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A KINETIC STUDY OF $C(2^1S_0)$ IN THE PHOTOLYSIS OF C_3O_2 BY ATOMIC ABSORPTION SPECTROSCOPY

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SUMMARY

Electronically excited carbon atoms, $C(2^1S_0)$, have been monitored by time-resolved resonance absorption following their generation in the low wavelength pulsed irradiation of carbon suboxide. The kinetic decay has been studied in the presence of a number of added gases. The results indicate that the atom in this energized state is produced *via* a secondary process and the mechanism of its formation is discussed in terms of the photolysis of the radical C_2O in a singlet state. Rate data for the collisional removal of $C(2^1S_0)$ by He, H_2, N_2, CO, CH_4 and C_3O_2 are reported and compared with existing data in the literature.

INTRODUCTION

The kinetic study of the low lying states of atomic carbon arising from the $2p^2$ configuration, namely, $C(2^3P_J)$, $C(2^1D_2)$ and $C(2^1S_0)$, is particularly attractive from the viewpoint of elucidating the relationship between chemical reactivity and electronic structure. The very weak spin orbit coupling in this light atom[1] especially justifies the separation of spin and orbital motion that is normally assumed when correlating specific electronic states of reactants and products for atom–molecule reactions[2] *via* the "least symmetrical complex"[3]. Furthermore, $C(2^1D_2)$ and $C(2^1S_0)$, respectively 1.263 and 2.684 eV above the 2^3P_J ground state[1], are highly optically metastable[4] and hence all of these three low lying states are amenable to investigation by atomic absorption spectroscopy, permitting a comparison of rate data derived from the same direct experimental method.

A sizeable body of kinetic data has now been obtained for the reactions of $C(2^3P_J)$ and $C(2^1D_2)$. Braun and coworkers[5] have employed kinetic spectrographic absorption of the atomic resonance lines in the vacuum ultra-violet to

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obtain rate data for these atoms, following their generation by the vacuum ultra-violet flash photolysis of carbon suboxide. Although $C(2^1S_0)$ was also observed and monitored during these experiments, the mechanism of its formation was uncertain, the low quantum yield and its high order dependence on flash intensity suggesting generation by a secondary photolysis process. For this reason, reliable kinetic measurements could not be obtained in this type of experiment, *viz.*, by monitoring the atomic concentration at a fixed time delay as a function of the pressure of reacting gas. Braun *et al.*[5] were able, however, to place an upper limit on the rate constant for the reaction of $C(2^1S_0)$ with hydrogen of 5×10^{-12} cm^3 molecule^{-1} s^{-1}. The main body of data for $C(2^1S_0)$ has been derived from Meaburn and Perner's[6] atomic absorption measurements at $\lambda = 247.8$ nm on this state following pulsed radiolysis of a number of carbon compounds. Some kinetic information may be inferred from the half-lives that were reported[7,8], although the decay kinetics were not unequivocably established. Wolf and coworkers[9] have observed both $C(2^1D_2)$ and $C(2^1S_0)$ by atomic resonance absorption spectroscopy in a flow system, following plasmolysis of organic compounds, but kinetic data were not described. The authors[7,10–13], have employed time-resolved photoelectric atomic resonance absorption spectroscopy to make extensive kinetic studies of $C(2^3P_J)$ and $C(2^1D_2)$, following their generation by flash photolysis of carbon suboxide. The purpose of the present work is to determine the feasibility of kinetic studies of the more highly excited $C(2^1S_0)$ state in this type of system, where the entire decay of the atomic concentration is monitored in a single shot experiment, and further, to investigate the mode of photolytic generation of $C(2^1S_0)$. Rate data for this atomic state are reported, and are compared with the existing data in the literature.

EXPERIMENTAL

A major experimental difficulty in the study of $C(2^1S_0)$ by atomic resonance absorption spectroscopy is the relatively low quantum yield of this species resulting from the vacuum ultra-violet photolysis of C_3O_2 ($\sim$ 2%)[5]. For this reason, it is necessary to employ comparatively high energies ($>$1000 J) to obtain an adequate yield of the atom at time delays beyond the scattered light disturbance ($\sim$ 100 μs) commonly experienced in measurements of this kind. The experimental system described in this paper represents a variation upon the apparatus employed previously by the authors[7,11–13] for the study of atomic carbon. It was designed with the aim of permitting the use of relatively high energies to yield significant photolyses of gaseous molecules at wavelengths down to the transmission cut-off of LiF at $\lambda = \sim 110$ nm.

A diagram of the lamp and vessel assembly is shown in Fig. 1. The basic housing was of a cylindrical brass construction (1 = 14.5 cm, i.d. = 9 cm, end flange diameter = 13 cm) with end flanges attached by means of "Viton" O-ring

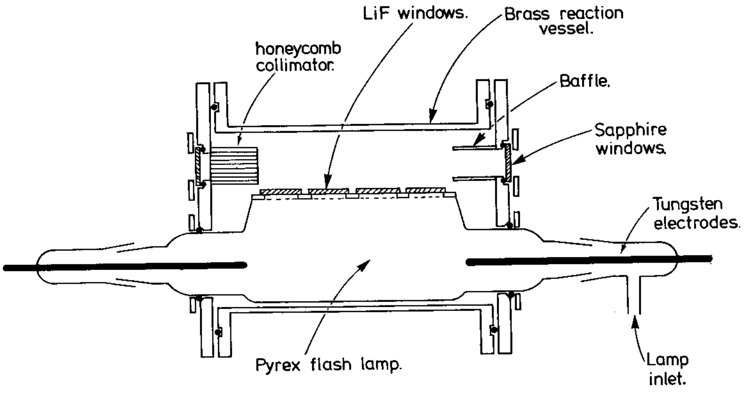


Fig. 1. Schematic diagram of lamp and vessel assembly for low wavelength pulsed irradiation. (Entry ports to reaction vessel and thermocouple not shown.)

seals. The outer space comprised the reaction vessel and the inner, the photolysis lamp, photolysis taking place through four lithium fluoride port holes (22 mm diameter). This may be contrasted with the coaxial system employed previously[7,11–13], essentially using the arrangement described in detail by Donovan[14] for the study of $S(3^1S_0)$, in which the annular space comprised the lamp and the inner cylinder, the vessel. The end flanges were fitted with pumping and filling ports and with a hermetically sealed thermocouple. The Pyrex lamp was attached to these flanges by means of vacuum seals using O-rings. The lamp volume in the region of the discharge was maximized to eliminate shock wave damage to the LiF windows. The lamp cross-section was basically D-shaped with the LiF windows cemented by means of Araldite epoxy resin to the flat surface. The present system offers the potential advantage of permitting temperature dependent studies which were not feasible with the previous arrangement.

Optical measurements were made along an axis opposite to the photolysis lamp windows, through sapphire windows, sealed to the end flanges by means of O-rings. Baffle systems, comprising a honeycomb collimator at the exit window and a cylindrical collimator at the entrance window, were employed to reduce scattered light. The complete interior of the reaction vessel and the outside of the flash lamp, with the exception of the windows, were painted black to reduce scattered light.

The shape of the light pulse from the photolysis lamp ($C = 10\ \mu F$, $V =$ 15–18 kV, $E = 1125$–1620 J), as measured by monitoring the scattered light, was found to be markedly dependent on wavelength, the peak intensity at short wavelength ($\lambda = 200$ nm) occuring at longer times ($\sim 30\ \mu s$) than at longer wavelength ($\lambda \gtrsim 300$ nm) ($\sim 10\ \mu s$). The intensity at short wavelength was critically dependent on gas filling. Thus N_2 gave rise to a considerably greater intensity than Xe at $\lambda = 200$ nm, in fact, the yield of $C(2^1S_0)$ was found to be negligible when employing xenon, and a lamp filling of 6.65 kN m^{-2} of N_2 was used throughout. The lamp was fired by means of high voltage switching using an ignitron (B.T.H. BK 66). The reproducibility of the photoflash lamp was poor at high energies unless a fresh lamp filling was employed for each flash to minimize random variations in the shape and intensity of the pulse. There was further, a significant drop in the light transmission of the LiF windows over a series of 20–30 flashes and the flash energy was gradually increased during a series of runs to compensate partially for this effect. The lamp was dismantled and the LiF windows were repolished, principally to remove deposits of sputtered Pyrex, and annealed between each of such a series of experiments.

Subsequent to photolysis, $C(2^1S_0)$ was monitored in absorption by means of the resonance transition at $\lambda = 247.8$ nm $[C(3^1P_1) \rightarrow C(2^1S_0)$, gf $= 1.8$[15]] derived from a microwave discharge through a quartz flow lamp (1% CO in He, $p_{total} = 106$ N m^{-2}, incident power = 80–100 W). An external H.T. filter unit was used to eliminate inherent ripple (~ 5%) in the output from the microwave generator employed (E.M.I. Type T1001). The atomic line was separated by means of a 1 m grating monochromator (Higler and Watts Monospek 1000, Czerny-Turner mount, blaze wavelength = 300 nm, 1200 lines/mm) used in the first order with 100 μm slits during kinetic experiments. This line was free from extraneous radiation from CO and CO^+ at the spectral resolution employed. The resulting signals were detected by means of a photomultiplier (E.M.I. 9783QB) mounted at the exit slit of the monochromator and used at very low gain with a high photon flux and with an overall voltage across the dynode chain of 550 V. The output was fed into a current-to-voltage converter employing a fast settling operational amplifier[16]. The time constant used in the detection circuit was 2 μs. Scattered light prevented kinetic measurements being made during the first 100 μs subsequent to the flash. The resulting photoelectric pulses, representing time-dependent light absorption by $C(2^1S_0)$, were displayed on a storage oscilloscope (Tektronix type 564B, Time Base 2B67, Type 3A7 differential comparator) using an offset voltage facility to increase the effective size of the oscilloscope screen. The traces were then photographed for kinetic analysis.

Materials

The gases He, N_2, CO, H_2, CH_4 and C_3O_2 were all employed as described previously[11].

RESULTS

Figure 2 shows a typical oscilloscopic trace, illustrating the attenuation of radiation at $\lambda = 247.8$ nm $[C(3^1P_1) \rightarrow C(2^1S_0)]$ following the low wavelength pulsed photolysis of C_3O_2. Our analysis of such traces is based upon an absorption law of the Beer–Lambert form:

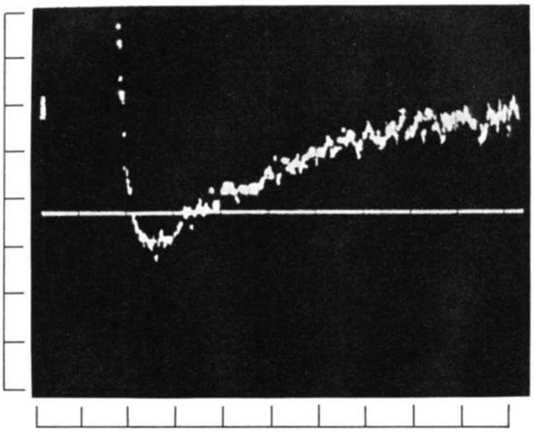


Fig. 2. Oscilloscope trace indicating the decay of $C(2^1S_0)$ obtained by monitoring the absorption of light at $\lambda = 247.8$ nm $[C(3^1P_1) \leftarrow C(2^1S_0)]$. Vertical scale = 0.2 V per division, true baseline offset 1.50 V below indicated baseline. Horizontal scale = 50 μs per division. $p_{C_3O_2} = 0.27$ N m^{-2}, $p_{\text{total with He}} = 6.65$ kN m^{-2}; $E = 1125$ J.

$$I_{tr} = I_0 \exp -(\varepsilon\, lc) \qquad \text{(i)}$$

Experimental verification of this law[17] was not possible in this case owing to the systematic variation in the degree of photolysis from shot to shot (see below) and particularly, to the uncertainty in the mechanism of the generation of $C(2^1S_0)$. However, this law has proved satisfactory in studies of $C(2^3P_J)$ and $C(2^1D_2)$ in this laboratory[7,10-13] and others[18] provided the degree of absorption is low ($\lesssim 50\%$). In the present experiments, the degree of absorption was always $\lesssim 30\%$.

Although the decay of $C(2^1S_0)$ may conceivably be expected to show some deviation from pseudo-first order kinetics in some of the experiments described, the signal to noise ratio was not generally adequate in this work to demonstrate any such effects. Kinetic analysis of the traces was therefore based on the best least squares fit to a pseudo first-order decay. Thus we assume:

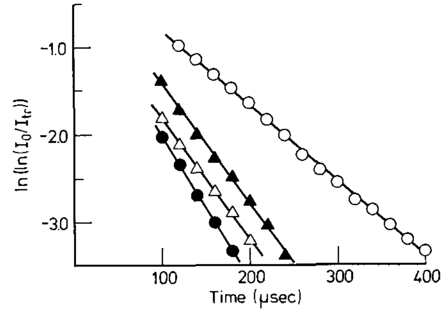
$$\frac{-\mathrm{d}[C(2^1S_0)]}{\mathrm{d}t} = k'[C(2^1S_0)]$$

whence, from eqn. (i), a plot of ln $[\ln(I_0/I_{tr})]$ against time yields a straight line of slope $-k'$, the overall first-order decay coefficient. Good first order plots were, in fact, generally obtained. Figure 3 shows typical first order plots obtained for the decay in the presence of methane.

The rate of decay (k') was found to be strongly dependent on the initial carbon suboxide pressure employed. Figure 4 shows a plot of k' against $P_{C_3O_2}$ from a series of four experiments performed consecutively, *i.e.* minimizing the effect of systematic variation of window transmission. The rate of decay was also influenced to a lesser extent by variations in the degree of photolysis at a fixed initial C_3O_2 pressure. Although the photolysis energy was often systematically varied to compensate partially for this deterioration, experiments were, in fact, necessarily performed over a wide range of initial degrees of photolysis. An estimate of the extent of photolysis in any individual experiment could be made by extrapolating the first order plot back to "zero time" which we take as corresponding to the peak of the photolysis pulse at low wavelength. Thus, we obtain the "initial" relative concentration, C_0, of $C(2^1S_0)$, namely,

$$C_0 = \ln (I_0/I_{t(\mathrm{peak})}) \times \text{const.} \qquad \text{(iii)}$$

The effect of the extent of photolysis upon the decay rate, is illustrated in Fig. 5, where values of k' are plotted against the corresponding values of C_0 at a constant C_3O_2 pressure. This plot shows a small but significant increase in rate at high initial yields of $C(2^1S_0)$, this increase indicating rapid removal of the excited atom by the photolysis products. Extrapolating to zero degree of photolysis, we obtain an intercept in Fig. 5 which we attribute to reaction of $C(2^1S_0)$ with the paren



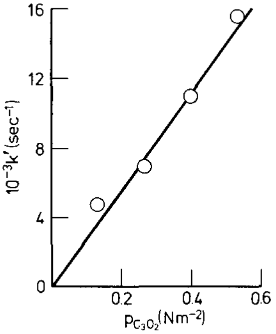


Fig. 3. First-order plots for the decay of $C(2^1S_0)$ in the presence of methane. $p_{C_3O_2} = 0.27$ N m^{-2}, $p_{\text{total with He}} = 6.65$ kN m^{-2}; $E = 1125$ J. p_{CH_4} (N m^{-2}): ○, 0.0; ▲, 0.67; △, 2.0; ●, 3.0.

Fig. 4. Plot of first-order rate coefficient (k') for the decay of $C(2^1S_0)$ against the initial pressure of C_3O_2. $p_{\text{total with He}} = 6.65$ kN m^{-2}; $E = 1620$ J.

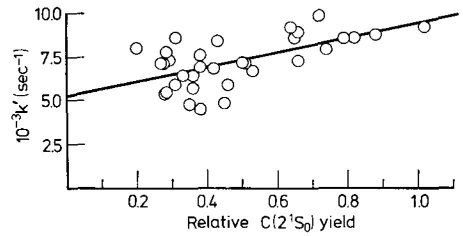


Fig. 5. Plot of first-order rate coefficient (k') for the decay of $C(2^1S_0)$ as a function of the $C(2^1S_0)$ photolysis yield. $p_{C_3O_2} = 0.27$ N m^{-2}, $p_{\text{total with He}} = 6.65$ kN m^{-2}; $E = 1125$–1620 J.

molecule C_3O_2. This yields a value of 1×10^{-10} cm^3 molecule^{-1} s^{-1} for the second order rate constant, consistent with the data in Fig. 4. From the intercept in Fig. 4, we may also place an upper limit on the rate of deactivation of $C(2^1S_0)$ by He of $< 2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

Two distinct effects on the decay traces of $C(2^1S_0)$ could be distinguished upon adding reagent gas. With some gases, a pronounced increase in the rate of decay, *i.e.* in k', was observed due to reaction or deactivation of $C(2^1S_0)$ directly with the added gas. Alternatively, however, it was often found that a gas would decrease the concentration of $C(2^1S_0)$ during the period of observation (100–500 μs), without significantly affecting the decay rate measured during this period. This strongly suggests that the added gas is removing a precursor of $C(2^1S_0)$ which must, in accordance with Braun *et al.*'s[5] original hypothesis, be generated *via* a secondary process. The problem in analyzing the present data lay in distinguishing between these two effects, which in general occurred concurrently. The procedure adopted was to carry out experiments with varying pressures of added gas, with frequently interposed experiments in the absence of the gas. It was then possible, by interpolation, to express the initial relative yield of $C(2^1S_0)$ for a given pressure of added gas as a fraction of the corresponding yield in the absence of added gas. We assume a simple mechanism involving a precursor P for the formation of $C(2^1S_0)$ during the photolysis flash of the form:

$$C_3O_2 + h\nu \xrightarrow{R_1} P + \text{other products} \tag{1}$$

$$P \xrightarrow{R_2} C(2^1S_0) \tag{2}$$

$$P + M \xrightarrow{k_M} \text{other products} \tag{3}$$

where R_1 and R_2 are the rates of processes (1) and (2), and k_M is the second order rate constant for removal of the precursor P by M. Since the decay rate of $C(2^1S_0)$ is relatively slow, the production rate during the photolysis flash may be written:

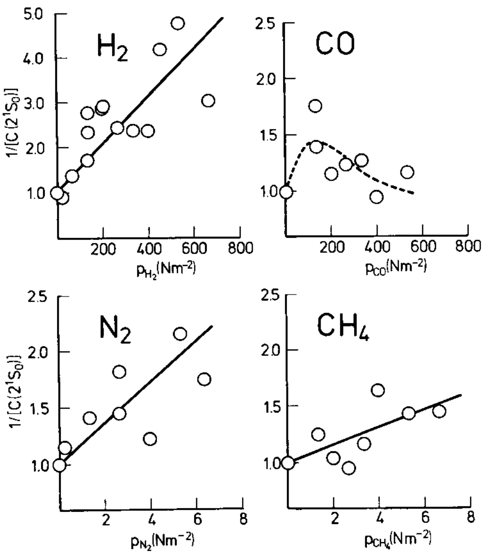
$$\frac{\mathrm{d}C[(2^1S_0)]}{\mathrm{d}t} \simeq \frac{R_1R_2}{R_2 + k_M[M]} \tag{iv}$$

Making the further simplification that R_1 and R_2 are constant during this period, for the initial relative yield of $C(2^1S_0)$:

$$[C(2^1S_0)] = \frac{A}{B + k_M[M]} \tag{v}$$

where A and B are constants. Although the derivation of eqn. (v) neglects depletion of the parent molecule, C_3O_2, and assumes a very simple square wave form for the photolysis pulse, the expression should provide a reasonable description of the variation in the *relative* yield of $C(2^1S_0)$ as a function of the pressure of added gas M. A plot of $1/[C(2^1S_0)]$ against [M] should therefore approximate to a straight line whose slope is proportional to k_M. These plots, which are essentially of the Stern–Volmer type, are illustrated for H_2, CO, N_2 and CH_4 in Fig. 6. It can be seen that, in spite of the considerable experimental scatter (it may be noted that a plot of this type exaggerated the experimental error at low yield, where measurements are least precise), H_2, N_2 and CH_4 give plots consistent with the above analysis, whereas the behaviour with added CO is anomalous. Table 1 gives relative values of k_M obtained by this procedure, expressed relative to $k_{H_2} = 1$.

Figure 7 illustrates the effect of added gases on the decay coefficient k' for removal of $C(2^1S_0)$. The slopes of these plots yield second order rate constants for reaction of $C(2^1S_0)$. These rate constants, which, for the reasons discussed below, we regard as upper limits, are listed in Table 2, together with the values for C_3O_2 and He obtained above. The data are compared with those obtained by Braun *et al.*[5], and those derived from the half-lives reported by Meaburn and Perner[6].



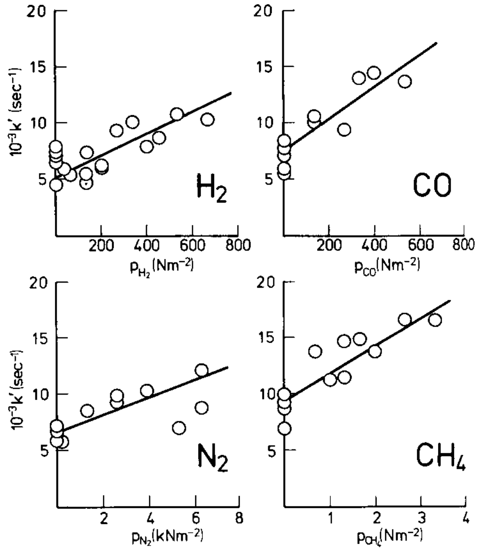


Fig. 6. Stern–Volmer type plots for the effect of added gases on the yields of $C(2^1S_0)$. $p_{C_3O_2} = 0.27\ N\ m^{-2}$, $p_{\text{total with He}} = 6.65\ kN\ m^{-2}$; $E = 1125$–1620 J.

Fig. 7. Plot of first-order rate coefficients (k') for the decay of $C(2^1S_0)$ in the presence of various gases. $p_{C_3O_2} = 0.27\ N\ m^{-2}$, $p_{\text{total with He}} = 6.65\ kN\ m^{-2}$; $E = 1125$–1620 J.

TABLE 1

RELATIVE RATES FOR THE REMOVAL OF THE REACTIVE INTERMEDIATE IN THE PHOTOCHEMICAL GENERATION OF $C(2^1S_0)$

Gas	H_2	CO	N_2	CH_4
Rel. rate	1	—	0.03	29

TABLE 2

RATE DATA FOR REACTIONS OF $C(2^1S_0)$ (k, cm^3 $molecule^{-1}$ s^{-1}, 300 K)

Gas	This work	Braun *et al.*[5]	Meaburn and Perner[6]
C_3O_2	1×10^{-10}		
He	$<2 \times 10^{-15}$		
H_2	$\leqslant 4 \times 10^{-14}$	$<5 \times 10^{-12}$	$\sim 2 \times 10^{-14}$
CO	$\leqslant 6 \times 10^{-14}$		$\leqslant 3.5 \times 10^{-16}$
N_2	$\leqslant 3 \times 10^{-15}$		
CH_4	$\leqslant 10^{-11}$		$\sim 3 \times 10^{-14}$

DISCUSSION

The results obtained in this work confirm the hypothesis of Braun *et al.*[5] that $C(2^1S_0)$ is generated *via* a secondary photolysis process. Braun's conclusion was based on the observation that the production of $C(2^1S_0)$ by photolysis of C_3O_2 exhibited a higher than unit order dependence on light intensity, in contrast with the lower states of atomic carbon, $C(2^3P_J)$ and $C(2^1D_2)$. The present experiments have established that the addition of certain gases which are relatively unreactive towards $C(2^1S_0)$ (as evidenced by direct measurement of the decay rate) can, nevertheless, reduce the yield of $C(2^1S_0)$, and must therefore be reacting with a precursor of the atom. Braun *et al.*[5] have tentatively suggested that this precursor may be the radical C_2O.

The generation of C_2O by the ultra-violet photolysis of C_3O_2 has been firmly established[19–26].

$$C_3O_2 + h\nu \rightarrow C_2O + CO \tag{4}$$

It has been shown that C_2O is produced in the ground triplet state ($^3\Sigma$) at wavelengths above ~ 290 nm, and in an excited singlet state ($^1\Delta$ or $^1\Sigma$) in the wavelength region 240–290 nm, both by direct spectroscopic observation[25,26], and by product analysis in static photochemical systems[19–24]. Bayes[21] has made simple molecular orbital calculations of the radical C_2O. These indicate a $^3\Sigma$ ground state with $^1\Delta$ and $^1\Sigma$ states lying approximately 0.5 and 0.8 eV above the ground state. In the present system, the bulk of the photolysis occurs at wavelength below 200 nm owing to the very much greater absorption coefficient of C_3O_2 in this region[27]. Here the major process has been established as[5]:

$$C_3O_2 \rightarrow 2CO + C \tag{5}$$

with the carbon atoms generated principally in the ^3P state (~ 80%) and the majority of the remainder in the ^1D state. The wavelength threshold for the generation of $C(2^1S_0)$ by direct photolysis is 139.4 nm[28], and in view of the lower lamp output, and the lower intensity of the C_3O_2 absorption continuum at these lower wavelengths[27], it is not surprising that the ^1S atom does not appear to be produced significantly in the primary process. The low wavelength photolysis mechanism, however, does lead to further possible avenues for the generation of C_2O radicals by exothermic reactions of the type:

$$C(2^3P_J) + C_3O_2 \rightarrow 2C_2O \tag{6}$$

$$C(2^1D_2) + C_3O_2 \rightarrow 2C_2O \tag{7}$$

Previous measurements have established that both $C(2^3P_J)$[10,11] and $C(2^1D_2)$[7,12,13] react very rapidly with C_3O_2. There remains the possibility of the formation of C_2O radicals by recombination with CO added, or formed in the primary photolysis process:

$$C(2^3P_J) + CO + M \rightarrow C_2O + M \tag{8}$$

Measurements of the third order rate constant for process (8) have been made hitherto[11] and yield a value of 6.3×10^{-32} cm^6 molecule^{-2} s^{-1} (M = He).

Efficient photodissociation of C_2O to form ground state CO ($^1\Sigma^+$) and $C(2^1S_0)$ would require C_2O to be in a singlet state. For the photodissociation processes:

$$C_2O(^1\Delta) \rightarrow CO(^1\Sigma) + C(2^1S_0) \tag{9}$$

$$C_2O(^1\Sigma) \rightarrow CO(^1\Sigma) + C(2^1S_0) \tag{10}$$

we obtain threshold wavelengths of (278.2–207.7) nm and (295.5–217.1) nm, respectively, dependent on the value employed (384–238 kJ/mol) for $\Delta H^0{}_f$ of C_2O ($^3\Sigma$)[29–31]. Morrow and McGrath[25] have observed diffuse spectra in the region 445–310 nm which they attribute tentatively to singlet states of C_2O, and report continuous absorption at shorter wavelengths.

In Table 1 we present relative rate data from the plots in Fig. 7 which pertain to the removal of the precursor to $C(2^1S_0)$. Although the numerical values obtained here should be regarded with some caution, in view of the crudeness of the analysis, what is perhaps most significant is the anomalous behaviour upon addition of CO. Increasing quantities of this gas appeared firstly, to decrease, and then increase the yield of $C(2^1S_0)$. It may be noted that CO might be expected to increase the rate of production of C_2O *via* reaction (8). Although the C_2O will probably be formed initially in a triplet state (reaction of $C(2^1D_2)$ with CO will result in quenching to the ground state[5,7]), interconversion between the closely spaced electronic levels of C_2O could lead to an increased photolysis yield of $C(2^1S_0)$ *via* a singlet state of C_2O.

The present results therefore add weight to the hypothesis that C_2O photolysis provides the source of $C(2^1S_0)$ in this system. The origin of the C_2O, whether by direct photolysis, or *via* reaction of carbon atoms with the parent molecule as in reactions (6), (7) and (8) remains to be resolved. Some conclusions regarding this may be drawn from the data obtained in this work. Thus, it may be seen that addition of very small quantities of H_2, CO, CH_4, N_2, sufficient to compete effectively with other species in the system in deactivating $C(2^1D_2)$[7], cause an insignificant change in the $C(2^1S_0)$ yield. Reaction (7) may therefore be discounted as a major route to the formation of $C(2^1S_0)$. Further, the amounts of H_2, CH_4 and N_2 which were required (Fig. 6) to cause a significant reduction in the yield of $C(2^1S_0)$, would only cause a small reduction in the amount of $C(2^3P_J)$ present *during the photolysis flash*, on the basis of our existing measurements for the rates of reaction of the ground state atom[10,11]. It would appear, therefore, that reaction (6) can only account for a small proportion of the C_2O responsible for the $C(2^1S_0)$ yield. We are consequently led to the conclusion that, in the absence of added CO, direct photolysis of C_3O_2 provides the principal source of singlet C_2O in our system. We may note that each of the molecules CO_2[32] and COS[14] in their ground $^1\Sigma$ states, yield $O(2^1S_0)$ and $S(3^1S_0)$ *via* photodissociation in their intense low wavelength absorption continua. The molecular orbital calculations of Bayes[21] indicate that the molecular orbital manifolds of CO_2 and C_2O exhibit a close resemblance.

The complexity of the present system leads us to regard the kinetic data obtained for the decay of $C(2^1S_0)$ with some caution. It has been shown (Fig. 5) that $C(2^1S_0)$ can react with the products of photolysis, as well as with the parent molecule, C_3O_2. $C(2^1S_0)$ is a minor product of the photolysis by comparison with $C(2^3P_J)$ and $C(2^1D_2)$, and we cannot discount the possibility that the decay of $C(2^1S_0)$ in the presence of added gases may be affected by interaction with the products of reaction of these lower states of the carbon atom. We therefore regard our present results as providing upper limits on the rate constants for reactions of $C(2^1S_0)$. For this reason, the data are not necessarily inconsistent with those derived from the work of Meaburn and Perner (Table 2). We may emphasize that the present experiments constitute the first detailed measurements on the kinetic decay of $C(2^1S_0)$. What is clear from this work is confirmation of the conclusion that $C(2^1S_0)$ is appreciably less reactive than the less highly excited $C(2^1D_2)$ state[7], with all of the added gases employed. This behaviour parallels that of the analogous states oxygen and sulphur atoms, and may be interpreted in terms of the effect of spin and orbital symmetry on the pathways available for reaction[2].

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