Photochemical 2 + 2 Cycloaddition *via* a Cation-radical Chain Reaction

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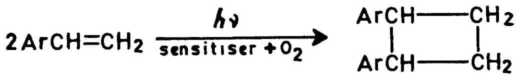
Summary Photochemically-induced 2 + 2 cycloaddition of *N*-vinylcarbazole occurs *via* a novel chain reaction involving propagating cyclobutane cation-radicals.

PREVIOUSLY we have shown that 2 + 2 cycloaddition of *N*-vinylcarbazole (I) may be induced by both thermal[1] and photochemical[2] methods. For a wide range of sensitisers[2] the latter technique gives quantitative yields of cyclodimer but only in the presence of catalytic quantities of dissolved oxygen, *i.e.* (Ar = 9-carbazolyl):



$$2\mathrm{ArCH{=}CH_2} \xrightarrow[\text{sensitiser}+\mathrm{O_2}]{h\nu} \begin{array}{l}\mathrm{ArCH{-}CH_2}\\ \;\,|\qquad\;\; |\\ \mathrm{ArCH{-}CH_2}\end{array}$$

(I) (II)(*trans*-)

Chloranil and anthraquinone were found to function as photosensitisers in the absence of oxygen[2] and recently we have shown that fluorenone behaves similarly in Me_2CO, but apparently requires catalytic amounts of oxygen for the much slower reaction in MeOH. In all cases, however, dissolved oxygen (air) markedly increased the rates of cyclodimerisation. Replacing air by pure oxygen did not increase overall rates of cycloaddition indicating that the concentration of dissolved oxygen in air-saturated solutions (*ca.* 10^{-3}M) was sufficient to swamp the photochemical intermediates.

Quantum yields for chloranil- and fluorenone-sensitised cyclodimerisation of (I) have now been determined (Table) and were significantly in excess of unity, indicative of a chain reaction. In order to account for these observations the mechanisms previously suggested[1,2] for 2 + 2 cycloaddition of (I) must be modified to include the cyclobutane cation radical (VI) as a chain carrier. (For the sake of clarity $O_2^{\bullet-}$ or Sens$^{\bullet-}$ counterions are omitted from the propagation steps).

The initiation mechanism applies equally well to singlet or triplet excited states, although the former are thought to be mainly involved. Equilibria between open chain and cyclised cation-radicals such as (V) and (VI) will obviously be affected by the steric and electronic nature of substituents and (V) may be diverted to open-chain dicationic species in the presence of an excess of oxidant.[1,4] Experimental proof of the reverse process *i.e.* one-electron oxidative ring-opening of (II) [to give derivatives of (V)] has already been obtained.[5]

Quantum yields (ϕ_d)[a] *for photosensitised*[b] *cyclodimerisation of* N-*vinylcarbazole*[c] *at* 25°

Sensitiser	Concentration	Solvent	Atmosphere	ϕ_d
Chloranil	3×10^{-3}M	Me_2CO	Air	$8\cdot5 \pm 0\cdot1$
Chloranil	3×10^{-3}M	Me_2CO	N_2	$4\cdot3 \pm 0\cdot2$
Chloranil	10^{-3}M	MeOH	Air	$2\cdot9 \pm 0\cdot2$
Chloranil	10^{-3}M	MeOH	N_2	$1\cdot1 \pm 0\cdot1$
Fluorenone	(2×10^{-4}–10^{-2}M)	Me_2CO	Air	$3\cdot6 \pm 0\cdot4$
Fluorenone	10^{-2}M	Me_2CO	N_2	$2\cdot1 \pm 0\cdot3$

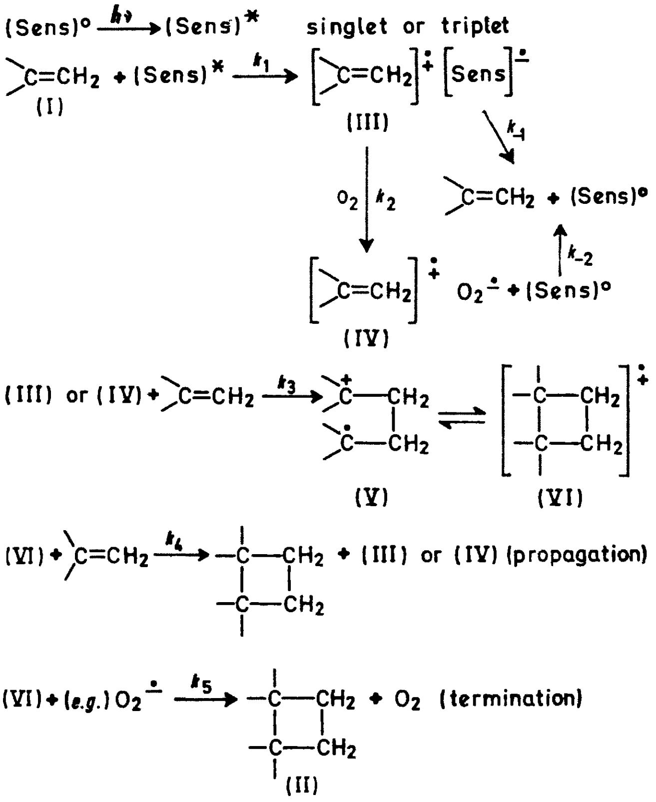
[a] ϕ_d = [no. of moles of cyclodimer (II)]/(no. of moles light quanta absorbed): determined by ferrioxalate actinometry as described in ref. 3.

[b] Irradiation by 250w Medium Pressure mercury lamp through a 405 nm interference filter.

[c] [*N*-Vinylcarbazole] = 0·1M.

The extent of intervention by molecular oxygen will depend on the relative values of k_{-1}, k_{-2}, and k_3, which in turn reflect both the stability of anion radicals formed from carbonyl sensitisers, and solvation characteristics of the ion-pairs (III) and (IV). Similar factors govern the ratios k_{-1}/k_3, k_{-2}/k_3, and k_4/k_5, accounting for the variation in quantum yield with changing reaction conditions. Apparent unit quantum yields, reported previously for dye sensitisers,[2] could then result from fortuitous combinations of the rate coefficients.

Charge-transfer spectra between *N*-vinylcarbazole (I) and *N*-ethylcarbazole [used as a model for the cyclodimer (II)] and chloranil have been determined in CH_2Cl_2. The spectra show maxima at 493 and 615 nm for (I) and 524 and 672 nm for the saturated homologue. Thus the ionisation potential of (I) may be estimated[6] to be approximately 3·6 kcal greater than that of the cyclobutane (II). The heat of polymerisation of (I) is 18 kcal mole^{-1},[7] and taking cyclobutane strain energy to be 26 kcal mole^{-1},[8] the cyclodimerisation of (I) may be estimated to be exothermic overall by approximately 10 kcal mole^{-1}. It follows therefore that the initiation reaction (III) [or (IV)] + (I) → (VI) will be exothermic by about 13 kcal mole^{-1}, while the propagation step (VI) + (I) → (III) [or(IV)] will be endothermic by only *ca.* 3—4 kcal mole^{-1}. This novel chain mechanism is therefore supported by simple thermochemical considerations, suggesting that similar processes, involving both cation radicals[9] or anion radicals, may be found other suitably activated systems.



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