Photo-oxidation of Carbanions: the Reactivity of Singlet Oxygen with 9-Benzenesulphonylfluoren-9-yl Anion

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Summary The oxidation of 9-substituted fluoren-9-yl anions to fluorenone by molecular oxygen in t-butyl alcohol is markedly accelerated by irradiation of added dye sensitisers (*e.g.*, rose bengal) or by direct excitation of the carbanion, singlet oxygen being involved in both cases.

A RECENT report[1] that dimedone is oxidised by singlet oxygen, in basic solution prompts us to report some results on the photo-oxidation of carbanions. Fluoren-9-yl anions (FlX^-) react readily with ground-state molecular oxygen ($^3O_2$) to give fluorenone (Fl:O).[2] The mechanism is thought to involve rate-limiting transfer of an electron from the carbanion to oxygen[3] giving a fluorenyl radical and superoxide ion, collapse of which would lead to a fluorenyl hydroperoxide ion (Equation 1). We reasoned that the carbanion could be converted directly into the fluorenyl hydroperoxide ion by reaction with singlet molecular oxygen ($^1O_2$) (Equation 2) and that this might be a cleaner and more rapid reaction than the thermal oxidation.

$$Na^+FlX^- + {}^3O_2 \rightarrow FlX\cdot + O_2^{-}\cdot Na^+ \rightarrow Fl(X)O\cdot O^-Na^+ \rightarrow Fl:O \qquad (1)$$

$$Na^+FlX^- + {}^1O_2 \longrightarrow Fl(X)O\cdot O^-Na^+ \longrightarrow Fl:O \qquad (2)$$

Irradiation of a dye, such as rose bengal (λ_{max} 550 nm), known to sensitise the production of $^1O_2$,†[4] in solution in air- or oxygen-saturated t-butyl alcohol containing Na^+FlX^- ($X = SO_2Ph$ or COPh), generated from the parent 9-substituted fluorene by an excess of sodium t-butoxide, led to rapid and quantitative formation of fluorenone. The disappearance of the carbanion followed a first-order kinetic

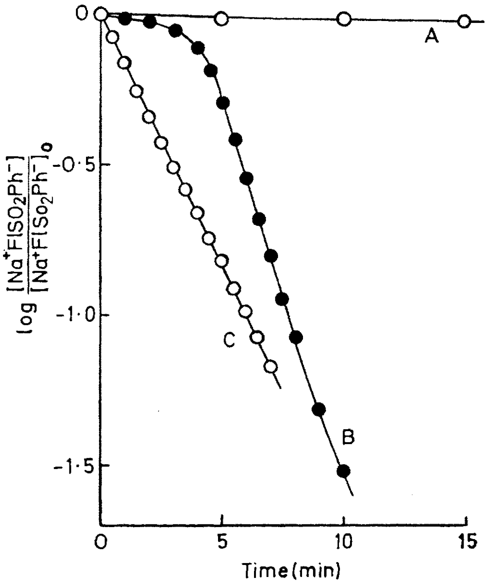

FIGURE 1. *Effect of light on the oxidation of* $Na^+FlSO_2Ph^-$ (*ca.* 10^{-4} M) *by molecular oxygen in t-butyl alcohol at* 30°. A: *Thermal reaction.* B: *Direct irradiation* (ca. 360 *nm*). C: *Rose-bengal sensitised reaction* (ca. 550 *nm*).

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† Eosin Y, cryptocyanine, and azulene have also been used successfully.

law for >90% reaction (Figure 1), consistent with Reaction (3) if $k_d \gg k_c[\mathrm{Na^+FlX^-}]$.

$$^3\mathrm{O_2} \underset{k_d}{\overset{h\nu\text{-sensitiser}}{\rightleftarrows}} {}^1\mathrm{O_2} \xrightarrow[k_c]{\mathrm{Na^+FlX^-}} \mathrm{Fl{:}O} + \mathrm{Na^+XO^-} \qquad (3)$$

The oxidation of $\mathrm{Na^+FlSO_2Ph^-}$ could also be accelerated by direct excitation of the carbanion (λ_{max} 368 nm) using light from a Phillip's O5/J6 source. The kinetic form (Figure 1) is more complex than that of the dye-sensitised reaction but oxidation is again quantitative.

Quantum yields for fluorenone formation (Φ_F) have been determined by conventional methods for photo-oxidation under both sets of conditions using a range of concentrations of $\mathrm{Na^+FlSO_2Ph^-}$. Assuming that the reaction scheme is that in Equation (3) for both dye-sensitised and direct photo-oxidation of the carbanion and that the carbanion concentration ($[\mathrm{Na^+FlX^-}]$) does not change appreciably during the period of measurement (< 5% conversion of $\mathrm{Na^+FlX^-}$ into Fl:O), it can be shown that Φ_F is related to $[\mathrm{Na^+FlX^-}]$ and the quantum yield for singlet oxygen formation (Φ_O) as shown in Equation (4). The experimental results in the Table fit Equation (4) and linear

$$\frac{1}{\Phi_F} = \frac{1}{\Phi_O} \times \left(1 + \frac{k_d}{k_c[\mathrm{Na^+FlX^-}]}\right) \qquad (4)$$

regression analysis yields values for Φ_O and k_d/k_c. Although photo-oxidation under the two sets of conditions gives very different Φ_F and Φ_O values, the values of k_d/k_c are very close, supporting the view that both the direct and dye-sensitised formation of fluorenone involve reaction of the carbanion with singlet oxygen, at least in the initial stages. The values of k_d/k_c are very small which indicates that the carbanion is highly reactive towards singlet oxygen (more than twice as reactive as 2,5-dimethylfuran,[5] relatively high concentrations—0·01M—of which inhibit carbanion oxidation when added to reaction mixtures). This could have important implications in preparative organic chemistry, even in situations where carbanion formation from its precursor is far from complete.

Quantum yields for fluorenone formation in the direct and rose-bengal sensitised photo-oxidation of 9-*benzenesulphonylfluoren*-9-*yl anion in t-butyl alcohol at* ca. 30°

Filter	Sensitised 546 ± 2 nm[a]		Direct 368 ± 2 nm[a]	
10^4 $[\mathrm{Na^+FlSO_2Ph^-}]$ (M)	% Conversion	Φ_F	% Conversion	Φ_F
2·0	3·9	0·24	4·4	0·012
3·0	3·4	0·32	—	—
4·0	3·0	0·38	3·5	0·018
6·0	2·4	0·44	2·7	0·021
8·0	2·0	0·51	2·3	0·024
10·0	1·8	0·55	—	—
Φ_O	0·80 ± 0·03[b]		0·035 ± 0·002	
10^4 k_d/k_c (M)	4·6 ± 0·2		3·8 ± 0·3	

[a] Bandwidth at one-half the maximum transmission.

[b] Literature values,[4] 0·76 (methanol), 0·78 (ethanol), 0·74 (propan-1-ol), 0·73 (n-butanol).

That the photo-oxidation of $\mathrm{Na^+FlSO_2Ph^-}$ is more complicated than suggested by Equation (2) is indicated by the following evidence. Fluorenone formation always lags behind carbanion disappearance to a small but significant extent, indicating that a metastable intermediate (I) is produced. In direct photo-oxidation of $\mathrm{Na^+FlSO_2Ph^-}$, the maximum rate of disappearance of the carbanion occurs when the concentration of (I) (obtained by difference) is greatest. Interruption of irradiation in a rose-bengal sensitised aerial oxidation of $\mathrm{Na^+FlSO_2Ph^-}$ after about 40% of the initial concentration of carbanion had been consumed revealed that the carbanion continued to be transformed into fluorenone at a rate faster than the normal thermal oxidation as long as (I) was present (Figure 2). The apparent stoicheiometry of this light-induced dark reaction from the results of Figure 2 is $2\mathrm{FlSO_2Ph^-} + (\mathrm{I}) \longrightarrow 3\mathrm{Fl{:}O}$, but comparison with runs in t-butyl alcohol saturated with oxygen suggests that the rate of reaction is also dependent on the oxygen ($^3\mathrm{O_2}$) concentration.

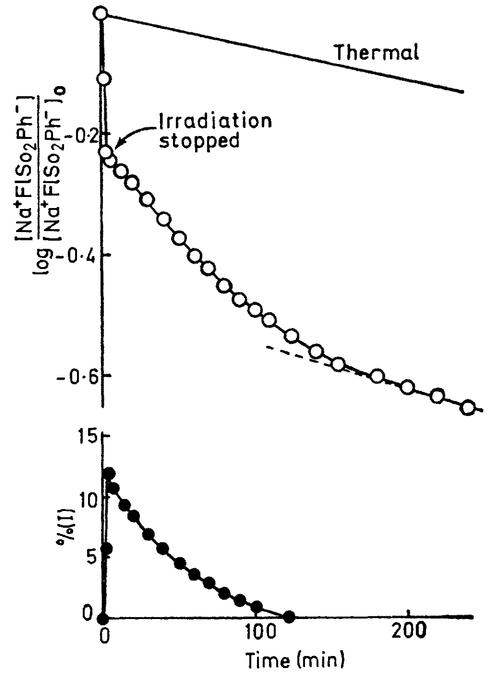

FIGURE 2. *Consumption of carbanion and production of metastable intermediate* (I) *in an interrupted, rose-bengal sensitised aerial oxidation of* $\mathrm{Na^+FlSO_2Ph^-}$ *in t-butyl alcohol at* 30°.

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