THE PHOTOCHEMISTRY OF 1,2-CYCLOBUTANEDIONE IN THE GAS PHASE

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Summary

The gas phase photochemistry of 1,2-cyclobutanedione (CBD) has been studied for the first time at five wavelengths between 400 and 500 nm, at which it is excited to its first $\pi^* \leftarrow n_+$, $^1B_1 \leftarrow {}^1A_1$ excited state. Major products were CO and C_2H_4, and a simple primary dissociation is indicated:

$$CBD + h\nu \longrightarrow 2CO + C_2H_4 \tag{1}$$
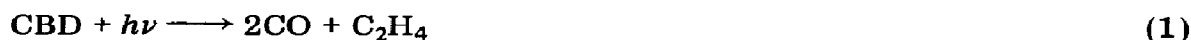
In the initial stages of the photolysis, $[C_2H_4] < 0.5[CO]$, and it is suggested that a second primary process

$$CBD + h\nu \longrightarrow X + CO \tag{2}$$

occurs, in which X is tentatively identified as cyclopropanone, which is lost by secondary decomposition and polymerization.

Quantum yields of C_2H_4 were measured and varied from about 0.7 to 1.0, increasing with decreasing wavelength. The addition of CO_2 reduced the yields of C_2H_4, and pressures for 50% quenching between 300 and 800 Torr were measured, increasing with decreasing wavelength. Fluorescence was also observed from the system; relative quantum yields were measured which decreased at the shorter wavelengths. An emission spectrum is reported, excited at 488.0 nm. Oxygen had a small quenching effect on the emission, which appears to be singlet rather than triplet emission. A low resolution absorption spectrum is also reported, and shows complex sharp vibrational structure. Mechanisms are suggested for the photolysis and the light emission, and comparisons are made with glyoxal and cyclobutanone.

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1. Introduction

The thermal decomposition and the photolysis of several α-dicarbonyl compounds have been examined in recent publications from this laboratory [1 - 4]. The compound 1,2-cyclobutanedione (CBD) is of special interest because it is locked into the less stable cis configuration, which has been observed only in glyoxal and then only in one part per thousand in equilibrium with the trans isomer [4]. It is also of interest for comparison with other cyclic carbonyl compounds, particularly cyclobutanone, which have been very much studied [5]. The thermal decomposition of CBD was recently examined in this laboratory [6] and elsewhere [7] and appears to proceed by a clean unimolecular dissociation into C_2H_4 + 2CO. The photolysis of CBD vapour, which has apparently not been studied before, is described in the present paper.

2. Experimental details

The apparatus and techniques for handling CBD were as previously described [6]. The cylindrical quartz photolysis cell was 10 cm long and 5 cm in diameter. The reaction vessel, gas-handling manifold, quartz spiral pressure gauge and reagent storage trap were all enclosed in an air thermostat usually held at 56 °C, hot enough to avoid condensation at the pressures employed but low enough so that thermal decomposition was negligible.

The light source was a 625 W tungsten–halogen lamp, focused on the slit of a monochromator which gave a bandwidth of about 20 nm (at half-height) at selected wavelengths between 400 and 500 nm. Light intensities were measured after transmission through the cell using a Scientech 362 power meter; extinction coefficients for the actual wavelengths and bandwidths used for photolysis were measured in this way, and the number of quanta of light absorbed by the CBD vapour was calculated, after appropriate window corrections, to obtain quantum yields. The incident flux was between 10^{14} and 10^{15} photons s^{-1}.

Fluorescence measurements were made in the usual T-shaped cell, using an IP21 RCA photomultiplier with a sharp cut-off filter to remove most of the exciting light. The extent of absorption was always small enough to avoid attenuation effects.

Following photolysis, products were removed through traps at -196, -78 and 0 °C. Gases volatile at -196 °C were collected with a Toepler pump and gas burette and analysed by gas chromatography on a molecular sieve column with a thermal conductivity detector. Gases volatile at -78 °C were then collected in a similar way and analysed on Porapak Q by flame ionization detection. In a series of experiments to measure the effect of CO_2 on the photolysis, CBD vapour was irradiated in a spiral of Pyrex tubing (8 mm in outside diameter) which also served as a pick-up for the gas chroma-

tograph, injecting products directly onto the column without condensation or other handling.

CBD was prepared as described previously [6, 8] and had no impurities detectable by nuclear magnetic resonance analysis or by gas chromatography.

3. Results

3.1 Absorption spectrum

Figure 1 shows part of a low resolution absorption spectrum of CBD vapour in the visible region, taken with a 1 m Spex spectrometer and a 2 m absorption cell at about 50 °C. The spectrum shows sharp complex vibrational structure and, at high resolution, sharp rotational structure. A detailed analysis of the spectrum will be published elsewhere [9]. The photolysis was studied at the five wavelengths (two are shown in Fig. 1) 493.3, 481.8, 457.3, 447.6 and 417.9 nm, which are centred on the vibrational bands listed with their assignments in Table 1. Also shown are extinction coeffi-
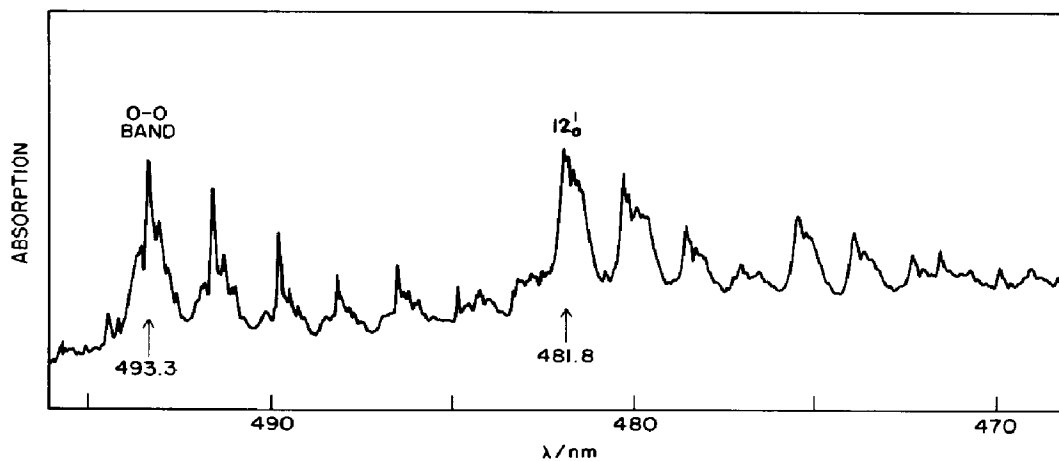

Fig. 1. Low resolution absorption spectrum of CBD vapour. The arrows show the two longest wavelengths used in the photolysis.

TABLE 1

Wavelengths used for photolysis of 1,2-cyclobutanedione

Wavelength (nm)	Absorption band vibrational assignment	Molar decadic extinction coefficient (M^{-1} cm^{-1})
493.3	0−0	14.8
481.8	12_0^1	19.2
457.3	2_0^1	11.2
447.6	$2_0^1 12_0^1$	8.8
417.9	$2_0^2 12_0^1$	2.95

ν_2, carbonyl stretch; ν_{12}, asymmetric carbonyl wag [9].

cients measured at the same bandwidths used in the photolysis; with many sharp features in the spectrum, these values can vary strongly with wavelength and bandwidth.

3.2. Products of the photolysis

CO and C_2H_4 were the only products of any importance that were positively identified and measured by mass spectrometry and gas chromatography (traces of CH_4 and CO_2, less than 0.1% of the CO, were also detected, and even smaller amounts of ketene). A third product X was also formed in substantial amounts and was very probably cyclopropanone, but we were unable to make a positive identification. Evidence for the formation of X and its identity was as follows.

(a) Initial production of C_2H_4 was always less than half that of CO, but with increasing time of photolysis the $[C_2H_4]/[CO]$ ratio rose to about 0.5, the value expected if these were the only products (Fig. 2).

(b) The volume of gases condensable at $-196\ ^\circ C$ and volatile at $-78\ ^\circ C$ collected in the gas burette was always more than the quantity of C_2H_4 measured by gas chromatography. A white polymer was deposited throughout the parts of the vacuum line exposed to these products, making gas volume measurements uncertain, but the amount of extra gas present was approximately that expected if the deficit of C_2H_4 indicated by the $[C_2H_4]/[CO]$ ratio were due to cyclopropanone formation.

(c) A variety of attempts to detect and identify cyclopropanone were unsuccessful. These included mass spectrometry (with and without gas chromatography), IR absorption of the gaseous products and UV absorption, with measurements both during and immediately after photolysis of CBD vapour in a 2 m tube. No absorption was detectable around 310 nm where cyclopropanone is reported to absorb [10].
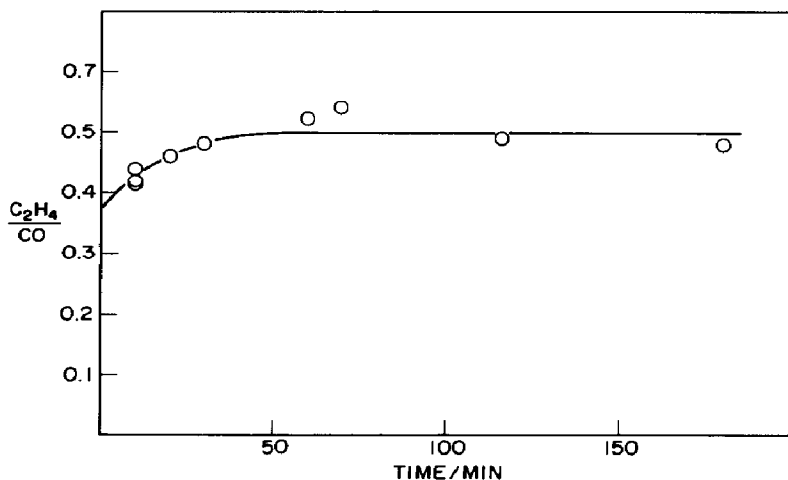

Fig. 2. Product ratio *vs.* time of irradiation in the photolysis of CBD at 493.3 nm.

(d) When the photodecomposition of CBD exceeded a few per cent, polymer formation became evident in the photolysis cell itself. In a few experiments with a 488 nm argon ion laser used to obtain a fluorescence spectrum, polymer formation on the front window was visible within seconds.

All these observations are more or less compatible with the reported properties of cyclopropanone [10, 11], particularly its tendency to polymerize. The behaviour of the $[C_2H_4]/[CO]$ ratio in Fig. 2 suggests that cyclopropanone is a transient product which decomposes to C_2H_4 plus CO, which is somewhat at variance with the report that it disappears thermally mostly by polymerization rather than fragmentation [11]. The very low partial pressures of cyclopropanone in the present system may favour fragmentation; photolysis, which does yield C_2H_4 plus CO [10], does not seem likely, since cyclopropanone apparently does not absorb light above about 350 nm; photosensitization by energy transfer from CBD might be a possibility.

If it is assumed that the photolysis of CBD proceeds by the two channels

$$CBD + h\nu \longrightarrow C_2H_4 + 2CO \qquad\qquad (1)$$

$$CBD + h\nu \longrightarrow X + CO \qquad\qquad (2)$$

values of the initial relative yields of reactions (1) and (2) can be calculated from the $[C_2H_4]/[CO]$ ratio taken from the intercept in Fig. 2 and from similar plots at other wavelengths; these are shown in Table 2.

TABLE 2

Initial product ratios and quantum yields in the photolysis of 1,2-cyclobutanedione

Wavelength (nm)	Initial $[C_2H_4]/[CO]$	$R_2/(R_1 + R_2)$	Quantum yields of C_2H_4	Relative emission
493.3	0.37	0.41	0.69	1.00
481.8	0.38	0.39	0.79	1.36
457.3	0.37	0.41	0.88	0.63
447.6	0.47	0.11	0.94	0.54
417.9	0.49	0.04	0.99	0.066

3.3. Quantum yields of C_2H_4

The high sensitivity of the flame ionization detector permitted measurement of C_2H_4 yields (but not CO yields) at very low conversions and reaction times. Yields were linear with time and should have been close to true initial values, thus avoiding complications caused by dissociation of product X and polymer formation on windows etc. The quantum yields of C_2H_4 measured in this way are shown in Table 2. An overall uncertainty of ±15% can be estimated in these values.
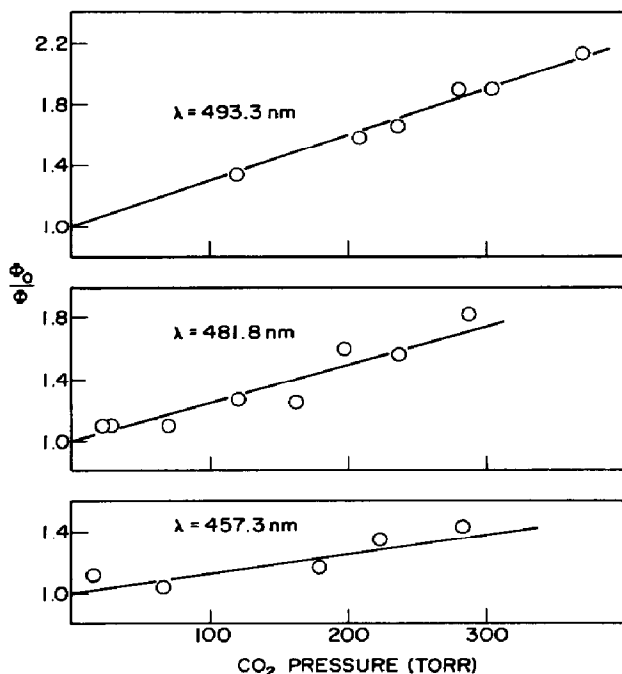
Fig. 3. Effect of CO_2 on the quantum yield Φ of C_2H_4 (Φ_0, yield in the absence of CO_2; CBD pressure, 0.6 Torr; T = 25 °C).

The effect of pressure on the quantum yield of C_2H_4 was tested by adding CO_2; the results for three wavelengths are shown in reciprocal plots in Fig. 3 and appear to follow a simple Stern–Volmer relation.

3.4. Fluorescence

Moderately intense fluorescence was observed at all wavelengths used in the photolysis. Intensities were measured at five wavelengths and were normalized for differences in the incident light intensity and the extinction coefficient to obtain relative quantum yields, all shown in Table 2. Within the narrow range of pressure employed (0.5 - 4.7 Torr) these yields were independent of pressure. No allowance was made for possible changes in the emission spectrum with changing wavelength of the exciting light, and all measurements were made with a single sharp cut-off filter (Corning 3486; 50% transmission at 525 nm) between the fluorescence cell and the photomultiplier tube. This may have discriminated against possible emission at wavelengths below the cut-off value with excitation at the shorter wavelengths.

The fluorescence intensity was too low to obtain an emission spectrum with the tungsten lamp and monochromator used to measure relative yields, but a spectrum was obtained using an argon ion laser giving an output of several watts at 488 nm; this is shown in Fig. 4. Most of the strong features observed can be identified with hot bands in the absorption spectrum [9]; a detailed analysis of the emission spectrum will be published elsewhere
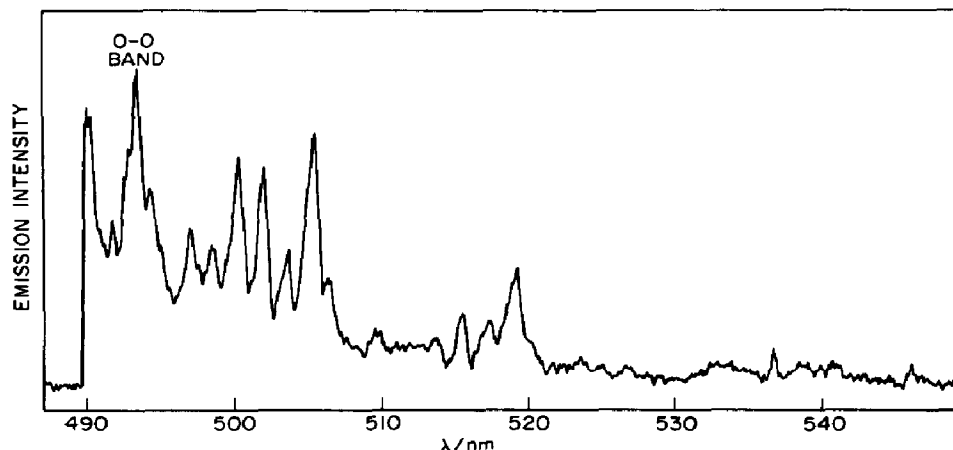
Fig. 4. Low resolution spectrum of emission from CBD excited at 488.0 nm at a pressure of about 0.5 Torr.

[12]. We are thus observing fluorescence from the excited singlet state, and not triplet emission. The spectrum in Fig. 4 is not corrected for the response of the photomultiplier; there was also some attenuation with increasing wavelength owing to polymer formation on the entrance window and consumption of CBD during the spectrometer scan.

Oxygen showed a moderate quenching efficiency for the fluorescence excited at 493.3 nm, shown in a reciprocal plot in Fig. 5; this sort of behaviour is that expected for quenching of a short-lived excited singlet state rather than of a long-lived triplet state, supporting the conclusion reached from the emission spectrum that we are observing fluorescence rather than triplet emission.

The data in Fig. 5 were obtained immediately after the exciting light was admitted to the cell. On continuing irradiation, the fluorescence in-
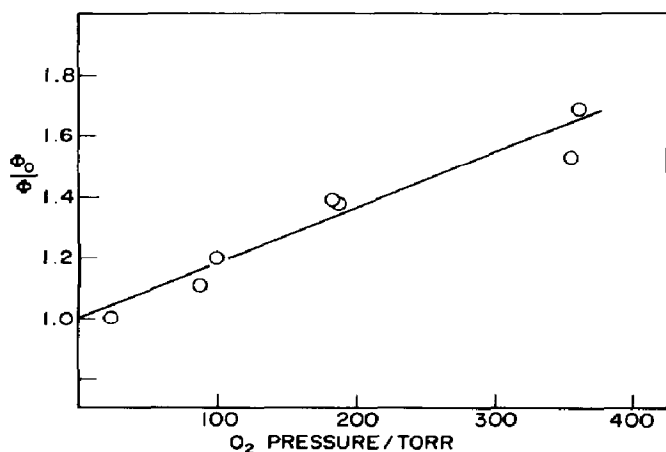

Fig. 5. Quenching by oxygen of the emission from CBD excited at 493.3 nm (CBD pressure, 1.57 Torr; $T = 56\ ^{\circ}$C).

tensity remained constant for several minutes, then began to rise sharply and finally levelled out at a value many times higher than that observed from CBD in the absence of oxygen. The rate of rise in the intensity increased with increasing pressures of CBD and oxygen. This complex behaviour was not investigated further; it appears that a reaction product must be formed in the presence of oxygen that fluoresces more efficiently than CBD itself.
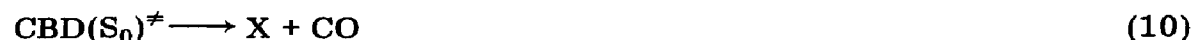
4. Discussion

The first excited singlet state of CBD, the state excited in the present study, corresponds to a $\pi^* \leftarrow n_+$, $^1B_1 \leftarrow {}^1A_1$ allowed transition, closely analogous to that of cis-glyoxal for which the 0-0 band lies at 487.5 nm, just 5.8 nm to the blue of that for CBD [9]. Both the cis and the trans isomers of glyoxal exhibit a complex photophysics and photochemistry [4, 5, 13 - 15]. Two dissociation channels are observed:

$$(HCO)_2 + h\nu \longrightarrow H_2CO + CO \tag{3}$$

$$(HCO)_2 + h\nu \longrightarrow H_2 + 2CO \tag{4}$$

At very low pressures (less than 0.05 Torr) dissociation follows a collisionless crossing to high levels of the ground state, and a pressure dependence of the channel ratio has been attributed to vibrational deactivation of the ground state [4]. At higher pressures, collision-induced crossing to the triplet state predominates; fluorescence is efficiently quenched, with a pressure for 50% quenching of less than 0.1 Torr, and the decomposition proceeds through the triplet state.

The lack of quenching of CBD fluorescence at CBD pressures up to 4.7 Torr and the relative inefficiency of oxygen as a quencher (Fig. 5) both point to a much shorter lifetime for the excited singlet state of CBD than for that of glyoxal. As in most carbonyl $\pi^* \leftarrow n$ systems, there is no reason to expect the excited singlet state to be itself dissociative, especially when excited in the 0-0 band, and the short lifetime of CBD can most probably be attributed to a fast radiationless transition to the ground state. The important processes in the CBD system can be summarized:

$$CBD(S_0) + h\nu \longrightarrow CBD(S_1) \tag{5}$$

$$CBD(S_1) \longrightarrow CBD(S_0) + h\nu(fluor) \tag{6}$$

$$CBD(S_1) \longrightarrow CBD(S_0)^{\neq} \tag{7}$$

$$O_2 + CBD(S_1) \longrightarrow quenching \tag{8}$$

$$CBD(S_0)^{\neq} \longrightarrow C_2H_4 + 2CO \tag{9}$$

$$CBD(S_0)^{\neq} \longrightarrow X + CO \tag{10}$$

where S_0 and S_1 denote the ground state and the first excited singlet state and $\neq$ indicates vibrational excitation. The observed effect of CO_2 on the photolysis is probably due to collisional deactivation of $S_0^{\neq}$:

$$CO_2 + CBD(S_0)^{\neq} \longrightarrow CBD(S_0) + CO_2 \qquad (11)$$
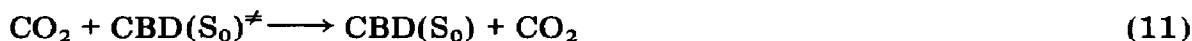
Deactivation of S_1 by CO_2 cannot be completely ruled out; CO_2 is about twice as efficient in suppressing C_2H_4 formation as oxygen is in quenching the fluorescence, about the difference expected if deactivation of the same species were involved. The difficulty with this is that the species produced on deactivation of S_1 (probably S_0 or perhaps the triplet T_0) would almost certainly retain enough energy to dissociate, since S_1 excited at 493.3 nm would contain a total energy about 20 kcal mol^{-1} in excess of the activation energy for decomposition of the ground state [6], and further deactivating collisions would be required to suppress formation of C_2H_4. In the same way reaction (11) must be a stepwise process, and with decreasing excitation wavelength more energy must be removed. Table 3 summarizes the results of the quenching experiments with CO_2 taken from Fig. 3. These data, both the absolute values of the pressure needed for quenching half the decomposition and its variation with excess energy, appear to be roughly what would be expected for collisional deactivation of the vibrationally excited ground state of CBD.

In the thermal decomposition of CBD, it was argued that reaction (9) was a concerted process, as the observed activation energy of 39 kcal mol^{-1} appeared to be too low to permit formation of a biradical intermediate [6]. In the photolysis there is enough energy for biradical formation, although the lower-energy concerted path would still be favoured unless there was a large difference in frequency factor; isotopic photochemical experiments such as those used in the pyrolysis [7] would be informative. If reaction (9) is concerted, it bears some analogy to reaction (4) in glyoxal, which has attracted much attention [15, 16]. The decomposition of CBD also invites comparison with that of cyclobutanone

$$\text{Cyclobutanone} \longrightarrow C_2H_4 + CH_2CO \qquad (12)$$

$$\text{Cyclobutanone} \longrightarrow \text{cyclopropane} + CO \qquad (13)$$

TABLE 3

Effect of CO_2 on the yield of C_2H_4

Wavelength (nm)	Pressure (Torr) of CO_2 for 50% quenching	Relative rate of quenching	Energy (kcal mol^{-1}) of $S_0^{\neq}$	
			Total	Excess[a]
493.3	340	1.00	57.9	18.6
481.8	404	0.94	59.2	19.9
447.6	776	0.44	63.9	24.6

[a] Energy in excess of the activation energy for dissociation of 39.3 kcal mol^{-1}.

particularly with regard to the ring contraction with extrusion of CO (reaction (13)). In the thermal decomposition [17], reaction (13) is of very minor importance (about 0.5%); the analogous reaction (10) (if $X \equiv$ cyclopropanone) could have occurred to a similar extent in the thermolysis of CBD and would probably not have been detected [6, 7]. In the photolysis of cyclobutanone [5], reaction (13) becomes much more important, varying from about 30% to 45%, depending on wavelength, and appears to proceed largely through the triplet state. If, as we tentatively suggest, reaction (10) is responsible for the deviation of the $[C_2H_4]/[CO]$ ratio from 0.5, the estimates of the extent of its occurrence in Table 2 indicate an importance at 493.3 nm comparable with that of reaction (13) in the cyclobutanone photolysis. At shorter wavelengths reaction (10) appears to decrease in importance (the reverse of the wavelength dependence of reaction (13) in cyclobutanone). This decrease may be only apparent, however, in as much as cyclopropanone may well be formed with enough vibrational energy to decompose to C_2H_4 plus CO, products indistinguishable from those of reaction (9); this decomposition would become more important with decreasing wavelength. The analogous reaction of cyclopropane occurs in the cyclobutanone photolysis, but here the product, propylene, is easily distinguished from the products of reaction (12).

It is interesting that ketene was not a significant product in either the thermolysis or the photolysis of CBD, although it is the main product in the thermolysis of the 1,3-cyclobutanedione isomer [7]. A search was also made, using classical flash photolysis with long-path photographic detection, for a possible C_2O_2 intermediate [18]. No absorption, either transient or long lived, was detectable between 300 and 800 nm except for that of CBD itself.

The present initial study of CBD leaves many questions unanswered about the photophysics and photochemistry. Glyoxal and cyclobutanone, to each of which CBD bears some resemblance, have been studied for decades and neither is fully understood. Much more work on the photochemistry of CBD is clearly needed; it is unfortunately much less tractable experimentally than its two analogues, especially with regard to stability, polymer formation in the photolysis, and product analysis. Studies are continuing.

Acknowledgments

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