The Question of the Role of Singlet Oxygen in the Dye-sensitised Photo-oxygenation of α-Oxo-carboxylic Acids

By R. Stephen Davidson* and Dean Goodwin
(*Department of Chemistry, University of Leicester, Leicester* LE1 7RH)
and Gerald Smith
(*Davy Faraday Laboratory of the Royal Institution, Albermarle St., London* W1X 4BS)

Summary The dye-sensitised photo-decarboxylation of α-oxo-carboxylic acids in the presence of oxygen has been studied by laser flash photolysis and by utilising solvent isotope effects and the results show, contrary to previous claims, that singlet oxygen does not play a significant role.

Recently there have been several reports[1-4] upon the dye-sensitised photo-oxygenation of α-oxo-carboxylic acids in which decarboxylation occurs and carboxylic acids are produced. There is evidence for the intermediacy of percarboxylic acids[1,4] and a species (probably an oxygen–α-oxo-carboxylic acid adduct) which is capable of epoxidising alkenes.[4]

Evidence for the participation of singlet oxygen in the dye-sensitised reactions is: (i) the reactions are slowed down by the addition of β-carotene (a known quencher of singlet oxygen, but also a quencher of the excited singlet and triplet state of dyes[1]), and (ii) the observation of an apparent solvent isotope effect.[3] We[2] and others[3] have previously shown that the decarboxylation of α-oxo-carboxylic acids can be sensitised by dyes in the absence of oxygen and therefore there is the possibility that in the photo-oxygenation reactions, decarboxylation is occurring by more than one mechanism. In order to ascertain the role of singlet oxygen we have studied the ability of the acids to quench singlet oxygen (using the technique of laser flash photolysis) and solvent isotope effects.[5]

The rates of reaction of α-oxo-acids with singlet oxygen were measured using the method developed by Wilkinson[6] and Kearns[7] in which the oxo-acids compete for singlet oxygen with 1,3-diphenylisobenzofuran. The results are shown in Table 1. Laser flash photolysis of aerated methanolic solutions of Methylene Blue containing the α-oxo-acids shows the presence of a transient produced by reaction of the triplet dye with the acid. The transient appears to be the same as that observed by Kayser and Young,[8] *i.e.*, a radical derived from a Methylene Blue molecule. Analysis of the kinetics gave the rate constants for reaction of the dye with the acids and these are shown in Table 1. The rate constants given in Table 1 demonstrate that the acids react with the triplet dye far more efficiently than with singlet oxygen.

Table 1. Rate constants for reaction of α-oxo-carboxylic acids with singlet oxygen and Methylene Blue in aerated methanolic solutions[a]

Acid	Singlet oxygen k_q/l mol^{-1} s^{-1}	Methylene Blue k_r/l mol^{-1} s^{-1}
Phenylpyruvic acid	$<7 \times 10^6$ [b]	3×10^8
α-Oxoglutaric acid	3—4×10^6	$6{\cdot}5 \times 10^8$
3,3-Dimethyl-2-oxobutyric acid	*ca.* 1×10^6	$4{\cdot}5 \times 10^8$

[a] The solutions were flash photolysed (λ = 694 nm) using 15 ns, 1 J single pulses from a Q-switched ruby laser. [b] The formation of transient species absorbing at the monitoring wavelength of 410 nm made it difficult to measure the bleaching of the 1,3-diphenylisobenzofuran. Thus the acid concentration was kept as low as possible but this introduces large errors and therefore we can only give an upper limit for this rate constant.

The availability of the rate constants in Table 1 enabled meaningful solvent isotope studies to be carried out.[9] If singlet oxygen is solely responsible for oxidation the kinetics of the reaction will be described by equation (1).

$$-\mathrm{d}[\text{Acid}]/\mathrm{d}t = I\phi_{\mathrm{T}}k_{\mathrm{q}}[\text{Acid}]/(k_{\mathrm{d}} + k_{\mathrm{q}}[\text{Acid}]) \qquad (1)$$

I = Light intensity. ϕ_{T} = Triplet yield of dye. k_{d} = Unimolecular decay constant for singlet oxygen.

Since the k_{q} values for the oxo-acids are so low, the use of a low concentration of the acid, *e.g.*, 1×10^{-4} M, will mean that the rate of reaction is largely controlled by k_{d}. Thus the rate of reaction should be considerably higher in deuterium oxide ($k_{\mathrm{d}} = 5 \times 10^4\ \mathrm{s}^{-1}$)[10] than for water ($k_{\mathrm{d}} = 5 \times 10^5\ \mathrm{s}^{-1}$).[5] The rates of photo-oxidation of the oxo-acids were determined by following their rates of

TABLE 2. Solvent isotope effect upon the dye-sensitised photo-oxidation of α-oxo-carboxylic acids[a]

Acid (Concentration/M)	Dye (Concentration/M)	Rate in H_2O /mol min^{-1}	Rate in D_2O /mol min^{-1}	Isotope effect; Rate D_2O/Rate H_2O
α-Oxoglutaric acid (10^{-4})	Rose Bengal (2×10^{-6})	$0{\cdot}152 \pm 0{\cdot}012 \times 10^{-6}$	$0{\cdot}169 \pm 0{\cdot}024 \times 10^{-6}$	$1{\cdot}17 \pm 0{\cdot}21$
α-Oxoglutaric acid (10^{-4})	Methylene Blue (2×10^{-6})	$0{\cdot}122 \pm 0{\cdot}024 \times 10^{-6}$	$0{\cdot}187 \pm 0{\cdot}034 \times 10^{-6}$	$1{\cdot}65 \pm 0{\cdot}60$
α-Oxoglutaric acid (2×10^{-2})	Rose Bengal (10^{-3})	$0{\cdot}158 \pm 0{\cdot}011 \times 10^{-4}$	$0{\cdot}247 \pm 0{\cdot}079 \times 10^{-4}$	$1{\cdot}61 \pm 0{\cdot}61$
Phenylpyruvic acid (10^{-4})	Rose Bengal (2×10^{-6})	$0{\cdot}204 \pm 0{\cdot}02 \times 10^{-6}$	$0{\cdot}205 \pm 0{\cdot}051 \times 10^{-6}$	$1{\cdot}04 \pm 0{\cdot}35$
Phenylpyruvic acid (10^{-4})	Methylene Blue (2×10^{-6})	$0{\cdot}179 \pm 0{\cdot}015 \times 10^{-6}$	$0{\cdot}212 \pm 0{\cdot}008 \times 10^{-6}$	$1{\cdot}2 \pm 0{\cdot}15$

[a] The reported results are usually the mean of four determinations and all have been subjected to least squares analysis.

consumption by polarography.† The results are shown in Table 2. It is readily seen that the reactions display a remarkably small solvent isotope effect and for the oxidation of α-oxoglutaric acid sensitised by Rose Bengal, the magnitude of the effect is not markedly dependent upon the concentration of the acid. One concludes that either singlet oxygen is not involved in the reaction or else the oxidation is occurring predominantly by the dye–acid interaction and this is swamping the contribution made by the singlet oxygen reaction. From equation (2)[9] and the results given in Table 1 it is possible to calculate that the isotope effects for phenylpyruvic acid, α-oxoglutaric acid, and 3,3-dimethyl-2-oxobutyric acid should be 1·4, 2·0, and 1·4 provided that N_t and N_0 are either unity or of similar magnitude. The fact that the measured isotope effects are smaller than the calculated values may indicate that $N_0 < N_t$. The fact that the observed values for a particular acid apparently vary with the sensitiser used is probably a reflection of the fact that the isotope effect falls within the limits of experimental reproducibility. The previously reported, small solvent isotope effects[3] vary considerably in the range 1—2 and therefore the results cannot be taken as evidence for the participation of singlet oxygen.

$$\frac{-\mathrm{d}[\mathrm{Acid}]}{\mathrm{d}t} = \frac{N_t I \phi_T k_r[\mathrm{Acid}]}{(k_{d_1} + k\mathrm{O}_2[{}^3\mathrm{O}_2] + k_r[\mathrm{Acid}])} + \frac{N_0 I \phi_T k\mathrm{O}_2[{}^3\mathrm{O}_2] k_q[\mathrm{Acid}]}{(k_{d_1} + k_{\mathrm{O}_2}[{}^3\mathrm{O}_2] + k_r[\mathrm{Acid}])(k_d + k_q[\mathrm{Acid}])} \qquad (2)$$

I = Light intensity. ϕ_T = Quantum yield of triplets for the sensitiser. k_d = Unimolecular decay constant for singlet oxygen. k_{d_1} = Unimolecular decay constant for the triplet dye. k_{O_2} = Bimolecular rate constant for quenching dye triplets by oxygen. $[{}^3\mathrm{O}_2]$ = Concentration of oxygen in solution. N_t = Fraction of triplet dye–acid collisions which result in chemical reactions. N_0 = Fraction of singlet oxygen–acid collisions which result in chemical reactions.

Our results show that singlet oxygen plays little, if any, role in the Rose Bengal and Methylene Blue sensitised photo-oxygenation of α-oxo-carboxylic acids. The dye–acid interaction is obviously an important reaction but one cannot rule out that some reaction at least occurs *via* an intermediate such as the superoxide anion.[4]

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