Photolysis of 1,1-Dichloro-2,2-diarylethenes in the Presence of Oxygen. Formation of Highly Unstable Dioxetanes

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The photolysis of 1,1-dichloro-2,2-bis(4-methoxy-phenyl)ethene, 1,1-dichloro-2,2-bis(4-tolyl)ethene and 1,1-dichloro-2,2-diphenylethene in the presence of oxygen has been investigated by flash photolysis and by steady-state photolysis. These experiments showed that the corresponding benzophenones were formed as primary photoproducts. After vapour phase photolysis, carbonyl chloride was identified by mass spectrometry. It is suggested that these products are formed by ring cleavage of unstable dioxetanes. By flash photolysis short-lived intermediates (k 150 $-$ 300 s^{-1}) were detected. On the basis of the UV absorptions, the chemical properties and the Arrhenius activation parameters, these intermediates are assigned as 1,2-dioxetanes.

The environmental fate of pesticides, especially photochemical transformations and degradation, has received much attention.[1] Major breakdown products of DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) and Methoxychlor (1,1,1-trichloro-2,2-bis(4-methoxyphenyl)ethane) are DDE (1,1-dichloro-2,2-bis(4-chlorophenyl)ethene) and DMDE (1,1-dichloro-2,2-bis(4-methoxy-phenyl)ethene), respectively.[2,3] Photolysis of DMDE under a variety of conditions leads to the formation of 4,4′-dimethoxybenzophenone and 1-chloro-2,2-bis(4-methoxyphenyl)ethene, and the isomerization product 1-chloro-2-(2-chloro-4-methoxyphenyl)-2-(4-methoxyphenyl)ethene (cis and trans).[4] Analogous products have been reported for the photolysis of DDE.[4,5]

We have studied the mechanism of the photooxidation of DMDE (1a) and the related compounds 1,1-dichloro-2,2-bis(4-methylphenyl)-ethene (1b) and 1,1-dichloro-2,2-diphenylethene (1c) by flash and steady-state photolysis.
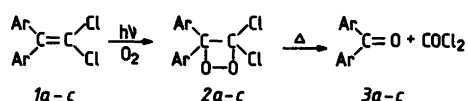
Scheme 1. a, Ar $=$ 4-CH$_3$OC$_6$H$_4$; b, Ar $=$ 4-CH$_3$C$_6$H$_4$; c, Ar $=$ C$_6$H$_5$.

RESULTS

Flash photolysis of compounds 1a $-$ c. Flash photolysis with Pyrex-filtered light ($\lambda > 300$ nm) of aerated $10^{-5} - 10^{-3}$ M solutions of compounds 1a $-$ 1c (Scheme 1) in cyclohexane showed that short-lived transients (Fig. 1) were formed. The transients decayed in first order reactions (Fig. 2). The first order rate constants (Table 1) were independent of
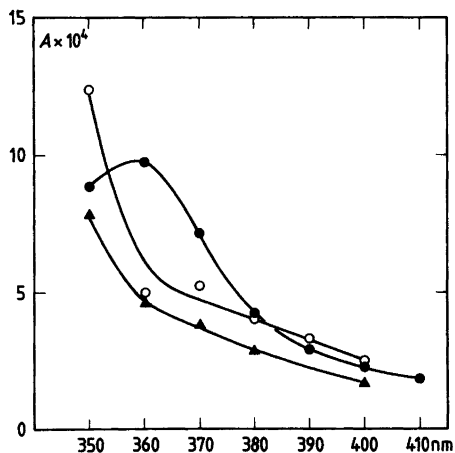
Fig. 1. UV spectra of dioxetanes 2a (●), 2b (○) and 2c (▲) obtained by flash photolysis at room temperature. Intensity in absorbance (1 cm).
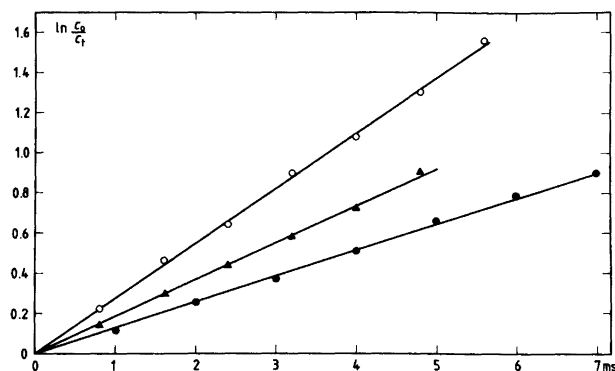
Fig. 2. First order plots of oscilloscope traces at 350 nm. ●, *2a*, 19.7 °C; ○, *2b*, 21.5 °C; ▲, *2c*, 20.5 °C.

the concentrations of compounds *1a−c*, and the intensity of the signals were nearly unchanged after eight flash excitations of the same solution. The rate constants were likewise independent of the number of excitations. If the solutions were degassed prior to flash photolysis, no absorbing species were observed. The signals diminished in intensity if solutions were flushed with nitrogen, but reappeared if deaerated solutions were flushed with oxygen. The appearance of the transient absorptions is therefore the result of a photochemical reaction between the starting materials and oxygen.
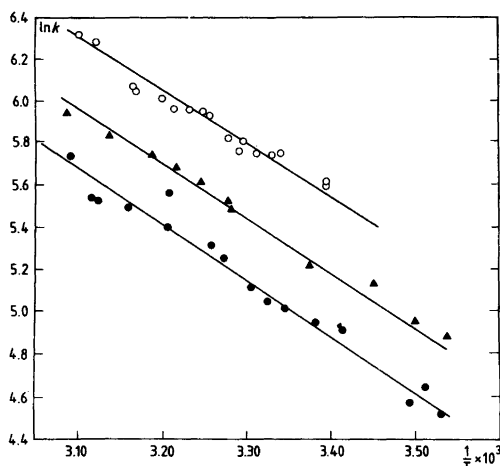

Fig. 3. Arrhenius plots of the first order rate constants for the decay of dioxetanes *2a* (●, correlation coefficient of the plot (*r*) 0.985), *2b* (○, *r* = 0.981) and *2c* (▲, *r* = 0.997).

By varying the temperature of the flash excited solutions, activation parameters for the decaying species were obtained (Table 1) from the Arrhenius plots (Fig. 3).

The chemical properties of the transients were investigated by addition of either butanethiol (10^{-2} M), acetic acid (10^{-2} M) or butaneamine (10^{-2} M) prior to flash photolysis in cyclohexane. However, the lifetimes of the intermediates were independent of the presence of these compounds. This shows that the transients are neither free radicals nor compounds reacting fast with weak acids or bases.

In order to identify primary reaction products, 10^{-4} M solutions of compound *1c* in cyclohexane were flashed once. The combined solutions were then evaporated, dissolved in MPH (isopentane −methylcyclohexane, 1:3) and analyzed by emission spectroscopy at 77 K. This gave a phosphorescence spectrum (with a progression of bands) identical to that of benzophenone.

No intermediates were observed when flash photolysis of *1a−c* was carried out in 96 % ethanol and benzophenone was not detected when solutions of *1c* were flashed once. The photochemical fate of *1a−c* in ethanol was not investigated further. By flash photolysis in Freon 113 (see below) only very weak signals were detected. This was probably due to the partial light absorption of the solvent at 300 nm.

Steady-state photolysis in liquid solution. Benzophenones are photoreduced when irradiated in hydrogen donating solvents.[6] Preparative photolysis was therefore carried out in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) in which benzophenones are unable to photoreduce.

Table 1. Arrhenius activation parameters for the decay of dioxetanes $2a-c$ in cyclohexane. The figures were calculated using a least squares analysis. $\Delta S^{+} = 19.15 \, (log_{10} A - 13.23)$ J/deg. mol at 25 °C.

	2a	2b	2c
E_a/(kJ/mol)	21.6 (1.0)	19.3 (1.0)	19.9 (0.5)
A/s^{-1}	9.1×10^5 (3.7×10^5)	7.0×10^5 (2.7×10^5)	6.5×10^5 (1.3×10^5)
ΔS^{+}/(J/deg. mol)	-139 (3)	-141 (3)	-142 (2)
k/s^{-1} (25 °C)	151 (3)	294 (4)	207 (2)

After photolysis in this solvent the corresponding benzophenones were isolated as the only major products. After photolysis ($\lambda > 300$ nm) of *1a*, 4,4'-dimethoxybenzophenone (*3a*) was isolated in 72 % yield (based on reacted starting material). Compounds *3b* and *3c* were isolated in 77 and 18 % yields, respectively.

Steady-state photolysis in the gas phase. A small sample of *1c* was photolyzed ($\lambda > 300$ nm) at 120 °C (40 °C above the melting point) in the presence of air. Besides starting material only benzophenone (30 %) was detected and identified by GC – MS. Probably, non-volatile polymeric material was also formed. Unexpectedly, no photoisomers of *1c* were detected. An analogous experiment with benzophenone showed that 30 % of the initial amount of benzophenone had been consumed.

Carbonyl chloride, which is highly reactive towards traces of water, was identified after photolysis of compounds *1a – c* in the gas phase (as above). It was identified by mass spectrometry.

DISCUSSION

By photolysis of compounds *1a – c* in Freon 113, benzophenones *3a – b* were isolated in high yields, and photolysis in the gas phase showed that the remaining part of the starting materials was converted into carbonyl chloride. After single flashes of solutions of *1c*, benzophenone was identified by low temperature emission spectroscopy. The latter experiment eliminates that benzophenone is formed in a secondary photochemical reaction. 4,4'-Dichlorobenzophenone has been identified in the same way from flash photolysis of DDE.[7]

These experiments suggest that *3a – c* and carbonyl chloride are formed in thermal reactions from unstable intermediates, which are assigned as the dioxetanes *2a – c*. This assignment is based on the following observations: (i) The intermediates

were shown by flash photolysis to be the result of a photochemical reaction with oxygen ($[O_2] = 0.01$ M in oxygen-saturated cyclohexane[8]). (ii) The lifetime of the intermediates was unaffected by the presence of butanethiol. Free radicals are therefore excluded as candidates for the assignments of structure (*e.g.*, the biradical obtained by formal cleavage of the O – O bond in a 1,2-dioxetane) and radicals are probably not precursors in the formation of the observed intermediates. An oxirane *O*-oxide[9] can probably also be excluded, since this species would be expected to react fast with added nucleophiles (butaneamine). (iii) The intermediates absorbed above 400 nm, in agreement with the observation that 1,2-dioxetanes (with few exceptions) are yellow due to a low intensity tail-end absorption[10] (the absorption coefficient of the intermediates at 350 nm must be greater than the absorption coefficient of benzophenone at this wavelength (100 l/mol cm)). (iv) 1,2-Dioxetanes usually decompose with negative entropies of activation.[10]

The activation parameters (E_a) for the thermal decomposition of 3,3-diphenyl-1,2-dioxetane and 3,3-bis(4-methoxyphenyl)-1,2-dioxetane are 87.5 and 95.0 kJ/mol, respectively.[11] In terms of relative rates, the two methoxy substituents accelerate the rate of decay by a factor of 3.9. The small substituent effect observed, was assigned to the breaking of the O – O bond, *i.e.*, a stepwise cleavage is favoured over a concerted cleavage. The effect of substituents was noted to be similar to the effect observed for the decomposition of benzoyl peroxides.[11]

The high energy content of dioxetanes substituted with two chlorine atoms (*2a – c*) is evident from the very low activation energies (Table 1). Substituents on the phenyl groups only play minor roles and, unlike the 3,3-diaryldioxetanes, the two methoxy substituents in *2a* have diminished the rate constant of

decomposition from 207 s^{-1} in *2c* to 151 s^{-1} (Table 1). It has previously been reported that the dioxetane containing two 4-chloro substituents (the dioxetane from DDE) decays with $k = 745$ s^{-1}.[7] Surprisingly, two 4-methyl groups (*2b*) accelerate the rate of decomposition (294 s^{-1}) relative to *2c*. A rationalization of these rates in view of the Hammett equation therefore fails. We conclude that the ring cleavage of *2a*−*c* may probably not be accomodated by the mechanism proposed for the ring cleavage of 3,3-diaryl-1,2-dioxetanes.

EXPERIMENTAL

Compounds. Compounds *1a*−*c* were prepared according to Refs. 3 and 12 and recrystallized three times from aqueous ethanol. ε_{300} (*1a*) 11 000 l/mol cm, ε_{300} (*1b*) 900 l/mol cm, and ε_{300} (*1c*) 150 l/mol cm. All solvents used (except Freon 113) were of spectroscopic grade. 1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113) was obtained as a technical product. It was fractionally distilled, the fraction boiling at 46.0−47.0 °C (atm. pressure) was used as solvent in the steady-state photolysis. It was shown by mass spectrometry and ^{1}H NMR spectroscopy to contain less than 1 % of 1,2-dichloro-1,1-difluoroethane, a compound with boiling point 47.8 °C.

Flash photolysis. The flash lamp (quartz) was filled with air, and the light was filtered with Pyrex glass ($\lambda > 300$ nm). Flash energies were 200 J (a 4 μF capacitor charged to 10 kV). The analyzing light beam was passed through a monochromator, through the reaction cell (10 cm) and through a second monochromator with a photomultiplier on the exit slit.

Emission spectroscopy. After collection of 250 ml of a 10^{-4} M solution of compound *1c* in cyclohexane, exposed to one flash, the solution was evaporated to dryness and the residue dissolved in 1 ml of MPH (isopentane − methylcyclohexane, 1:3). After cooling to 77 K the phosphorescence spectrum was recorded on a Perkin-Elmer Hitachi MPF-3 spectrophotometer, excitation wavelength 360 nm. The spectrum obtained was identical to the emission spectrum of benzophenone, recorded under the same conditions.

Gas phase photolysis of compound 1c. Compound *1c* (4.1 mg) was placed in a dry Pyrex cuvette. It was then sealed and the tip of the cuvette was heated in an oil bath to 125−135 °C. The cuvette was irradiated for 20 h with a 150 W Xenon lamp. Determination of reaction products was performed by means of gas chromatography (Perkin-Elmer F 11 or a Varian 2700 Aerograph with a 2 m × 3.25 mm column with Perkin-Elmer O. V. 17 on AW-DMCS Chromosorb G, 80 − 100 mesh, temperature 225 °C and nitrogen as carrier gas) after addition of an internal standard (diphenylmethane). The compounds (starting material 67 % and benzophenone 30 %, based on reacted starting material) were identified by GC-MS (Varian CH 7A Mass Spectrometer). When benzophenone (0.9 mg) was irradiated under similar conditions, 28 % was photolyzed.

Gas phase photolysis of 1a−c. *Identification of carbonyl chloride.* Compounds *1a*, *1b* or *1c* (3 − 10 mg) were placed in a dry Pyrex cuvette, equipped with a stopcock and an outlet tube fitting the gas inlet of the mass spectrometer. The tip of the cuvette was dipped into an oil bath held at a temperature of 15 − 30 °C above the melting point of the compound. The vapour was photolyzed for 15 − 18 h using an external 1000 W high pressure mercury light source. The cuvette was then cooled in liquid nitrogen and connected to the gas inlet of the mass spectrometer (Varian Mat 311A). Carbonyl chloride was identified from the peaks at m/e 98, 96 (M$^{\cdot +}$) and m/e 65, 63 (M$^{\cdot +}$ − Cl).

Photolysis in Freon 113. Compounds *1a*, *1b* or *1c* in Freon 113 (650 ml, 10^{-3} M) were photolyzed for 15 h in a 1 l photolysis flask using an internal 100 W medium pressure mercury light source. The light was filtered through Pyrex, and the temperature of the solution did not exceed 15 °C during photolysis. After evaporation of the solvent the residue was separated by preparative thin-layer chromatography (PLC) on silica gel (Merck PF$_{254+366}$) using chloroform as eluent. In each experiment only two compounds appeared under UV light: Starting materials and benzophenones *3a*−*c*. The benzophenones were identified by comparison with authentic samples.[13] 45 % of compound *1a* reacted during the 15 h of photolysis, and 4,4'-dimethoxybenzophenone was isolated in 72 % yield (based on reacted starting material). For compounds *1b* and *1c* the figures were 30 % (77 % yield of 4,4'-dimethylbenzophenone) and 37 % (18 % yield of benzophenone), respectively.

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