RATE COEFFICIENT FOR THE REACTION OH + HO$_2$ = H$_2$O + O$_2$ AT 1 ATMOSPHERE PRESSURE AND 308 K

R.A. COX, J.P. BURROWS and T.J. WALLINGTON *

Environmental and Medical Sciences Division, AERE, Harwell, Oxfordshire, OX11 0RA, UK

The rate coefficient for the reaction OH + HO$_2$ = H$_2$O + O$_2$ has been determined from measurements of the steady-state absorption of HO$_2$ at 210 nm, in low-frequency square-wave modulated photolysis of O$_3$ + H$_2$O mixtures. The value obtained was $(9.9 \pm 2.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 308 K and 1 atm pressure.

1. Introduction

The kinetics of the reaction

$$OH + HO_2 = H_2O + O_2 \qquad (1)$$

have been the subject of numerous studies over a number of years. Measurement of the rate coefficient is experimentally difficult and there remains substantial disagreement between the apparent value of k_1 obtained at high pressure (1 atm) [1—4] and the value from low-pressure flow systems [5—8]. In view of the importance of this reaction in atmospheric chemistry and in combustion, an understanding of the kinetics of this reaction is of high priority.

We have recently reported [9] an extensive study of the photolysis at 254 nm of dilute ozone—water vapour mixtures, in which reaction (1) plays an important kinetic role. The molecular modulation technique was used to monitor OH and HO$_2$ by UV absorption. A value of $k_1 = (6.2^{+4.0}_{-2.0}) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was obtained by computer fitting the in-phase and in-quadrature components of modulated absorption. However there was considerable uncertainty in k_1 because of problems encountered in describing the data accurately over all time periods, and the inability to observe directly the steady state of HO$_2$, which is required to determine k_1 from this

system. We have now developed a novel multichannel detection system for the molecular modulation spectrometer, in which the fully time-resolved waveform for absorption during a low-frequency modulated photolysis cycle is recorded. This greatly facilitates the extraction of kinetic information, particularly in situations of complex kinetic behaviour, such as for radical + radical reactions. The application of this system for the determination of k_1 from measurements of HO$_2$ in O$_3$ + H$_2$O photolysis is reported here.

2. Experimental

Gaseous mixtures of O$_3$, H$_2$O and O$_2$, diluted in either He, Ar, or N$_2$ at 1 atm pressure flowed through the 120 cm × 2.5 cm jacketed silica reaction vessel which was illuminated by square-wave modulated 254 nm light from up to three 40W low-pressure Hg lamps (Philips T-UV 40). Absorption was monitored on a beam from a D$_2$ lamp, which traversed the long axis of the cell before dispersion on a Spex "Doublemate" monochromator and detection with a photomultiplier. The details of the arrangement have been given before [10].

In the present work, the photocurrent was digitised and fed to an internally preprogrammed microcomputer (Harwell type 65380 MOUSE) controlled externally through a CBM PET 3032. A $\tau/200$ s gate in MOUSE divided the signal waveform during each suc-

* Present address: Department of Physical Chemistry, University of Oxford, Oxford, UK.

cessive photolysis cycle (period = τ s) into 200 channels which were stored separately in a buffer memory After signal accumulation over a preset time, the memory contents were transferred to the PET and displayed This process was repeated until sufficient signal averaging had been achieved. Baseline correction and calculation of absorption from a separately recorded reference signal was then carried out on-line using stored calibration data The minimum gating time was 1 ms, determined by the speed of operating instructions in MOUSE. The noise level in a single channel was equivalent to 1 5 X 10^{-4} absorption units from a 1800 s averaging time, after correction for the relative large baseline changes due to O_3 absorption

O_3 was generated by silent electrical discharge in a flow of pure O_2 and mixed flows of dry and H_2O-saturated carrier gas to achieve the required gas composition All experiments were conducted at 1 atm pressure and 308 K

3 Results

Fig 1 shows a profile of absorption versus time for

HO_2 monitored at 210 nm during the 1 Hz square-wave modulated photolysis of an O_3–H_2O–O_2–He mixture On photolysis, HO_2 absorption rises rapidly ($t_{0.5}$ = 15 ms) to a constant steady-state value When the lamps switch off a slower decay ($t_{0.5}$ = 75 ms) of HO_2 occurs. Since the photolysis period is finite, HO_2 does not decay to zero; only the change in HO_2 concentration during the cycle is detected.

The following reactions describe the production of OH and HO_2 in this system.

$$O_3 + h\nu = O(^1D) + O_2(^1\Delta), \tag{2}$$

$$O(^1D) + H_2O = 2OH, \tag{3}$$

$$OH + O_3 = HO_2 + O_2 \tag{4}$$
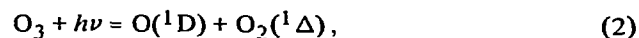
Removal of HO_2 and OH occurs principally via reaction (1) In our previous work it was shown that at photolysis periods $\tau \geqslant 0$ 2 s OH absorption exhibited a square waveform consistent with its removal by reactions (4) and (1) with a lifetime of 2–4 ms under the experimental conditions in fig 1 Thus OH is to a good approximation in steady state throughout the "lamp on" period and almost zero during the "lamp off" period Removal of HO_2 also occurs via the
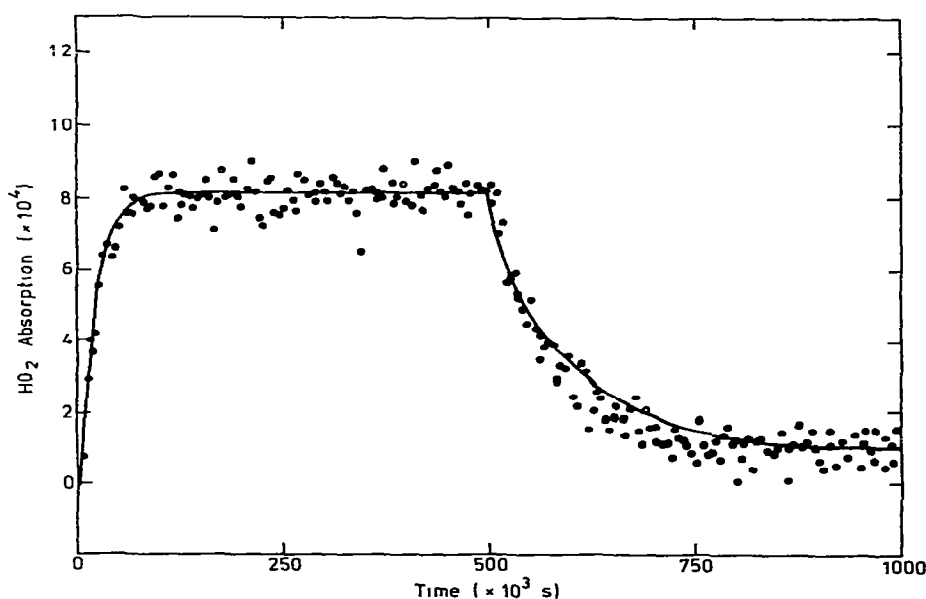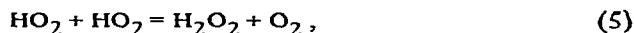

Fig 1 Absorption—time profile for HO_2 monitored at 210 nm in a 1 lamp photolysis at 254 nm of 3 5 X 10^{15} molecules cm^{-3} O_3 in the presence of 9 2 X 10^{16} molecules cm^{-3} H_2O in 1 atm He Modulation frequency· 1 Hz Averaging time 1800 s Full line shows curve fitted using k_1 = 9 0 X 10^{-11} cm^3 $molecule^{-1}$ s^{-1} and k_5 = 2 9 X 10^{-12} cm^3 $molecule^{-1}$ s^{-1}

slower reactions

$$HO_2 + HO_2 = H_2O_2 + O_2 , \qquad (5)$$

$$HO_2 + O_3 = OH + 2O_2 , \qquad (6)$$

and these dominate the decay in the dark, when OH is at very low concentration

For the limiting case when $k_1[OH] \gg k_5[HO_2] + k_6[O_3]$, the following expression may be obtained for the steady-state HO_2 absorption, A_{ss}.

$$A_{ss} = \sigma i[HO_2] = \sigma l k_4[O_3]/k_1 \qquad (1)$$

Fig 2 shows a plot of A_{ss} as determined from data such as in fig 1 against the average O_3 concentration present in the cell for experiments with different initial $[O_3]$ The extent of O_3 loss in the cell due to photodissociation and attack by OH and HO_2 was normally $\approx 30\%$ The HO_2 absorption showed a linear dependence on O_3 as required by eq. (1) The slope of the line through the origin gives $k_4/k_1 = 5.6 \times 10^{-4}$ using $\sigma(HO_2) = 4.3 \times 10^{-18}$ cm^2 at 210 nm [11] The con-

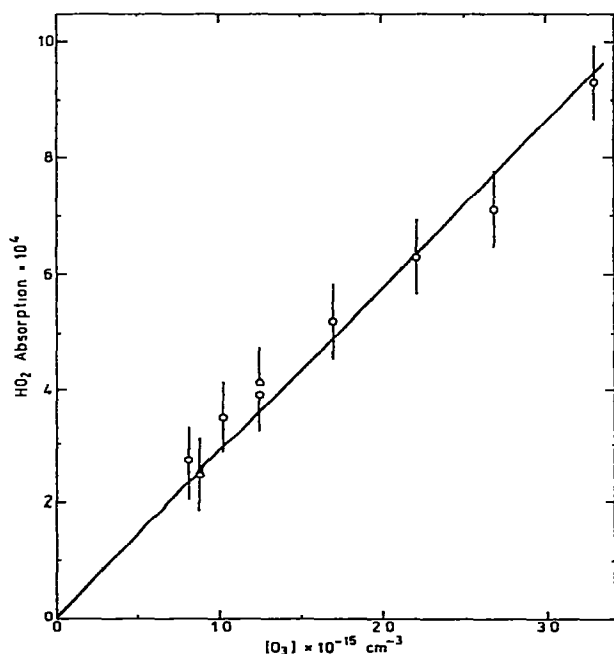sensus value for k_4 at 308 K $(7.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} [12]) then yields a value of $k_1 = 1.28 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at this temperature.

This value of k_1 must be considered an upper limit since (a) the steady-state absorption of HO_2 is underestimated from the data due to the residual HO_2 present at the end of a cycle, and (b) other reactions such as (5) and (6) could have a significant effect on the HO_2 steady state and hence on the value determined for k_4/k_1. The uncertainty introduced from these approximations was eliminated by computer simulation of the absorption—time curves. The Harwell programme FACSIMILE [13] with an associated non-linear least-squares fitting routine was used to integrate the kinetic equations generated from the reaction mechanism shown in table 1 and obtain "best fit" values of the rate coefficient k_1. All other rate coefficients were taken from recent reviews [12,14] except for k_5 which was either fixed at 2.2×10^{-12} cm^3 molecule^{-1} s^{-1} or fitted in the calculation.

A summary of the values of k_1 obtained from 37 experiments with varying light intensity, H_2O, O_3 and diluent gas is given in table 2. In all cases the absorp-

Fig. 2. Plot of steady-state HO_2 absorption obtained from HO_2 modulation observed during 1 Hz modulated, 3 lamp photolysis of O_3–H_2O–He mixtures, against O_3 concentration $[H_2O] = 3.5 \times 10^{17}$ molecules cm^{-3}.

Table 1
Mechanism of ozone—water vapour photolysis

Reaction	Rate coefficient at 308 K (cm^3 molecule^{-1} s^{-1})
$O_3 + h\nu = O(^1D) + O_2(^1\Delta)$	$2.2(-2)$[a](s^{-1})
$O_3 + h\nu = O(^3P) + O_2$	$2.2(-3)(s^{-1})$
$O(^1D) + O_2 = O(^3P) + O_2(^1\Sigma)$	$4.0(-11)$[b]
$O(^1D) + H_2O = 2OH$	$2.2(-10)$
$OH + O_3 = HO_2 + O_2$	$7.2(-14)$
$OH + H_2O_2 = H_2O + HO_2$	$1.6(-12)$
$OH + HO_2 = H_2O + O_2$	see text
$OH + OH = O(^3P) + H_2O$	$1.8(-12)$
$OH + OH + M = H_2O_2 + M$	$7.5(-12)$[b]
$HO_2 + HO_2 = H_2O_2 + O_2$	see text
$HO_2 + O(^3P) = OH + O_2$	$4.0(-11)$
$HO_2 + O_3 = OH + 2O_2$	$1.6(-15)$
$O(^3P) + O_2 + M = O_3 + M$	$7.6(-15)$[b]
$O_2(^1\Delta) + O_2 = 2O_2$	$1.7(-18)$
$O_2(^1\Delta) + O_3 = O(^3P) + 2O_2$	$4.5(-15)$
$O_2(^1\Sigma) + M = O_2 + M$	$5.0(-16)$
$O_2(^1\Sigma) + O_3 = O(^3P) + 2O_2$	$1.8(-11)$

[a] Photolysis rate determined as described in ref. [9].
[b] For experiments with N_2 or Ar present, rate coefficients for three-body reaction with M = N_2 or Ar and quenching of $O(^1D)$ by N_2 were used.

Table 2

Rate coefficients for reaction $OH + HO_2 = H_2O + O_2$ from computer simulations

Diluent gas [a]	Lamps	$10^{-17}[H_2O]$ (molecule cm^{-3})	$10^{11}k_1$ (cm^3 molecule^{-1} s^{-1})
He(14)	3	0 39–5 35	9 3 ± 1.4
He(15)	1	0 39–5 35	9 8 ± 1 6
He(10)	1 3	0 39–1.0	8 8 ± 1 7
He(12)	1 3	2 0–5 35	10.2 ± 1.3
Ar(4)	1 3	0 76–1 66	10 7 ± 1 3
N$_2$(4)	1 3	3 09–5 38	11 8 ± 2.8

[a] Number of experiments shown in parentheses

tion—time data were well described over the entire cycle including the rise and fall to and from the steady state, as is illustrated in fig 1. The fitted values of k_1 were well defined, typically with statistically derived 95% confidence limits of ±9%, and showed no systematic variation with any of the experimental variables The mean value of $(9\ 9 ± 1\ 7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} is however ≈25% lower than that calculated from the HO$_2$ steady state plotted in fig 2 The computed residual HO$_2$ absorption was ≈8 × 10^{-5}, i e. 9% and 28% respectively of the highest and lowest observed steady-state absorption Clearly the higher value of k_1 obtained from the analysis using eq (1) arises in large part from an underestimation of the true steady state from the absorption—time profiles The remaining difference between the values of k_1 obtained from the two methods is due to the neglect of other HO$_2$ loss processes For the conditions of the experiment at the highest [O$_3$] plotted in fig 2, the effective loss rate for HO$_2$ in steady state by reaction with OH, HO$_2$, O$_3$ and O(^{3}P) were 75, 8.2, 5.2 and 2 6 s^{-1}, showing that loss by routes other than reaction (1) were minor but significant

The fitted values of k_5 were much less well defined than k_1, the statistical confidence limits being typically ± a factor of 2 The values ranged from $2\ 5 \times 10^{-12}$ to $8\ 0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} with a mean of $4\ 4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} This is a factor of 2 higher than the value measured at 308 K and with 3 Torr H$_2$O present [9], i.e. 2.2×10^{-12} cm^3 molecule^{-1} s^{-1}, and this is believed to arise from the approximation used to correct the waveform for underlying absorption due to O$_3$ in the present work. The correction is made assuming that O$_3$ consumption occurs only during illumination but non-negligible con-

tribution from reaction (6) during HO$_2$ decay leads to a higher apparent HO$_2$ decay rate during the dark period, after correction Since the fitted value of k_5 is largely determined by this part of the waveform, the value is too high. The fitted value of k_1 was, however, not sensitive either to the value of k_5 used in the simulation or to the absorption—time data during HO$_2$ decay. The error in k_1 arising from these factors is therefore small

The other uncertain aspect of the chemistry of this system is the reactions governing O(^{3}P), since the excited molecular states of O$_2$ are involved However it was found that the fitted value of k_1 was insensitive to the rate of the reaction O(^{3}P) + HO$_2$ = OH + O$_2$, because it does not constitute an overall sink for HO$_x$ radicals The parameters upon which k_1 is largely dependent are σ(HO$_2$), k_4 and the measured [O$_3$] The overall uncertainty, including errors on these parameters, is estimated to be ±25% The resultant value of k_1 is therefore

$$k_1 = (9\ 9 ± 2.5) \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

at 308 K

4 Discussion

The value of k_1 obtained in this study is in excellent agreement with recent values near $1\ 0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} obtained from investigations conducted at high pressures using steady-state photolysis [1,2], flash photolysis [3] and pulse radiolysis [4]. It is, however, significantly higher than the range 2×10^{-11} to 5×10^{-11} cm^3 molecule^{-1} s^{-1} favoured by Chang and Kaufman [7] in their strongly argued

paper based on a number of low-pressure discharge flow experiments conducted by themselves and others [5,6] and also on simple rate theory. However, the most recent discharge flow experiments [8,15] give values near 6×10^{-11} cm^3 molecule^{-1} s^{-1}, indicating that some of the earlier work was in error

All the determinations of k_1 to date are to a certain extent indirect, inasmuch as numerical modelling techniques and rate coefficients for competing reactions are required to obtain the value of k_1 The kinetic behaviour of HO_2 and OH in the O_3 + H_2O photolysis system has been well characterised in our previous study [9] and this lends confidence that the analysis presented above is soundly based and that k_1 is well defined by the measurements

Recent studies of the analogous atom-transfer reactions HO_2 + HO_2 = H_2O_2 + O_2 and HO_2 + ClO = $HOCl$ + O_2 have shown that these reactions exhibit abnormal pressure and temperature dependences, indicative of the involvement of a short-lived intermediate complex. The possible involvement of complex formation in the OH + HO_2 reaction cannot be ruled out, particularly if the difference between the low- and high-pressure results is real, and k_1 is pressure dependent. Since the theoretical understanding of this type of process is incomplete, prediction of the temperature and pressure dependence of k_1 cannot be soundly based and experimental determination of the effect of these variables is urgently needed

The multichannel detection technique for molecular modulation combined with numerical simulation appears to offer considerable promise for investigation of radical + radical reactions in photochemical systems by kinetic spectroscopy. In future work it is planned to investigate other reactions of HO_2 and OH with radical species.

References

[1] W B. DeMore and E Tschuikow-Roux, J. Phys. Chem 78 (1974) 1447
[2] W B DeMore, J Phys. Chem 83 (1979) 1113
[3] C J Hochanadel, T J Sworski and P J Ogren, J. Phys. Chem 84 (1980) 3274
[4] R.R Lu, R A. Gorse, M C. Sauer Jr. and S Gordon, J. Phys Chem 84 (1980) 819.
[5] J P. Burrows, G W. Harris and B A. Thrush, Nature 267 (1977) 233
[6] W Hack. A.W Preuss and H G. Wagner, Ber. Bunsenges. Physik. Chem 82 (1978) 1167.
[7] J S Chang and F. Kaufman, J. Phys. Chem. 82 (1978) 1683
[8] B A Thrush and J P T Wilkinson, Chem. Phys. Letters 81 (1981) 1
[9] J P Burrows, R A. Cox and R G Derwent, J. Photochem 16 (1981) 147.
[10] R A Cox, R G. Derwent, A.E J Eggleton and H.J. Reid, J. Chem Soc. Faraday I 75 (1979) 1648.
[11] T T. Paukert and H.S Johnston, J Chem. Phys. 56 (1972) 2824.
[12] D L. Baulch, R.A Cox, R F Hampson Jr, J.A. Kerr, J Troe and R.T. Watson, J. Phys Chem Ref. Data 9 (1980) 295
[13] E.M. Chance, A R Curtis and C.R. Kirby, AERE Report R-8775 (1977)
[14] R F. Hampson Jr and D Garvin, eds, Reaction Rate and Photochemical Data for Atmospheric Chemistry (1977), NBS Special Publication 513 (1978)
[15] L F Keyser, J Phys Chem, to be published