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Journal of Photochemistry and Photobiology A: Chemistry 157 (2003) 275–281

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Laboratory investigation of the photooxidation of formaldehyde combining FTIR analysis of stable species and HO_2 detection by the chemical amplifier technique

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Received 3 June 2002; received in revised form 11 December 2002; accepted 6 January 2003

Abstract

The photodissociation of formaldehyde in air at one atmosphere pressure and room temperature has been investigated in a 977 L photoreactor by in situ analysis of stable species by FTIR absorption spectroscopy and of peroxy radicals, HO_2, by the chemical amplifier technique, after sampling. The photodissociation coefficient of the channel $H_2CO + h\nu\ (+O_2) \rightarrow 2\,HO_2 + CO$ (1) determined experimentally was found consistent with that calculated from the absorption spectrum of H_2CO and the spectral distribution of the photolysis light. The rate constant k_{-3} of the thermal decomposition of the adduct formed in the reaction $HO_2 + H_2CO \leftrightarrow HOCH_2O_2$ (3, −3) was determined and found at the lower limit of the range of the literature values. This study confirms the potentiality of the chemical amplifier technique in combination with other analytical techniques to investigate chemical mechanisms of atmospheric interest in photoreactors.

Keywords: FTIR analysis; 2,4-Dinitrophenylhydrazine; EDTA

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1. Introduction

Photooxidation of formaldehyde has been recognized for a long time to be important in both the polluted and natural troposphere, as a source of HO_2 radicals, a component of the HO_x (OH, HO_2) radicals which control the oxidation processes and ozone formation. Photooxidation of formaldehyde has also been recently suggested to contribute to additional HO_x sources in the upper troposphere as a result of convective injection of lower tropospheric formaldehyde or its precursors like acetone (e.g. [1] and ref. therein). The HO_2 radicals are produced in the radical channel (1) of the H_2CO photolysis which compete with the molecular channel (2):

$$H_2CO + h\nu(+O_2) \rightarrow 2HO_2 + CO \quad (1)$$

$$H_2CO + h\nu \rightarrow H_2 + CO \quad (2)$$

The recommended quantum yields [2] indicate that the radical channel (1) increases in importance from 340 nm ($\Phi_1 = 0$) to become dominant at wavelengths shorter than 320 nm. These quantum yields have been derived from continuous or pulsed photolysis experiments where the CO and H_2 end product yields were measured [3–7]. The relative quantum yield for the production of radical products, H and HCO (channel (1)), have been very recently measured directly using chemical amplification with subsequent detection by chemical ionisation mass spectrometry [8]. Photolysis experiments have also provided information on the reaction of HO_2 with H_2CO which occurs in the laboratory in the presence of concentrations of H_2CO higher than a few ppm. This reaction produces formic acid, HCOOH, following the mechanism:

$$HO_2 + H_2CO \leftrightarrow HO_2CH_2O \leftrightarrow HOCH_2O_2 \quad (3,–3)$$

$$HOCH_2O_2 + HOCH_2O_2 \rightarrow 2HOCH_2O + O_2 \quad (4)$$

$$HOCH_2O_2 + NO \rightarrow HOCH_2O + NO_2 \quad (5)$$

$$HOCH_2O + O_2 \rightarrow HCOOH + HO_2 \quad (6)$$

This mechanism has been investigated in photoreactors with continuous irradiation and in situ monitoring of the stable

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doi:10.1016/S1010-6030(03)00066-2

species by infrared absorption [9–12], and in a pulsed photolysis study with in situ NO_2 monitoring by UV absorption [13]. In further pulsed and modulated photolysis studies [14,15], this chemical system has been more completely characterized by in situ monitoring of the peroxy radical intermediates HO_2 and $HOCH_2O_2$ using either UV absorption spectroscopy for both species [14] or UV absorption and laser diode infrared absorption spectroscopy for $HOCH_2O_2$ and HO_2, respectively [15]. Another study has to be mentioned where the HO_2 and $HOCH_2O_2$ radical concentrations where measured by ESR spectroscopy after cryo-trapping [16]. These different studies have led to recommended values for the rate constants of reactions 3 and −3, but with still significant uncertainties, specially for reaction −3.

In this paper we report a study of the photooxidation of formaldehyde in air at atmospheric pressure using a large volume photoreactor, with both in situ analysis of stable products by FTIR, and of peroxy radicals using the chemical amplifier technique. This latter has been essentially developed so far by several groups including ours for field measurements of peroxy radicals. The aims of the present work were to test the validity of the results given by the chemical amplifier used by deriving from the experiments photochemical and kinetic data for the photooxidation of formaldehyde consistent with the existing ones.

2. Experimental

The experimental set up combined the photoreactor of the LISA laboratory in Paris with the chemical amplifier developed at the CNRS-LCSR laboratory in Orléans.

2.1. Photoreactor

The photoreactor of LISA has been described previously [17]. It consists of a 977 L Pyrex glass tube (45 cm diameter, 6 m length) and aluminum alloy end flanges. The reactor is equipped with 40 fluorescent lamps centered on 360 nm (Philips TL03) and 40 centered on 420 nm (Philips TL05). The analytical system includes and infrared (FTIR) absorption spectroscopy, and HPLC for carbonyls analysis after sampling in the reactor. The FTIR system, used in this work, comprises a multireflection White mirrors mounted in the reactor and a FTIR spectrometer (Bomem DA8-ME). The optical path which can be adjusted from 12 to 672 m was set up at 156 m for these experiments.

For this study, the light intensities in the chamber were determined in a separate set of experiments using NO_2 photolysis. NO_2 was introduced in the chamber and photolyzed under the same conditions as those used during H_2CO photolysis experiments. NO_2, NO and ozone were monitored and the photolysis frequency of NO_2 (J_{NO_2}) was derived by fitting the experimental and calculated concentration-time curves. The obtained J_{NO_2} value was found equal to $(2.87 \pm 0.12) \times 10^{-3}\,s^{-1}$. These uncertainties are determined during the FACSIMILE software fitting procedure. After having determined the best value for the constant by fitting, the solver makes some further iterations by slightly modifying each fitted constant in order to estimate the sensitivity of the fit. Using this information, it calculates final uncertainties for a confidence range of 95%. Errors on the fitted date, i.e. errors due to the quantification of NO_2, NO and ozone in infrared spectra are taken into account in this procedure. To obtain the actinic flux spectrum, the relative emission spectrum inside the chamber was recorded using a LiCOR 1800 spectroradiometer and scaled to give the experimental J_{NO_2} (see Fig. 1).

The infrared spectra of HCHO and HCOOH were calibrated by flushing known amounts of the vapor of these compounds (determined by measuring the pressure into a calibrated 0.55 L Pyrex bulb) into the chamber. For HCHO sample were taken in 2,4-dinitrophenylhydrazine solution and their derivatized products were analyzed using HPLC following the method described by Kuwata et al. [18], NO, NO_2 and ozone spectroscopic parameters were taken from the HITRAN database [19]. The integrated band intensities (IBI–neperian logarithm) used for these compounds were $(3.03 \pm 0.13) \times 10^{-17}\,cm^2$/molecule between 3000 and 2630 cm^{-1}, for HCHO, and $(3.39 \pm 0.2) \times 10^{-17}\,cm^2$/molecule between 1160 and 1050 cm^{-1} for HCOOH.

2.2. Chemical amplifier

The chemical amplifier described here was developed in our laboratory. Similarly to those built to determine peroxy radical concentrations in the atmosphere [20–22], it follows the principle established by Cantrell and Stedman [20]. The chemical amplification technique relies on the HO_x-catalyzed conversion of NO into NO_2 in the presence

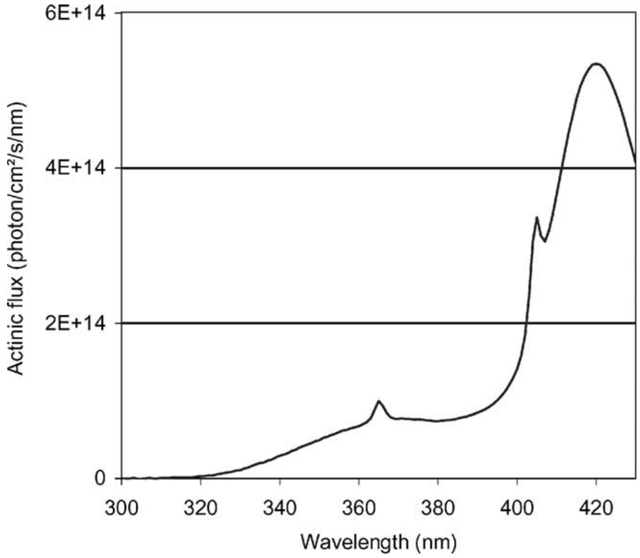

Fig. 1. J_{NO_2} scaled emission spectrum of photolysis lamps inside the chamber (actinic flux) in the range 300–430 nm.

of CO by the following reaction cycle:

$$HO_2 + NO \rightarrow NO_2 + OH$$

$$OH + CO \rightarrow CO_2 + H$$

$$H + O_2(+M) \rightarrow HO_2$$

The NO_2 concentration is then accurately determined by chemiluminescence. In the above chain the main termination processes are:

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

$$HO_2 + NO_2(+M) \rightarrow HO_2NO_2$$

$$HO_2 + \text{wall} \rightarrow \text{radical loss}$$

The HO_2 concentration sampled into the amplification cell can be determined by $[HO_2]_0 = \Delta\,[NO_2]/LC$ where NO_2 is the NO_2 concentration produced and LC is the chain length of the amplification cycle. The chain length which is defined as the ratio between the chain propagation and termination rates is determined from the measurements of $\Delta[NO_2]$ as mentioned above, and $[HO_2]_0$, using a calibrated source of HO_2. The calibrated HO_2 source used was the photolysis of a H_2O/air mixture at 185 nm and 1 atm pressure [23]. LC values obtained with our amplifier were typically 120, which is comparable to the values obtained with the other existing amplifiers.

The amplification cell is a pyrex tube (1.45 cm inner diameter, 14 cm length), where the chain reaction takes place when NO (3 ppmv), CO (10%) and N_2, as the diluent, are flowed together through it. The sampling of the gaseous mixture in the photoreactor is made through a hole of 4 mm diameter drilled at the top of a cone. The flow rate of the sampled gas is 1 STP $l\,min^{-1}$.

The amplification cell was set into the photoreactor, its axis being perpendicular to that of the photoreactor. The top of the sampling cone was located a few millimeters below the lower FTIR beam array. The cell was surrounded by a stainless steel jacket to prevent photolysis of the gaseous mixture inside the cell. NO_2 was detected by the chemiluminescence of a luminol solution. Experiments have been carried out to optimize the composition of the solution making negligible the influence of formic acid produced in the photolysis of H_2CO (reaction 6) under certain conditions. It is known that acids reduce the chemiluminescence intensity signal. This effect was made negligible by replacing NaOH by KOH. The composition of the luminol solution used in this work was 10^{-4} M luminol (Aldrich, purity ≥98%), 1 M KOH (Aldrich, purity ≥85%), 10^{-2} M Na_2SO_3 (Aldrich, purity ≥98%) and 10^{-2} M EDTA (ethylene diamine tetra acetic acid) (Aldrich, purity ≥99%). Besides, it was verified that formaldehyde has no effect on the luminescence signal intensity.

The chemical amplifier was calibrated for HO_2 before and after each series of photolysis experiments since the amplification cell had to be taken out of the photoreactor, and coupled to the calibrated source of HO_2. NO_2 was calibrated everyday using a known $NO_2/O_2/N_2$ (Alphagaz) containing 1 ppm of NO_2 (±5%). The measured values of LC could differ by up to 20%. The LC value considered for a series of experiments was the average between the ones measured before and after the series of experiments.

The procedure followed for each experiment started by pumping the photoreactor down to 2×10^{-3} mbar under irradiation during 2 h. The photoreactor was then filled with synthetic air (Alphagaz, nitrogen, oxygen 80–20 K) at a pressure slightly higher than one atmosphere, and formaldehyde was added at a controlled partial pressure from a depolymerized paraformaldehyde/synthetic air mixture contained in a flask. After homogenization the aldehyde air mixture was irradiated during 2 h during which the concentrations of the stable species (H_2CO, CO and HCOOH) were monitored by FTIR analysis. In the meantime, the chemical amplifier was calibrated everyday for NO_2, in the range 0–100 ppbv. After the two first hours, the gaseous mixture maintained under irradiation was sampled through the chemical amplifier for peroxy radical analysis.

3. Results

3.1. *HO_2 detection in the photolysis of H_2CO/air mixtures*

A first expected result is the detection of peroxy radicals by the chemical amplifier technique in the photolysis of H_2CO/air mixtures. The detected radicals are mainly HO_2 as discussed below. Fig. 2 shows the amplification signal intensity as a function of the number of lamps switched on (the same numbers of the two types of lamps, centered on 360 and 420 nm, are switched on). The signal intensity without amplification corresponds mainly to the addition of 30 ppbv of NO_2 to the detection cell. This addition was necessary due to a non linear response of the detector for low concentrations (less than 5 ppbv) of NO_2. Fig. 2 shows a decrease of the amplification signal when the number of lamps switched on is decreased, and a similar increase when the number of lamps switched on is increased in a similar way. Moreover, the intensity of the chemiluminescence signal is found to be proportional to the square root of the number of lamps switched on, as shown from the plots of Fig. 3. This behavior is consistent with the kinetic equation obtained by calculating the steady state concentration of HO_2 radicals from their production by reaction (1) and consumption by the reaction:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{7}$$

The steady state equation is:

$$[HO_2] = ((J_1/k_7)[H_2CO])^{1/2}$$

where J_1 is the photolysis coefficient of the radical channel (1) and k_7 the rate constant of reaction (7). This equation

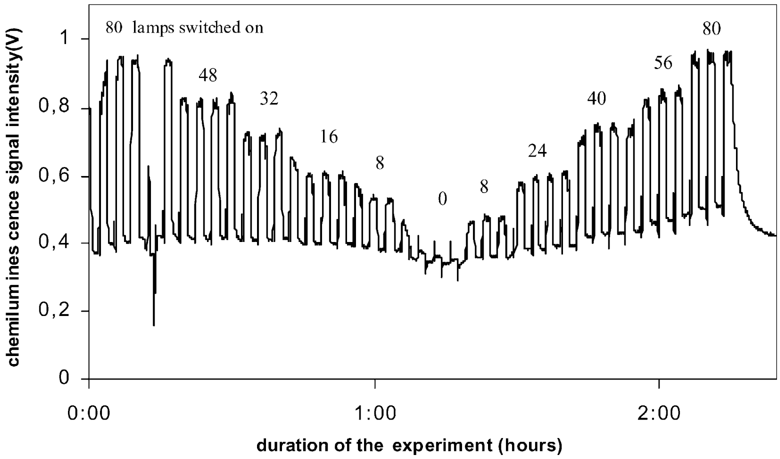

Fig. 2. Photolysis of formaldehyde (5.3 ppmv) in air: intensity of the chemiluminescence signal as a function of the number of lamps switched on.

also assumes that the equilibrium (3, −3) is achieved. This is the case since the time constant of this equilibrium (<0.1 s) is much lower than the time constant of the HO_2 measurement. The concentration of H_2CO, $[H_2CO]$, being almost constant during the time of the experiment in Fig. 2, as observed from FTIR measurements, $[HO_2]$ is proportional to the square root of J_1. Since the intensity of the chemiluminescence signal is proportional to $[HO_2]$, and J_1 is proportional to the total intensity of the lamps switched on, which, in turn, is proportional to the number of lamps switched on, then, the intensity of the chemiluminescence signal has to be proportional to the square root of the number of lamps switched on. This is effectively observed (Fig. 3).

3.2. Photolysis experiments at low H_2CO concentration

A series of photolysis experiments have been carried out using low HCHO concentrations, ranging from 228 to 566 ppbv. Under these conditions, the measured maximum concentrations of HO_2, corresponding to the 80 lamps switched on, were in the range 43–78 pptv. Under these conditions the loss of HO_2 through the reactions:

$$HO_2 + H_2CO \leftrightarrow HOCH_2O_2 \tag{3,–3}$$

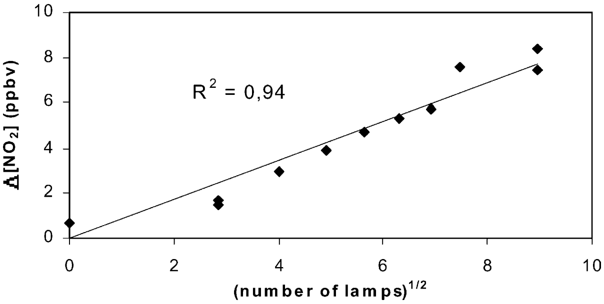

Fig. 3. Photolysis of formaldehyde (220 ppbv) in air: intensity of the chemiluminescence signal ($\Delta[NO_2]$), as a function of the square root of the number of lamps switched on.

$$HOCH_2O_2 + HO_2 \rightarrow HOCH_2OOH + O_2 \tag{8}$$

can be considered to be negligible compared to the self-combination of HO_2 (7). Considering the recommended value for the equilibrium constant $K = k_3/k_{-3} = 5 \times 10^{-16}\,cm^3$/molecule [24] at 298 K, the $[HOCH_2O_2]/[HO_2]$ ratio is effectively low at the low H_2CO concentrations used (the ratio is 0.007 for 566 ppbv of H_2CO). This low ratio also indicates that the amplification signal is mainly due to HO_2, the contribution of the hydroxy methylperoxy radical, $HOCH_2O_2$ being negligible.

The measured HO_2 and H_2CO concentration data can be used to calculate the photolysis rate coefficients J_1 and J_2 of the two channels of the H_2CO photolysis:

$$H_2CO + h\nu(+O_2) \rightarrow 2HO_2 + CO \tag{1}$$

$$H_2CO + h\nu \rightarrow H_2 + CO \tag{2}$$

The rate coefficient J_1 is obtained from the equation resulting from the application of the steady state approximation for the HO_2 radicals: $J_1 = k_7\,[HO_2]^2/[H_2CO]$. The values obtained for J_1 from this expression are reported in Table 1 together with the measured HO_2 and H_2CO concentrations for the experiments carried out. The resulting mean value of J_1 is $(1.43 \pm 0.86) \times 10^{-6}\,s^{-1}$ where the error is mainly the experimental error on the HO_2 concentration which is estimated to be ±30%.

This J_1 value can be compared to the one calculated from the parameters of the expression $J_1 = \sum I_\lambda \sigma_\lambda \Phi_{1\lambda}$, where I_λ is the total intensity of the two lamps integrated over $d\lambda$, σ_λ the absorption cross section of H_2CO and $\Phi_{1\lambda}$ the quantum yield of reaction 1 at the wavelength λ, respectively. σ_λ and $\Phi_{1\lambda}$ are averaged values over $d\lambda$ ($d\lambda$ has been taken as 1 nm). The calculations have been made using the actinic flux previously determined for the two series of lamps (centered on 360 and 420 nm, respectively (see Fig. 1)) and the recommended values for σ [25] and Φ_1 [2]. The J_1 value calculated in this way is $(1.13 \pm 0.04) \times 10^{-6}\,s^{-1}$. It must

Table 1
H_2CO and HO_2 concentrations and experimentally derived values of J_1 and J_1/J_2 (see text)

$[HCHO]_0 \times 10^{-12}$ (molecule/cm^3)	t (s)	$[HO_2]_t \times 10^{-9}$ (molecule/cm^3)	$[HCHO]_t \times 10^{-12}$ (molecule/cm^3)	J_1 (s^{-1}) $\times 10^6$	J_1/J_2
9.93 ± 0.12	2640	2.27 ± 0.68	9.31 ± 0.32	1.61 ± 0.68	0.31 ± 0.20
9.48 ± 0.05	1980	2.14 ± 0.64	9.20 ± 0.10	1.45 ± 0.59	0.28 ± 0.12
5.63 ± 0.04	4620	1.58 ± 0.47	5.03 ± 0.14	1.45 ± 0.60	0.28 ± 0.13
9.15 ± 0.10	16620	1.82 ± 0.54	6.39 ± 0.85	1.51 ± 0.71	0.29 ± 0.15
7.89 ± 0.07	10320	1.65 ± 0.50	6.01 ± 0.40	1.31 ± 0.57	0.25 ± 0.12
14.10 ± 0.04	9840	2.21 ± 0.66	11.20 ± 0.26	1.27 ± 0.53	0.24 ± 0.11

be pointed out that Madronich and Weller [26] have shown that the use of a lower resolution induce additional errors in the photolysis frequencies determination. In our case this errors are 0.1% for J_{NO_2}, and 3% for both J_1 and J_2. The calculated value for J_1 is then $(1.13 \pm 0.10) \times 10^{-6}\,s^{-1}$.

This value is in good agreement with the experimentally derived value of $J_1 = (1.43 \pm 0.86) \times 10^{-6}\,s^{-1}$. Besides, the J_2 value calculated similarly as J_1 from the expression $J_2 = \sum I_\lambda \sigma_\lambda \Phi_{2\lambda}$, yields $J_2 = (5.21 \pm 0.19) \times 10^{-6}\,s^{-1}$. This leads to $J_1/J_2 = 0.22 \pm 0.02$ to be compared with the value $J_1/J_2 = 0.27 \pm 0.24$ obtained from the experimentally derived value of J_1 and calculated J_2.

The good agreement between the calculated and experimentally derived values of J_1 and J_1/J_2 validates the present peroxy radical measurements by the chemical amplification technique.

3.3. Photolysis experiments at high H_2CO concentrations

A second series of experiments have been made using higher concentrations of H_2CO, in the range 2.04–5.57 ppmv in order to investigate the (3, −3) equilibrium. In that case the reaction of HO_2 with H_2CO and subsequent reactions are effectively no more negligible. A direct evidence of the occurrence of this process is the observation of formic acid by FTIR. The yield of HCOOH is for instance 3.5% in the experiment with an initial concentration of 4.47 ppmv for H_2CO (Fig. 4). The concentration time profiles of H_2CO, HCOOH, and the measured steady state concentration of HO_2 were fitted to the calculated ones using for the simulation the mechanism reported in Table 2. The aim of the fitting procedure was to determine the rate constant of reaction (−3) which appears to be the most uncertain kinetic parameter in this mechanism. The rate constants for the other reactions which were used as fixed parameters are from [24]. The photolysis coefficient of channel (1), J_1, was also derived from the simulation calculations. In the calculations it has to be taken into account that the measured concentration of peroxy radicals corresponds both to HO_2 and $HOCH_2O_2$, the contribution of this latter being no more negligible at the high concentrations of H_2CO used. This contribution was 20% or less, considering that the chain length in the amplification cell was the same for HO_2 and $HOCH_2O_2$, which is a reasonable assumption.

The experimental conditions of two experiments which have been simulated are the following: initial concentration of H_2CO: 1.11×10^{14} and 5.01×10^{13} molecule/cm^3; stationary concentration of peroxy radicals, $[HO_2] + [HOCH_2O_2]$: 5.48×10^9 and 5.36×10^9 molecule/cm^3, respectively. The obtained rate constant for the thermal decomposition of the $HOCH_2O_2$ adduct (reaction −3) was: $k_{-3} = 35 \pm 5\,s^{-1}$ and

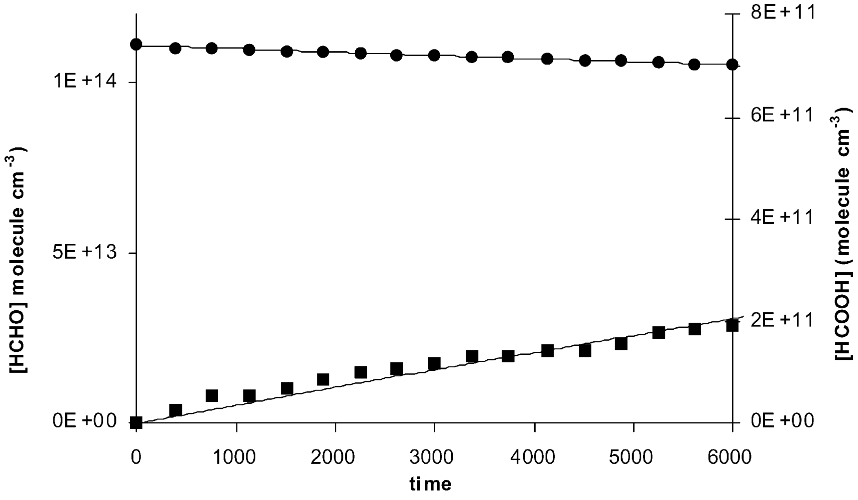

Fig. 4. Formation kinetics of HCOOH in the photolysis of H_2CO in air. $[H_2CO]_0 = 4.5$ ppmv.

Table 2
Rate constant data used in the simulation calculations of the photolysis of H_2CO in air at atmospheric pressure and room temperature

Reaction number	Reactions	k (298 K) (cm^3/(molecule s))
1	$H_2CO + h\nu(+O_2) \rightarrow 2HO_2 + CO$	See text
7	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.9×10^{-12}
3	$HO_2 + H_2CO \rightarrow HOCH_2O_2$	7.9×10^{-14}
−3	$HOCH_2O_2 \rightarrow HO_2 + H_2CO$	See text
8a	$HOCH_2O_2 + HO_2 \rightarrow HOCH_2OOH + O_2$	7.2×10^{-12}
8b	$HOCH_2O_2 + HO_2 \rightarrow HCOOH + H_2O + O_2$	4.8×10^{-12}
4	$HOCH_2O_2 + HOCH_2O_2 \rightarrow 2HOCH_2O$	5.5×10^{-12}
9	$HOCH_2O_2 + HOCH_2O_2 \rightarrow HCOOH + CH_2(OH)_2 + O_2$	7.0×10^{-13}
6	$HOCH_2O + O_2 \rightarrow HCOOH + HO_2$	3.5×10^{-14}

The rate constants are from [14].

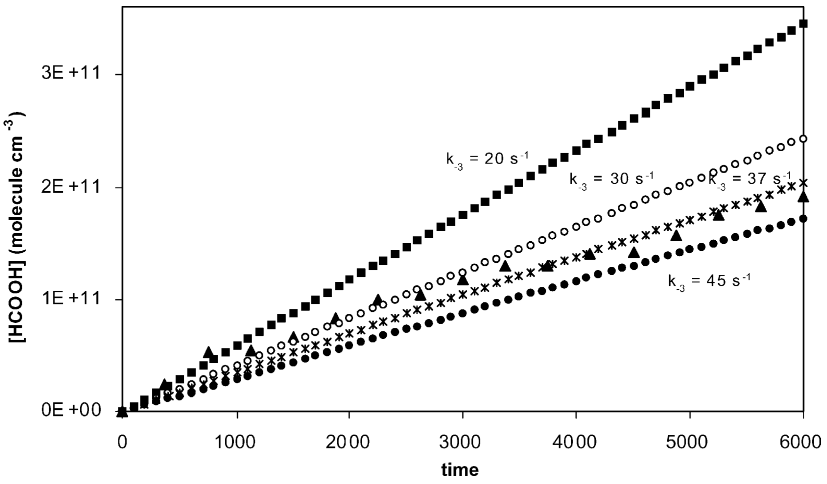

Fig. 5. Sensitivity of HCOOH formation kinetics to k_{-3}: experimental plots (▲), calculated curves with $k_{-3} = 20\,s^{-1}$ (■), $30\,s^{-1}$ (○), $37\,s^{-1}$ (✱), $45\,s^{-1}$ (●). $[H_2CO]_0 = 4.5$ ppmv.

$21 \pm 7\,s^{-1}$, respectively. The mean value is ($28 \pm 14\,s^{-1}$). It has to be mentioned that the HCOOH concentration profiles were very sensitive to k_{-3} (Fig. 5), whereas the peroxy radical concentrations were mostly sensitive to the photolysis rate of H_2CO (Fig. 6). The obtained ratios J_1/J_2 were 0.13 and 0.24.

The present determination of k_{-3} can be compared with the literature values which have previously been discussed in detail [14]. The range of the literature values is rather large since it is comprised between $1.5\,s^{-1}$ [27] and around $150\,s^{-1}$ [12,14] at 298 K. However, the lowest of these two values have been reevaluated to $30\,s^{-1}$ [13] by fitting the

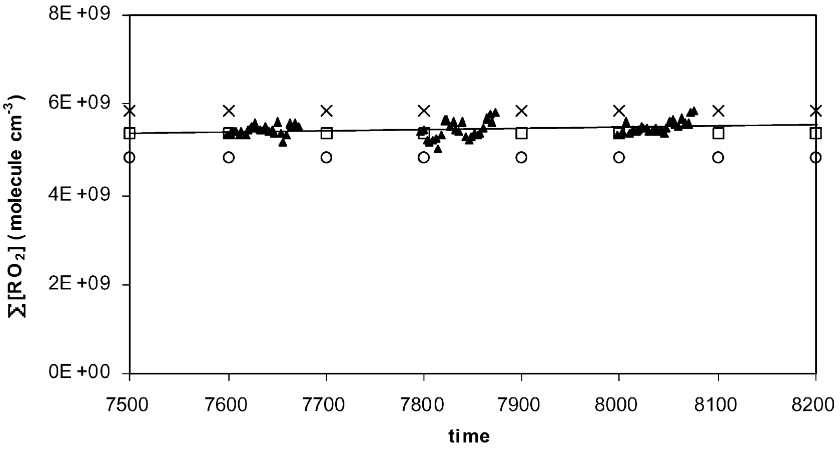

Fig. 6. Sensitivity of peroxy radical concentrations to J_1/J_2: experimental plots (▲), calculated RO_2 concentrations with $J_1/J_2 = 0.1$ (○), 0.13 (□) and 0.16 (×). $[H_2CO]_0 = 4.5$ ppmv.

experimental data of Su et al. [27,9], using an improved chemical mechanism. The value $k_{-3} = 20\,s^{-1}$ with the uncertainty range 10–40 s^{-1} has been obtained at 273 K by Barnes et al. [12]. In this latter work the decay of HO_2NO_2 (source of HO_2 by thermal decomposition) was monitored in the presence of formaldehyde. The decay of HCHO and formation of HCOOH and $HOCH_2O_2NO_2$ were determined as a function of time. The k_{-3} value obtained at 298 K would be 170 s^{-1} at 298 K, using the temperature dependent expression $k_{-3} = 2.0 \times 10^{12} \exp[(-7000 \pm 2000)/T]\,s^{-1}$ determined by Veyret et al. [14]. The uncertainty on this k_{-3} value is yet rather large considering the uncertainties on k_{-3} at 273 K and that on its temperature dependence. The k_{-3} determination of Veyret et al. at 298 K, interpolated from measurements at 295 and 308 K, is 126 s^{-1} with the uncertainty range 60–190 s^{-1}. Therefore our present determination, 28 ± 14, corresponds to the lower limit of the range of the existing k_{-3} values at 298 K.

4. Conclusion

The present study of the continuous photolysis of H_2CO in air at atmospheric pressure by combining in situ analysis of stable species by FTIR and peroxy radicals by a chemical amplifier has provided data for photodissociation coefficient of H_2CO (J_1), and thermal decomposition of the $HOCH_2O_2$ adduct (k_{-3}) consistent with the literature data. This confirms the potentiality of the chemical amplifier associated to photoreactors to investigate chemical mechanisms of atmospheric interest.

Acknowledgements

The French Programme of Atmospheric Chemistry (PNCA) of CNRS for support.

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