



Photochemical Electron Transfer Across a Liquid/Liquid Interface: Methylene Blue-Sensitized Decarboxylation of Substituted Carboxylic Acids

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Abstract: Methylene Blue photocatalyzed electron transfer reactions of some substituted carboxylic acids across the water/benzene interface lead to efficient decarboxylation of these acids and the utility of this procedure has been demonstrated by the synthesis of some dihydrobenzopyran and dihydrobenzofuran derivatives.

Photochemical charge separation has relevance to a variety of applications ranging from solar energy conversion^{1,2} to organic synthesis.³⁻⁶ The highly efficient back electron transfer between the radical ion-pairs that are generated in close proximity as a result of light absorption is a major factor affecting the efficiency of these processes. Several microheterogeneous systems such as micelles, colloids and membranes have been employed in efforts to control the back electron transfer.^{1,7-9} An interface that has not been well investigated for such applications is the liquid/liquid interface. There is considerable interest in the development of new methods for decarboxylating organic acids due to the synthetic importance of such transformations and several reports have recently appeared on the use of photoelectron transfer catalysis for this purpose. However, with few exceptions¹⁰⁻¹² most of the studies deal with the mechanistic aspects.¹³⁻¹⁹ We have recently observed that the liquid/liquid interface can be utilized to bring about efficient photoelectron transfer catalysed decarboxylation of substituted carboxylic acids. Methylene Blue (MB⁺), dissolved in water has been found to bring about efficient decarboxylation of some substituted carboxylic acids, dissolved in benzene to give alkyl radicals. This process has been utilized for the synthesis of some dihydrobenzopyran and dihydrobenzofuran derivatives. Dihydrobenzopyran and dihydrobenzofuran derivatives are important in a number of biological and pharmacological applications.²⁰⁻²³ Therefore any method for the generation of such compounds will be synthetically important.

Irradiations were carried out (in a well-type photoreactor using Pyrex-filtered output of a 450 W Hanovia medium pressure mercury lamp) of a mixture of 2 mmol of acid, dissolved in 200 ml of benzene and 0.2 mmol of Methylene Blue, dissolved in 100 ml of water, under vigorous stirring. N₂ was flushed through the solution during irradiation and the exit gas was passed through saturated solutions of Ba(OH)₂. The extent of decarboxylation was estimated by weighing the precipitated BaCO₃ (Table 1). Although Methylene Blue photosensitized decarboxylation of N-arylglycine has been reported²⁴ none of the acids used in the present study underwent MB⁺ photosensitized decarboxylation in homogeneous solvent systems such as water, acetonitrile, and water/acetonitrile to any considerable extent (<1%). Efficient photodecarboxylation occurred only when an immiscible solvent system consisting of water and benzene was used. On excitation by

Pyrex-filtered light, MB^+ will be selectively excited, leading to the formation of its triplet state ($\phi\ ^3\text{MB}^{+*} = 0.52$).²⁵ Electron transfer can take place across the liquid/liquid interface between $^3\text{MB}^{+*}$ in water and the acid in benzene which will be followed by a proton exchange in order to maintain the charge balance. The $\text{RXCH}_2\text{CO}_2^\cdot$ radicals thus formed will undergo rapid decarboxylation to generate the corresponding alkyl radicals.¹¹

Table 1 shows the efficiencies of photodecarboxylation of the different acids studied. The efficiencies with which these acids partition into the water phase in the water/benzene experiments are also included in Table 1. These results suggest that the acids which partition more efficiently into water photodecarboxylate less efficiently. With respect to photoinduced electron transfer, both 2-allylphenoxyacetic acid and phenoxyacetic acid are expected to behave similarly. However, due to the preferential solubilization of phenoxyacetic acid in water photoinduced electron transfer for this acid will take place within the water layer itself, where rapid back electron transfer would prevent the decarboxylation process. These results confirm that the liquid/liquid interface plays an important role in the control of back electron transfer processes.

Table 1. Distribution of acid in water and the CO_2 yield by MB^+ sensitized photodecarboxylation.

Sl. No.	Acid used	Distribution of acid in water (%)	Decarboxylation (%)
1.	2-Allylphenoxyacetic acid	3.2	86
2.	1-Allyl-2-naphthoxyacetic acid	1.0	76
3.	2-(Prop-1-enyl)phenoxyacetic acid	4.7	50
4.	2-Allyl-4-chlorophenoxyacetic acid	1.8	43
5.	2-Naphthoxyacetic acid	1.2	36
6.	Phenoxyacetic acid	47.8	24
7.	p-Methoxyphenylacetic acid	18.7	<1

The synthetic utility of these systems was probed by studying the photodecarboxylation of 2-allyl- and 2-propenyl- aryloxyacetic acid derivatives. For example, MB^+ photosensitized reaction of 2-allylphenoxyacetic acid under the conditions described above led to 86% decarboxylation. The benzene layer was washed with water and analysed on a gas-chromatograph (Hewlett-Packard 5890-Series (II)) using authentic samples and an internal standard. The major products were identified as 3-methylchroman (4, 50%), 2-allylanisole (5, 20%) and 2-allylphenol (6, 18%) (Scheme 1). Major photoproducts from the substrates that we have investigated are illustrated in Table 2. In all these studies some amount of MB^+ remain unchanged after photolysis. Since only catalytic amounts of MB^+ were used (10% of the acid concentration), the efficient decarboxylation that is observed suggests that the semireduced dye is being oxidised by alkyl radicals.

Apart from bringing about efficient photodecarboxylation of the acids, use of the liquid/liquid interface also facilitates the separation of the photosensitizer from the reaction mixture. This process can therefore form a convenient route to the synthesis of many benzopyran and benzofuran derivatives.

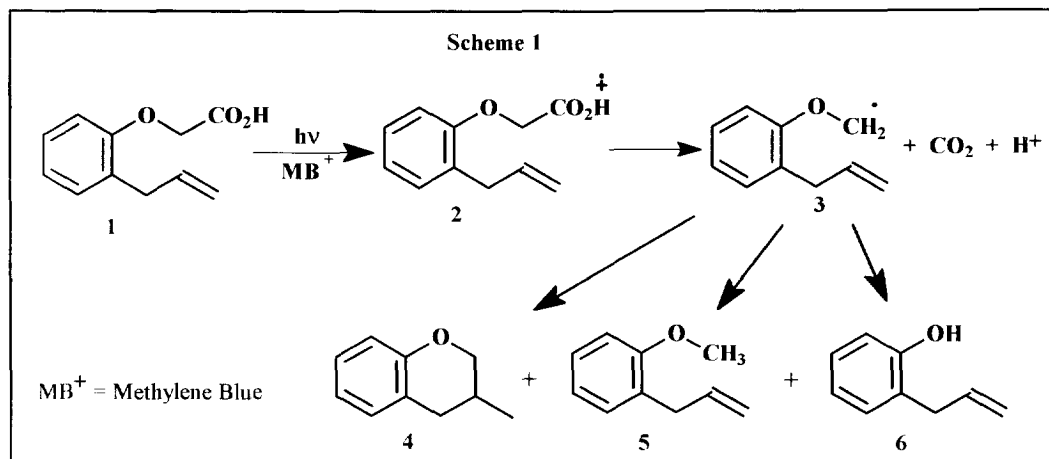


Table 2. Major Photoproducts from the Acids Used

Sl No	Acid used	Photoproduct	Yield(%)
1)			50
2)			70
3)			55
4)			74

Further efforts are in progress to elucidate the role of the liquid/liquid interface in enhancing photodecarboxylation and also to design suitable sensitizers in order to increase the range of acids that can be decarboxylated using this procedure.

We thank the Department of Science and Technology and the Council of Scientific and Industrial Research, Government of India for financial support of this work. This is document No. RRLT-PRU 47 from the Regional Research Laboratory, Trivandrum.

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(Received in UK 4 November 1994; revised 20 December 1994; accepted 21 December 1994)