

Short Communication

Singlet and triplet state photodecomposition of tetramethyl-1,3-cyclobutanedione

RALPH SPAFFORD and MARTIN VALA

Department of Chemistry, University of Florida, Gainesville, Fla. 32601 (U.S.A.)

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The direct and xanthone-photosensitized decomposition of tetramethyl-1,3-cyclobutanedione (TMCBD) has been investigated. The quantum yields for TMCBD disappearance and dimethylketene (DMK) production have been determined. The triplet decomposition of TMCBD is shown to yield DMK exclusively. Infrared analyses of the direct and photosensitized photolysates have revealed that the known product, tetramethylcyclopropanone (TMCP), is formed solely via the excited singlet state. The possible mechanisms for the photodecomposition are discussed. It is suggested that the decarbonylation to TMCP proceeds via a concerted pathway.

The photochemical degradation of TMCBD is known to yield TMCP and DMK among other products. Although this photodecomposition reaction has been extensively investigated [1 - 8] the identification of the specific electronic excited states involved in the decomposition process has never been made. Previous attempts at photosensitization and quenching of photoexcited TMCBD have been unsuccessful. This has led to the tentative suggestion that the photoreaction occurs solely in the excited singlet state [3]. Although the exact location of the lowest triplet state of TMCBD was not known at the time of these studies, it has recently been reported ($E_T = 72.5 \text{ kcal mol}^{-1}$) [9]. Because of the current interest in the photoreactivity of cyclic ketones, we have reinvestigated the direct and photosensitized decomposition of TMCBD and report here on the successful photosensitization of TMCBD with xanthone ($E_T = 74 \text{ kcal mol}^{-1}$) [10] in the non-polar solvent CCl_4 .

In Table 1 the quantum yields for the disappearance of TMCBD, which were determined by vapor phase chromatography*, and the quantum yields for the production of DMK, which were determined by infrared band intensities† [11], are given. These results show that DMK is formed via both

*A Varian Aerograph Model 90P gas chromatograph with a 5 in \times 0.25 in SS column of 3% SE-30 on Diatomite CLO 100/120 was used.

†A Perkin-Elmer 237 B infrared spectrophotometer was used. The value of the integrated intensity of the 2124 cm^{-1} carbonyl stretch band ($1.9 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$) found by Haller and Srinivasan [11] was used. IR determinations were carried out as soon as possible after the cessation of photolysis (usually less than 5 min and not more than 10 min). The peak intensities were not noticeably time dependent within this period.

TABLE 1

Quantum yields of TMCBD decomposition and DMK formation under direct and photosensitized irradiation conditions

Molecular species ^a	Quantum yield ^b	Direct (D) or photosensitized (PS) ^c	Percentage conversion range ^d (%)
-TMCBD	0.42 ± 0.05	D	7-19 (8)
-TMCBD	0.08 ± 0.02	PS	12-37 (6)
+DMK	0.33 ± 0.02	D	7-16 (6)
+DMK	0.15 ± 0.01	PS	12-20 (4)

^a-TMCBD, disappearance of TMCBD; +DMK, appearance of DMK.

^bErrors quoted are one standard deviation calculated using the number of runs shown in parentheses in the fourth column; actinometer, 2-hexanone in pentane. (The disappearance of 2-hexanone was monitored via gas chromatography; the value of 0.327 for the quantum yield of hexanone disappearance was used [24].) The quantum yields quoted for DMK refer to the total amount of DMK formed. The efficiency of triplet energy transfer from xanthone to TMCBD is unknown since all attempts at quenching of the triplets have been unsuccessful. The quantum yields given here were determined assuming unit efficiency.

^cSensitizer, xanthone. (The relative extinction coefficients of xanthone and TMCBD at 313 nm are 3.5×10^3 and $15 \text{ l mol}^{-1} \text{ cm}^{-1}$, respectively. Concentrations of xanthone used were calculated so that 99.8% of the excitation radiation was absorbed by the xanthone.) Solvent, CCl_4 ; excitation wavelength, 313 nm; merry-go-round apparatus. All samples were deoxygenated to 10^{-4} - 10^{-5} Torr using a freeze-pump-thaw procedure after which the sample tubes were flame sealed.

^dThe number of runs are given in parentheses.

excited triplet and singlet states. By comparing the quantum yield for photosensitized TMCBD decomposition with that for photosensitized DMK formation (and realizing that 1 mol of TMCBD will decompose to 2 mol of DMK) it is possible to conclude that the sole photoproduct of decomposition via the triplet state is DMK. In addition, this leads to the conclusion that TMCP is formed exclusively via an excited state other than the lowest triplet. The reactive state may be an excited singlet or highly excited vibrational levels of the ground state*. The present experiments do not allow a definite choice to be made.

The infrared spectra of the photolysates from direct and photosensitized experiments were scanned in the region between 2500 and 1500 cm^{-1} . TMCP is known [7, 11, 12] to exhibit a carbonyl stretching vibration at 1840 cm^{-1} . As can be seen in Fig. 1 only the directly photolyzed solution

*Whether TMCP is produced from the excited singlet of TMCBD or in high vibrational levels of the ground singlet after internal conversion is open to question. Recent vapor phase pyrolysis experiments [13] indicate that TMCP is one of the major products at temperatures above 360°C . This result should be treated cautiously, however, since it is not clear whether a comparison of products obtained via an equilibrium thermo-lysis method and a non-equilibrium photolysis method is valid.

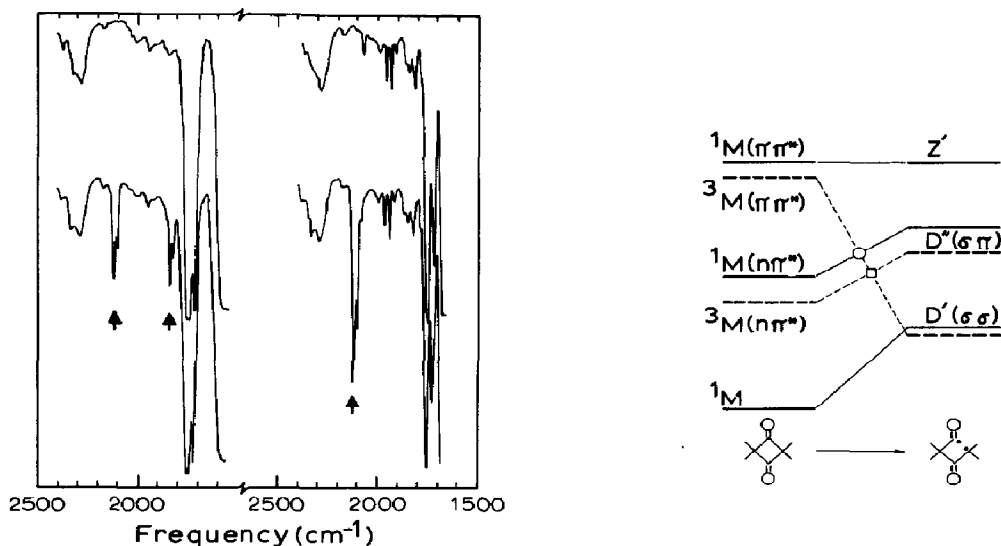
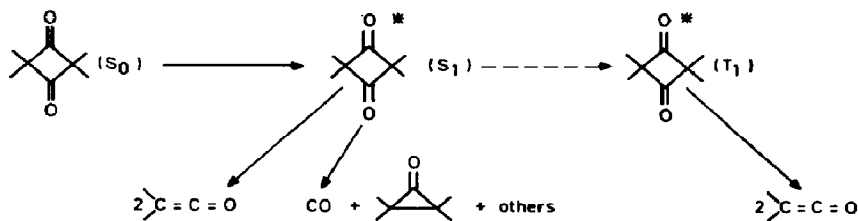


Fig. 1. Infrared spectra of unphotolyzed and photolyzed TMCBD in CCl_4 . Left-hand side, top, unphotolyzed TMCBD; left-hand side, bottom, directly photolyzed TMCBD; the arrows indicate the formation of DMK (2124 cm^{-1}) and TMCP (1840 cm^{-1}). Right-hand side, top, unphotolyzed TMCBD with xanthone photosensitizer; right-hand side, bottom, photosensitized TMCBD; the arrow indicates the production of DMK (2124 cm^{-1}). The irradiation times of the two runs are not the same.

Fig. 2. Salem state correlation diagram for a $\sigma(\sigma, \pi)$ tritopic reaction when D' is below D'' where D' and D'' are two diradical states and Z' is the first zwitterionic state: \circ singlet potential surface crossing for planar and non-planar TMCBD geometries; \square triplet potential surface crossing for non-planar TMCBD geometry. (Diagram adapted from ref. 15, Fig. 17.)

exhibits the 1840 cm^{-1} band. Within the limits of detectability, no indication of any such band was observed in the photosensitized solution. This provides strong support for our suggestion that TMCP is formed via the singlet state manifold*. Furthermore, the known 2124 cm^{-1} band of DMK can be seen in both direct and photosensitized photolysates, confirming its production via both singlet and triplet states. The overall scheme of TMCBD photolytic degradation is therefore



*We estimate that in the photosensitized experiments a band of about 10% the intensity of that observed in the direct photolysis experiments would have been easily detectable. This sets an upper limit for the quantum yield of TMCP formation via the triplet mechanism as 0.03. (See also footnote to previous page.)

The mechanisms by which these photoreactions occur are of considerable current interest. There is some indirect evidence which points to a concerted process for the decarbonylation of TMCBD to yield TMCP. In several recent papers [14 - 16] Salem and coworkers have examined theoretically the α -cleavage of saturated ketones. They have shown that there exist sizeable barriers to α -cleavage upon excitation to $^3n\pi^*$, $^3\pi\pi^*$ and $^1n\pi^*$ excited states. The higher lying excited $^1\pi\pi^*$ state has been shown to correlate (apparently without any potential energy surface crossings) with the lowest zwitterionic (singlet) product state (*cf.* Fig. 2). Burr and Dewar [17] and later Hoffmann [18] showed that the electronic structure of the cyclopropanone biradical is predominantly zwitterionic in character. Since we have shown that TMCP is formed via the singlet manifold and it is known that its biradical electronic structure is zwitterionic, it is reasonable to infer that excitation to the TMCBD $^1n\pi^*$ state(s) will not yield TMCP via a biradical mechanism. However, favorable symmetry and energy correlations between reactant and product electronic states exist for a concerted process. The driving force behind the singlet exclusivity of the TMCBD \rightarrow TMCP decomposition is most probably the zwitterionic (oxyallyl) singlet electronic structure of the product.

It is of interest to compare the photodegradation of TMCBD with that of cyclobutanone (CB). Lee and Lee [19] have shown that in its triplet $n\pi^*$ state CB decarbonylates to yield cyclopropane (which subsequently forms propylene), whereas in its singlet $n\pi^*$ state CB rapidly undergoes internal conversion to high vibrational levels of its ground state and forms ketene and ethylene products there. The striking difference in CB and TMCBD triplet state photoproducts (cyclopropane and dimethylketene, respectively) is due to the preference of the TMCBD decarbonylation product (TMCP) for a singlet (oxyallyl) degradation pathway. Although the triplet products are very different, the singlet state photoproducts of CB and TMCBD are similar (except for TMCP, of course). They both yield a ketene photoproduct (CB giving ketene and ethylene and TMCBD forming dimethylketene) which suggests that a similar degradation mechanism is operative.

It appears likely that the singlet decomposition of both CB and TMCBD (with the exception of the formation of TMCP) proceeds via a biradical intermediate. The probability of this mechanism occurring hinges on the magnitude of the barriers to α -cleavage. As Turro *et al.* [20] have recently pointed out, small-ring ketones possess appreciable strain energy which may be used to surmount thermodynamic barriers to biradical formation. Provided this strain energy is sufficient, it is possible to create a $\sigma\sigma$ biradical in its ground state (see Fig. 2). For a planar decomposition intermediate, Salem and coworkers [14 - 16] have shown that there is a favorable intersystem crossing (mixing) between the high lying $^3\pi\pi^*$ state (which becomes the biradical $\sigma\sigma$ state) and the $^1n\pi^*$ state (indicated by a circle in Fig. 2). No such mixing exists between the $^3\pi\pi^*$ ($\sigma\sigma$) and $^3n\pi^*$ states in a planar intermediate since their symmetries are different. This restriction is lifted, however, for a non-planar decomposition intermediate (indicated by a square in Fig. 2). In fact,

it has been shown [21, 22] that the excited singlet and triplet states of TMCBD and CB are distorted in a non-planar fashion via out-of-plane carbonyl wagging vibrations. Thus excitation to the $^1n\pi^*$ and $^3n\pi^*$ states of TMCBD and CB may lead to the biradical ring-opened intermediate, provided the strain energy exceeds the energy barrier to α -cleavage. Indeed, Hemminger and Lee [23] have presented evidence that the bond dissociation in the $^1n\pi^*$ state of CB may be as low as $3.8 \text{ kcal mol}^{-1}$, which they attribute to a significant amount of ring strain.

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