Chemical Sensitization. The Chemical Initiation of Photochemical Reactions in the Absence of Light

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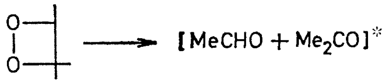
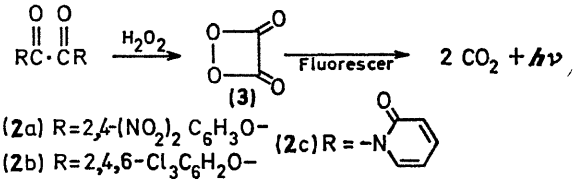
Summary Photochemical reactions of phenanthraquinone, 4-methoxy-4′-nitrostilbene, and *o*-tolylpropane-1,2-dione occur in the dark on admixture with oxalic acid derivatives and hydrogen peroxide.

Recently White, Wiecko, and Roswell[1] reported the first examples of the use of chemically generated excited states as sensitizers for photochemical reactions. They used the dioxetan[2] (**1**) to generate an excited state of acetone or acetaldehyde which acted as the energy donor. We report some independent observations of a related phenomenon.

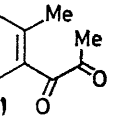
(**1**)



Bis-(2,4-dinitrophenyl) oxalate (**2a**), bis-(2,4,6-trichlorophenyl) oxalate (**2b**), and bis-(2-pyridon-1-yl)glyoxal (**2c**) have been reported to chemiluminesce with hydrogen peroxide in the presence of rubrene (or other fluorescers) with high quantum efficiencies, 0·23, 0·18, and 0·16 respectively.[3] A high-energy intermediate has been demonstrated in these reactions which is postulated to be the dioxetandione (**3**).[4] Decomposition of (**3**) is catalysed by certain fluorescent compounds with emission of light. Spontaneous decomposition is slower and yields no light.



We have generated (**3**) in the presence of several photochemically reactive compounds and find that the chemical energy of (**3**) can cause photochemical transformations even when no light is emitted. For example, treatment of a benzene solution, 3×10^{-3} M in *o*-tolylpropane-1,2-dione (**4**) and $1{\cdot}8 \times 10^{-2}$ M in bis-(2,4-dinitrophenyl) oxalate (**2a**), with an excess of anhydrous hydrogen peroxide in glyme yielded 3% of the known photo-product,[5] 2-methyl-2-hydroxyindanone (**5**), without visible light emission. Since the quantum yield for the photochemical reaction was found to be ϕ_{4050} *ca.* 0·8, and a 6-fold excess of the oxalate was employed, the chemical sensitization efficiency $\phi_{\mathrm{CS}} = 0{\cdot}03/6(0{\cdot}8) = 0{\cdot}006$.



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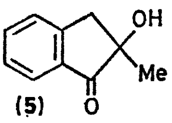

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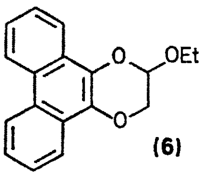

(6)

A lower yield, but higher chemical sensitization efficiency was achieved on treatment of 5×10^{-3} M-phenanthraquinone and 2×10^{-2} M-(**2a**) in ethyl vinyl ether with hydrogen peroxide. Although only a 1% yield of the photo-adduct[6] (**6**) was obtained, the quantum yield for the photochemical reaction is low, $\phi_{4050} = 0{\cdot}06$, hence $\phi_{\mathrm{CS}} = 0{\cdot}04$.

The highest efficiencies and yields were obtained using *trans*-4-methoxy-4′-nitrostilbene (*S*, 64 kcal/mole) as the reactant (Table). These reactions produced emission which was visually indistinguishable from the fluorescence emission of the *trans*-stilbene. A maximum yield of 9% of the *cis*-isomer was obtained. Although these yields are somewhat lower than those reported by White, *et al.*,[1] the chemical sensitization efficiencies are significantly higher than the maximum ϕ_{CS} *ca.* 0·01 of the previous work.

Chemical sensitization of trans-4-*methoxy*-4′-*nitrostilbene by oxalate derivatives in benzene*[a]

	[Oxalate][b]	[*trans*-Stilbene]	Yield *cis*-stilbene	ϕ_{CS}[c]
(**2a**)	5×10^{-3} M	1×10^{-3} M	6%	0·030
(**2a**)	$7{\cdot}5 \times 10^{-3}$	2×10^{-3}	6	0·040
(**2a**)	2×10^{-2}	4×10^{-3}	9	0·045
(**2b**)[d]	4×10^{-2}	8×10^{-3}	2	0·010
(**2c**)[e]	$1{\cdot}5 \times 10^{-2}$	2×10^{-3}	6	0·020

[a] Suspensions of the reactants were treated dropwise with an excess of 0·1 N-H_2O_2 in anhydrous dimethoxyethane at room temperature. Reactions were complete within 10 min. [b] Incompletely dissolved. [c] ϕ_{CS} = (yield) [*trans*-stilbene]/[oxalate] $\phi_{t\rightarrow c}$ where $\phi_{t\rightarrow c} = 0{\cdot}40$ (ref. 7). [d] Contained 5×10^{-2} M-NaOAc (suspension). [e] Contained 1×10^{-2} M-$CCl_3{\cdot}CO_2H$.

The reported failure of these authors to observe chemical sensitization with oxalates is interesting. We also found that the reactions failed with unsubstituted *trans*-stilbene. The failure to produce stilbene isomerization may be due to the high energy of *trans*-stilbene singlet (84 kcal/mole) relative to the energy available for electronic excitation in (**3**) which has not yet been demonstrated to be greater than 71 kcal/mole.[4] Nevertheless there may be structural as well as energetic requirements for excitation of an acceptor. This would not be unexpected since evidence for orbital symmetry requirements in energy transfer has previously been given,[8] and ability of acceptors to catalyse the decomposition of (**3**) further implies that structural factors may be involved.

Attempts to improve the yields of these reactions have so far been unsuccessful. The use of larger amounts of oxalates may have failed to give increased yields due to the accumulation of oxalate decomposition products which may act as quenchers. We are currently investigating other chemical energy sources which do not yield quenchers.

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