Tetrahedron Vol 39, No 14, pp 2373 to 2379, 1983
Printed in Great Britain

0040-4020/83 $3.00 + .00
Pergamon Press Ltd

FACTORS AFFECTING DYE SENSITISED PHOTO-OXIDATION REACTIONS; THE EFFECT OF OXYGEN CONCENTRATION AND ITS USE TO PROBE THE MECHANISM OF DECARBOXYLATION OF α-OXO-CARBOXYLIC ACIDS AND ESTERS

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(*Received in UK* 22 *March* 1983)

Abstract - The dye sensitised photo-oxidation of α-oxo-carboxylic acids and esters leads to the production of carbon dioxide. The yield of carbon dioxide is dependent upon the oxygen concentration. This, together with the fact that carbon dioxide evolution can be observed in the absence of oxygen, is in accord with the view that the decarboxylation reactions involve an initial dye-substrate interaction rather than a singlet oxygen mediated reaction.

Dye sensitised photo-oxygenation reactions involving singlet oxygen are known to be insensitive to changes in oxygen concentration, above a critical minimum level.[1,2] In contrast, reactions which involve radicals e.g. the dye sensitised oxidation of amines,[1] show a dependency upon oxygen concentration. Similarly, oxidation reactions occurring via an electron transfer process, e.g. dye-sensitised photo-oxygenation of trans-stilbene,[2] are subject to an oxygen concentration dependence.

We now report upon the effects of changes in oxygen concentration in dye sensitised photo-oxidative decarboxylations of α-oxo-carboxylic acids[3,4,5,6,7,8] and their esters.[9,10] A singlet oxygen mechanism was proposed for the dye sensitised decarboxylation of the α-oxo-carboxylic acids.[3,5,6] However, we[7] and others[8] have since shown that singlet oxygen is not involved to a significant extent and a mechanism involving interaction between the α-oxo-carboxylic acid and the triplet dye has been proposed.[7] To substantiate this proposal dye sensitised decarboxylations of α-oxo-carboxylic acids have been carried out, the reaction mixtures being flushed with gases having a range of oxygen concentrations. Similar experiments were performed using α-oxo-carboxylic esters, which are shown to undergo sensitised photo-oxidative decarboxylation with a variety of dyes. The only previous reports regarding the dye-sensitised decarboxylation of esters have concerned esters which have a strong tendency to enolise.[9,10] A mechanism involving the enol form of the esters was proposed for these reactions.[9,10]

α-Oxo-Carboxylic Acids

Results and Discussion

The carbon dioxide yields obtained under argon (0.0001% oxygen), pure oxygen, air (carbon dioxide free), nitrogen (O.F.N., 0.001% oxygen) and commercial grade nitrogen (up to 5% oxygen) from the dye sensitised decarboxylation of α-oxo-glutaric acid and pyruvic acid are shown in Tables 1-3. The effect of a change in the oxygen flow rate, upon the yield of carbon dioxide is illustrated in Table 2, whilst Tables 2 and 3 highlight the variation in carbon dioxide yields obtained using Rose Bengal from two different sources. By comparison the results in Table 4, of the dye sensitised photo-oxidation of citronellol under the same conditions used for the acids above, show the expected trends for a singlet oxygen mediated reaction i.e. very little reaction at very low oxygen concentrations but no significant difference in reac-

TABLE 1 Yields of carbon dioxide from the irradiation of pyruvic acid (2×10^{-2} M) sensitised by Rose Bengal (B.D.H.; 0.02g/25 mls) under different gases, flushed through at 10 mls/min, in (A) methanol/pyridine and (B) acetonitrile/pyridine (4:1 v/v) solutions, after 6 and 20 hrs irradiation, using a 2% aqueous potassium chromate light filter solution.

	Carbon dioxide yields (%)			
	(A)		(B)	
	6 hrs	20 hrs	6 hrs	20 hrs
Argon	9.7	28.1	12.2	39.6
Nitrogen (O.F.N.)	7.5	20.0	8.1	24.3
Nitrogen (commercial)	7.1	20.0	*	*
Air (carbon dioxide free)	12.4	58.7	34.5	98.9
Oxygen	6.8	28.5	17.7	63.9

*Yield not determined

TABLE 2 Yields of carbon dioxide from the irradiation of α-oxo-glutaric acid (2×10^{-2}M) sensitised by Rose Bengal (B.D.H.; 0.02g/25 mls) under the conditions given in Table 1.

	Carbon dioxide yields (%)			
	(A)		(B)	
	6 hrs	20 hrs	6 hrs	20 hrs
Argon	9.8	42.7	9.1	37.4
Nitrogen (O.F.N.)	6.2	17.9	5.8	22.2
Nitrogen (commercial)	6.4	20.6	6.7	29.2
Air (carbon dioxide free)	20.3	105.9	22.1	113.4
Oxygen	11.5	51.3	11.7	54.0
Oxygen[(a)]	*	*	17.3	116.3

(a) - rate of oxygen flushing 20 mls/min *Yield not determined.

TABLE 3

Yields of carbon dioxide from the irradiation of α-oxo-glutaric acid (2×10^{-2} M) sensitised by Rose Bengal (Eastman-Kodak; 0.02g/25 mls) under the conditions given in Table 1.

	Carbon dioxide yields (%)	
	(A)	
	6 hrs	20 hrs
Argon	11.9	33.0
Nitrogen (O.F.N.)	10.0	26.2
Nitrogen (commercial)	8.4	24.3
Air (carbon dioxide free)	19.2	75.5
Oxygen	11.7	45.8

TABLE 4

Rate of photo-oxidation of citronellol (2×10^{-2} M) sensitised by Rose Bengal (B.D.H.; 0.02g/25 mls) under the conditions given in Table 1, using acetonitrile as solvent.

	Rate of consumption of citronellol (Ms^{-1})
Argon	0
Nitrogen (O.F.N.)	0
Air (carbon dioxide free)	4.6×10^{-6}
Oxygen	4.6×10^{-6}

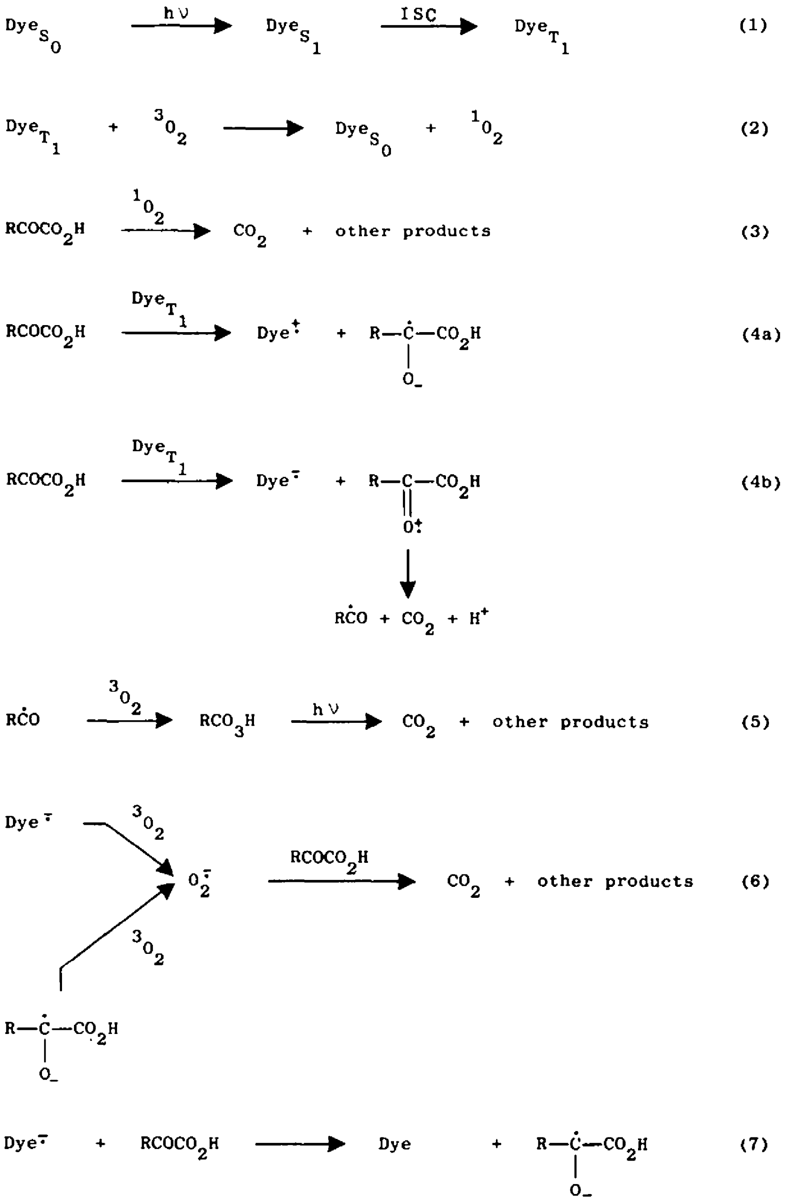
-tion rate between oxygen and air flushed solutions.

These results confirm the previous finding that decarboxylation of α-oxo-carboxylic acids occurs even in the absence of oxygen.[3,4,5] The discrepancy between our low yields and those previously reported under anaerobic conditions may have arisen as a consequence of leakage of air into the nitrogen line used in the earlier study.[4]

For all the α-oxo-carboxylic acids studied the yields of carbon dioxide were found to be in the order: air > oxygen > argon > nitrogen. These results can be used to give an insight into the relative importance of each of several possible interactions between the α-oxo-carboxylic acid, the triplet dye and oxygen. These are outlined in Scheme 1.

Since singlet oxygen has been shown not to be involved to a significant extent in the dye sensitised decarboxylations of α-oxo-carboxylic acids,[7,8] path (2) and the subsequent path (3) may be disregarded. Radical processes (paths (4a) and (4b)) could lead to carbon dioxide production by a mechanism involving superoxide anions (path (6)) or as a consequence of the scavenging of acyl radicals (produced via path (4b)) by oxygen to yield peracids (path 5).[3,5] The latter may subsequently undergo decarboxylation (path (5)).[11] A combination of paths (4b) and (5) therefore increases the theoretical maximum yield of carbon dioxide to two moles per mole of α-oxo-carboxylic acid.[12]

Scheme 1



As there is no oxygen present when the reaction mixtures are flushed with argon the radical pathway (4b) is the only feasible route to carbon dioxide production. The small concentration of oxygen in the solutions flushed with nitrogen is able to scavenge acyl radicals (path (5)), thus paths (4a) and (4b) both lead to decarboxylation. However, quenching of the triplet dye by oxygen will reduce the efficiency of path (4), below that observed under argon, so higher yields of carbon dioxide will be obtained under argon than under nitrogen (Tables 1-3). Regeneration of the dye may be accomplished, even in the absence of oxygen, via reaction of the radical anion of the dye with the α-oxo-carboxylic acid (path (7)).

Under aerated conditions paths (4a), (4b), (5) and (6) can all lead to decarboxylation. The oxygen concentration will allow efficient scavenging of acyl radicals, to yield more than one molar equivalent of carbon dioxide as a result of per-acid formation (path (5)), and a greater yield of superoxide anion (path (6)). Consequently quenching of the triplet dye by oxygen will be unable to counteract the increased yields of carbon dioxide produced via the remaining triplet dye molecules.

Quenching of the triplet dye by oxygen will be most marked under pure oxygen. The yield of singlet oxygen from triplet benzophenone has been observed to increase from 50% in air saturated solution to 90% in oxygen saturated benzene solution, the inefficiency in aerated solution being attributed to incomplete oxygen quenching of the triplet benzophenone.[13] The resultant reduction in efficiency of path (4) will lead to fewer radicals being available to be scavenged by oxygen, hence a lower yield of carbon dioxide will be produced under oxygen than under air.

2. α-Oxo-carboxylic esters

Results and discussion

Table 5 shows the yields of carbon dioxide produced from dye sensitised photo-oxygenation of a range of α-oxo-carboxylic esters using methylene blue and rose bengal as sensitisers. A variety of dyes (Table 6) were found to sensitise the decarboxylation of methyl pyruvate. The methylene blue sensitised photo-oxygenation of methyl pyruvate yielded carbon dioxide in both methanol-pyridine and acetonitrile-pyridine (4:1 v/v) solvent mixtures. In the case of n-hexyl pyruvate (Table 7) glc analysis of the products from the rose bengal sensitised photo-oxidation revealed the formation of n-hexanol. However n-hexane, hexene or hexaldehyde were not detected. The effect of oxygen concentration upon the rose bengal sensitised decarboxylation of methyl pyruvate (Table 8) was therefore of interest in ascertaining the mechanism of decarboxylation of α-oxo-carboxylic esters.

TABLE 5 Yields of carbon dioxide from the dye[a] sensitised photo-oxygenation of α-oxo-carboxylic esters in acetonitrile/pyridine (4:1 v/v) solutions using a 2% aqueous potassium chromate light filter solution.

α-oxo-carboxylic ester (10^{-2} M)	Irradiation time (hrs)	Yield (%) of carbon dioxide	
		Methylene Blue	Rose Bengal
Methyl pyruvate	20	39	54
Ethyl pyruvate	20.25	*	37
Ethyl pyruvate	20.5	21	*
Isopropyl pyruvate	18	15.5	23
n-Butyl pyruvate	18	30	34
t-Butyl pyruvate	18	27	29
n-Hexyl pyruvate	18	21	34
Benzyl pyruvate	18	24.5	26
Ethyl benzoyl formate	19	14	14
2-(1-naphthyl)ethyl pyruvate	18	28	51
2-(2-naphthyl)ethyl pyruvate	18	29	45
2-(2-naphthyl)ethyl α-oxo-octanoate	18	47	43

*Yield not determined.

(a) Dye concentration = 0.02g/25 mls. Slight bleaching of the dye occurred during the course of the irradiation in each case.

TABLE 6 Yields of carbon dioxide from the dye sensitised photo-oxygenation of methyl pyruvate (10^{-2} M) in acetonitrile/pyridine (4:1 v/v) solution.

Sensitiser(a)	Irradiation time (hrs)	Light filter (aqueous solution)	Yield (%) of carbon dioxide
Rose Bengal	20.5	Saturated $NaNO_3$	76.3
Methylene Blue	19	Saturated $NaNO_3$	59.3
Methylene Blue (b)	19	Saturated $NaNO_3$	36
Rhodamine B	18	2% K_2CrO_4	45
Erythrosin B	18	2% K_2CrO_4	70.3
Tetraphenylporphyrin	18	2% K_2CrO_4	28

(a) Rose Bengal/Methylene Blue = 0.02g/25 mls; Rhodamine B/Erythrosin B = 0.02g/50 mls; tetraphenylporphyrin OD = 0.8 @ 514 nm.

(b) Methanol/pyridine (4:1 v/v) solution.

TABLE 7 Yields of carbon dioxide from the photo-oxygenation of n-hexyl pyruvate sensitised by Rose Bengal (B.D.H.; 0.02g/25 mls) in various solutions using a 2% aqueous potassium chromate light filter solution.

n-hexyl pyruvate concentration (M)	Solvent (4:1 v/v)	Irradiation time (hrs)	Yield (%) of carbon dioxide
5×10^{-2}	MeCN	18	8
3.3×10^{-2}	MeCN/quinoline	20	15(a)
2×10^{-2}	MeCN/pyridine	18	17.3

(a) n-hexanol (25% by glc).

TABLE 8

Yields of carbon dioxide from the irradiation of methyl pyruvate (2×10^{-2} M) sensitised by Rose Bengal (B.D.H.; 0.02g/25 mls)in acetonitrile /pyridine (4:1 v/v) solution for 18 hrs under the conditions given in Table 1.

	Yield of carbon dioxide (%)
Argon	17.4(a)
Nitrogen (O.F.N.)	12.0
Nitrogen (commercial)	11.4
Air (carbon dioxide free)	42.5
Oxygen	27.1

(a) The high yield of carbon dioxide obtained in the absence of oxygen can only be accounted for by the presence of small quantities of water which enable the dye to be regenerated.

Since the same trend in carbon dioxide yields produced under a range of gases, i.e. air > oxygen > argon > nitrogen was obtained for the decarboxylation of methyl pyruvate (Table 8) and α-oxo-carboxylic acids (Tables (1-3) we consider it improbable that a singlet oxygen mediated reaction is the major route to carbon dioxide production from methyl pyruvate. Although a singlet oxygen mechanism was proposed for the dye sensitised photo-oxygenation of the enol tautomers of some α-oxo-carboxylic esters [9,10] no evidence e.g. solvent isotope effects and quenching studies, was presented to support such a mechanism.

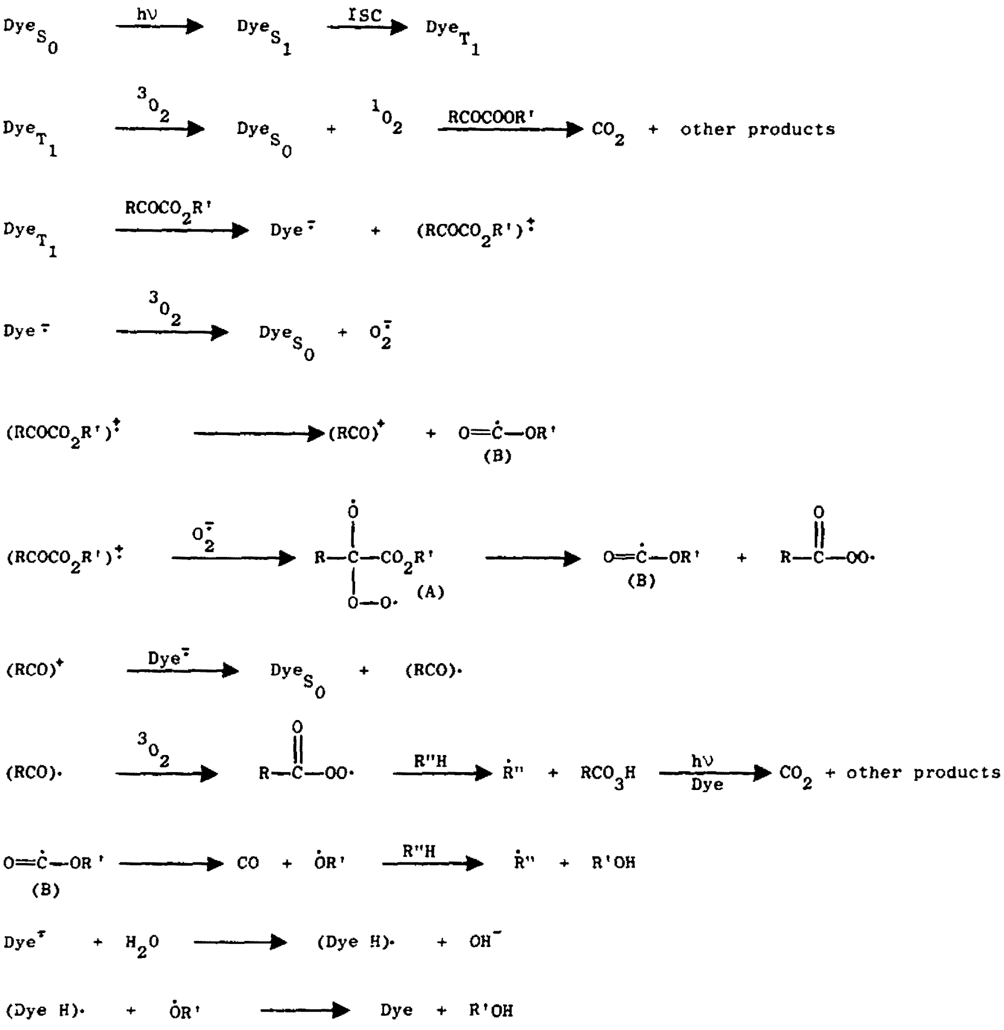
From the finding that the efficiency of decarboxylation is dependent upon oxygen concentration, together with the earlier observation that α-oxo-carboxylic esters are capable of undergoing electron transfer reactions,[14] the following mechanism (Scheme 2) is proposed to account for the observed carbon dioxide production under dye sensitised photo-oxygenation conditions.

A species similar to (A) in Scheme 2 has been proposed as an intermediate in the direct photo-oxygenation of α-oxo-carboxylic acids[8] and their esters.[15] Such an intermediate has also been suggested for the direct photo-oxidation of non-conjugated ketones (e.g. menthone)[16] and as a possible intermediate in the analogous reactions of 1,4-dicarbonyl compounds.[17]

The formation of per-acids has been demonstrated in the direct photo-oxygenation of α-oxo-carboxylic esters.[8] Per-acetic acid has been shown to undergo rose bengal sensitised decarboxylation under both degassed and aerated conditions.[11]

Decarboxylation of species (B) would result in the formation of a second mole of carbon dioxide from the ester. The resultant radical (R') could undergo hydrogen abstraction to yield R'H. However, the yields of carbon dioxide from methyl pyruvate were always well below 100% and no n-hexane formation was detected during the dye sensitised photo-oxygenation of n-hexyl pyruvate, so decarboxylation of species (B), in of decarbonylation, is considered unlike-

Scheme 2



EXPERIMENTAL

GLC analyses were recorded on a Perkin Elmer Sigma 3 gas chromatograph using a Perkin Elmer 10% SE 30, chromosorb W 60-80 mesh, column.

Potassium chromate (BDH), Rhodamine B (BDH), erythrosin B (Sigma), α-oxo-glutaric acid, ethyl pyruvate, methylene blue (metal free), methyl pyruvate, pyruvic acid, quinoline (all Aldrich), rose bengal (BDH and Eastman-Kodak), methanol (Fisons AnalaR) and acetonitrile (Cambrian Chemicals) were used as supplied. Pyridine (Fisons) and citronellol (Aldrich) were distilled prior to use. n-Butyl pyruvate, t-butyl pyruvate, benzyl pyruvate, isopropyl pyruvate, n-hexyl pyruvate, 2-(1-naphthyl)ethyl pyruvate and 2-(2-naphthyl)ethyl pyruvate were prepared by the reaction of the appropriate alcohol with pyruvoyl chloride,[18] under the conditions previously described.[19] Ethyl benzoyl formate was prepared by an analogous route using benzoyl formyl chloride and ethanol. Similarly, 2-(2-naphthyl)ethyl α-oxo-octanoate was prepared from 2-oxo-octanoyl chloride and 2-(2-naphthyl)ethanol. Spectral and physical data confirmed the structure of the prepared esters.

We thank Miss Maria Schmidt for the sample of tetraphenylporphyrin. All gases were passed through aqueous solutions saturated with barium hydroxide, in order to remove any traces of carbon dioxide, prior to use. The oxygen concentrations of the gases were:-
argon, < 0.0001%; nitrogen (OFN), 0.001%; nitrogen (commercial) < 5%.
Photolysis tubes containing the acid and ester solutions (25 mls) were continuously flushed (∿ 10 mls/min) with the appropriate gas, whilst being irradiated within a circular array of fluorescent daylight lamps (Cryselco, 8 x 20 W). Irradiations with each of the five gases were carried out simultaneously ensuring that the rate of flushing was the same for all the gases. Following irradiation the solutions were flushed for a further 2 hrs, to remove any residual carbon dioxide, the exit gases being passed through a saturated aqueous solution of barium hydroxide. The precipitated barium carbonate was weighed and the percentage yield of carbon dioxide calculated on the basis of one mole of carbon dioxide being generated per mole of α-oxo-carboxylic acid or ester. The reactions using citronellol were flushed for 45 mins prior to irradiation and allowed to flush for

30 minutes, after a sample had been taken for glc analysis, before further irradiation. Consumption of the citronellol was followed by glc analysis.

Product analysis of the n-hexyl pyruvate reaction by glc was carried out by comparison with authentic samples of n-hexanol, n-hexane, hexene and hexaldehyde.

Further factors affecting the decarboxylation of α-oxo-carboxylic acids.

Yields of carbon dioxide from the dye sensitised decarboxylation of α-oxo-carboxylic acids were also found to be dependent upon the flow rate of oxygen (Table 2). By doubling the rate of oxygen flushing the yields of carbon dioxide were increased. Hence, it was necessary to ensure that each of the five gases was being flushed through their respective reaction mixtures at the same rate.

The source of the rose bengal also affected the carbon dioxide yields (Tables 2 and 3). Rose bengal samples from a variety of sources have been found to have different photophysical properties[11] which could account for the discrepancy in carbon dioxide yields from BDH and Eastman Kodak rose bengal samples.

These findings demonstrate that caution must be taken when results obtained using dyes from different sources are being compared.

We thank the SERC for a maintenance grant (J.E.P.) and The City University for a fellowship (D.G.).

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