

Photodecomposition of 1,2-Dioxetanes

CORNELIA NEIDL and JOACHIM STAUFF

Institut für physikalische Biochemie
der Universität Frankfurt am Main

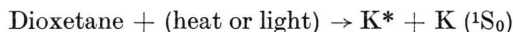
(Z. Naturforsch. **32b**, 1102-1103 [1977]; received March 2, 1977)

1,2-Dioxetanes, Photodecomposition, Luminescence Spectra Flash Photolysis

Diadamantyldioxetane, trimethyldioxetane and tetramethyldioxetane were photolyzed by light of $\lambda > 260$ nm. The spectral distribution of the quanta emitted during photo-induced decomposition of dioxetanes was found to be different from fluorescence and phosphorescence of ketones. Flash photolysis experiments showed the absorption of a short-lived intermediate. It was concluded, therefore, that photolysis of dioxetanes is not a concerted process but involves at least one precursor of the final product ketone.

Introduction

According to several investigations of LECHTKEN *et al.*¹ the luminescence produced by photoinduced decomposition of Tetramethyldioxetane (TMD) does not differ from the fluorescence and phosphorescence of acetone:



(K^* = electronically excited ketone). Therefore, it had been assumed that in principle the photochemical reaction should follow the same pathway as the thermal decomposition. In both cases a concerted splitting of the C-C- and O-O-bonds should take place. On the other hand it was reported² that photolysis of some other dioxetanes led to products like alcohols and diketones, which could only be explained if one assumed a biradical-like intermediate. It is also known, that peroxides like Di-*tert*-butyl-peroxide are disrupted at their O-O-bonds, if they are excited by light ($\lambda > 260$ nm)^{3,4}.

We want to report on some results of photolysis experiments we have done with solutions of Diadamantyldioxetane (DAD), Trimethyldioxetane (TriMD) and TMD which prove the existence of an intermediate which is neither identical with a ketone in its excited singlet nor its triplet state.

Experimental

DAD was prepared by the method of ADAM *et al.*⁵. An ultimately pure sample free from adamantanone

Requests for reprints should be sent to Prof. Dr. J. STAUFF, Institut für Physikalische Chemie und und Kolloidchemie, Sandhofstraße, Gebäude Nr. 75a, D-6000 Frankfurt a. M.

was obtained by column-chromatography of the raw product (cyclohexane over silica gel). TriMD was synthesized as described by KOPECKY and MUMFORD⁶. We obtained TMD after the method of TURRO *et al.*⁷. Diluted solutions were used in all experiments (10^{-3} - 10^{-4} molar in *n*-heptane, *n*-pentane or decahydronaphthalene). Delayed photoluminescence was measured with a phosphorimeter 10 ms after excitation of the sample. The phosphorimeter consisted of a Farrand fluorimeter which was equipped with two light choppers. Flash photolysis experiments were done in a 20 cm long, double-walled, quartz-cell. The outer jacket was filled with a 1.5% aqueous CuSO_4 -solution³. Samples were degassed by four freeze-thaw cycles. We used a continuous light source for analysis. The duration of the photolysis-flash was 48 μsec (half-height). The decay curves were stored on a transient recorder.

Results and Discussion

The luminescence spectrum of DAD in decahydronaphthalene (20 °C) is shown in Fig. 1, curve 1. It was obtained immediately after exposure to light of the sample and excited by light of 300 nm. In contrast to the spectra observed by other investigators the luminescence maximum is situated at the region of 350-360 nm. Under the same conditions, TMD shows a spectrum with the luminescence maximum in the same region (Fig. 2). If the solutions were irradiated continuously within the spectrometer the maxima were displaced towards longer wavelengths and the original band disappeared. Finally, we obtained a pure ketone-spectrum.

Why has this effect not been observed by other investigators? The answer is given by the following

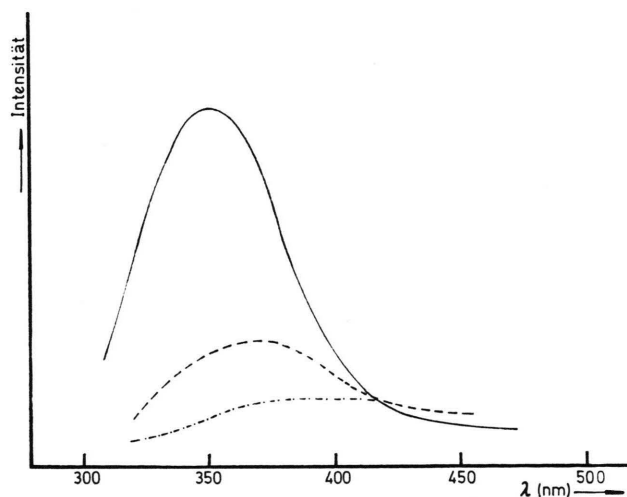


Fig. 1. Emission-spectra of DAD during photolysis with 300 nm (corrected spectra);

- 1 ——— start spectrum,
- 2 - - - - spectrum after 16 h irradiation,
- 3 - · - · - spectrum after 42 h irradiation.

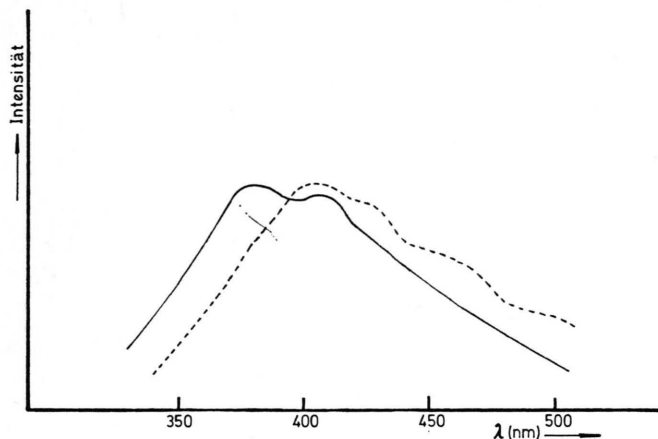


Fig. 2. Fluorescence Spectra of TMD (excited by 300 nm) (curve 1 and curve 2 are not on the same scale!);

- 1 ——— TMD in decaline,
2 - - - - TMD plus acetone in decaline.

simple experiment: Addition of small amounts of the ketone (formed upon illumination of the dioxetane) to the photolyzing solutions caused the disappearance of the shorter wavelength maxima and the appearance of the ketone bands as the only observable ones (Fig. 2, curve 2). The presence of ketone leads to a strong quenching of the short-wavelength maximum which must be due to an energy-transfer to the ketone molecule. Therefore, the dioxetanes have to be carefully purified – ketones must not be present – in order to observe the described effect. The TMD-spectrum (Fig. 2, curve 2) shows some ketone-bands indeed, which must originate from ketone-impurities still present. Addition of 1,3-pentadiene as a typical triplet-quencher diminished the intensity of the whole luminescence spectrum of DAD. Tri-*tert*-butyl-phenol – a well-known radical scavenger – led to a quenching of the whole luminescence spectrum. Phosphorescence measurements with a delay-time of 10 ms at 77 K showed the same maximum at 350–360 nm as the normal luminescence-spectrum at room temperature. Flash photolysis revealed the absorption of an intermediate (λ_{abs} about 350 nm) with a lifetime of $3 \cdot 10^{-3}$ sec. The kinetical analysis revealed the decay-function being of mixed first

and second order. The lifetime of the first order term was approximately 20 times higher in deoxygenated solutions. Under the same conditions, adamantanone did not give any effect.

These experiments prove the formation of an intermediate during the course of the photolytic decomposition of 1,2-dioxetanes, which cannot be identified with a long-lived excited state of the ketone or the peroxide. The ketone can be excluded because of the difference of the emission spectra – ketone fluorescence and phosphorescence bands are situated in the region of 400–470 nm. Most convincing is the quenching of all spectral bands by tri-*tert*-butyl-phenol (TTB) at the same time. TTB quenches triplet-states only to a small extent⁷ but reacts rapidly with radicals. Therefore, the intermediate (found in the flash-photolysis-experiments) is not consistent with a quenching-mechanism of a triplet state which should proceed by a diffusion-controlled reaction with rate constants of at least 10^7 . Energy-transfer from intermediates to the final product ketone in the ground state occurs when the latter is either added or produced in the course of the decomposition of 1,2-dioxetanes. Being diffusion-controlled, the transfer reaction could take place within 10^{-9} to 10^{-10} sec. The excitation process has about the same or greater velocity. Therefore, our measurements do not contradict the results of the single-photon-counting experiment made by LECHTKEN and STEINMETZER¹. According to these authors excited ketone is formed from dioxetane within 10^{-8} to 10^{-9} sec upon illumination. Because they observed only the ketone emission bands one has to assume that the ketone (*e.g.* acetone) was excited by energy-transfer from dioxetane or from the intermediate. The intermediate should reasonably be identified with the biradical formed by scission of the O–O-bond, for it can be shown that the UV spectra of dioxetanes are very similar to those of normal peroxides². Therefore, the same excitation process should take place and similar photoreactions are to be expected. This diradical should not be the same as the one arising during the thermal decomposition⁸. 1,4-Biradicals may have rather different chemical behaviour depending whether they are produced by thermal or photolytic fission⁹.

The financial support of the “Deutsche Forschungsgemeinschaft” (AZ Sta 4/64) is greatly appreciated.

¹ P. LECHTKEN and H. C. STEINMETZER, Chem. Ber. **108**, 3159 [1975].

² W. ANDO and K. WATANABE, Tetrahedron Lett. **47**, 4127 [1975].

³ J. CALVERT and J. PITTS (Jr.), Photochemistry, Wiley & Sons, N. Y. 1966.

⁴ C. NEIDL, Dissertation, Frankfurt/Main 1976.

⁵ J. H. WIERINGA, J. STRATING, H. WYNBERG, and W. ADAM, Tetrahedron Lett. **2**, 169 [1972].

⁶ K. KOPECKY and C. MUMFORD, 51st Ann. Conf. Chem. Inst. of Canada, Vancouver B. C., June 1968.

⁷ H. CHR. STEINMETZER, P. LECHTKEN, and N. J. TURRO, Liebigs Ann. Chem. **1973**, 1986.

⁸ I. SIMO and J. STAUFF, Chem. Phys. Lett. **34**, 326 [1975].

⁹ T. A. GIBSON and L. M. STEPHENSON, J. Am. Chem. Soc. **96**, 5624 [1974].