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PHOTOCHEMISTRY WITHOUT LIGHT - REACTION OF ACTIVE OXALATE ESTERS WITH ANTHRACENOPHANES

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Summary. Certain anthracenophanes undergo photochemistry without light, sensitised by active oxalates. Although the quantum yield of sensitisation is extraordinarily high, no direct evidence for the expected radical cation intermediate has been found.

It has been amply demonstrated[1,2] that excited states generated by chemical means undergo the expected photochemical reactions. However most of these reactions have been the result of excited triplet ketone formation during dioxetan decomposition, and few other potentially useful reactions have been investigated. The most effective chemiluminescent system is that of the reaction between electronegatively substituted oxalate esters and hydrogen peroxide[3]. Attempts to extend the initial observations[2] of photochemistry without light resulted in doubt being cast on the applicability of the reaction for this purpose[4]. A further reason for wishing to investigate oxalate reactions is the fact that, in spite of extensive and elegant research[3], the ultimate source of the excitation remains unclear.

Since a characteristic of the reaction is the ease with which excited states are produced from polynuclear aromatic hydrocarbons, we initially attempted to carry out the well known photochemical dimerisation of anthracene using bis-dinitrophenyl oxalate. No trace of dimer was observed, the only products being the apparent carboxyphenylation of the anthracene as a result of free radical side reactions. A similar failure was observed in the attempted dimerisation of acenaphthylene[4]. We decided to examine the anthracenophanes (1(a), n=2 and 1(b) n=4) as providing more suitable substrates for such a reaction.

Not only is the isomerisation likely to be favoured, but such sandwich compounds form particularly stable, and hence more easily detectable radical cations[5]. We have postulated electron transfer reactions involving such ions in the oxalate reaction[6], but they are so far unobserved, in spite of the successful extension of the concept to other systems[7]. A promising technique for the detection of the radical ion pairs is based on the modulation of luminescence intensity by resonance absorption of microwave radiation in an external magnetic field[8,9]. This e.s.r. method is capable of detecting a steady state concentration of 20 radical pairs per sample. We were unable to observe any perturbation of the light intensity, and it may be that the lifetime of the radical pair (4) is much shorter than the 10^{-8} s typical of the successful experiment already reported[8]. We also failed to observe any signals using other fluorescers such as 9,10-dimethylanthracene.

The anthracenophane 1(a) readily undergoes photochemical isomerisation with a quantum yield[10] of 0.3, but does not fluoresce[11]. Treatment of solutions of 1(a) in dimethoxyethane with 2 and H_2O_2 gave the results in Table 1. The reaction was followed by loss of absorption at 380 or 420 nm, and shown to be reversible on heating. The chemical sensitisation yield (ϕcs) is the highest yet observed and clearly confirms that in some cases at least, the oxalate system can be used for photochemistry without light. The yields obtained are not optimal since the concentration of the poorly soluble anthracenophane acceptor is considerably below that necessary for maximum quantum yield in the oxalate system. Lower chemical sensitisation quantum yields (ϕcs) were obtained using oxalate 3, with ϕcs rising as the ratio of oxalate to anthracenophane concentration falls from 10.9 (ϕcs 0.11) to 1.9 (ϕcs 0.21).

The isomerisation occurs with an efficiency ten times greater than any previously observed with this system, suggesting that the trans-annular interaction (which will stabilise the radical cation) is responsible. This proposition is most easily examined by comparing light intensity with that of other light yielding reactions. The <u>fluorescent</u> anthracenophane 1(b) was thus essential to the experiment[12]. Since it also undergoes dimerisation (ϕcs 0.06) and hence consumption, a comparison of quantum yield of emission does not accurately reflect efficiency. However a comparison of initial intensities[13] will provide suitable data. The values obtained for 1(b), diphenylanthracene and anthracene are shown in Table 2 and plot of log $\frac{I^{\circ}_{CL}}{\phi_F}$ against E_S was linear (slope 0.165, correlation coefficient 0.9999).

Recent demonstrations[14] that the dimerisation of olefins otherwise typical of photochemical reactions takes place through radical cation intermediates suggested that the high efficiency of isomerisation in the case of the anthracenophanes may be an alternative indication of the intermediacy of such ions. However no isomerisation was observed when 1(a) was treated with a variety of reagents known to result in reactions via the radical cation[15,16] including WCl_6 and diphenylpicrylhydrazyl with $SnCl_4$ or $AlCl_3$ and CH_3NO_2. We conclude that the anthracenophane isomerisation is efficiently accomplished by the chemical generation of the singlet excited state.

<u>Table 1</u>

<u>Reaction of anthracenophane 1(a) with oxalate 2</u>

10^5[1a]/M	10^4[2]/M	R($\frac{[2]}{[1a]}$)	Yield Y%	Y/R	ϕcs
5.76	10.1	17.5	91	0.052	0.17
5.76	5.06	8.8	69	0.078	0.26

Reactions run in dimethoxyethane, H_2O_2 in t-BuOH 0.12 M 45.5°C; ϕcs = Y/R x 0.3,

Na salicylate 1.0 x 10^{-6} M.

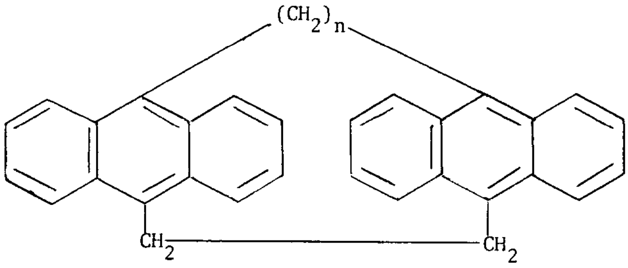
Table 2

1b, Diphenylanthracene (DPA) and anthracene (A) as acceptors in the oxalate reaction.

Fluorescer	$I_{max}^{(a)}$(rel.)	ϕ_F	$\log_{10}\frac{I_{max}}{\phi_F}$	E_S(K. cal.)^b
1b	550	0.014	2.595	60.5
DPA	500	0.84	0.775	71.5
A	54	0.36	0.175	75.4

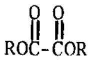
(a) Corrected for phototube response. $[H_2O_2]$ 0.12 M $[Fluorescer]$ 1.6 x 10^{-5} M, [2] 1.2 x 10^{-3} M, Na salicylate 1.0 x 10^{-6} M.

(b) Calculated from fluorescence and absorption spectra[17].



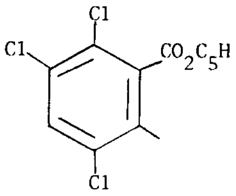
1(a) n = 2

1(b) n = 4

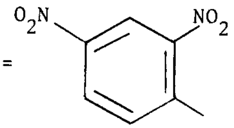


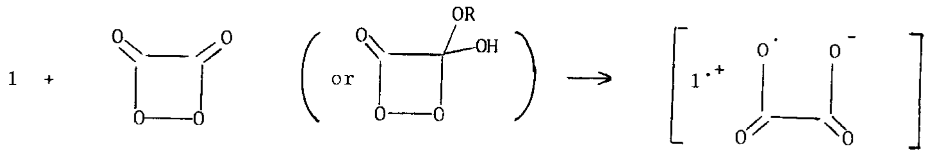
$$ROC(=O)-C(=O)OR$$

2, R =



3, R =





$$\longrightarrow 1^{\cdot +}\ CO_2^{\cdot -} + CO_2 \longrightarrow 1^* + 2CO_2$$

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