

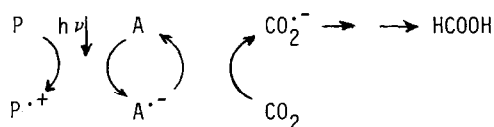
IS CARBON DIOXIDE PHOTOREDUCTIBLE BY MONOELECTRONIC TRANSFERS UNDER VISIBLE LIGHT?

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*ABSTRACT : A reaction presented as a photosensitized reduction of carbon dioxide is in fact a photooxidation of the aromatic sensitizers.*

A photochemical reduction of  $\text{CO}_2$  into formic acid was presented by Tazuke and Kitamura<sup>(1)</sup> using a coupled system of electron donor and acceptor sensitizers in aqueous acetonitrile. The following scheme was proposed for the reaction mechanisms :



where P = perylene (Pe) or pyrene (Py) and A = 9,10 dicyanoanthracene (DCNA) or p.dicyanobenzene (DCB).

Although thermodynamic objections were possible in certain cases (as for the electron transfer from  $\text{DCNA}^{\cdot-}$  to  $\text{CO}_2$ ) it seemed interesting to us to examine the physicochemical criteria governing this process involving monoelectronic steps in a homogeneous medium. It would be a very simple system when compared with the more elaborate ones mimicking photosynthesis by the way of highly organized media<sup>(2-5)</sup>.

In preliminary experiments the results of Tazuke were indeed reproduced. However, it was found that, if oxygen is carefully excluded from the reaction medium, no formic acid is formed (runs 1 and 2). Thus, the origin of the acid could not be  $\text{CO}_2$ .

It was confirmed that the reaction is photosensitized : when the light is cut off or without the aromatic sensitizers, the acid doesn't form (runs 3 and 4). Experiments made in the presence of triethylamine showed that the initiation of the reaction by an electron transfer quenching, leading to the radical anions of the sensitizers does not lead to formic acid (runs 12 and 13). The coupling of the sensitizers is not necessary (runs 5 to 7). Impurities present in acetonitrile are not the source of the acid : the reaction works in other solvents (run 9).

DCNA is known as a photoinitiator forming singlet oxygen ( $^1\text{O}_2$ ) or superoxide anion ( $\text{O}_2^{\cdot-}$ )<sup>(6-8)</sup>. Run 10 gives benzaldehyde, which may be the outcome of a reaction of stilbene with  $^1\text{O}_2$ <sup>(9)</sup>. However, when  $^1\text{O}_2$  is produced in the presence of Rose Bengal and stilbene, no formic

acid is found (run 15) nor is it formed when  $O_2^-$  is introduced to initiate the reaction (run 14) in the presence of Pe.

A higher consumption of the sensitizers is observed in those experiments where formic acid is produced. We can conclude that formic acid is one of the products of very complex photooxidation and fragmentation reactions of the aromatic sensitizers themselves. Similar behaviors have already been detected (<sup>10</sup>) and this type of degradation seems to be rather general (runs 8, 10 and 11).

TABLE : PHOTSENSITIZED FORMIC ACID FORMATION<sup>a</sup>

Run N°	Experimental Conditions	Sensitizers (conc.)x10 <sup>4</sup> M.L <sup>-1</sup>	[HCOOH] <sup>b</sup> x10 <sup>3</sup> M.L <sup>-1</sup>
1	CH <sub>3</sub> CN-H <sub>2</sub> O <sup>c</sup> , CO <sub>2</sub> , air	Pe-DCNA (2.0 - 2.5)	0.95
2	" , CO <sub>2</sub>	" (2.1 - 2.3)	0
3	" , CO <sub>2</sub>	-	0 <sup>d</sup>
4	" , air	-	0 <sup>d</sup>
5	" , "	Pe (2.3)	1.15
6	" , "	DCNA (2.72)	0.90
7	" , "	Py (2.27)	1.03
8	" , "	Pe-St <sup>e</sup> (2.0 - 57.3)	3.85
9	DMSO-H <sub>2</sub> O <sup>c</sup> , "	Pe (2.35)	5.50
10	" , "	St <sup>e</sup> (5.84)	3.10
11	" , "	PhCHO (119)	7.68
12	CH <sub>3</sub> CN-H <sub>2</sub> O <sup>c</sup> , "	Pe <sup>f</sup> (2.15)	0
13	" , "	DCNA <sup>f</sup> (2.72)	0
14	" , "	Pe <sup>g</sup> (2.10)	0
15	" , "	St <sup>h</sup> (57.3)	0

a. 20 mL of reaction mixture, gas bubbling during 16 h, high pressure mercury lamp (Hanau Q300), Pyrex vessel ( $\lambda > 300$  nm); b. Detected by VPC as a cyclohexyl methylester obtained by reaction with BF<sub>3</sub>-cyclohexylmethanol; c. 95-5, d. Same result with sensitizers but without light; e. St=stilbene; f. with 0,72 M.L<sup>-1</sup> triethylamine; g. Without light, 0.10 Mole.L<sup>-1</sup> of K<sub>2</sub>O<sub>2</sub> added; h. 3.42.10<sup>-2</sup> Mole.L<sup>-1</sup> of Rose Bengal added, visible light.

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