Cation-radicals: Oxygen Catalysis in the Photosensitised Cyclodimerisation of Aromatic Enamines

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WE have investigated the photosensitised cyclodimerisation of the enamines (I)—(IV) in methanol and, for each enamine, the product cyclobutane has the same structure as that obtained from the metal-catalysed reaction. (See Scheme 1 in the accompanying communication[1]).

The reactions show common features markedly different from those of conventional organic photosensitised reactions: (*a*) A wide range of sensitisers is efficient (Table) and reaction occurs even when the sensitiser has a lowest excited triplet-state energy (E_T) substantially less than that expected for a carbazole derivative. Direct energy transfer from sensitiser to substrate is therefore excluded.

(*b*) With all sensitisers (except anthraquinone and chloranil) and all enamines, *cyclodimerisation occurs only when oxygen is present in the system.* In the absence of oxygen there is essentially no photochemical reaction of the enamines (II)—(IV). For (I), photosensitisation in the absence of oxygen leads to rapid polymerisation. This will be discussed in detail elsewhere.

(*c*) Yields of cyclobutanes (Ia)—(IVa) are essentially quantitative if irradiation is prolonged and the precipitated dimers are periodically filtered off.

(*d*) Direct photolysis of the enamines (I)—(IV) with, or without, oxygen does not produce the cyclobutane dimer and, by use of wavelength filters, it was shown that the sensitiser is the primary absorbing species in all cases.

Detailed kinetic studies on the dimerisation of (I) have been carried out with a tungsten-filament lamp, with Rhodamin 6G as sensitiser. For sensitiser concentrations $< 10^{-5}$M the rate of dimerisation was first-order in sensitiser and first-order in (I) with an activation energy of 4 kcal. mole^{-1}. The solubility of oxygen in methanol at 25°, $6\cdot5 \times 10^{-3}$M, was not increased in the presence of 0·1M-enamine. Rates of dimerisation are not increased by the use of pure oxygen, instead of air, to saturate the solutions. Therefore oxygen must play a catalytic function and is present in sufficient excess over the photochemical intermediates. This is borne out by the absence of products containing oxygen.

Photosensitisers for cyclodimerisation[a] *of* (I)—(IV)

Sensitiser	λ_{max} (nm.) in MeOH	E_T (kcal.mole^{-1})
Acetophenone	320	74
Benzophenone	332	69
Anthraquinone	324	63
Chloranil	363	
2,4,6-Triphenylpyrylium tetrafluoroborate	405	53
Acriflavin	461	49
Rhodamin 6G	523	
Methylene Blue	646	33
(Carbazole)		(70)

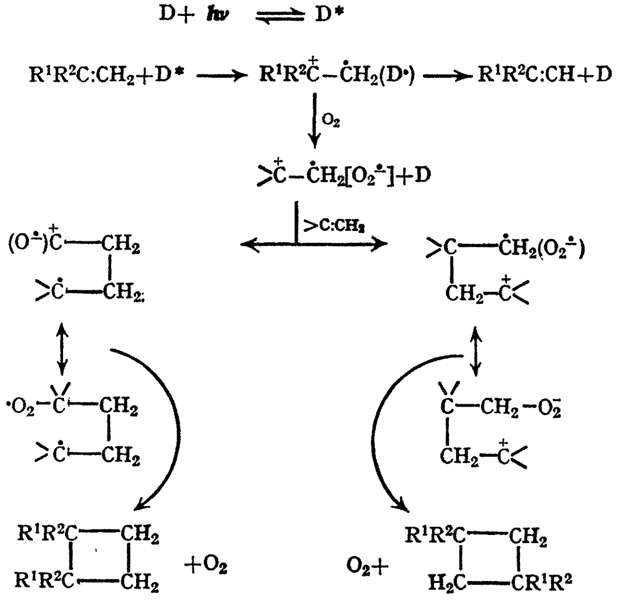
[a] Typically 10^{-2}—10^{-1}M-enamine, 10^{-6}—10^{-3}M-sensitiser. Irridation, for the carbonyl sensitisers, was by a 250w medium-pressure mercury discharge lamp and by a 1 kw tungsten lamp for the dye sensitisers. Glass vessels were used, in a constant temperature bath situated 20 inches from the lamp housing. Precipitation of dimer occurred after approximately 30 min. irradiation.

By means of suitable interference filters and ferrioxalate actinometry,[2] it was shown that for the photodimerisation of (I) with both acriflavine (at 436 nm.) and 2,4,6-triphenylpyrylium tetrafluoroborate (at 405 nm.) the quantum yield for cyclobutane formation was 1·1 ± 0·1. This result, together with the complete quenching of the powerful fluorescence of both 2,4,6-triphenylpyrylium tetrafluoroborate and Rhodamine 6G at enamine concentrations $\geqslant 10^{-2}$M, leads us to assume that excited singlet states of these sensitisers are involved in the cyclodimerisations. For the other types of sensitiser it is not possible to characterise the excited intermediates.

The similarity between metal-catalysed[1] and photocatalysed cyclodimerisations of (I)—(IV) is made even more striking by the observation that for *N*-vinyl-enamines (I) and (II), free-radical copolymerisation of added methyl methacrylate occurs readily in the photo-reactions. In contrast, addition of methyl methacrylate to the photoreactions of the *C*-vinyl-enamines (III) and (IV) has no effect on the dimerisation, and no homopolymers or copolymers are formed.

Sensitisers such as Rose Bengal and Eosin, which are particularly useful for generation of singlet oxygen species, are comparatively inefficient in promoting the cyclodimerisation of (I)—(IV). Thermal generation of singlet oxygen *via* the hypochlorite–peroxide reaction[3] does not bring about cyclodimerisation of (I). It is reasonable to conclude therefore that the catalytic effect of oxygen in the photosensitised processes is not due to intermediate sensitisation of singlet oxygen formation. By analogy with the metal-catalysed reactions we suggest the mechanism shown in the Scheme to explain these highly efficient photodimerisations.

The rate-determining initial step involves electron transfer from enamine to the excited sensitiser D*. If the initial redox ion-pair re-forms enamine and ground-state sensitiser, then the observed fluorescence quenching would result. Interception of this intermediate redox ion-pair by dissolved oxygen would lead to a new ion-pair involving superoxide ion, simultaneously regenerating ground-state sensitiser. Reaction of the cation-radical–superoxide complex with an excess of enamine would follow the paths A or B according to the expected cation stabilities as discussed for metal catalysis.[1] Free-radical activity would then be expected only for the *N*-vinyl-enamines—as observed experimentally.



SCHEME

Additional confirmation of the reaction scheme was provided by the observation that copper(I) heptanoate (10^{-3}M)—completely ineffective as a thermal catalyst for dimerisation of (I)—can be used instead of oxygen as co-catalyst for the photo-reaction, by using Rhodamine 6G with light of wavelength > 500 nm. Use of copper(II) ion to intercept the initial photo-produced ion-pair would yield intermediates identical with those suggested for the metal-catalysed processes.[1] It is thus possible to understand why the oxidising agents anthraquinone and chloranil were effective sensitisers in the absence of oxygen.

The cyclodimerisations described illustrate a new and highly efficient reaction pathway for organic photochemistry and point the way to further development of oxidation processes involving a combination of visible light sensitiser and oxidising metal ion.

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[1] F. A. Bell, R. A. Crellin, H. Fujii, and A. Ledwith, preceding communication.

[2] C. G. Hatchard and C.A. Parker, *Proc. Roy. Soc.*, 1956, *A*, **235**, 518.

[3] C. S. Foote, *Accounts Chem. Res.*, 1968, **1**, 104, and references cited therein.