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FLASH PHOTOLYSIS OF 1,1-DICHLORO-2,2-BIS(4-CHLOROPHENYL)ETHENE (DDE) IN THE PRESENCE OF OXYGEN. FORMATION OF A HIGHLY UNSTABLE DIOXETANE

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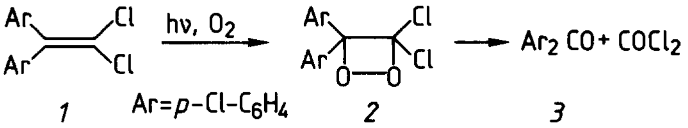
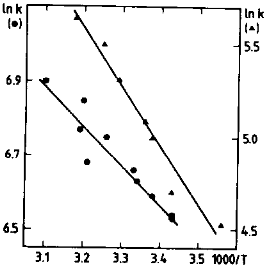
The photochemistry of 1,1-dichloro-2,2-bis(4-chlorophenyl)ethene (DDE, 1) which is accumulating in nature as a product of the pesticide DDT has previously been the subject of investigation[1] and several products have been identified.



A flash photochemical study ($\lambda_{ex} > 300$ nm) using aerated 10^{-5}-10^{-4} M solutions of DDE in ethanol ($\lambda_{max} = 246$ nm, $\varepsilon_{max} = 18000\ M^{-1}cm^{-1}$) and cyclohexane showed that a transient, absorbing below 400 nm, was formed. The transient decayed following first order kinetics, $\underline{k}_{EtOH} = 163\ s^{-1}$ and $\underline{k}_{cyclohex.} = 746\ s^{-1}$ at 25° C. The activation parameters were evaluated (Table) from the Arrhenius plot (Fig.). When solutions were degassed or deaerated with nitrogen or when the viscous ethylene glycol was used as solvent no signal was detected. The intermediate is therefore the result of a photochemical reaction of DDE with oxygen. In order to identify the products, samples were flash photolysed once and the residue after evaporation dissolved in EPA[2] and analysed by emission spectroscopy at 77 K. This gave phosphorescence spectra (with a progression of bands) identical to a spectrum of 4,4'-dichlorobenzophenone



Arrhenius plots of the first order rate constants for the decay of 2 in cyclohexane (o) and ethanol (Δ)

	96% EtOH	C_6H_{12}
A/s^{-1}	7.0×10^6	2.6×10^4
$\Delta S^{\ddagger}$/cal/deg mol	-29±8	-40±5
$\Delta H^{\ddagger}$/kcal/mol	5.7	2
$\Delta G^{\ddagger}$/kcal/mol	14.4	13.5

Activation parameters at 25° C for the decay of 2, evaluated from the Arrhenius plot

(3). On the basis of this and the following experiments the intermediate was identified as the 1,2-dioxetane, 2. 1,2-Dioxetanes are yellow due to tail-end absorption[3] and decompose into carbonyl compounds, usually with negative entropies of activation.[3]

Steady-state photolysis (λ > 300 nm) of DDE in benzene in the presence of air or oxygen gave 3 (35-37%) as the only major product. Compound 3 could not be isolated after steady-state photolysis of DDE in ethanol and cyclohexane, in which benzophenones are photoreduced.[4] Since phosgene is highly reactive towards traces of water and towards photolysis[5] it could not be detected or trapped with ammonia after photolysis in liquid solution. However, DDE vapour was photolysed (λ > 300 nm) at 110° C in the presence of air and the phosgene formed could be identified by mass spectrometry. TLC showed that compound 3 was also formed. The intermediate observed by flash photolysis is thus identified as the dioxetane, 2[6].

Dioxetanes are often prepared by cycloaddition between singlet oxygen and an alkene.[3] Singlet oxygen might be generated during photolysis by energy transfer from the triplet state of DDE. However, DDE did not react with singlet oxygen, prepared by dye-sensitization using rose bengal or methylene blue in ethanol[4] and the high-energy sensitizer, Michler's ketone, (in benzene) was also inefficient. It is therefore concluded that 2 or a precursor of 2 is formed in a reaction between excited DDE (singlet or short-lived triplet) and ground state oxygen. This type of reaction appears to be unknown.

The high energy content of a dioxetane substituted with two chlorine atoms is evident from the very low heat of activation. The small value of $\Delta S^{\ddagger}$ could be due to a sterically hindered transition state or, since one of the triplet states of the resultant carbonyl compounds is often significantly populated,[3] due to spin inversion in the transition state. The solvent effect (Table) indicates that the transition state is less polar than the educt. The polar carbonyl groups are probably not formed in the transition state and a stepwise cleavage involving a biradical intermediate is therefore favoured over a concerted cleavage.[7]

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