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THE PHOTO-SENSITISED DECARBOXYLATION OF α-KETO-CARBOXYLIC ACIDS

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It was recently reported[1] that irradiation of oxygenated methylene blue solutions containing α-keto-carboxylic acids or their anions resulted in the production of carbon dioxide. The proposal was made that the decarboxylation reaction involves attack by singlet oxygen upon the carboxylic acid. The intermediacy of singlet oxygen in the reaction was inferred from the observation that light, oxygen and the dye are all essential for reaction to occur and that addition of β-carotene retards the reaction.

Contrary to these claims, we find that the decarboxylation of α-keto-carboxylic acids and their anions can be sensitised by methylene blue and other dyes (rose bengal, riboflavin,[2] rhodamine B) in the absence of oxygen and that in fact oxygen retards the reaction. The pertinent results are shown in the Table.

TABLE. Yields of Carbon Dioxide from Irradiation of Solutions of Dyes containing α-Keto-glutaric Acid. (0.02 M)

State of Acid	Solvent	Irradiation Time	Yield (%)[a] of Carbon Dioxide			
			Methylene Blue[b]		Rose Bengal[b]	
			N_2	O_2	N_2	O_2
Free	Methanol	20 h	25.5	31.5	-	-
	Acetonitrile	20 h		59		
Pyridinium Salt	Methanol/ Pyridine	20 h	33 [c]	58 [c]	100 [c]	84 [c]
Pyridinium Salt	Acetonitrile/ Pyridine	20 h	None[d]	120 [e]	72	200 [e]
Pyridinium Salt	Methanol/ Pyridine	6 h	31	35.5	48	25.5
Sodium Salt	Methanol	20 h		<10 [f]	None[f]	38

a - Calculated on the basis of one mole CO_2 being generated per mole of acid; b - Potassium chromate filter solution; c - Irradiation for longer periods did not improve yields; d - Sensitiser bleached, colour restored by oxygen; e - i.e. more than one mole of CO_2 is being produced per mole of acid; f - Sensitiser undergoes irreversible chemical change.

The retarding effect of oxygen can be clearly seen for the reaction sensitised by rose bengal (6 h irradiation). For methylene blue as sensitiser, the yield of carbon dioxide after 6 h irradiation in nitrogen flushed solutions represents very nearly the maximum yield of this product whereas for the reaction in oxygenated solution only 61% of the total amount of carbon dioxide has been involved. Further points of interest include the fact that in some cases more than one mole of carbon dioxide per mole of acid is generated and that in the methylene blue reactions, the lack of carbon dioxide formation in nitrogen flushed solutions is due to bleaching of the dye.

The pyridinium salt of α-keto-glutaric acid quenches the fluorescence of rose bengal and methylene blue. In the case of rose bengal, the quenching is efficient when the concentration of the acid is the same as that employed in the reactions, whereas this is not the case for methylene blue.

The described results establish that there is a reaction pathway in the dye-sensitised decarboxylation of α-keto-carboxylic acid which does not involve singlet oxygen. Clearly, this pathway involves attack by an excited state of the dye upon the acid. The fact that oxygen retards the reactions suggests that the triplet state of the dye is responsible for reaction. The excited singlet state of the dye does not appear to be involved since a) oxygen should not quench this reaction (due to the short singlet lifetimes of the dye), and b) the reaction with methylene blue is relatively efficient although under the experimental conditions its excited singlet state is very inefficiently quenched by the acid or its anion. There is the possibility that in oxygenated solutions, there is a duality of mechanisms i.e. reaction can occur by attack of singlet oxygen and the excited dye upon the acid. Recently it was shown that the dye sensitised oxidation of amines involved competition between two distinct mechanistic pathways.[3] The observation that addition of β-carotene retards the decarboxylation reactions may be due to its quenching action on either singlet oxygen or the excited singlet and triplet states of the dye.[4]

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