

Short Communication

Formation of electronically excited C₂O and C₂ radicals by the laser photolysis of C₃O₂ at 193 nm

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1. Introduction

Two primary processes have been proposed for the photolysis of C₃O₂: the breaking of one C—C bond [1 - 7]



and the breaking of two C—C bonds [8, 9]



Step (2) is energetically possible at wavelengths below 200 nm, and the photodecomposition in step (1) leading to the triplet ground state of C₂O is observed below 320 nm. Below 290 nm formation of C₂O in a low-lying metastable singlet state has been postulated from photochemical studies [3, 4]. More recently Donnelly *et al.* [10] have identified ground state C₂O after the 266 nm photolysis of C₃O₂ by laser-induced fluorescence (LIF). In a subsequent LIF experiment Pitts *et al.* [11, 12] recorded fluorescence spectra of the A ³Π_i → X ³Σ⁻ band system and confirmed the spectroscopic constants obtained in absorption measurements in the gaseous phase [13] and in an argon matrix [14].

The C₂O radical has been proposed as a precursor of the CO* observed in hydrocarbon-oxygen flames [15 - 17]; its formation in the C₃O₂ + O reaction system has recently been demonstrated using LIF [18].

Umemoto *et al.* [19] have investigated the multiphoton dissociation of C₃O₂ at 193 nm and have observed electronically excited C₂* radicals, C* atoms and CO* molecules. They explained the formation of C₂* by the reaction



which had previously been suggested by Kunz *et al.* [20].

In this short communication we report an investigation of the single-photon photolysis of C₃O₂ at a wavelength of 193 nm which produces electronically excited C₂O* A ³Π_i radicals. We also associate the observed

C_2^* emission due to the $d\ ^3\Pi_g \rightarrow a\ ^3\Pi_u$ transition with the occurrence of both primary processes (1) and (2) in the C_3O_2 photolysis.

2. Experimental details

The C_3O_2 was prepared by the dehydration of malonic acid with phosphorus pentoxide [21], purified by trap-to-trap distillation and diluted with argon to a $[C_3O_2]/[Ar]$ ratio of 1/20. The purity of the C_3O_2 was 99% as determined by mass spectroscopy. The purity of the argon was 99.997% (Messer Griesheim). All experiments were carried out at room temperature under flow conditions in a black-anodized cubic aluminium cell of dimensions 15 cm \times 15 cm. The total pressure was measured using an MKS Baratron capacitance manometer. Two types of laser systems were used. The photolysis of C_3O_2 was carried out using the ArF line (193 nm) and the KrF line (248 nm) of a rare gas halide excimer laser (Lambda Physik type EMG 102) with pulse durations of 15 ns and output energies of 150 mJ and 200 mJ respectively. A pulsed dye laser (Quantel YG 481) with an output energy of 50 mJ and a pulse duration of 10 ns was used for the fluorescence excitation of C_2O produced in the ground state by the photolysis of C_3O_2 at 248 nm (KrF line). The fluorescence spectra were observed at right angles to the laser beams using a Spex monochromator (focal length, 22 cm) equipped with a grating (1200 lines mm^{-1}) blazed at 500 nm. EMI 9558 B and Varian VPM 159 A photomultiplier tubes were used for the spectral region below 800 nm and between 800 nm and 1 μm respectively. The photomultiplier output signals were processed using a boxcar integrator.

3. Results and discussion

In the 193 nm photolysis using an unfocused ArF excimer laser beam emissions were observed in the spectral region from 620 nm to about 1 μm , which was the detection limit of the photomultiplier. This emission was attributed to the $A\ ^3\Pi_i \rightarrow X\ ^3\Sigma^-$ transition of the C_2O radical. To identify the transition, the C_2O fluorescence spectrum was produced by C_3O_2 photolysis at 248 nm in combination with LIF. Figure 1 shows parts of both spectra. The positions of the band peaks strongly suggest that the emission is caused by $C_2O^* A\ ^3\Pi_i$. The decay of both emissions exhibited the same lifetime (of the order of 50 μs) which can be related to the previously observed lifetime of $C_2O^* A\ ^3\Pi_i$ [12].

The 638 nm dye laser beam populated the (1, 1, 1) vibrational level with $^3\Sigma^-$ symmetry of the $A\ ^3\Pi_i$ state recently reported by Pitts *et al.* [11]. The spectral shift of the fluorescence to the excitation wavelength agrees within error limits with multiples of the three ground state fundamentals (1978, 379 and 1074 cm^{-1}) given by Devillers and Ramsay [13] and Jacox *et al.* [14]. The LIF spectrum shows additional emissions which have not been assigned. The unidentified emissions may come from the population of other vibrational levels of $C_2O^* A\ ^3\Pi_i$. The photochemical studies performed by Bayes [3] indicate that irradiation of C_3O_2 at wavelengths below 290 nm produces C_2O radicals in a low-lying metastable singlet state. The maximum

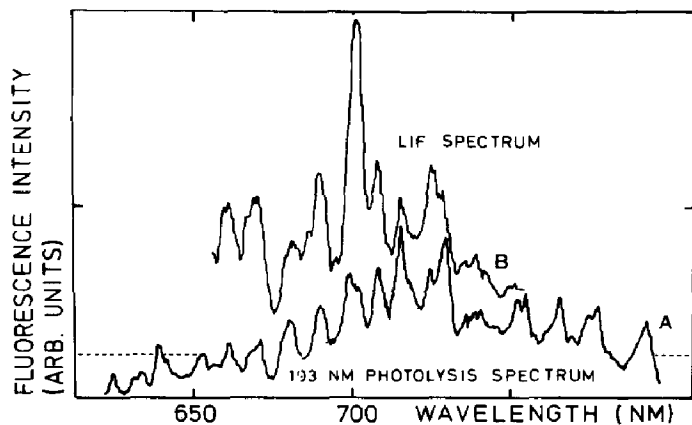


Fig. 1. Curve A, emission observed in the ArF (193 nm) photolysis of 15 mTorr C_3O_2 diluted with argon at 800 mTorr; curve B, laser-induced fluorescence of C_2O excited at 638 nm. The C_2O was produced by the KrF (248 nm) photolysis of C_3O_2 at 200 mTorr diluted with argon at 1.8 Torr. Spectrum B was recorded with a delay of 100 μs between the photolysis pulse and LIF excitation. The intensities were not corrected for the photomultiplier response (EMI 9558 B). The LIF spectrum is overlapped by scattered laser light below 650 nm. As indicated in the figure, the two spectra have different zero lines.

yield for this was found near 250 nm where 90% of the C_2O appeared to be formed in the singlet state. In the present measurements the photolysis at 193 nm generated C_2O^* in the $A^3\Pi_i$ state. Since the dissociation of C_3O_2 into triplet C_2O and singlet CO is forbidden by the spin conservation rule, Willis and Bayes [4] suggested intramolecular crossing to a triplet state of C_3O_2 which decomposes to the triplet C_2O and singlet CO ground states. In the present study the C_2O^* observed in the C_3O_2 photolysis at 193 nm was formed over a time period of 5 - 10 μs . No explanation can be given for such a delayed build-up mechanism, but it is possible that the time required for the formation of $C_2O^* A^3\Pi_i$ is due to either the existence of a transient triplet precursor state of C_3O_2 or a slow C_2O singlet-triplet transition. Furthermore the reaction



cannot be excluded on energetic grounds [22 - 24]. Reaction (4) should lead to a quadratic dependence of the C_2O^* emission intensity on the laser power because carbon atoms and CO are formed in steps (1) or (2) by photolysis at 193 nm. However, the observed linear increase in the emission intensity with increasing laser power indicates that reaction (4) is not important. The C_2O^* emission is quenched by argon at a half-pressure of 2 Torr. The spectral distribution was unchanged within this pressure range.

Photolysis of C_3O_2 at 193 nm, but not at 248 nm, produced, in addition to C_2O^* , emissions of the C_2 Swan system ($d^3\Pi_g \rightarrow a^3\Pi_u$), particularly the "high pressure bands" from the vibrational level $v' = 6$. This system exhibits a lifetime of the order of some microseconds and not the expected

radiative lifetime of 120 ns [25]. This result may indicate that it is produced by secondary reactions. Umemoto *et al.* [19] discussed the kinetics of the Swan emission with the assumption that the C_3O_2 photolysis at 193 nm produced carbon atoms by process (2) as well as C_2O radicals by process (1) which subsequently form C_2^* by reaction (3). They considered that C_2O is present in the first excited singlet state a $^1\Delta$. However, they gave no explanation supporting the production of C_2O a $^1\Delta$. In the present work the intensity of the high pressure bands was independent of pressure when argon was added as a carrier gas in the range from 1 to 10 Torr. This means either that a long-living precursor state like a $^1\Delta$ is not involved in the production of C_2^* or that this metastable state is not quenched by argon.

Further work is necessary to determine whether the C_3O_2 photolysis at 193 nm yields C_2O a $^1\Delta$ in addition to C_2O A $^3\Pi_i$.

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