Photochemistry and Photophysics of Glycolaldehyde in Solution

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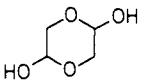
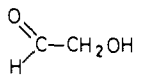
Abstract: The end products for the photolysis of glycolaldehyde in aqueous solution have been monitored by mass spectrometric, FTIR, ^{1}H NMR, ^{13}C NMR, and UV–vis spectroscopic techniques. Methanol, carbon monoxide, formaldehyde, and malonaldehyde are the major photochemical products and are in accord with earlier CIDNP studies. The quantum yields of fluorescence for glycolaldehyde and a series of related alkanal compounds in solution are reported for the first time; they are all in the range $\Phi_F = 0.71–0.84 \times 10^{-3}$. The singlet state decay kinetics for glycolaldehyde and ethanal were followed in more detail by measurement of their fluorescence lifetimes in solution with use of a synchrotron radiation source. The results may be explained in terms of emission from "free" and hydrogen-bonded singlet $n\pi^*$ excited states of the carbonyl compounds in water.

The photochemistry and photophysics of the simple sugars in solution are neither well documented nor understood. Glycolaldehyde is arguably the simplest possible sugar being the first is an homologous series of aliphatic hydroxyaldehydes. In the solid state it has been shown by infrared and Raman spectroscopic techniques[1] to exist exclusively as the compound 2,5-dihydroxy-1,4-dioxane (I), a cyclic dimer of glycolaldehyde (II). However, in nonaqueous solvents, ^{1}H NMR studies show that the free monomer (II) is observed as a minor component (6% in Me_2SO-d_6) of a complex equilibrium mixture consisting mainly of five- and six-membered cyclic dimers in approximately equal proportions.[2] In aqueous solutions, a large amount of hydrated glycolaldehyde (III) is formed; Colins and George[3] have estimated from integration of the ^{1}H NMR spectrum of a 0.1 mol dm^{-3} D_2O solution that 4% of the equilibrium mixture is analyzed as monomer, whereas 70% exists as its hydrate. In contrast with the nonaqueous solution results, only 9% of the solid glycolaldehyde is maintained as the dioxan dimer (I), and 17% is produced as the dioxolan dimer (IV).



I



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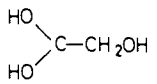

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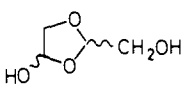

IV

The rate of monomer appearance has been measured in Me_2SO, methanol, and water solutions with ^{1}H NMR,[2] dilatometric,[4] and cryoscopic methods:[5] a simple first-order rate dependence was found in each case. In aqueous solutions the kinetics of the monomerization processes for glycolaldehyde and a related carbonyl compound, dihydroxyacetone [$CH_2(OH)CO\,CH_2(OH)$], have been measured and suggested[4] to exhibit the same general pH-dependent behaviour which has been observed for the mutarotation of D-glucose.[6] In view of the above rate studies, it is surprising that the absorbance at $\lambda_{max} = 256$ nm reported for glycolaldehyde in water was found to be independent of time and pH.[1] These results are contrary not only to the well-established dimer/monomer kinetics for solutions but also to the UV spectra of the isoelectronic aliphatic aldehydes where $\lambda_{max} \simeq 277$ nm. No subsequent UV studies have been reported in the literature.

The primary photochemistry of glycolaldehyde has been examined by Seifert and Bargon[7] using Chemically induced dynamic nuclear polarization (CIDNP). They presented evidence for the α-cleavage of an excited triplet state of $CH_2(OH)CHO$ leading to the formation of formyl and hydroxymethyl radical pairs inside a solvent cage. It was proposed that the two radicals then either recombined to give parent glycolaldehyde or disproportionated to form methanol and carbon monoxide. No direct observation of the products was made although they are those expected by analogy with the photolysis of simple aliphatic aldehydes such as ethanal. There are no reports of luminescence from glycolaldehyde in solution.

The primary photochemistry of higher sugars have been more completely studied due to the commercial interest in irradiated foodstuffs. Laurent[8] and Morre[9] have reported the formation of malonaldehyde in photolyzed, basic solutions of glucose. The presence of malonaldehyde was readily established by its UV spectrum, and the red pigment formed upon treatment with 4,6-dihydroxy-2-mercaptopyrimidine (2-thiobarbituic acid). Photochemical reactions have also been utilized for the decarbonylation of derivitized sugars where Norrish type 1 processes predominate.[10]

The aim of the present research is twofold: (i) to monitor the end products for photolysis of glycolaldehyde in solution in order to evaluate the importance of the α-cleavage photochemical mechanism proposed on the basis of CIDNP data; and (ii) to investigate luminescence from excited electronic states of glycolaldehyde in solution to ascertain the photophysical effect of an hydroxyl functional group on the carbonyl chromophore.

Experimental Section

Glycolaldehyde was purchased from Sigma Chemical Co. Ltd. (batch 12F-0697) and dried under a vacuum of less than 10^{-4} mbar for at least 24 h. Other batches were examined but deemed unsuitable for the present photochemical study as they were found to contain traces of pyridine of the order 100 ppm (w/w). The impurity was evident in the UV spectra as a shoulder at 256 nm; it is not unexpected as the preparative method utilized commerically for glycolaldehyde involves pyridine.[11] Dihydroxyacetone was purchased from Sigma Chemical Co. Ltd. (batch 40F-0246) and stored in a desiccator over silica gel below 273 K. Ethanal propanal, butanal, and acetone (BDH Chemicals Ltd.) were bulb-to-bulb distilled and analyzed by mass spectrometry. None of the compounds showed peaks of greater than 1% of the parent ion at masses greater than the parent mass; all exhibited satisfactory cracking patterns. Analar water and trichloroacetic acid were purchased from BDH

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Chemicals Ltd. Dimedone (Aldrich Chemical Co. Ltd.), 4,6-dihydroxy-2-mercaptopyrimidine (Aldrich Chemical Co. Ltd.), and 2,4-dinitrophenylhydrazine (Fisons PLC) were used as supplied. Thin-layer chromatography (TLC) was carried out on precoated silica plates with a 254-nm fluorescer (Merck 5554). These were spotted with 20 μL of the analyte with use of a micropipette (Drummond microcap), and then the plates were eluted in either dichloromethane/ethanol (19/1) or ethylacetate/hexane (1/3). The plates were then visualized with either 254 nm UV light, iodine vapor, or aqueous potassium permanganate applied as a spray. The method of Smith et al.[12] was used for analysis of malonaldehyde.

UV spectra were recorded on either a Pye-Unicam SP8-500 or an SP8-100. ^{13}C NMR were obtained on a Jeol FX 100L FT-NMR instrument operating at 25.05 MHz with use of standard operating conditions. Gas-phase infrared spectra were recorded on a Digilab FTS-20V FTIR spectrometer at 2 cm^{-1} resolution in a 10 cm path length gas cell equipped with potassium bromide windows. Mass spectra were acquired on an SMS Dataquad 200 spectrometer by leaking the gas to be analyzed directly into the analyzer head. Corrected luminescence spectra were measured with a Perkin-Elmer LS.5 spectrofluorimeter plus a 3600 Data station and PECLS software. Quantum yields were calculated by the method of Winfield et al.[13] relative to quinine sulfate in 1 N sulfuric acid (Φ_F = 0.546 at 293 K).[14] A low-temperature accessory based on the design described by Winfield et al.[15] was used for the measurement of luminescence spectra at 90 K.

Fluorescence lifetime measurements for the aldehydes were carried out with use of the beam-line HA12 of the electron storage ring at the SERC Daresbury Laboratory. The storage ring was operated in single-bunch mode, giving light pulses of 200 ps duration with a repetition frequency of 3.1 MHz. The synchrotron radiation was dispersed by a Spex 1500 SP Czerny-Turner monochromator, and an excitation wavelength of 280 nm (band pass 3 nm) was used. Fluorescence was detected at right angles to the excitation beam with use of a Mullard XP2020Q photomultilier and an LF40 filter ($\lambda > 400$ nm). The samples were contained in a standard fluorescence cell (1 cm × 1 cm cross-section), and a Ludox solution was used to determine the pump profile after each luminescence measurement. Fluorescence lifetimes were determined by measuring successive time intervals between photomultiplier pulses (after a constant fraction discrimination) and the zero-time reference signal from the storage ring, using a time-to-amplitude converter (TAC). Output pulses from the TAC were accumulated in a multichannel analyzer, and the decay profiles were recorded locally on a PDP 11/04 computer. Data storage and analysis were performed on the NAS7000 main-frame computer at Daresbury.

Light from a 250-W medium-pressure mercury lamp (Thorn) was focussed with a quartz lens into the sample contained in a cuvette (1 cm × 1 cm cross section). A grease- and mercury-free vacuum line was used for degassing samples by the freeze–pump–thaw method (10^{-5} mbar at 77 K) with the photolysis experiments. The samples were maintained at 288 K by placing the cells in a water-cooled metal block.

Results

Kinetic Measurements in Aqueous Solution. The UV spectrum of glycolaldehyde in water observed in the present studies exhibits marked time- and pH-dependent behavior, in contrast to the results of Michelson and Klaboe[1] reported above. A broad absorption with λ_{max} = 278 nm grows in and reaches an absorbance maximum after approximately 3 h. By analogy with other simple aldehydes the band is assigned to the $n-\pi^*$ transition of free monomeric glycolaldehyde. In fact, freshly made solutions show a very weak absorbance at 278 nm, indicating the presence of a small amount of monomer in the mainly dimeric solid. The complex nature of the aqueous solution precludes measurement of the concentration of free monomer and hence the molar extinction coefficient of glycolaldehyde. However, in the absorbance range 0.04–0.84 the monomer absorption follows the Beer–Lambert law and an absorbance/concentration ratio of 0.020 ± 0.002 mg^{-1} mL was measured.

A series of UV spectra for 0.1 M aqueous solutions of $CH_2(OH)CHO$ were measured as a function of time and pH at 291 K. The data obtained in these experiments gave good correlation when the monomerization was treated as a first-order rate process. The rate coefficient vs. pH profile shown in Figure 1 indicates that pH has a minimum effect on the rate coefficient in the range 4.0–6.0, which is qualitatively similar to measurements made for the mutarotation of D-glucose.[6] The value for $k_{291}^{7.0}$, the rate coefficient at 291 K and pH 7.0, was determined to be 0.085 ± 0.005 min^{-1}. In order to establish the mechanistic significance of these results a similar set of experiments was performed for 0.1 M aqueous solutions of dihydroxyacetone. In contrast to the suggestions of Bell,[4] the general behavior for the monomerization of dihydroxyacetone was not found to be similar to the dissolution of glycolaldehyde or mutarotation of D-glucose. The rate coefficient vs. pH profile exhibits a minimum at pH 3.4 with no extended pH region of constant effect: these data are summarized

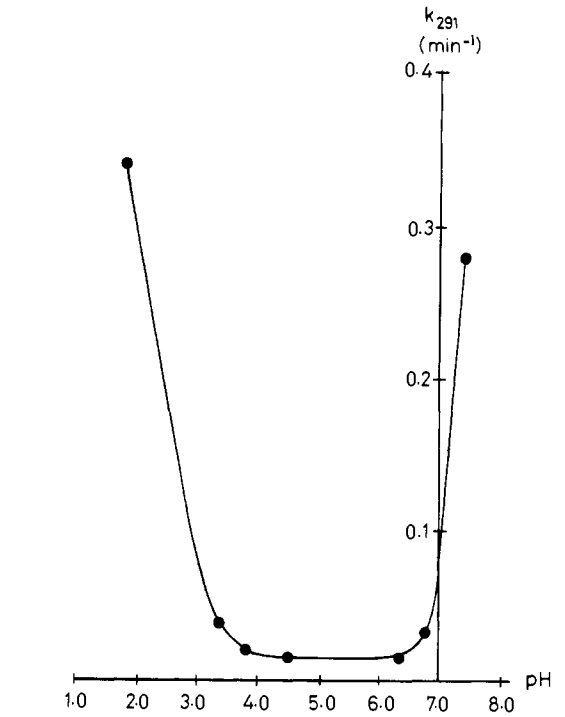

Figure 1. Rate coefficient, k_{291}, vs. pH plot for glycolaldehyde dissolution in water.

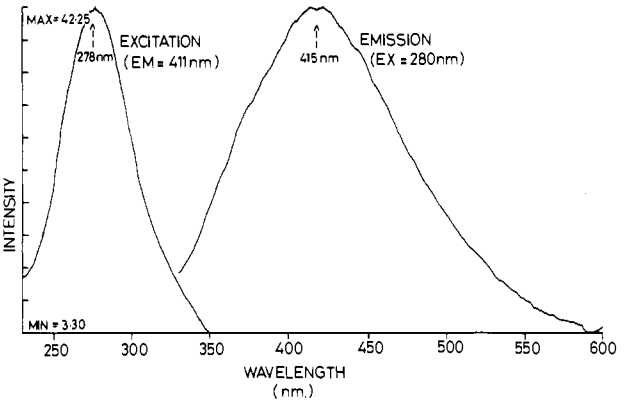

Figure 2. Corrected emission and excitation spectra for glycolaldehyde in water.

Table I. Variation of Rate Coefficient for Dihydroxyacetone Monomerization with pH in Aqueous Solution at 291 K

pH	rate coefficient, min^{-1}	pH	rate coefficient, min^{-1}
1.10	0.271 (±0.005)	4.55	0.034 (±0.005)
1.80	0.085 (±0.005)	5.40	0.068 (±0.005)
2.20	0.040 (±0.005)	6.20	0.133 (±0.005)
2.90	0.013 (±0.005)	7.10	0.204 (±0.005)
3.50	0.004 (±0.005)	8.00	0.337 (±0.005)
4.00	0.009 (±0.005)	8.80	0.806 (±0.005)

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Table II. Fluorescence Characteristics of Some Carbonyl Compounds in Aqueous Solution

compound	λ_{max}(emission), nm	λ_{max}(excitation), nm	$10^3\Phi_F$[a]
glycolaldehyde	415	278	0.79 (0.03)
propanal	410	276	0.73 (0.01)
butanal	412	286	0.71 (0.02)
ethanal	406	276	0.84 (0.03)
acetone	407	265	1.17 (0.03)

[a] Figures in parentheses represent standard deviation of the measurement.

in Table I. The results obtained in this study are quantitatively similar to those observed for the mutarotation of D-fructose.[6] The value for $k_{291}^{7.0}$, the rate coefficient at 291 K and pH 7.0, was determined to be 0.200 ± 0.005 min^{-1}.

Quantum Yield of Fluorescence Measurements. The corrected fluorescence emission and excitation spectra for glycolaldehyde are shown in Figure 2. The emission band is broad and unstructured with a maximum intensity at λ = 415 nm. The corrected excitation spectrum is identical with the UV absorption spectrum described above. No changes in the emission spectra were observed when they were measured at 90 K.

The quantum yield of fluorescence, Φ_F, for glycolaldehyde in water was measured as 0.79×10^{-3} (standard deviation, 0.03×10^{-3}) relative to quinine sulfate in 1 N sulfuric acid. For comparison, the corrected emission and excitation spectra of ethanal, propanal, butanal, and acetone in water were measured along with their respective Φ_F values. The results are summarized in Table II.

Fluorescence Lifetime Measurements. Attempts to measure the fluorescence lifetimes of glycolaldehyde and related simple alkanals with use of a frequency-doubled argon ion laser (λ = 257 nm) as the source of excitation with a single-photon counting apparatus met with difficulties. The low extinction coefficients, typically 10–30 mol^{-1} dm^3 cm^{-1}, and the low fluorescence yields (ca. 10^{-3}) of the aldehydes led to data accumulation times of the order of 3 h. Over this period there was considerable drift in the time base of the laser, and irreproducible data were obtained. These experimental problems were overcome by use of the synchrotron radiation source (SRS) located at the SERC Daresbury Laboratory. The tunability of the SRS allowed optimization of the excitation conditions while its high repetition rate and stability allowed reliable data aquisition; 2×10^4 counts were taken as a standard condition with a typical collection time of 15 min. The fluorescence decay for all the aldehydes studied was monitored over the 1024 channels at both 0.020 and 0.078 ns ch^{-1}.

The decay of glycolaldehyde fluorescence following excitation at 280 nm is shown in Figure 3a. The profile was fitted to both two and three exponential decay functions, giving the same two significant lifetime parameters, τ_1 and τ_2, in each case. The dominant τ_1 factor (A_1 = 0.040 ± 0.003) was determined to be 1.60 ± 0.10 ns whereas a value for τ_2 of 0.30 ± 0.05 ns (A_2 = 0.023 ± 0.003) was obtained. The third lifetime parameter, τ_3, of little statistical significance (A_3 = 0.003 ± 0.001), which varied considerably with background subtraction (τ_3 = 7.0 ± 1.0 ns), was also measured for the three-exponential fitting. The autocorrelation and residuals for this latter fit are shown in parts b and c of Figures 3, respectively, and, when viewed with the calculated χ^2 value of 1.34, they indicate that an adequate description of the decay profile is provided by the τ_1 and τ_2 lifetimes given above. The variable and small contribution of τ_3 to the overall fit may be accounted for by the presence of a low level of luminescent impurity.

The data for ethanal were treated in the same way as for glycolaldehyde and lead to a τ_1 value of 2.10 ± 0.10 ns (A_1 = 0.040 ± 0.004) and a τ_2 value of 0.17 ± 0.02 ns (A_2 = 0.015 ± 0.005). Again two- and three-exponential fits gave the same values for these lifetimes and a χ^2 = 1.30 was calculated for the higher level of fitting.

Photolysis Products of Glycolaldehyde in Solution. The UV absorption spectra of both aerated and degassed aqueous solutions

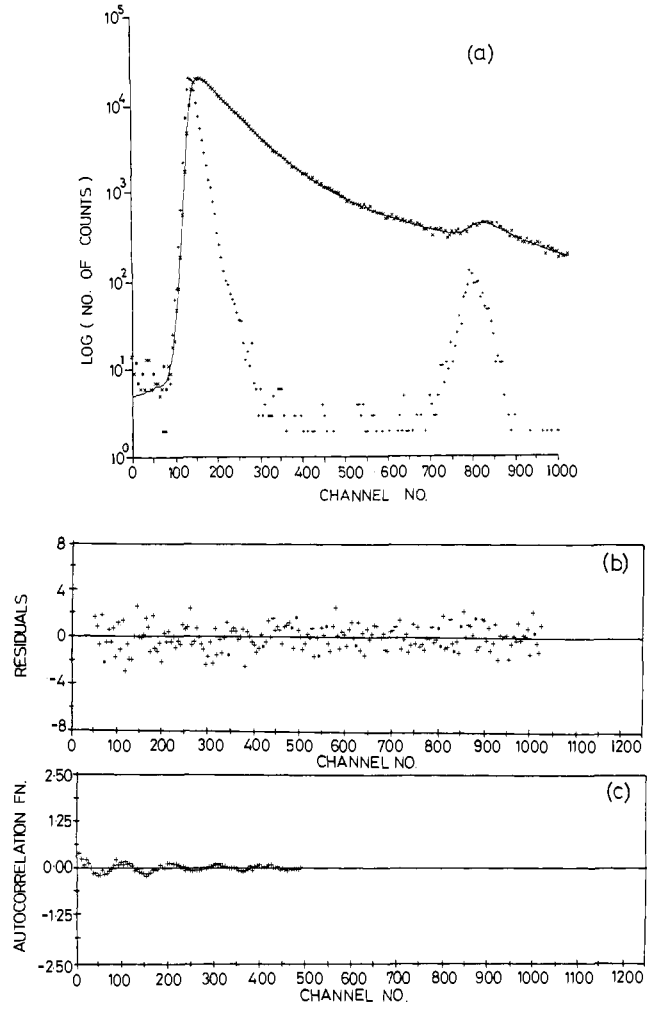

Figure 3. Fluorescence lifetime study for glycolaldehyde in water: (a) decay profile (0.02 ns ch^{-1}); (b) residuals; (c) autocorrelation function.

of glycolaldehyde show considerable changes on photolysis with a medium-pressure mercury lamp. The broad parent peak centered on λ = 278 nm is lost in a new, more strongly absorbing band with λ_{max} = 245 nm as shown in Figure 4. This new feature shifts to λ_{max} = 268 nm upon addition of a mild base such as sodium hydrogen carbonate. Treatment of a photolyzed solution with 4,6-dihydroxy-2-mercaptopyrimidine in 15% trichloroacetic acid at 80 °C gave a deep red coloration with λ_{max} = 530 nm. The same coloration was produced when authentic malonaldehyde was treated in the same manner. The UV spectrum of malonaldehyde shows the same pH dependence as the photolyzed solution with λ_{max} = 245 nm in acidic or neutral solutions and λ_{max} = 268 nm in basic solution. This pH dependence is due to the ionization of the weakly acidic 1,3-dicarbonyl species. Malonaldehyde has been previously identified as a product of photolyzed basic glucose solutions.[8,9]

The ^{13}C NMR spectrum of glycolaldehyde in D_2O is very complex; solutions photolyzed for 5 h show a vareity of new peaks with the most intense of these measured at 83 ppm. This chemical shift is identical with that of aqueous formaldehyde. In solutions which were photolyzed for up to 12 h a weak signal at 50 ppm is observed and is identical with that obtained when an authentic sample of methanol is added to unphotolyzed glycolaldehyde solutions.

Gas bubbles were observed during the photolysis of both aerated and deaerated solutions of glycolaldehyde. The product gas was isolated by performing the irradiation in a sealed cell and then transferring the gas to an evacuated infrared cell. Analysis by FTIR clearly showed the presence of carbon monoxide ($\bar{\nu}$ = 2143 cm^{-1}) as did mass spectrometry (m/e 28, 16, 12). Neither technique indicated the presence of carbon dioxide, and in the mass

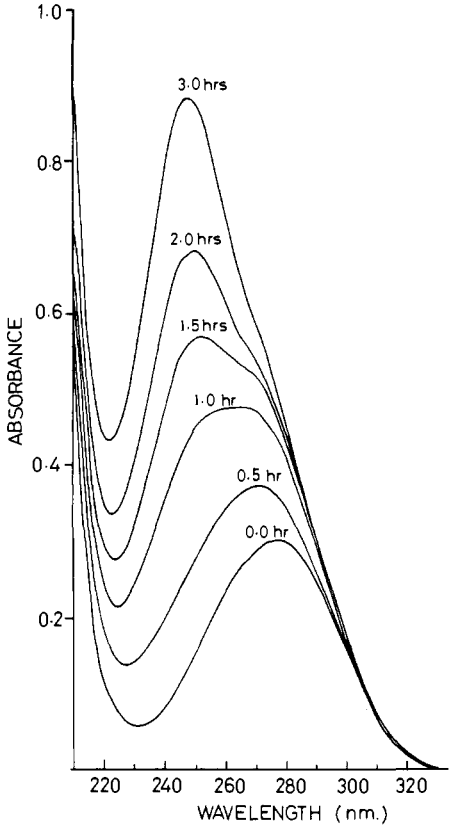

Figure 4. Effect of photolysis by medium-pressure mercury lamp on glycolaldehyde in water.

spectrum only background quantities of molecular hydrogen were detected.

The concentrations of the products identified above, namely, methanol, carbon monoxide, malonaldehyde, and formaldehyde, will be discussed below as will possible mechanisms for their formation.

Discussion

Dissolution Kinetics for Glycolaldehyde in Water. In aqueous solutions glycolaldehyde has been shown to exist in several structural forms by a variety of spectroscopic techniques. ^{1}H NMR studies have indicated that 4% of the complex equilibrium mixture can be attributed to free monomer, $CH_2(OH)CHO$.[3] However, the Beer–Lambert plot obtained in this work indicates that this proportion is closer to 7–9% if it is assumed that the molar extinction coefficient for glycolaldehyde is similar to that of ethanal and proponal (ϵ_{max} = 9 and 12 mol^{-1} dm^3 cm^{-1}, respectively). This would appear to be a good assumption in view of the quantitative and qualitative similarities observed for the fluorescence lifetimes and quantum yields of the aldehydes.

The dissolution of dimeric glycolaldehyde (2,5-dihydroxy-1,4-dioxane) to its monomeric form has been found to follow a simple first-order rate equation: the values obtained for the rate coefficient over the pH range 1.80–7.40 are in agreement with those given by Bell and Hirst,[4] who used dilatometry to measure the change in molar volume as dimer was converted to monomer. The wide range of linearity found for the pH dependence of the rate coefficient in the monomerization process is similar to that found for the mutarotation of D-glucose[6] in which the rate-determining step is not a simple proton transfer but involves a hydrogen-bonded substrate–solvent–catalyst (SSC) intermediate complex.[16]

In contrast, to the observations made by Bell,[4] the dissolution of dimeric dihydroxyacetone was not found to follow the same pH–rate coefficient profile measured for the production of glycolaldehyde monomer from its solid form. Instead, the kinetic dependence was determined to be identical with that found for the mutarotation of D-fructose,[6] which exhibits a clear minimum point at a pH value of 3.40. It may be concluded that the formation of an SSC complex is disfavored by the electronic and/or steric factors involved when the intermediate substrate is a ketone rather than an aldehyde.

The experiments described above for glycolaldehyde were performed by monitoring the appearance of a broad, weak absorption band in the UV spectrum centered at 278 nm. The $n\pi^*$ transition for $CH_2(OH)CHO$ has been previously assigned to a feature with λ_{max} = 256 nm. It is clear from the present study that this latter assignment is in error and can be attributed to a pyridine impurity since (i) the monomerization kinetics followed by UV spectroscopy are similar to those measured by dilatometric methods; (ii) the $n\pi^*$ transition for related alkanals are found in the λ_{max} = 278 nm spectral region; and (iii) doping batch 12F-0697 with traces of pyridine produces identical UV spectra to those obtained with other batches of glycolaldehyde purchased from Sigma Chemical Co.

Luminescence of Aldehydes in Solution. The corrected fluorescence emission and excitation spectra of glycolaldehyde in water closely resemble those of the simple carbonyl compounds ethanal, propanal, butanal, and acetone as can be seen in Table II. The quantum yields of fluorescence for the alkanals and glycolaldehyde in solution have not been measured before although some data relative to an arbitrary Φ_F value for propanal of unity have been reported.[17] The measurements in this work for the aldehydes are all in the range $\Phi_F = 0.71–0.84 \times 10^{-3}$. The result obtained for acetone ($\Phi_F = 1.17 \times 10^{-3}$) is in good agreement with the value published by Testa and O'Sullivan[18] ($\Phi_F = 1.0 \times 10^{-3}$ in *n*-hexane relative to a value of 0.09 for tryptophan).

The photophysics of glycolaldehyde and its analogue ethanal in water can be discussed in some detail as fluorescence lifetime measurements for these compounds were made in addition to the determination of their fluorescence quantum yields. A comparion of the results will give a direct indication of the intramolecular effect of an hydroxyl group on the lowest $n\pi^*$ singlet state of a carbonyl chromophore.

Two significant lifetime parameters, τ_1 and τ_2, were measured when the fluorescence decay profiles were fitted to both two and three experimental functions. The values of τ_1 for glycolaldehyde and ethanal were 1.60 ± 0.10 and 2.10 ± 0.10 ns, respectively, with the corresponding measurements for τ_2 being 0.30 ± 0.05 and 0.17 ± 0.02 ns. The calculated pre-exponential factors, A_1 and A_2, for the two compounds indicate that τ_1 is the dominant contribution to the decay profile in each case: for glycolaldehyde A_1 = 0.040 ± 0.004 and A_2 = 0.023 ± 0.005 while A_1 = 0.040 ± 0.004 and A_2 = 0.015 ± 0.005 for ethanal. Fluorescence lifetimes, τ_F, have been measured previously for propanal and butanal in hexane.[17] The observed decay kinetics of these aldehydes are apparently less complex than those observed in this study as only one lifetime was given for each compound. However, the reported τ_F values (2.3 ns for propanal and 1.7 ns for butanal with λ_{ex} = 310 nm) are in good agreement with the τ_1 parameters obtained for glycolaldehyde and ethanal in water. Furthermore, the value for τ_F of 2.10 ns measured for ethanal in the gas phase (λ_{ex} = 300 nm)[19] is in excellent agreement with the present results for its τ_1 in water. However, the complex decay kinetics observed (and expected) for a carbonyl $n\pi^*$ excited state in a hydrogen-bonding solvent means that τ_1 cannot be necessarily identified with the fluorescence lifetime of "isolated" monomer aldehyde.[20]

In a recent report, Biczók et al.[21] have reported bi-exponential decay characteristics for a series of alkanones in isooctane at 298 K. They ascribed the origin of a short-lived component (0.32–0.48 ns) to the formation of a nonfluorescent excimer in a reversible

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process. This event cannot be ruled out for the present study of glycolaldehyde and ethanal. However, an entirely separate coupled system to explain the data in this study can be proposed. The physical model is based on the existence of both "free" and hydrogen-bonded $n\pi^*$ excited states[22] for the aldehyde compounds in water. Recent experiments[23] and calculations[24] have shown the importance of including hydrogen-bonding effects in appropriate solvents for the study of blue shift phenomena with carbonyl $n\pi^*$ transitions. The observation of two significant lifetime parameters, τ_1 and τ_2, for glycolaldehyde and ethanal in water suggest that hydrogen bonding may also have a specific influence on the decay characteristics of $^1n\pi^*$ states. It would also appear that intramolecular hydrogen bonding between the hydroxyl and carbonyl functional groups in glycolaldehyde has an insignificant effect on photophysics of the $^1n\pi^*$ state as the τ and A factors for both $CH_2(OH)CHO$ and CH_3CHO are similar. A good test for this model would be fluorescence lifetime measurements of glycolaldehyde in aprotic media. However, the dimer solid is insoluble in solvents such as chloroform and cyclohexane.

Photochemistry of Glycolaldehyde in Aqueous Solution. Fourier transform infrared and mass spectrometric analysis of the gas evolved during the photolysis of glycolaldehyde in water showed it to be carbon monoxide with no trace of carbon dioxide or hydrogen. The extrusion of carbon monoxide from aldehydes in solution is well-known and is often accompanied by small amounts of hydrogen.[25] It is possible that hydrogen was being produced in these reactions but the amounts were not detectable in comparison with the mass spectrometer background level. The formation of CO is in accordance with the CIDNP study of Seifert and Bargon,[7] who performed no end-product analysis.

The ^{13}C NMR of glycolaldehyde in deuterium oxide shows two major peaks at 65 and 91 ppm which have been assigned by Barker et al.[26] to the hydrated monomer. A closer examination reveals many more features of which only one is readily assignable: the peak at 205.8 ppm appears as a doublet in the off-resonance spectrum and can therefore be assigned to the formyl carbon of the free monomer. A more sophisticated NMR study (^1H ^{13}C NMR double quantum filtered COSY)[27] has allowed an assignment of the other peaks and will be the subject of a separate report.

In the ^{13}C NMR spectrum of photolyzed glycolaldehyde solution there are a number of new signals produced of which two, namely, formaldehyde (83 ppm) and methanol (50 ppm), have been identified. When samples were doped with these two compounds, the signals observed were coincident with the peaks in the photolyzed solution. Methanol was seen only in solutions exposed to extended photolysis (ca. 12 h) although this is likely to be due to the poor sensitivity of ^{13}C NMR for the detection of methanol, the limit of detection being approximately 0.25 mol dm^{-3} or 5% of the glycolaldehyde concentration. In dilute aqueous solution, formaldehyde exists as the hydrate methanediol, and it is this species to which the peak at 83 ppm is ascribed. Quantitative TLC of the dimedone derivative of formaldehyde shows that after photolysis the concentration of formaldehyde in aerated 0.25 mol dm^{-3} solutions of glycolaldehyde is ca. 5×10^{-3} mol dm^{-3}. Formaldehyde was detected by ^{13}C NMR in both aerated and degassed solutions, indicating that its formation is not effected by the presence of oxygen. Hence it is proposed that H_2CO is formed in the solvent cage as a disproportionation product of the formyl and hydroxy methyl radicals in addition to the reaction producing methanol and carbon monoxide. Reactions 1 and 2 are both exothermic.

$$(H\dot{C}O + \dot{C}H_2OH) \rightarrow H_2CO + H_2CO \quad (1)$$

$$(H\dot{C}O + \dot{C}H_2OH) \rightarrow CH_3OH + CO \quad (2)$$

Seifert and Bargon[7] argued that in acidic solution photolysis of glycolaldehyde produced methanolic acid although no mechanism was proposed. In this work ^{13}C NMR spectroscopy provided no evidence for the formation of methanoic acid, ethylene glycol, glycolic acid, or ethanoic acid.

The major change in the UV absorption spectrum of glycolaldehyde in solution upon medium-pressure mercury arc photolysis has been shown to be due to the formation of malonadehyde, a three-carbon 1,3-dialdehyde. The compound is formed at the same rate regardless of the amount of oxygen present in the solution. Malonaldehyde readily forms the enolic tautomer and is moderately acidic. The anion shows an intense $n-\pi^*$ absorption band at 268 nm while in acid solution the feature becomes less intense and is shifted to 245 nm. The UV spectrum and absorbance of the red pigment formed upon treatment with 4,5-dihydroxy-2-mercaptopyrimidine both indicate that in a 0.25 mol dm^{-3} solution of glycolaldehyde photolyzed for 5 h the concentration of malonaldehyde is ca. 2–6 ppm. The photoproduct has been detected in photolyzed aqueous solutions of formaldehyde in sodium bicarbonate (0.01 mol dm^{-3}). Photolysis of 0.05 mol dm^{-3} formaldehyde solutions under the same conditions used for the glycolaldehyde experiments produced no detectable carbon monoxide or malonaldehyde; the detection limit for the latter compound is 0.1 ppm.

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