The Gas-Phase Photochemistry of Oxalic Acid¹

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The photolysis of oxalic acid has been studied in the gas phase at wavelengths from 257 to 313 nm, corresponding to excitation of the $\tilde{A}({}^{1}A_{u},\pi^{*} + n_{+})$ first excited singlet state. Products were CO₂, CO, H₂O, and HCOOH, all formed linearly with time and with product ratios independent of wavelength and added gases. It is concluded that two primary processes occur, yielding CO₂ + HCOOH and CO₂ + CO + H₂O, respectively, with the yield of the first about 2.6 times that of the second. Weak fluorescence has been observed accompanying the photolysis. The mercury (${}^{3}P_{1}$)-photosensitized decomposition was also studied and was very similar to the direct photolysis, after correcting for secondary decomposition of formic acid. The infrared multiphoton decomposition of oxalic acid vapor was also briefly examined by using a pulsed CO₂ laser operating at 935 cm⁻¹. The same two processes were observed, but with yields of CO approaching those of CO₂ and the second process thus more important than the first. Mechanisms in the three systems are discussed. It is suggested that the ultraviolet photolysis may proceed through the dihydroxymethylene radical, formed directly from the excited state, while the infrared multiphoton decomposition probably involves a simple decomposition of the vibrationally excited ground state.

Introduction

Few studies of the reactions of oxalic acid vapor have been reported probably because of its low vapor pressure and ease of thermal decomposition. The thermal decomposition³ appears to be a simple homogeneous unimolecular dissociation into CO₂ and HCOOH with an activation energy of 30 kcal/mol and a frequency factor of 8×10^{11} s⁻¹. The photolysis, which apparently has not been studied before, is of interest for comparison with that of other α -dicarbonyl compounds such as glyoxal and biacetyl which have been very thoroughly investigated. In addition to the ultraviolet photolysis, we have studied the mercury-photosensitized decomposition of oxalic acid and the multiphoton infrared decomposition.

Experimental Section

Apparatus and techniques were similar to those used previously in this laboratory.⁴ Ultraviolet photolysis was done in a cylindrical quartz vessel, 5 cm in diameter and 10 cm long. A Pyrex vessel of similar dimensions, fitted with NaCl windows, was used for the infrared experiments. Anhydrous oxalic acid (Aldrich) was stored in a cold finger at about 25 °C and warmed to give the desired vapor pressure as required after thorough pumping to remove volatile gases immediately before use. Reaction vessels, cooled storage finger, stopcocks, and gas manifold were all enclosed in an air thermostat held at 115 °C. Product analysis was done by fractionation at -196 and -78 °C, and measurement by gas buret and gas chromatography.

A 1000-W Hg–Xe arc lamp, fitted with a matching monochromator with a bandwidth of about 20 nm, was used for the ultraviolet photolysis. An Oriel 5-W low-pressure Hg lamp was used for the mercury-photosensitized decomposition, with a Vycor filter to remove the 185-nm radiation. For the infrared experiments, a Lumonics Model 203 pulsed CO₂ TEA laser, described previously,^{4,5} was used, operating at a frequency of 935 cm⁻¹. The laser beam was stopped down to about 1-cm diameter, and a Ge lens of 200-cm focal length gave a gently converging beam. Experiments were done at three fluences of about 2,3, and 6 J/cm², obtained by placing the lens at distances of 80, 100, and 130 cm, respectively, from the center of the reaction vessel.

Results

Absorption Spectrum. The gas-phase absorption spectrum, not measured previously, is reported in detail elsewhere;⁶ a low-res-

olution spectrum is shown in Figure 1. The absorption above 255 nm has been assigned to excitation of the first excited singlet state, $\tilde{A}(\pi^*-n_+)$, with its origin at 313 nm. The broad features evident in Figure 1 correspond approximately to excitation of the carbonyl stretching vibration, ν_2' , in the upper state. At higher resolution, a more complex vibrational structure and some rotational structure are evident. At wavelengths below 255 nm, a second, stronger absorption sets in, probably the beginning of a $\pi^*-\pi$ transition. Present photolysis studies were restricted to the first transition.

Ultraviolet Photolysis. The photolysis was studied at wavelengths of 258, 277, 300, and 313 nm, corresponding to maxima in Figure 1, and at pressures between 0.1 and 8 torr, all at 115 °C. Products observed were CO₂, CO, H₂O, and HCOOH. Figures 2 and 3 show typical plots of the yield of CO₂ and CO as a function of time for the photolysis at 300 nm and for the "blank" thermal reaction in the dark.⁷ The intercepts in these plots appear to be caused by thermal decomposition in the solid oxalic acid reservoir during vaporization, while the slopes correspond to the gas-phase photolysis (plus thermal reaction) and the gas-phase thermal reaction alone. Similar behavior was found at all wavelengths. The ratio CO_2/CO for the photolysis (corrected for the thermal reaction) was 3.6 ± 0.5 , apparently independent of reaction time, pressure, and wavelength. The ratio H_2O/CO was approximately unity, while the ratio HCOOH/CO₂ was about 0.5, both ratios independent of reaction time, wavelength, and pressure. Traces of H_2 were observed, apparently formed almost entirely in the initial thermal decomposition during vaporization, amounting to about 4% of the CO_2 formed in the same process. Hydrogen is not a significant photolysis product.

The photolysis of oxalic- d_2 acid was studied briefly at two wavelengths. Its behavior was in all respects similar to that of oxalic- h_2 acid, except for the ratio CO₂/CO, which was 4.9 ± 0.2 , significantly higher than in oxalic- h_2 acid.

Light Emission in the Ultraviolet Photolysis. Weak light emission was observed from $\operatorname{oxalic} -d_2$ and $-h_2$ acid. This was studied in a conventional T-shaped fluorescence cell, with an IP21 photomultiplier to measure total emission transmitted by a Corning 7380 filter which blocked most of the exciting radiation. Excitation spectra are shown in Figure 4 and are seen to follow approximately the absorption spectra with little difference in the two isotopic species. Emission intensity was a linear function of oxalic acid pressure up to 1 torr (i.e., proportional to the light absorbed) and was independent of added air up to a pressure of 12 torr, indicating a fast emission with no collisional quenching, and no quenching

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⁽³⁾ G. Lapidus, D. Barton, and P. E. Yankwich, J. Phys. Chem., 68, 1863 (1964).

⁽⁴⁾ R. A. Back and J. M. Parsons, Can. J. Chem., **59**, 1342 (1981); **60**, 2692 (1982).

⁽⁵⁾ R. A. Back, Can. J. Chem., 60, 2542 (1982).

⁽⁶⁾ R. A. Back, Can. J. Chem., 62, 1414 (1984).

⁽⁷⁾ This is almost certainly a surface reaction, since the rate is much higher than the homogeneous one³ and CO as well as CO_2 is produced. The higher surface/volume ratio and the lower temperature in the present system both favor the surface reaction.



Figure 1. Low-resolution absorption spectra of oxalic- h_2 and $-d_2$ acid. The latter curve has been raised by 0.4 unit of absorbance. The lower line is an empty-cell blank.



Figure 2. Yields of CO_2 from the thermal reaction and the photolysis of oxalic acid vapor at 300 nm, a pressure of 0.5 torr, and temperature of 115 °C.

by oxygen, at these pressures. The emission was too weak to obtain its spectrum.

The $Hg({}^{3}P_{1})$ -Photosensitized Decomposition. Primary products were the same as in the direct photolysis, with production of CO and CO₂ again linear with time. Hydrogen is now a significant minor product, but the nonlinear time dependence (Figure 5) shows that it is largely secondary in origin. Secondary decomposition of formic acid seems a probable source of this hydrogen. The decomposition has been shown⁸ to proceed by two reactions

$$HCOOH + Hg^* \rightarrow H_2O + CO + Hg$$
(1)

$$\rightarrow H_2 + CO_2 + Hg$$
 (2)

with a ratio of reaction 1 to reaction 2 of about 3. The extent of decomposition of oxalic acid in the present system was appreciable (~10% at 30 min), and a simple calculation shows that the decomposition of formic acid expected if its cross section for Hg(³P₁) is similar to that of oxalic acid can account for the observed H₂. Furthermore, the CO₂/CO ratio from the mercury-photosensitized decomposition was appreciably lower than that of the direct photolysis (Figure 5). If the hydrogen produced is assumed to have come from reaction 2, and a value⁸ of 3.1 is taken for the ratio of reaction 1 to reaction 2, a correction can be made



Figure 3. Yields of CO from the thermal reaction and the photolysis of oxalic acid vapor at 300 nm, a pressure of 0.5 torr, and temperature of 115 °C.



Figure 4. Excitation spectra for emission from $\operatorname{oxalic} h_2$ and d_2 acid at a pressure of 0.6 torr. Emission intensity is in arbitrary units.

for CO and CO₂ produced in these reactions. The ratio CO₂/CO corrected in this way is seen in Figure 5 to be raised close to that for the direct photolysis. It may be noted that a similar secondary photolysis of formic acid was not a factor in the direct photolysis of oxalic acid because formic acid absorbs only very weakly at the wavelengths employed.

The Infrared Multiphoton Decomposition. The reported infrared spectrum of oxalic acid vapor shows no absorption in the region accessible with a CO_2 laser,⁹ although the solid-state spectrum has a strong double-headed band centered around 900 cm⁻¹ which has been assigned¹⁰ to an out-of-plane O-H bending mode which appears to be at a much higher frequency in the gas phase.⁹ We observed substantial decomposition, however, with

⁽⁸⁾ J. R. Bates and H. S. Taylor, J. Am. Chem. Soc., 49, 2438 (1927); P. Kebarle and F. P. Lossing, Can. J. Chem., 37, 389 (1959).

⁽⁹⁾ B. C. Stace and C. Oralratmanee, J. Mol. Struct., 18, 339 (1973).
(10) L. J. Bellamy and R. J. Pace, Spectrochim. Acta, 19, 435 (1963).
(11) Heats of formation taken from "Handbook of Chemistry and Physics", 62nd ed., CRC Press Inc., Boca Raton, FL, 1981-1982.



Figure 5. Yield of H_2 and the CO_2/CO product ratio vs. time from the mercury-photosensitized decomposition of oxalic acid vapor.



Figure 6. Product yield from the infrared multiphoton decomposition of oxalic acid vapor at a pressure of 0.5 torr and a fluence of 6 J/cm^2 . Dashed lines are for the concurrent thermal decomposition.

the P30 line of the 10.6- μ m band at 935 cm⁻¹, using the weakly focused beam as described. The unfocused beam gave no decomposition, and the absorption is obviously quite weak; it may perhaps involve absorption in the first overtone of an O-C-O bending vibration observed⁹ at 460 cm⁻¹.

Products were the same as in the ultraviolet photolysis: CO_2 , CO, HCOOH, and H₂O. Figure 6 shows the linear dependence of the yields of CO_2 and CO on the number of pulses, together with the concurrent thermal decomposition for which a correction was made as before. The ratio CO_2/CO was independent of the number of pulses and of the oxalic acid pressure between 0.1 and 0.5 torr but decreased slightly with increasing fluence from about 1.4 at the lowest fluence to 1.1 at the highest. The addition of air decreased yields of both products and increased the CO_2/CO ratio (Figure 7).

Discussion

Primary Processes. The present observations indicate that the photodecomposition of oxalic acid vapor by both ultraviolet and infrared radiation can be described as the sum of two processes:

$$C_2O_4H_2 \rightarrow CO_2 + HCOOH$$
 (3)

$$\rightarrow CO_2 + CO + H_2O \tag{4}$$

In the ultraviolet photolysis, the invariance of product ratios with





Figure 7. The effect of air on the infrared multiphoton decomposition of oxalic acid vapor at 0.4-torr pressure and a fluence of 6 J/cm². Yields in the top curves are relative to those in the pure vapor.



Figure 8. Energy relations (heats of formation) for reagents and products in the decomposition of oxalic acid vapor.¹¹ All numbers are in kcal/mol.

time and pressure suggests that these are primary unimolecular reactions and that reaction 4 is not simply reaction 3 followed by photodecomposition of formic acid. As noted earlier, the latter does occur with increasing conversion in the mercury-photosensitized reaction, although initially reactions 3 and 4 are both primary processes in this system also. The possibility remains in both cases that a fraction of the HCOOH produced in reaction 3 could be sufficiently excited vibrationally to decompose into CO and H_2O . The energetics of the system are shown in Figure 8, and while there is certainly enough excess energy in the ultraviolet photolysis to do this, the lack of dependence of product ratios on wavelength and pressure suggests that it does not occur.

In the infrared multiphoton decomposition, the product ratio is independent of the number of pulses, showing that secondary decomposition of formic acid building up over a series of pulses does not occur. Secondary decomposition within a single pulse also seems unlikely, since the fraction of oxalic acid decomposed per pulse in the irradiated zone was only about 1% at the highest fluence employed, while formic acid does not absorb the radiation used and does not decompose by itself. The decomposition of vibrationally excited formic acid formed in reaction 3 is less easily ruled out. While the product ratio was independent of oxalic acid

 TABLE I: Ratios of Products and Primary Processes in Oxalic Acid

 Decomposition

system	CO ₂ /CO	R_4/R_3	
thermal decomposition ³			-
127–190 °C	50	0.02	
direct photolysis	3.6	0.38	
mercury-photosensitized decomposition	3.3	0.43	
infrared multiphoton			
decomposition			
2 J/cm^2	1.38	2.6	
3 J/cm^2	1.30	3.1	
6 J/cm^2	1.12	7.8	

pressure from 0.1 to 0.5 torr, pressure dependence of the channel ratio in the multiphoton decomposition of a two-channel system can be complex,⁵ and the increase in CO_2/CO on the addition of air up to 5 torr could be caused partly by deactivation of oxalic acid itself during or after the laser pulse and partly by deactivation of excited formic acid. The small probability of decomposition in the laser beam suggests that the decomposition occurs without a great excess of energy above threshold, but even at threshold reaction 3 releases 65 kcal/mol of energy (Figure 8), a major portion of which could be deposited in the formic acid fragment. The activation energy for the unimolecular dehydration of formic acid¹² is 60 kcal/mol, and to account for the CO_2/CO ratio at the highest fluence, over 80% of the formic acid from reaction 3 must have decomposed. All things considered, it seems unlikely that such extensive decomposition occurred in the present system.

Table I summarizes initial product ratios from the several systems studied and relative rates of reactions 3 and 4.

Mechanisms of Decomposition. The thermal decomposition of oxalic acid, at temperatures up to 453 K, yielded only CO₂ and formic acid,³ from which an approximate upper limit for the relative rates of reactions 4 and 3 of $R_4/R_3 \leq 0.02$ might be estimated. In the multiphoton infrared decomposition, CO and H_2O are important products, and if it is assumed that these are formed by reaction 4, then in all the experiments, R_4 was greater than R_3 , and at the highest fluence, $R_4/R_3 = 7.8$. If reactions 3 and 4 are simple unimolecular processes, such a reversal in relative rates with increasing temperature implies that $A_4 > A_3$ and $E_4 > E_3$, where A and E are the usual Arrhenius parameters. If an effective "temperature" of about 1000 K is estimated for the infrared experiments at the highest fluence (based on the fractional decomposition per pulse, the Arrhenius parameters for reaction 3, and comparison with similar systems), then values of $A_4/A_3 = 800$ and $E_4 - E_3 = 9$ kcal/mol would account for the observed difference in R_4/R_3 between the thermal reaction and the infrared multiphoton decomposition.

Yankwich et al. suggested that reaction 3 proceeded by hydrogen transfer through a five-membered cyclic transition state.³ The energy probably required to form dihydroxymethylene makes this path unlikely, and a four-center transition state is more probable:

Formation of $CO_2 + CO + H_2O$ directly from *trans*-oxalic acid by a similar hydrogen transfer seems improbable, raising the possibility that the cis isomer is involved:

The cis isomer of oxalic acid is unknown, but *cis*-glyoxal has been observed spectroscopically and found to be 3.2 kcal/mol less stable than the trans isomer in the ground state.¹³ The barrier to rotation was estimated to lie between 4 and 14 kcal/mol, and the torsional frequency in oxalic acid⁶ suggests a similar or perhaps lower barrier.¹⁴ Equilibration between *cis*- and *trans*-oxalic acid should therefore be fast compared to reactions 3 and 4 ($E_3 = 30$ kcal/mol). The difference in activation energy between reactions 3 and 4 would then arise from the ΔH for cis-trans isomerization and perhaps also from a difference in activation energy between reactions 5 and 6.

In the ultraviolet photolysis, the lack of dependence of product ratios on wavelength and pressure points to a direct rapid decomposition of the excited state rather than decomposition of a vibrationally excited ground state populated by internal conversion. The latter should have shown a strong dependence on energy (and hence on wavelength and pressure) and, considering the excess energy available (Figure 8) compared to that probably available in the infrared photolysis, should have shown a much higher value of R_4/R_3 than observed. The very weak emission observed, again unaffected by pressure, also points to the fast removal of the excited singlet state.

There are also problems, however, with reactions 3 and 4 proceeding directly from the excited state, as one might have expected some dependence of R_4/R_3 on vibrational excitation of the \tilde{A} state, and hence on wavelength. A more attractive mechanism is the initial fast formation of CO₂ + HOCOH:

$$C_2O_4H_2(^{1}A_u) \longrightarrow O_{C_1}H_{C_2}O_{C_2} + C_2 + C_2H_{C_2}H_{C_2}O_$$

This may be regarded as similar to the type II process common in ketones, in which π^* -n excitation makes the carbonyl oxygen a ready acceptor for intramolecular hydrogen-atom transfer. Unlike the thermal reaction of oxalic acid, discussed earlier, excitation in the ultraviolet undoubtedly provides sufficient energy to produce dihydroxymethylene, which could then either decompose or isomerize:



If reactions 8 and 9 have similar energy requirements, or if HO-COH loses most of its vibrational excitation before reaction, values of the ratio R_8/R_9 and hence R_4/R_3 would be independent of the exciting wavelength, as observed.

Finally, the similarity of the product ratios from the mercury-photosensitized reaction and the direct photolysis suggests that the triplet state of oxalic acid might be an intermediate in reaction 7, yielding triplet HOCOH. Alternatively, singlet HOCOH from reaction 7 might be collisionally deactivated to the triplet state before reacting further, with the mercury-photosensitized reaction giving triplet HOCOH directly through the triplet state of oxalic acid. In either case, the triplet state of oxalic acid must be so short-lived that no collisional deactivation can occur.

Registry No. CO₂, 124-38-9; CO, 630-08-0; HCOOH, 64-18-6; Hg, 7439-97-6; C₂O₄H₂, 144-62-7.

 ⁽¹³⁾ G. N. Currie and D. A. Ramsay, Can. J. Phys., 49, 317 (1971); R.
 Y. Dong and D. A. Ramsay, Can. J. Phys., 51, 1463 (1973).

⁽¹⁴⁾ D. Ajo, G. Condorelli, I. Fragal, and G. Granozzi, J. Mol. Struct., 37, 160 (1977). These calculated values for both the energy difference and the barrier between the two isomers appear much too low. Sequence bands in the torsion vibration have been observed up to v = 6 in the ground state of the trans isomer, corresponding to 530 cm⁻¹, with no abnormal anharmonicity, and no bands have been observed at 130 °C in the ultraviolet spectrum that could be attributed to the cis isomer.⁶