 1080-liter quartz glass reactor equipped with a

long-path mirror system and a Bruker IFS 88 FTIR spectrometer [15]. $C_2H_5O_2$ and HO_2 radicals were generated by the near-UV irradiation of $C_2H_6/$ CH₃OH/Cl₂ mixtures in 1000 mbar of air diluent at 284, 298, or 312 K.

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

$$Cl + C_2H_6 \rightarrow C_2H_5 + HCl$$
(3)

$$C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$$
 (4)

$$CH_3OH + Cl \rightarrow CH_2OH + HCl$$
 (5)

$$CH_2OH + O_2 \rightarrow HO_2 + HCHO$$
 (6)

The decay of ethane and the formation of products were analyzed using FTIR spectroscopy with an optical pathlength of 484.7 m and a spectral resolution of 1 cm^{-1} . Infrared spectra were derived from 64 co-added interferograms. Ethane (99.95%) and synthetic air were purchased from Messer-Griessheim. The air was dried using a Messer-Griessheim Hydrosorb absorption tube. Methanol was purchased from Fluka and had a stated purity of > 99.8%. Reference spectra of C₂H₆, CH₃OH, and CH₃CHO were acquired by introducing authentic samples into the reaction chamber using calibrated volumes. The reference spectrum of ethyl hydroperoxide was taken from the library at Ford, $\sigma(842 \text{ cm}^{-1}) = 3.3 \times 10^{-18}$ cm² molecule⁻¹. Reactants and products were monitored by comparing calibrated reference spectra over the range 700–900 cm^{-1} with the recorded spectra. Initial concentrations of the gas mixtures were: $[C_2H_6] = 2, 4 \text{ or } 8 \times 10^{14}, [CH_3OH] = 7-8 \times 10^{14},$ and $[Cl_2] = 4 \times 10^{14}$ molecule cm⁻³ in 1000 mbar of air. The mixtures were irradiated for 4-21 min resulting in ethane consumptions of 6-36%.

3. Results

Following the UV irradiation of $C_2H_6/CH_3OH/Cl_2/air$ mixtures reactions (1) and (7) compete for the available $C_2H_5O_2$ radicals.

$$C_2H_5O_2 + HO_2 \rightarrow \text{products} \tag{1}$$

$$C_2H_5O_2 + C_2H_5O_2 \rightarrow \text{products} \tag{7}$$

Fortunately, the rate constant for reaction (1) is more than two orders of magnitude larger than that for reaction (7) $(k_1 = 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1};$ $k_7 = 5.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [16] at 298 K) and it is relatively straightforward to establish conditions where reaction (1) is the dominant fate of $C_2H_5O_2$ radicals. In the present work three sets of experiments (using $[CH_3OH]_o/[C_2H_6]_o = 1, 2, \text{ or } 4$) were performed at each of three different temperatures (284, 298, or 312 K). Using the Acuchem chemical kinetic modeling package [17] with the chemical mechanism given in Table 1 it can be calculated that for experiments employing $[CH_3-OH]_o/[C_2H_6]_o = 1, 2, \text{ or } 4$, reaction with HO₂ radicals accounts for 90.7, 98.6 or 99.6% of the loss of the $C_2H_5O_2$ radicals, respectively.

Fig. 1 shows typical IR spectra acquired before (A) and after (B) a 6.5 min irradiation of a mixture containing 3.65×10^{14} molecule cm⁻³ C₂H₆, 6.92 $\times 10^{14}$ molecule cm⁻³ CH₃OH, and 4×10^{14} molecule cm⁻³ Cl₂ in 1000 mbar of air at 284 K. Panel C shows the result of subtracting features attributable to C₂H₆ from panel B. Comparison of panel C with the reference spectra of C₂H₅OOH and CH₃CHO given in panels D and E shows the formation of these products. As with all product studies, careful attention needs to be paid to possible secondary chemistry in the system. To check for possible heterogeneous losses of C_2H_5OOH and CH₃CHO in the chamber, reaction mixtures were allowed to stand in the dark at 284 and 298 K for 30 min: there was no observable loss (< 2%) of either C_2H_5OOH and CH_2CHO . Fig. 2 shows a plot of the

Table 1

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Reaction mechanism
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Fig. 1. IR spectra acquired before (A) and after (B) a 6.5 min irradiation of a mixture containing 3.65×10^{14} molecule cm⁻³ C₂H₆, 6.92×10^{14} molecule cm⁻³ CH₃OH, and 4×10^{14} molecule cm⁻³ Cl₂ in 1000 mbar of air at 284 K. Panel C shows the result of subtracting features attributable to C₂H₆ from panel B. Reference spectra of C₂H₅OOH and CH₃CHO are given in panels D and E.

observed formation of C_2H_5OOH and CH_3CHO versus the loss of C_2H_6 following the irradiation of $C_2H_6/CH_3OH/Cl_2/air$ mixtures.

Rate constant $[cm^3 molecule^{-1} s^{-1}]$	Reference
5.7×10^{-11}	[18]
5.4×10^{-11}	[19]
8.0×10^{-12}	[16]
4.0×10^{-14}	[16]
1.9×10^{-14}	[16]
8.0×10^{-15}	[20]
2.9×10^{-12}	[18]
7.8×10^{-11}	[19]
9.8×10^{-11}	[21,22] ^a
9.0×10^{-12}	[21,22] ^a
	Rate constant [cm ³ molecule ⁻¹ s ⁻¹] $6.0 \times 10^{-4} s^{-1}$ 5.7×10^{-11} 5.4×10^{-11} 8.0×10^{-12} 4.0×10^{-14} 1.9×10^{-14} 8.0×10^{-15} 2.9×10^{-12} 7.8×10^{-11} 9.8×10^{-11} 9.0×10^{-12}

^aKinetic data from [21], mechanistic data by analogy to C₂H₅OH [22].



Fig. 2. Plot of the observed formation of C_2H_5OOH (filled symbols) and CH_3CHO (open symbols) versus the observed loss of C_2H_6 , curves are second order fits to aid visual inspection of the data trends.

The product data in Fig. 2 contain information concerning the branching ratio for reaction (1). To extract such information appropriate allowance must be made for two factors. First, it should be recognized that while the loss of C_2H_6 provides an accurate value for the amount of $C_2H_5O_2$ radicals formed in the system, not all of these $C_2H_5O_2$ radicals react with HO₂. As discussed above for the experiments using $[CH_3OH]_0/[C_2H_6]_0 = 1, 2, \text{ or } 4,$ reaction with HO₂ radicals accounts for 90.7, 98.6, or 99.6% of the loss of the C₂H₅O₂ radicals. Hence, the observed loss of C_2H_6 must be multiplied by either 0.907, 0.986, or 0.996 to obtain the amount of $C_2H_5O_2$ radicals which are lost via reaction (1). Second, and more importantly, the effect of secondary reactions of Cl atoms with C₂H₅OOH and CH₂CHO needs to be considered. The curvature shown in the yield plots in Fig. 2 indicate that C_2H_5OOH is consumed and CH_3CHO is produced by secondary reactions in the system. It is well established that Cl atoms react rapidly with both $C_{2}H_{5}OOH$ and $CH_{3}CHO$. Fortunately, the kinetics and mechanism of these reactions (and of the competing losses of Cl atoms via reaction with C_2H_6 and CH₃OH) are well understood and their effect can be explicitly calculated for each experiment using the chemical mechanism in Table 1.

Fig. 3 shows the result of taking the data in Fig. 2 correcting the observed C_2H_6 loss for that fraction which does not react with HO₂ radicals and correcting the observed C₂H₅OOH and CH₃CHO product vields for the effect of secondary reactions with Cl atoms. At this point it should be stressed that the chemical mechanism in Table 1 used to compute the corrections is taken entirely from the literature and has not been adjusted in anyway to 'fit' the data trend shown in Fig. 2. It is gratifying that corrections calculated using the chemical mechanism in Table 1 account for the curvature in Fig. 2 and result in the linear plots shown in Fig. 3. As seen from Fig. 3 within the experimental uncertainties there is no discernable effect of temperature, [CH₃OH]₀/ $[C_2H_6]_0$ concentration ratio, or consumption of C_2H_6 upon the product yields. The lines through the data in Fig. 3 are linear least squares fits which give yields of $(104 \pm 5)\%$ for C₂H₅OOH and $(2 \pm 4)\%$ for acetaldehyde and provide values of $k_{1a}/(k_{1a} +$ k_{1b}) = 1.04 ± 0.05 and $k_{1b}/(k_{1a} + k_{1b}) = 0.02 \pm$ 0.04 at 284-312 K. Quoted errors are 2 standard deviations from the linear least-squares analysis.



Fig. 3. Plot of the observed formation of C_2H_5OOH (filled symbols) and CH_3CHO (open symbols) corrected for secondary reactions involving Cl atoms (see text) versus the observed loss of C_2H_6 , corrected for the fraction which does not react with HO₂ radicals. Experiments were conducted in 1000 mbar of air diluent at either 284 (squares), 298 (circles), or 312 K (triangles).

4. Discussion

The aim of the present work was to provide mechanistic information to facilitate the accurate representation of reactions of alkyl peroxy radicals with HO₂ radicals in atmospheric models. Within the admittedly limited temperature range employed in the present work, there was no evidence for any effect of temperature on the products, and hence mechanism, of reaction (1). For purposes of atmospheric modeling, we recommend that the reaction of $C_2H_5O_2$ with HO₂ radicals should be represented by a single-reaction pathway giving hydroperoxide at all temperatures. A similar recommendation has been made recently for the reaction of CH_3O_2 with HO_2 radicals [16]. In the absence of information to the contrary, it seems reasonable to extend this recommendation to the reaction of all unsubstituted alkyl peroxy radical reactions with HO₂. It should be noted that substituted peroxy radicals such as CH_2CIO_2 , $CH_3C(O)O_2$, and $CH_3OCH_2O_2$ are well known to react with HO₂ via two reaction channels. Further work is needed to establish the temperature dependence of the branching ratios of such reactions.

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