Photolysis and OH-Initiated Oxidation of Glycolaldehyde under Atmospheric Conditions

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The photolysis and OH-initiated oxidation of glycolaldehyde ($HOCH_2CHO$), which are relevant atmospheric processes, have been investigated under different conditions using complementary methods in three different laboratories. The UV absorption cross sections of glycolaldehyde determined in two of the laboratories are in excellent agreement. The photolysis of glycolaldehyde in air has been investigated in a quartz cell with sunlamps and in the EUPHORE chamber irradiated by sunlight. The mean photolysis rate measured under solar radiation was $(1.1 \pm 0.3) \times 10^{-5}$ s^{-1} corresponding to a mean effective photolysis quantum yield of (1.3 ± 0.3). The major products detected were HCHO and CO, whereas CH_3OH was also observed with an initial yield around 10%. Evidence for OH production was found in both experiments using either OH scavenger or OH tracer species. Photolysis of glycolaldehyde was used as the OH source to measure the reaction rate constants of OH with a series of dienes by the relative method and to identify and quantify the oxidation products of the OH-initiated oxidation of 2-propanol. The different experiments suggest that OH is produced by the primary channel: $HOCH_2CHO + h\nu \rightarrow OH + CH_2CHO$ (1). The rate constant of the OH reaction with glycolaldehyde has been measured at 298 K using the relative method: $k_{glyc} = (1.2 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The product study of the OH-initiated oxidation of glycolaldehyde in air has been performed using both a FEP bag and the EUPHORE chamber. HCHO was observed to be the major product with a primary yield of around 65%. Glyoxal (CHOCHO) was also observed in EUPHORE with a primary yield of (22 ± 6)%. This yield corresponds to the branching ratio (≈20%) of the H-atom abstraction channel from the CH_2 group in the $OH + HOCH_2CHO$ reaction, the major channel (≈80%) being the H-atom abstraction from the carbonyl group. The data obtained in this work, especially the first determination of the photolysis rate of glycolaldehyde under atmospheric conditions, indicate that the OH reaction and photolysis can compete as tropospheric sinks for glycolaldehyde. Since glycolaldehyde is a significant oxidation product of isoprene whereas the photolysis of glycolaldehyde is a significant source of methanol, isoprene might contribute a few percent of the global budget of methanol.

Introduction

The gas-phase degradation of carbonyl compounds represents an important source of HO_x radicals in the atmosphere. This HO_x radical production enhances the oxidation capacity of the atmosphere and may significantly increase the concentrations of photochemical smog components. Aldehydes are thought to be a major class of the carbonyl compounds that may play such a role. They are emitted to the atmosphere as primary pollutants (from combustion, vegetation, or solvents) or are present as intermediate species in the oxidation of other volatile organic compounds (VOCs). In the gas phase, their principal degradation processes are controlled by reactions with OH, NO_3, and O_3 (for unsaturated compounds) and by photolysis.

Laboratory studies have shown that glycolaldehyde ($HOCH_2CHO$) is an oxidation product of a number of VOCs such as ethene,[1] isoprene,[2] 2-methyl-3-buten-2-ol (MBO)[3], and methyl vinyl ketone (MVK).[4] The total yield of glycolaldehyde amounts to 24% and 28% from the OH + isoprene reaction and the OH + MBO reaction, respectively.[5] Field measurements have shown that glycolaldehyde is present in the atmosphere, and it has been suggested that glycolaldehyde might be an important component of plumes from biomass fires.[6,7] Glycolaldehyde mixing ratios in the boundary layer of up to 3 ppbv have been previously measured.[8,9,10] Little data are available on the processes driving the atmospheric degradation of this hydroxyaldehyde. Niki et al. were the first to measure the rate constants for the Cl and OH reactions with glycolaldehyde, and they reported the only available oxidation study initiated by OH and Cl radicals.[11] Recently, Bacher et al. have determined the UV absorption spectrum of glycolaldehyde, studied its photolysis in an indoor smog chamber, and determined its reaction rate constant with OH radicals.[12] According to these two studies, the gas-phase atmospheric fate of glycolaldehyde seems to be controlled by both photolysis and reaction with OH radicals.

To get further insight into the atmospheric chemistry of glycolaldehyde, we have conducted a complementary study of the photolysis and OH-initiated oxidation of glycolaldehyde using different experimental conditions in three separate labo-

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ratories. At LCSR−Orléans, the UV spectrum, the OH reaction rate constant, and the resulting products were measured. The UV spectrum as well as the photolysis products were investigated at MPI-Mainz, and finally, the EUPHORE facility was used to study the photolysis rate and OH-initiated oxidation of glycolaldehyde.[5]

Experimental Section

The experimental systems and procedures used in the present study were the same as those described in a recent work from the same laboratories[13] and hence are only briefly summarized here.

Measurements of UV Absorption Cross-Sections. The UV absorption spectrum of glycolaldehyde was determined both at MPI-Mainz (0.3 nm resolution) and at LCSR/CNRS Orléans (0.1 nm resolution) using similar setups. Absorption cross sections were determined (211−330 nm, 298 ± 3 K and 0.15−0.5 Torr) in Mainz in a 63 cm long triple-jacketed cell equipped with heated quartz windows held at ∼ 60 °C in order to prevent deposition. The 256−316 nm absorption spectrum ($T = 333$ K, $P = 0.5-1.6$ Torr) was determined in Orléans in a 100 cm long double-jacketed Pyrex cell. The optical setup in both laboratories utilized a D_2 lamp as a light source and a detection system based on a monochromator/diode array detector (DAD) combination, using the Hg lines from a low-pressure Hg Penray lamp and the 213.8 nm line of Zn lamp for wavelength calibration. The measurements were performed in static conditions. Capacitance manometers 0−10 Torr were used in both laboratories for pressure measurements. As a precaution, the glycolaldehyde formed by heating its dimer was collected in a cold finger held in liquid N_2. The cell was then filled to the desired pressure utilizing the middle fraction of the glycolaldehyde that was distilled from the cold finger. The pressure in the cell was continuously monitored, and the observed small pressure drop during an optical scan did not exceed few percent. Average pressure was used for the evaluation of the cross sections.

Initially, a series of experiments were carried out (usually 3−4 independent determinations were made at each pressure) to establish the applicability of Beer−Lambert's law

$$\sigma(\lambda) = -\ln[I(\lambda)/I_0(\lambda)]/LC$$

where I and I_0 are the light intensities for the filled and the empty cell, respectively. L is the length of the absorption cell, and C is the concentration of the compound in the cell.

Subsequently, 10 additional spectral measurements were made at the highest possible concentration of glycolaldehyde.

Photolysis. The procedures used in the photolysis experiments were similar to those used for the study of the photolysis of acrolein and *trans*-crotonaldehyde described in a recent paper from the same groups.[13] We used two experimental facilities (i) TL12 sunlamps-quartz cell at MPI-Mainz[14] and (ii) EUPHORE outdoor smog chamber[15,16] which are briefly described below.

(i) Experiments Performed at MPI-Mainz. These experiments were performed in a 44.2 L quartz cell, equipped with 2 independent sets of White-optics mirror arrangements. Sapphire-coated aluminum mirrors were used for IR measurements, whereas MgF_2-coated aluminum mirrors were used for UV−visible absorption measurements. The base distance between the mirrors was 1.2 m. The IR and UV path lengths were tuned to 28 passes (33.6 m) and 8 passes (9.82 m), respectively. Photolysis was achieved by using TL12 sunlamps radially mounted around the cell (Philips 40 W, 275−380 nm, maximum at 310 nm). Concentration−time profiles of glycolaldehyde and its photolysis products were determined with a FTIR spectrometer by scanning the wavelength range of 450−4000 cm^{-1} at 0.5 cm^{-1} resolution. At the onset of photolysis, the spectra were averaged every 5 min and then, from 30 min and on, at 10 min intervals.

Qualitative and quantitative data analysis were carried out by comparing the reactant and the products spectra with reference spectra obtained in the same cell using calibration curves at corresponding pressures and resolution.

(ii) Experiments Performed at EUPHORE. A detailed description of the EUPHORE facility and the existing analytical equipment can be found in refs 15 and 16. It consists of two 200 m^3 independent hemispherical outdoor simulation chambers, made of FEP foil (more than 80% transmission of the solar radiation in the wavelength range 290−520 nm). Both chambers are equipped with FTIR spectrometers coupled with White-type multi-path mirror systems for in situ analysis (optical path lengths of 326.8 and 553.5 m). The IR spectra were recorded every 10 min by co-adding 550 interferograms with a resolution of 1 cm^{-1}. Gas chromatographs equipped with different detectors such as FID, PID, and ECD were also used for analysis. Species such as O_3, CO, and NOx were analyzed using specific analyzers (Monitor Labs 9810, Thermo Environment 48C, Monitor Labs 9841A and ECO−Physics CLD770 AL ppt with PLC 760 photolytic converter). Reactant and product concentrations were determined using calibrated reference spectra. Known amounts of glycolaldehyde were introduced into the chambers in the concentration range 0.6−1.8 ppm along with SF_6, which was used as a tracer in the determinations of the dilution rate caused by minor leaks by thermal expansion of the reaction mixture and by the sampling for analysis. In some experiments, cyclohexane or di-*n*-butyl ether (DNBE) was added to scavenge OH radicals or to estimate their concentration. The stability of the reaction mixtures prior to their exposure to sunlight, i.e., the possibility of dark reactions, was examined by starting the analytical sampling at least 30 min before the onset of photolysis.

The disappearance of DNBE is only due to its dilution in the chamber and to its reaction with OH radicals (see below). By assuming the [OH] radical concentration remains constant during the photolysis experiment, the following expression should apply:

$$\ln([\mathrm{glyc}]_0/[\mathrm{glyc}]_t) = (J + k_{\mathrm{OH}}[\mathrm{OH}] + k_{\mathrm{SF6}})t = k_{\mathrm{total}}t$$

The presence of an excess of cyclohexane ($[\mathrm{cyclohexane}]_0/[\mathrm{glycolaldehyde}]_0) > 20$ minimizes the consumption of glycolaldehyde due to a reaction with OH and the OH chemistry of the observed products. On the other hand, the use of the tracer, DNBE, enables estimation of the OH concentration in the chamber during the photolysis experiments. The OH concentration is derived from the first-order decay of the tracer concentration and it is then used to estimate the contribution of the OH reaction to the loss of glycolaldehyde.

OH-Initiated Oxidation. The OH-initiated oxidation of glycolaldehyde (kinetics and mechanism) has been investigated at CNRS/LCSR−Orléans and in the EUPHORE's outdoor simulation chambers.

(i) Experiments Performed at CNRS−Orléans. The setup used in Orléans consists of a 140 L FEP Teflon bag surrounded by 6 lamps emitting between 300 and 460 nm, centered at 365 nm (Philips, TL 20 W/05) and 6 lamps emitting between 270 and 400 nm, centered at 312 nm (T-20 M/20 W). The photolytic

light intensity and its spectral characteristics were controlled by the number and type of the lamps that were turned on, whereas the temperature was maintained at 298 ± 3 K by flowing air around the Teflon bag.

Glycolaldehyde was heated to ca. 70 °C and introduced into the bag by an air stream while the reference compounds used in the kinetic study were flushed from calibrated bulbs. The photoreactor was then filled to its full capacity with purified air. A Nicolet FTIR spectrometer (optical path length of 10 m and 1 cm^{-1} resolution) was used for analysis. The initial concentrations of glycolaldehyde were in the range of 40−55 ppm, and the photolysis period was 1−2 h. OH radicals were generated by the photolysis of nitrous acid, HONO, using the lamps centered at 365 nm. Relative rate constants were determined by comparing the reaction rate of glycolaldehyde to that of a reference compound

$$\mathrm{OH} + \text{glycolaldehyde} \rightarrow \text{products} \quad k_{\mathrm{glyc}}$$

$$\mathrm{OH} + \text{reference} \rightarrow \text{products} \quad k_{\mathrm{ref}}$$

Assuming that glycolaldehyde and the reference compound were consumed only by reaction with OH, k_{glyc} was then derived from the following equation:

$$\ln([\mathrm{glyc}]_0/[\mathrm{glyc}]_t) = (k_{\mathrm{glyc}}/k_{\mathrm{ref}}) \ln([\mathrm{ref}]_0/[\mathrm{ref}]_t)$$

where the subscripts 0 and t indicate concentrations before and at time t after irradiation, respectively.

(ii) Experiments Performed at EUPHORE. Both direct photolysis and OH-induced oxidation of glycolaldehyde were investigated. In the latter case, NO was added to initiate the OH radical formation under sunlight conditions. Unlike the Orléans experiments, the EUPHORE study did not include runs with added cyclohexane or DNBE.

Materials. Glycolaldehyde was prepared from its solid dimer (Aldrich) by gentle heating of previously degassed material by a heat gun. FTIR analysis has shown it to be free of detectable amounts of organic contaminants such as formaldehyde and methanol. 1,3-Dioxolane (99.99%) was obtained from Lambiotte; di-isopropyl ether (>99%), di-ethyl ether (>99%), di-*n*-butyl ether (> 99%), and isoprene (>99.5%) were obtained from Fluka; whereas acetaldehyde (99%), 2,3-dimethyl-1,3-butadiene (90%), 1,3-pentadiene (90%), and 2-propanol (99.5%) were bought from Aldrich. HONO was prepared by dropwise addition of an aqueous 1% $NaNO_2$ solution to a 30% sulfuric acid solution at room temperature and introduced directly into the chamber in an air stream.

Results and Discussion

UV-Absorption Cross Sections. The spectra, from Orléans and Mainz, determined in the ranges 256−316 and 211−330 nm, respectively, are shown in Figure 1, and the absorption cross sections derived are listed in Table 1. The absorption spectrum displays a broad unstructured absorption band, with a maximum near 282 nm. As can be clearly seen, the two spectra, Mainz at 298 K and Orléans at 333 K, agree quite well in the wavelength range 256−304 nm (within 10% or better). The absence of significant differences between the spectra might be considered as an indication that, at least in these wavelength range, the absorption cross sections are temperature independent. However, at the longer wavelength (λ > 304 nm), the relatively small cross sections could be less accurately determined because of the limit set by the highest allowed glycolaldehyde's pressure above which wall deposition could become a significant problem. Consequently, we estimate that the error in absorption cross sections is about ±25% for most of the wavelength range at λ > 304 nm and even higher at the longest wavelengths.

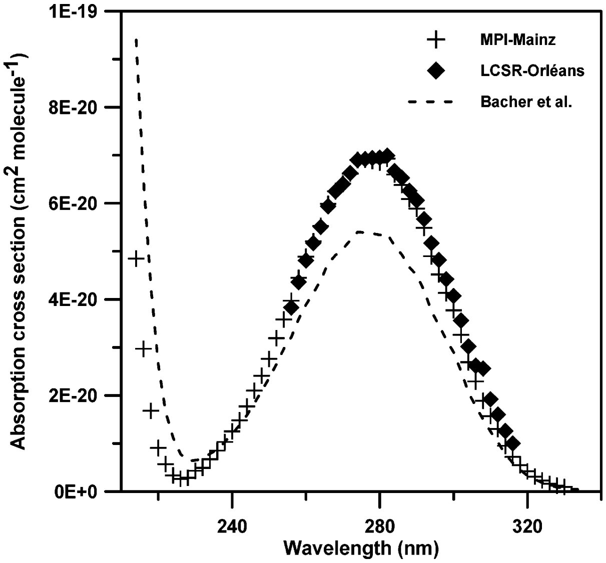

Figure 1. UV absorption spectra of glycolaldehyde.

Table 1 and Figure 1 include also the results of the spectral measurements of Bacher et al.[12] Comparison of these results with those of the present work reveals significant differences. Throughout most of the spectral range from 244 to 326 nm, the shape of the spectrum obtained by Bacher et al. and the Mainz spectrum are quite similar as indicated by the near constant σ(Mainz)/σ(Bacher) ratio of about 1.2 ± 0.1 throughout this range. These two spectra differ considerably at shorter wavelengths (λ < 244 nm), which are not relevant insofar as the atmospheric fate is considered. Examination of our experimental procedures and those of Bacher et al. does not reveal a cause for these discrepancies, since the procedure was quite similar and the measurements were carefully executed in all of these determinations. The observed differences may to certain extend reflect uncertainties in concentration measurements due to handling difficulties.

Photolysis. Since glycolaldehyde has UV absorption at wavelengths longer than 290 nm, it can undergo photolysis in the atmosphere similar to other aldehydes.[5] Photolysis experiments were therefore conducted to identify the products, to elucidate the photooxidation mechanism, and to determine its photolysis rate under atmospheric conditions.

Experiments in Mainz. Mixtures of 4−17 ppm of glycolaldehyde in synthetic air were irradiated with TL12 lamps (typically for 90 min) at four different pressures (300, 500, 700, and 760 Torr) and at (298 ± 2) K. The FTIR analysis was conducted using the glycolaldehyde band in the 2606.5−2996.6 cm^{-1} range. Dark experiments have shown that glycolaldehyde was consumed at a rate of 5%/h presumably due to wall loss. The experimental conditions and the observed photolysis removal rates are summarized in Table 2. The total removal rate, derived from the 11 experiments performed at different pressures, was found to be $k_{\mathrm{removal}} = (2.9 \pm 0.4) \times 10^{-4}\ s^{-1}$, independent of pressure in the 300−760 Torr of synthetic air. The main observed products were HCHO, CO, CH_3OH, and HCOOH with initial yields of (91 ± 24)%, (68 ± 16)%, (10 ± 2)%, and (4 ± 1)%, respectively. An example of kinetic and yield curves is presented in Figure 2. The carbon balance was estimated to be around 87%.

TABLE 1: Absorption Cross Sections[a] of Glycolaldehyde

λ (nm)	σ (Mainz)	σ (LCSR)	σ (Bacher et al.)
210			18.1
212	8.24		13.0
214	4.85		9.4
216	2.97		6.49
218	1.68		4.26
220	0.904		2.65
222	0.569		1.65
224	0.334		1.12
226	0.262		0.783
228	0.284		0.637
230	0.425		0.649
232	0.489		0.68
234	0.672		0.785
236	0.845		0.88
238	1.03		1.03
240	1.25		1.2
242	1.48		1.38
244	1.77		1.59
246	2.1		1.83
248	2.41		2.09
250	2.76		2.36
252	3.19		2.65
254	3.58		2.97
256	3.97	3.83	3.21
258	4.45	4.36	3.59
260	4.89	4.81	3.89
262	5.21	5.17	4.13
264	5.53	5.51	4.4
266	5.99	5.94	4.75
268	6.25	6.25	4.92
270	6.41	6.4	5.05
272	6.62	6.63	5.23
274	6.9	6.9	5.4
276	6.91	6.92	5.39
278	6.88	6.94	5.37
280	6.85	6.95	5.34
282	6.93	6.99	5.37
284	6.6	6.67	5.12
286	6.38	6.53	4.93
288	6.09	6.26	4.67
290	5.89	6.06	4.50
292	5.49	5.67	4.19
294	4.9	5.17	3.76
296	4.52	4.82	3.46
298	4.13	4.42	3.17
300	3.77	4.07	2.9
302	3.26	3.56	2.51
304	2.69	3.02	2.07
306	2.29	2.62	1.77
308	1.89	2.56	1.5
310	1.57	1.92	1.25
312	1.3	1.6	1.03
314	0.95	1.26	0.771
316	0.72	1.0	0.597
318	0.55		0.455
320	0.42		0.329
322	0.31		0.249
324	0.23		0.185
326	0.16		0.128
328	0.12		0.0875
330	0.096		0.0684
332			0.0439
334			0.0439

[a] 10^{-20} cm^2 molecule^{-1}.

Four photolysis experiments were also conducted in the presence of a 10−100 fold excess of cyclohexane. Mixtures of 3−30 ppm of glycolaldehyde and cyclohexane in synthetic air were irradiated with TL12 lamps (typically during 90 min) at 300 and 700 Torr and at (298 ± 2) K. Glycolaldehyde was found to be consumed with an average total removal rate of $k_{\text{removal}} = (1.5 \pm 0.2) \times 10^{-4}$ s^{-1}. This value is a factor of 2 lower than that obtained in the absence of cyclohexane. This difference indicates that, in our system in the absence of cyclohexane, an additional process contributes to glycolaldehyde's loss. The photolysis products were nearly the same as those observed in the absence of cyclohexane (HCHO, CO, CH_3OH, and HCOOH), except that the HCHO yields were somewhat lower, 81 ± 5%. The use of a high concentration of cyclohexane and the overlapping of its FTIR bands with those of the products made it difficult to quantify these products.

Experiments at EUPHORE. Five experiments have been conducted in June 1998 and 1999 either in the presence of cyclohexane (OH scavenger) or DNBE (OH tracer). The experimental conditions and the obtained photolysis rates are given in Table 3. An example of the concentration−time profiles is given in Figure 3. In the two experiments performed in the presence of the OH-tracer DNBE, the measured k_{DNBE} were found to be higher than those obtained in similar experiments with other aldehydes under the same conditions.[5] The higher consumption of DNBE can be attributed to the presence of OH at a higher concentration, which may be due to the existence of an additional OH source. Indeed, taking $k_{\text{OH+DNBE}} = 2.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1},[17] the OH radical concentrations were estimated from ($-\text{d[DNBE]}/\text{d}t) = k_{(\text{OH+DNBE})}$ [DNBE] [OH]) taking into account loss of DNBE by dilution. These concentrations were 3.7×10^5 and 2.7×10^5 molecule cm^{-3}, in the presence of glycolaldehyde, for the experiments done on June 19th and June 16th, respectively (see Table 3). These new values are considerably higher than that in absence of glycolaldehyde ([OH] $\approx 4 \times 10^4$ molecule cm^{-3}). These observations and those in the laboratory experiments, where the consumption of glycolaldehyde was found to be faster in the absence of the scavenger than in its presence, can be rationalized by assuming that OH is a product of glycolaldehyde photolysis.

The measured rates of glycolaldehyde photolysis, J_{glyc}, are reported in Table 3. In the presence of DNBE, J_{glyc} was calculated from the expression $J_{\text{glyc}} = k_{\text{total}} - k_{\text{SF6}} - k_{\text{glyc}}[\text{OH}]$, [OH] being derived from k_{DNBE}, as mentioned above. Table 3 also reports the experimental photolysis rate $J_{\text{exp}} = k_{\text{tot}} - k_{\text{SF6}}$. The effective quantum yield values of the glycolaldehyde photolysis, $\phi_{\text{eff}} = J_{\text{exp}}/J_{\text{glyc}}$, are respectively 1.5 and 1.4 in the experiments done on June 19th and June 16th. These values higher than unity values indeed suggest the OH reaction of glycolaldehyde. Besides, photolysis rates have been calculated using the absorption cross sections measured in this work along with the real solar actinic flux in Valencia on the day of the experiment and assuming quantum yield of unity. The obtained values, 9.3×10^{-6} and 7.2×10^{-6} s^{-1} for the experiments done on June 19th and June 16th, respectively, are in good agreement with the measured ones ($J_{\text{glyc}} = 9.2 \times 10^{-6}$ and 7.7×10^{-6} s^{-1}). This means that the primary quantum yield of the photolysis of glycolaldehyde is unity. Similar calculations for the experiments in the presence of cyclohexane (Table 3) gave higher $J_{\text{exp}}/J_{\text{calc}}$ values, which seems to indicate that the reaction of glycolaldehyde with residual OH could not be accurately estimated, due to the secondary chemistry of OH + cyclohexane, in the presence of residual NO_x in the chamber.

In the presence of DNBE, products formation yields are (54 ± 20)% for formaldehyde, (94 ± 20)% for CO, and (7 ± 1)% for HCOOH, whereas CH_3OH was qualitatively detected. The carbon balance deduced from these values is close to 100%. In the presence of cyclohexane, the CO yield was only about 70%, whereas formaldehyde and formic acid could not be accurately quantified due to the strong infrared absorption interferences of cyclohexane.

TABLE 2: Experimental Conditions and Results for the Photolysis of Glycolaldehyde Using Sunlamps (TL 12) at Mainz

	total pressure (Torr)					
	300		500	700		760
number of runs	2	2[a]	2	4	2[a]	3
$[Glyc.]_0$ (ppm)	4−6	2.8−3.7	7−12.3	13.4−16.7	7.5−28	4.3−9.1
Δ[Glyc.] (ppm)	1.8−2.3	0.7−0.8	2.7−5.6	5.3−6.8	2−5.6	1.8−3.3
$k_{removal}$ ($\times 10^{-4}$ s^{-1})	3.0 ± 0.3	1.6±0.2	2.9 ± 0.3	2.9 ± 0.4	1.5 ± 0.2	2.7 ± 0.3
yields (%)						
HCHO	101 ± 24		87 ± 17	80 ± 22	81 ± 5	95 ± 19
CO	69 ± 16		61 ± 11	81 ± 14		61 ± 13
HCOOH	12 ± 1		11 ± 2	11 ± 1		6 ± 1
CH_3OH	5 ± 1		3 ± 1	5 ± 1		4 ± 1

[a] Experiments conducted in the presence of an excess of cyclohexane (as an OH scavenger).

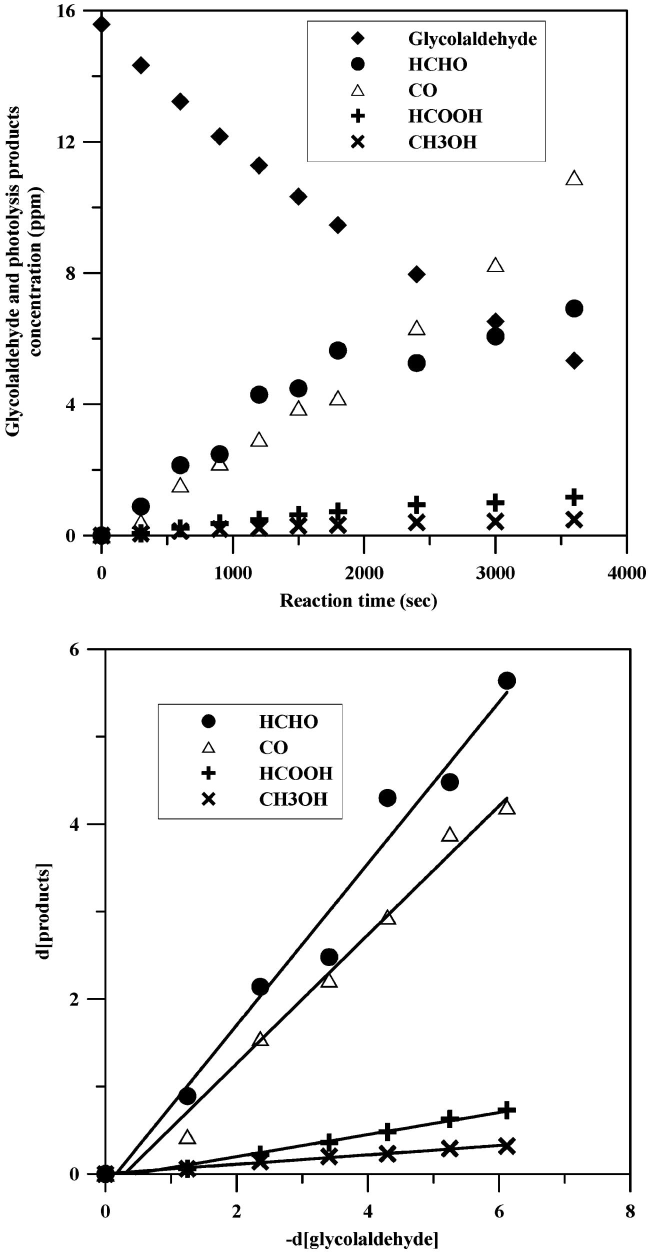

Figure 2. Concentration-time profiles of glycolaldehyde and products and product yields in the photolysis of glycolaldehyde (experiment performed at Mainz).

OH Production from the Photolysis of Glycolaldehyde. A series of independent experiments were conducted following the results obtained at Mainz and EUPHORE, which suggested that the photolysis of glycolaldehyde could lead to the production of OH radicals under radiation at wavelengths larger than 280 nm. The experiments were conducted using the photoreactor of Orléans and lamps centered on 312 nm (wavelength close to the maximum of absorption of glycolaldehyde at 282 nm). A gas chromatograph-flame ionization detector (GC-FID) was used for the quantitative analysis of the reactants. The gas mixtures were sampled at several reaction times, and the change in concentration of the compounds was monitored from integration of the chromatogram peaks. Chromatographic separation was achieved by using a DB− capillary column.

Two types of experiments were performed. In the first one, the photolysis of glycolaldehyde was used as the OH source to measure the reaction rate constants of OH with a series of dienes (isoprene, 2,3-dimethyl-1,3-butadiene, and 1,3-pentadiene) by the relative method. In the second type of experiments, the oxidation products arising from the OH reaction with 2-propanol were monitored.

(i) In the first series of experiments, two compounds (isoprene and another diene) were introduced in the reactor and their concentrations measured by GC. Blank runs were first performed, which consisted of the following steps: (1) Irradiating a mixture isoprene and dienes (in air) for a duration of 2−6 h. The analysis did not show any noticeable change in the concentrations of the used compounds. (2) Glycolaldehyde was then added to the mixtures and left for about 2−6 h without irradiation. Here also, no concentration change of the dienes was observed. (3) In the last step, when the lamps were switched on, the concentration of isoprene, 2,3-dimethyl-1,3-butadiene, and 1,3-pentadiene were found to decay by around 6%, 7.5%, and 5%, respectively. This led us to conclude that the OH radicals produced from the photolysis of glycolaldehyde were reacting with isoprene and the dienes

$$\mathrm{OH} + \text{isoprene} \rightarrow \text{products} \qquad k_{\text{isoprene}}$$

$$\mathrm{OH} + \text{diene} \rightarrow \text{products} \qquad k_{\text{dienes}}$$

Assuming that the two compounds are only consumed by reaction with OH, it can be shown that

$$\ln([\text{diene}]_0/[\text{diene}]_t) = (k_{\text{diene}}/k_{\text{isoprene}}) \ln([\text{isoprene}]_0/[\text{isoprene}]_t)$$

where the subscripts 0 and t indicate concentrations before irradiation and at time t after the starting of irradiation, respectively. Figure 4 shows an example of the obtained data from the photolysis of isoprene/2,3-dimethyl-1,3-butadiene/glycolaldehyde mixture. The ratios $k_{\text{diene}}/k_{\text{isoprene}}$ derived in different experiments were (1.28 ± 0.06) and (1.23 ± 0.06) for isoprene/2,3-dimethyl-1,3-butadiene, (1.07 ± 0.20) and (1.11 ± 0.20) for isoprene/1,3-*cis*-pentadiene, and (1.21 ± 0.16) and

TABLE 3: Experimental Conditions and Results for the Photolysis of Glycolaldehyde Using Solar Light at EUPHORE

experimental conditions	June 19, 1998	June 21, 1998	June 15, 1999	June 16, 1999	June 16, 1999
[Glyc.]$_0$ (ppm)	0.62	0.77	0.67	0.73	1.80
photolysis time	5 h 30 min	6 h	5 h	7 h	7 h
OH-tracer or scavenger (ppm)	DNBE 0.129	*c*-hexane 13.3	*c*-hexane 13.4	*c*-hexane 13.4	DNBE 0.129
$J(NO_2)$ (s^{-1})	10.0×10^{-3}	9.6×10^{-3}	9.5×10^{-3}	8.6×10^{-3}	8.1×10^{-3}
k_{total} (s^{-1})	$(2.0 \pm 0.2) \times 10^{-5}$	$(1.9 \pm 0.2) \times 10^{-5}$	$(2.4 \pm 0.2) \times 10^{-5}$	$(2.3 \pm 0.2) \times 10^{-5}$	$(1.8 \pm 0.2) \times 10^{-5}$
k_{SF6} (s^{-1})	$(6.4 \pm 0.6) \times 10^{-6}$	$(6.9 \pm 0.7) \times 10^{-6}$	$(9.4 \pm 0.9) \times 10^{-6}$	$(1.0 \pm 0.1) \times 10^{-5}$	$(7.1 \pm 0.7) \times 10^{-6}$
J_{exptl} (s^{-1})	1.36×10^{-5}	$(1.2 \pm 0.2) \times 10^{-5}$	$(1.4 \pm 0.2) \times 10^{-5}$	$(1.2 \pm 0.2) \times 10^{-5}$	1.09×10^{-5}
k_{DNBE} (s^{-1})	$(1.7 \pm 0.2) \times 10^{-5}$				$(1.5 \pm 0.2) \times 10^{-5}$
J_{glyc} (s^{-1})	$(9.2 \pm 1.4) \times 10^{-6}$				$(7.7 \pm 1.1) \times 10^{-6}$
J_{calcd} (s^{-1})	9.3×10^{-6}	8.7×10^{-6}		7.2×10^{-6}	7.2×10^{-6}

(1.13 ± 0.11) for isoprene/1,3-*trans*-pentadiene experiments. In addition, we have performed one experiment where OH was produced from the photolysis of H_2O_2 at 254 nm in the presence of isoprene and 2,3-dimethyl-1,3-butadiene (in the absence of glycolaldehyde). The obtained ratio $k_{diene}/k_{isoprene}$ was (1.25 ± 0.01) which is in good agreement with the data derived using glycolaldehyde as the OH source. These ratios are also compared with those derived from the rate constant data of the literature: $k(OH + \text{isoprene}) = 1.01 \times 10^{-10}$,[17] k(OH + 2,3-dimethyl-1,3-butadiene) $= 1.25 \times 10^{-10}$,[18] k(OH + 1,3-*cis*-pentadiene) $= 1.03 \times 10^{-10}$,[18] and k(OH + 1,3-*trans*-pentadiene) $= 1.14 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [determined during this work compared to isoprene]. From these literature data, the calculated ratios $k_{diene}/k_{isoprene}$ of 1.24 for 2,3-dimethyl-1,3-butadiene, 1.02 for 1,3-*cis*-pentadiene, and 1.13 for 1,3-*trans*-pentadiene are in good agreement with our results.

(ii) A second series of experiments was conducted to confirm that the photolysis of glycolaldehyde is a source of OH radicals. It consisted of irradiating a mixture of 2-propanol and glycolaldehyde in air. The runs were performed as follows: 2-propanol was first introduced in the chamber and left for 1−2 h in the dark and analyzed continuously by GC-FID/MS. No change was observed in its concentrations. Then, the mixture 2-propanol/air was irradiated for 1−2 h, and the 2-propanol concentration also showed a good stability. In a second step, glycolaldehyde was added to the mixture and left in the dark. The GC analysis did not show any change in the concentration of both compounds. Last, the 2-propanol/glycolaldehyde/air mixture was irradiated by the lamps emitting in the range 280−340 nm. In this last step, the analysis showed that both compounds decreased and acetone was formed. Acetone was produced following the OH-initiated oxidation of 2-propanol,[19] which represents another proof that OH was generated from the photolysis of glycolaldehyde in our experimental conditions.

Discussion on the Photolysis of Glycolaldehyde. The photolysis of glycolaldehyde may proceed through four primary

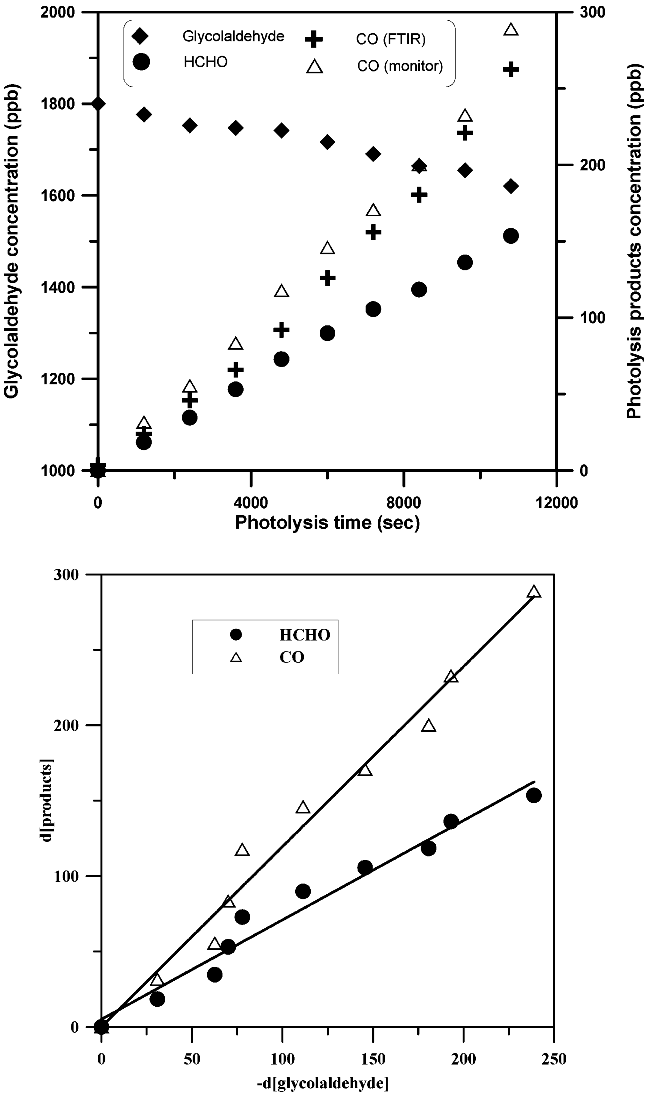

Figure 3. Concentration-time profiles of glycolaldehyde and products and product yields in the photolysis of glycolaldehyde in the presence of DNBE as OH tracer (experiment performed at EUPHORE).

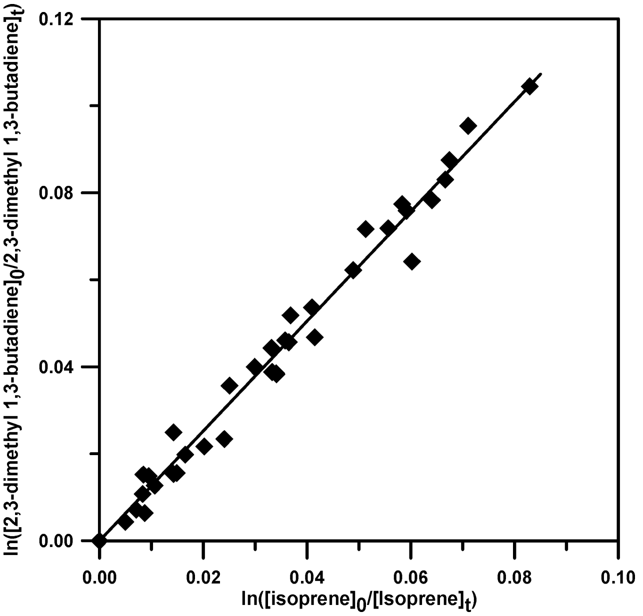

Figure 4. Relative rate plot for the reaction of OH radicals with 2,3-dimethyl-1,3-butadiene using isoprene as the reference compound (experiment performed at Orléans).

TABLE 4: Experimental Conditions and Results of Relative Reaction Rate Constant Measurements Performed in Orléans

[glycolal.]$_0$ (ppm)	reference compound	[ref]$_0$ (ppm)	expt no.	k_{glyc}/k_{ref}	k_{glyc} cm^3 molecule^{-1} s^{-1}
43−52	DIPE	40−50	2	1.06 ± 0.07	$(1.1 \pm 0.2) \times 10^{-11}$
42−53	DEE	49−56	3	0.98 ± 0.11	$(1.3 \pm 0.3) \times 10^{-11}$
43−47	1,3-dioxolane	45−49	2	0.98 ± 0.08	$(1.1 \pm 0.2) \times 10^{-11}$
44	acetaldehyde	55	2	0.92 ± 0.11	$(1.4 \pm 0.2) \times 10^{-11}$

thermochemically feasible processes[20,21]

$$HOCH_2CHO + h\nu \rightarrow OH + CH_2CHO \tag{1}$$

$$\rightarrow CH_2OH + HCO \tag{2}$$

$$\rightarrow CH_3OH + CO \tag{3}$$

$$\rightarrow H + HOCH_2CO \tag{4}$$

The high yields obtained for CO and HCHO suggest that channel (2) is the major photolysis channel of glycolaldehyde in our experimental conditions, HCHO and CO are rapidly produced from primary reactions of O_2 with CH_2OH and HCO

$$CH_2OH + O_2 \rightarrow HCHO + HO_2 \quad k = 9.6 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1\ 22} \tag{5}$$

$$HCO + O_2 \rightarrow CO + HO_2 \quad k = 5.2 \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1\ 22} \tag{6}$$

Methanol observed among the products indicates that the molecular channel (3) is also occurring. The difference between the loss rates of glycolaldehyde measured during the photolysis experiments conducted at Mainz with or without cyclohexane (OH scavenger), the high loss rate of di-*n*-butyl ether (OH tracer) measured in the presence of glycolaldehyde in the EUPHORE experiments and the measurements performed at Orléans, suggest the existence of the OH-radical formation channel (1). A low contribution of the reaction of CH_2CHO with O_2 to the OH production cannot be excluded considering the measured branching ratio of 0.15 for the OH forming channel of this reaction.[23] The radicals H and $HOCH_2CO$ formed from channel (4) react with oxygen leading to HO_2 and $HOCH_2C(O)O_2$, respectively. $HOCH_2C(O)O_2$ could react with HO_2 to produce stable compounds or other radicals. But, no characteristic products of this reaction have been observed.

Products yields obtained in Mainz and EUPHORE give indications on branching ratios of channels (1−3). These indications can be limited by the existence of a secondary chemistry. Hence, the difference between formaldehyde yields obtained in Mainz (91 ± 24)% and at EUPHORE (54 ± 20)% can be explained by the existence of another source of HCHO in experiments conducted at Mainz, which could be OH-initiated oxidation of glycolaldehyde, OH being produced by glycolaldehyde photolysis. Also, the CO yield is slightly higher at EUPHORE (94 ± 20)% than in Mainz (68 ± 16)% which may be due to additional formation of CO from the photolysis of formaldehyde. Moreover, the CH_2CHO radical, produced from channel (1), can be a source of HCHO

$$CH_2CHO + O_2 \rightarrow CH_2(OO)CHO \tag{7}$$

$$CH_2(OO)CHO\ (+RO_2) \rightarrow CH_2(O)CHO\ (+O_2) \tag{8}$$

$$CH_2(O)CHO \rightarrow HCHO + HCO \tag{9}$$

Finally, assuming that channel (4) is negligible, and the contribution of channel (3) equals the yield of CH_3OH (10%), the contribution of channels (1) + (2) equals 90%.

Our results can be compared to those obtained by Bacher et al.,[12] who have conducted a photolysis study on glycolaldehyde in the wavelength range 240−400 nm in a photoreactor using FTIR analysis. These authors have identified HCHO (41 ± 4)%, CO (54 ± 6)%, CO_2 (31 ± 6)%, HCOOH (7 ± 3)%, and CH_3OH (9 ± 2)% as photolysis products which accounted for about 70% of the reacted carbon. They have also noted that CO_2 yields were very variable similar to what we observed in Mainz and have detected glyoxal. The formation of glyoxal has been attributed to the reaction of glycolaldehyde with OH radicals, which could be produced by reaction of HO_2 with residual NO (present in the chamber) or by the following reactions:

$$HO_2 + HOCH_2C(O)O_2 \rightarrow HOCH_2C(O)OOH + O_2 \rightarrow CH_2OH + CO_2 + OH + O_2 \tag{10}$$

Bacher et al.[12] evoke the formation of $HOCH_2C(O)O_2$ via photolysis channel (4) and assign the yield of channel (4) to 15%, to account for their observation of glyoxal. These authors yet mentioned that the occurrence of reaction 10 was not consistent with their chlorine atom relative experiments, which yielded the same rate constant for the reaction with glycolaldehyde in N_2 and air. Bacher et al. further suggest that channel (2) is the major photolysis path forming CH_2OH +HCO (65−80%) and that the molecular channel CH_3OH + CO accounts for 15−20%. Our experiments indicate that the OH radicals are generated directly from the photolysis of glycolaldehyde and not from a photooxidation mechanism as proposed by Bacher et al.

Rate Constant Measurements for the OH Reaction with Glycolaldehyde. The rate constant for the reaction of OH radicals with glycolaldehyde was measured at (298 ± 3) K relative to the rate constants of the OH reaction with four reference compounds (diisopropyl ether, diethyl ether, 1,3-dioxolane, and acetaldehyde). After 50 min of mixing, several samples were taken to check for the wall loss of glycolaldehyde and the reference compounds. All compounds showed a good stability in the absence of OH with and without irradiation using 6 lamps centered at 365 nm. At least two experiments were conducted for each reference at different experimental conditions to check for the reproducibility of the measurements. In Table 4, the experimental conditions and the obtained rate constant ratios are given along with the derived rate constants for the reaction of OH with glycolaldehyde.

The rate constants of the reactions of OH with the reference compounds used to derive k_{glyc} were $(1.02 \pm 0.10) \times 10^{-11}$ for diisopropyl ether,[24] $(1.36 \pm 0.11) \times 10^{-11}$ for diethyl ether,[25] $(1.11 \pm 0.09) \times 10^{-11}$ for 1,3-dioxolane,[25] and $(1.53 \pm 0.08) \times 10^{-11}$ for acetaldehyde[26] (cm^3 molecule^{-1} s^{-1}). As shown in Table 4, the values obtained for the different references are in good agreement, and the recommended value is taken as the average of these values: $k_{glyc} = (1.2 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

The only kinetic studies of the reaction of OH with glycolaldehyde have been performed by Niki et al.[11] and recently by Bacher et al.[12] In both studies, the relative method with FTIR analysis was used. Niki et al. reported a value of (1.0 ± 0.2) ×

TABLE 5: Experimental Conditions and Results of the Photooxidation of Glycolaldehyde Performed in Orléans

expt no.	1	2	3	4	5
irradiation time (min)	150	140	120	120	80
$[Glyc.]_0$ (ppm)	52.6	66.7	49.7	52.3	41.4
Δ[Glyc.] (ppm)	4.1	5.1	4.9	4.8	3.1
concentration and yield (%)					
[HCHO] (ppm)	3	3.2	2.4	1.4	2.7
HCHO (%)	78 ± 10	57 ± 12	51 ± 8	82 ± 16	60 ± 8
[CO] (ppm)	0.6	0.9	0.9	0.5	0.7

10^{-11} cm^3 molecule^{-1} s^{-1} using acetaldehyde as reference ($k = 1.6 \times 10^{-11}$) and CH_3ONO as OH precursor. They reported a ratio of $k_{glyc}/k_{ref} = (0.63 \pm 0.08)$, which could be considered in agreement with our determination.

Bacher et al.[12] have also determined the rate constant for the reaction of OH radicals with glycolaldehyde. They used propene and acetaldehyde as reference compounds and photolysis of CH_3ONO or C_2H_5ONO in the presence of NO in air as OH sources. The obtained ratios k_{glyc}/k_{ref} were (0.49 ± 0.03) and (1.03 ± 0.13) with propene and acetaldehyde as references, respectively. Using k_{ref}(propene) $= 2.6 \times 10^{-11}$ and k_{ref}(acetaldehyde) $= 1.6 \times 10^{-11}$, these authors have obtained $k_{glyc} = (1.28 \pm 0.08) \times 10^{-11}$ and $(1.65 \pm 0.20) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. They made corrections for wall loss and photolysis of glycolaldehyde, which implied an overestimation of k_{glyc} of around 20%. After correction and averaging, they recommended $k_{glyc} = (1.1 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Our experimental result (1.2×10^{-11}) is in fair agreement with the ones obtained previously by Niki et al. (1.0×10^{-11}) and recently by Bacher et al. (1.1×10^{-11}). The measured k_{glyc} is close to the rate constants for the OH reactions with other simple aldehydes such as HCHO (1×10^{-11} [20]) and CHOCHO (1.15×10^{-12} [17]), which may indicate that the reaction is occurring mainly through abstraction of the H atom from the aldehydic group of $HOCH_2CHO$.

The experimental value has been compared to the estimated value using the structure−activity relationship (SAR) of Kwok and Atkinson,[28] $k_{glyc} = 2.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The calculated rate constant is nearly twice that of the experimental value. A recent experimental work published by Bethel et al.[29] led to the revision of the parameters used in SAR calculations. These authors have considered OH effects on α and β positions on H-atom abstraction. The new calculated value is $k_{glyc} = 4.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, higher than the first estimated one. Recently, a theoretical study was performed by Ochando-Pardo et al.,[30] and the overall rate constant at 298 K was calculated to be 3.8×10^{-11} cm^3 molecule^{-1} s^{-1}, in reasonable agreement with the experimental values obtained in this study, considering the number of factors which has to be accurately introduced in the theoretical calculation.

OH-Initiated Oxidation of Glycolaldehyde. The experiments of OH-initiated oxidation of glycolaldehyde have been performed in Orléans (laboratory studies using the same conditions as for the relative rate measurements with initial concentrations of glycolaldehyde of 45 to 60 ppm) and at EUPHORE (2 experiments were performed in June 2000 with initial concentrations of glycolaldehyde of 1 to 1.5 ppm under natural sunlight conditions).

Experiments Performed at Orléans. Several experiments have been performed in the Teflon bag in Orléans. OH radicals were produced by HONO photolysis using 6 TL12 lamps centered on 365 nm. There was no wall loss of glycolaldehyde in the dark. Experimental conditions, initial concentrations and obtained results are shown in Table 5.

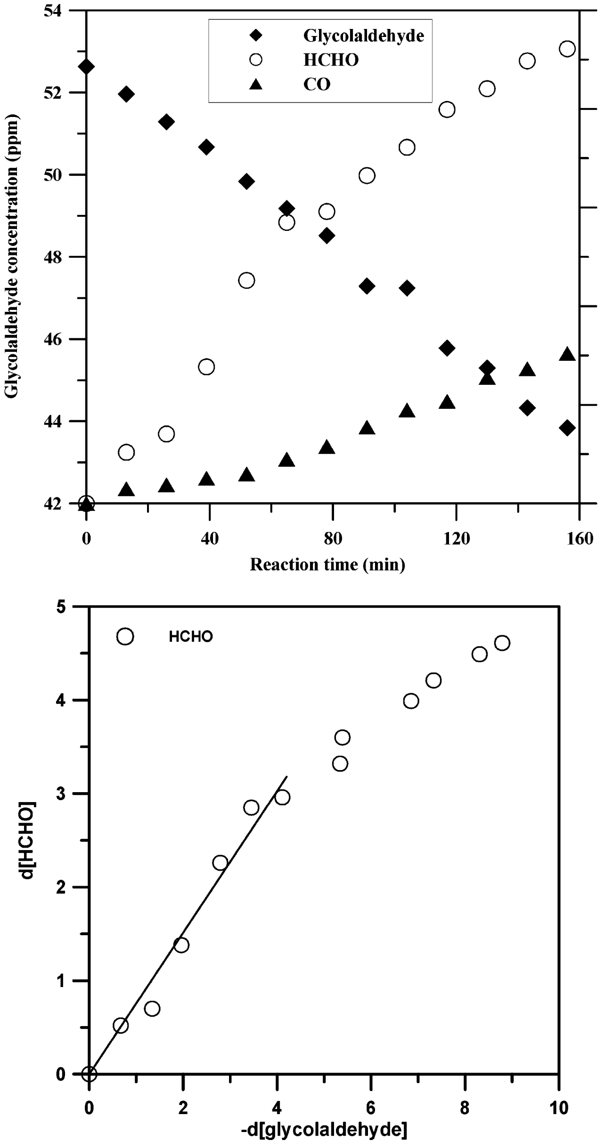

Figure 5. Concentration-time profiles of glycolaldehyde and products and product yields in the OH-initiated oxidation of glycolaldehyde in air (experiment performed at Orléans).

The IR spectra analysis has shown that glycolaldehyde oxidation gives HCHO and CO as major products and traces of formic acid. The concentration−time profiles of glycolaldehyde, HCHO, and CO are represented in Figure 5. These profiles indicate that formaldehyde is a primary product of the reaction, whereas CO is a secondary product. The primary yield obtained for formaldehyde is (66 ± 17)%. No PAN-type compound could be detected even with addition of NO_2 in one experiment.

Experiments Performed at EUPHORE. Two experiments of the OH-initiated oxidation of glycolaldehyde have been performed at EUPHORE using HONO as the OH source. Experimental conditions, initial concentrations, and obtained results are displayed in Table 6. In addition to formaldehyde and CO observed during the runs conducted at Orléans, glyoxal was also detected as a product of the reaction. The derived products yields are (64 ± 5)% for HCHO and (22 ± 6)% for CHOCHO. The carbon balance at the end of the experiment was found to be around 95%. Figure 6 shows concentration−time profiles of glycolaldehyde, HCHO, CO, and CHOCHO for one of the experiments. From this figure, one can note that formaldehyde and glyoxal are primary products, whereas the CO profile corresponds very likely to a secondary product.

TABLE 6: Experimental Conditions and Results of the Photooxidation of Glycolaldehyde Performed at EUPHORE

experimental conditions	June 7, 2000	June 8, 2000
irradiation time	3 h	4 h 10
$J(NO_2)\ s^{-1}$	7.2×10^{-3}	7.1×10^{-3}
$[Glyc.]_0$ (ppb)	1629	1016
Δ[Glyc.]	607	423
concentration (ppb) and yield (%)		
[HCHO]	437	286
HCHO (%)	59 ± 5	69 ± 3
[glyoxal]	169	101
glyoxal (%)	25 ± 6	18 ± 3
[CO]	227	208
$[ozone]_{max}$	413	382

Discussion on the OH-Initiated Oxidation of Glycolaldehyde. The initial reaction of OH radicals with glycolaldehyde can proceed according to 3 pathways, namely the H-atom abstraction from −CHO, $-CH_2-$, or −OH groups

$$HOCH_2CHO + OH \rightarrow HOCH_2C^{\bullet}O + H_2O \quad (11)$$

$$\rightarrow HOC^{\bullet}HCHO + H_2O \quad (12)$$

$$\rightarrow O^{\bullet}CH_2CHO + H_2O \quad (13)$$

According to the literature data on the OH reaction with hydroxy compounds, the H-atom abstraction from the HO−group (reaction 13) is of minor importance and can be considered as negligible in our study [e.g., ref 31]. The H-atom abstraction of the aldehydic group (reaction 11) forms the radical $HOCH_2$-CO, which will react with oxygen to produce the $HOCH_2C(O)$-O_2 radical. This latter reacts with NO or NO_2 to form $HOCH_2CO_2$ or $HOCH_2C(O)O_2NO_2$ according to the reactions

$$HOCH_2CO + O_2\ (+M) \rightarrow HOCH_2C(O)O_2$$

$$HOCH_2C(O)O_2 + NO \rightarrow HOCH_2 + CO_2 + NO_2$$

$$HOCH_2 + O_2 \rightarrow HCHO + HO_2$$

Decomposition of $HOCH_2CO$, which would have yielded primary CO product and $HOCH_2$ is unlikely considering the expected decomposition rate. For $HOCH_2CO$, Méreau et al.[32] have calculated by *ab initio* method an activation energy of 11.7 kcal mol^{-1}, and a rate constant of $3 \times 10^4\ s^{-1}$ at 1 atm and 298 K. The decomposition rate of $HOCH_2CO$ would be negligible compared to that of its reaction with O_2 in 1 atm of air at 298 K which was assumed to be around $10^6\ s^{-1}$.[32]

Reaction 12 proceeding by H-atom abstraction from the $-CH_2-$ group forms the HOCHCHO radical which reacts with O_2 leading to glyoxal

$$HOCHCHO + O_2 \rightarrow CHOCHO + HO_2$$

The series of the reactions given above leads to the observed primary products: HCHO and CHOCHO. Since we have not detected any PAN-type compound, it is likely that this PAN-type is unstable and readily dissociates.

The observation of glyoxal as primary product with a yield of (22 ± 6)% indicates that the H-atom abstraction from the $-CH_2-$ group (channel 12) has a branching ratio equivalent to this yield (≈20%) and that the H-atom abstraction from the −CHO group (channel 11) may have a branching ratio of around 80%.

Atmospheric Implications. The obtained data have been used to calculate the lifetime of glycolaldehyde toward OH reaction and photolysis using the expressions: $\tau_{OH} = 1/(k_{OH}[OH])$ and $\tau_J = 1/J$. Using an OH reaction rate constant of 1.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and an OH concentration ([OH]) of $2 \times 10^6\ cm^{-3}$,[33] the lifetime toward OH reaction is 11 h. Using the measured mean photolysis rate of $1.1 \times 10^{-5}\ s^{-1}$, the lifetime toward the photolysis is about 1 day at ground level. Therefore, the reaction with OH radicals and photolysis can compete as tropospheric sinks of glycolaldehyde. A potential atmospheric impact of the photolysis of glycolaldehyde is the generation of CH_3OH, with an estimated quantum yield of 10%. Since glycolaldehyde is generated as a secondary product in the photooxidation of isoprene with a total yield of 24%, the amount of CH_3OH generated can be estimated. Assuming that the photolysis process represents 1/3 of the total glycolaldehyde removal, and a quantum yield of 0.1 for the CH_3OH formation channel, the production of CH_3OH from isoprene will represent nearly 1% (exactly 0.8%) per molecule isoprene removed. Considering current global source estimates of 500 Tg of

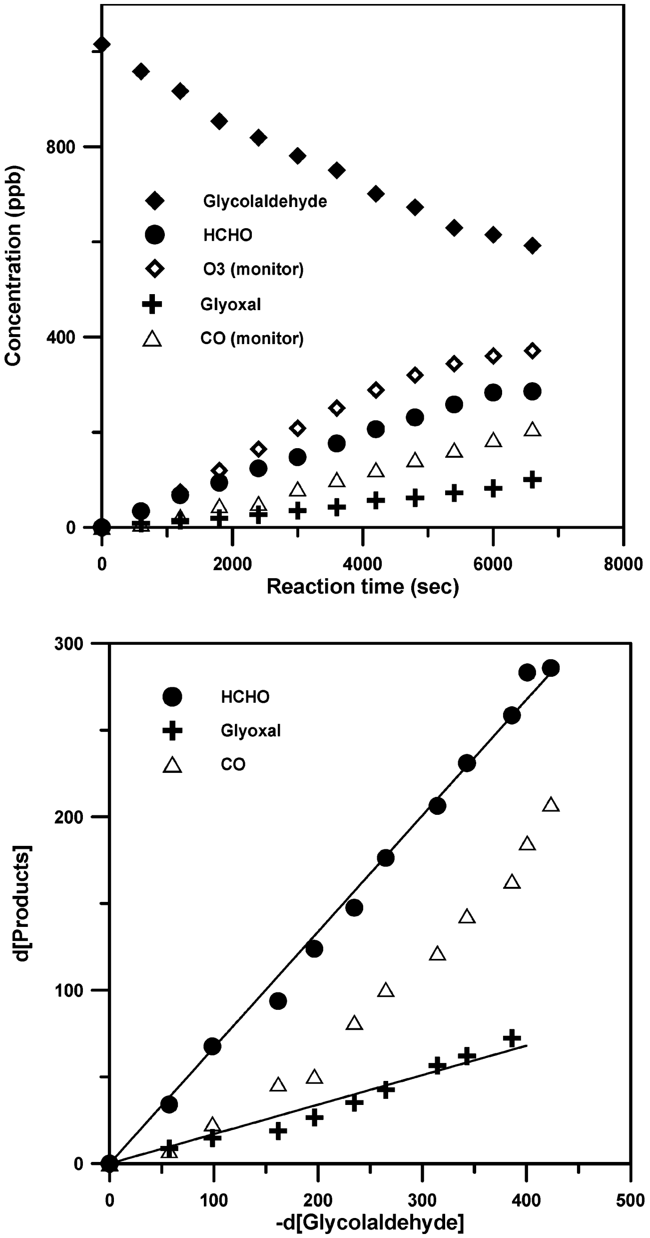

Figure 6. Concentration-time profiles of glycolaldehyde and products and product yields in the OH-initiated oxidation of glycolaldehyde in air (experiment performed at EUPHORE).

isoprene[34] and 200 Tg of methanol,[35] isoprene reaction would account for 2.5% in the global source of methanol. This is a potentially significant source considering the large uncertainties of the global source estimates of both isoprene and methanol. Methanol budget is a current atmospheric issue since it has a long lifetime in the lower troposphere, and will be transported in the upper troposphere or lower stratosphere.[35]

The atmospheric loss of glycolaldehyde through wet chemistry in hydrometeors may also be significant considering the Henry's law solubility constant of 4.1×10^4 M atm^{-1} estimated for glycolaldehyde.[36] This high value implies that wet deposition should not be ruled out in modeling the atmospheric fate of glycolaldehyde.

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