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THE DIRECT PHOTO-OXIDATIVE DECARBOXYLATION OF α-OXO-CARBOXYLIC ACIDS

R. Stephen Davidson and Dean Goodwin
(Department of Chemistry, The City University,
Northampton Square, London EC1V 0HB)

and

Geoffrey Turnock
(Department of Biochemistry, University of Leicester,
Leicester, LE1 7RH)

Summary

α-Oxo-carboxylic acids undergo photo-oxidative decarboxylation from both C-1 and C-2 positions, and reaction does not involve singlet oxygen: a mechanism involving an electron transfer reaction is postulated.

There has been considerable interest shown in ascertaining the mechanism of the dye-sensitised decarboxylation of α-oxo-carboxylic acids[1,2,3,4,5]. In many cases it was found that more than one mole of carbon dioxide was liberated from one mole of the α-oxo-carboxylic acid. We now report upon the photo-induced decarboxylation of α-oxo-carboxylic acids, which, in the presence of oxygen a similar situation arises.

Direct oxidation[6] of pyruvic acid, in the presence of oxygen, in a wide variety of solvents, leads to decarboxylation[7]. (Table 1). It has been previously noted that decarboxylation occurs when degassed solutions are employed[8], and that when the structure of the acid is suitable, e.g. α-oxo-decanoic acid, a Norrish Type II reaction leading to alkene production can occur[9]. We also find that other α-oxo-carboxylic acids undergo photo-induced decarboxylation in a variety of solvents, including those, e.g. methanol, which can lead to reduction of the α-oxo-carboxylic acid. (Table 2).

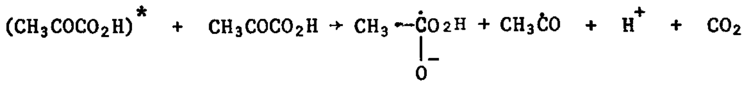
The longer irradiation period led to the production of more than one mole of carbon dioxide and it seemed reasonable to suppose that the first mole of carbon dioxide was derived from the carboxyl group and the second mole from the carbonyl group. To verify this hypothesis, reactions with 1-[^{14}C]-pyruvic acid and 2-[^{14}C]-pyruvic acid in aqueous acetonitrile were carried out. Irradiation in the absence of oxygen - which does not produce more than one mole of carbon dioxide, showed that this compound is cleaved from the carboxyl group. Thus with the 1-[^{14}C]-labelled acid the carbon dioxide was labelled with the correct level of activity. In the case of the 2-[^{14}C]-labelled acid, the carbon dioxide was not labelled. When the experiments were conducted in the presence of oxygen, labelled carbon dioxide was obtained from both acids. From the observation made by Jefford[1] that per-acids are intermediates in the dye sensitised reaction, we propose that the second mole of carbon dioxide is derived via per-acetic acid.

$$CH_3COCO_2H \xrightarrow[O_2]{h\nu} CH_3CO_3H \xrightarrow{h\nu} CO_2 + \text{other products}$$

That per-acetic acid will give carbon dioxide under the irradiation conditions utilised was verified[10]. The per-acid may also undergo sensitised decarboxylation; the pyruvic acid acting as a sensitiser. It is also known[11] that per-acetic acid gives carbon dioxide on direct irradiation in the absence of oxygen. The per-acids so produced may also undergo a Baeyer-Villiger reaction, but from the yields of carbon dioxide obtained this appears to be a minor route for reactions carried out under oxygen.

The inevitable question arises as to whether singlet oxygen is involved in the photo-oxidative decarboxylation process. It was found that the rate of decarboxylation of pyruvic acid in oxygenated deuteriochloroform compared with oxygenated chloroform is slightly faster (1.4 times), as is the rate of decarboxylation of α-oxo-glutaric acid in oxygenated acetonitrile/deuterium oxide (1:24) compared with oxygenated acetonitrile/water (1:24), (1.2 times), and if these are in fact solvent isotope effects, the difference in rate indicates that little, if any, of the decarboxylation occurs via singlet oxygen. (Table 3). There is a fallacy in this argument in that very small solvent isotope effects would be observed if the acid generated singlet oxygen and immediately reacted with it i.e. the reaction with singlet oxygen did not involve a diffusion process. Our previous measurements[5] of the rate constants for reaction of singlet oxygen with α-oxo-carboxylic acids suggest that because of their extremely low values a large solvent isotope effect should have been observed if singlet oxygen is involved.

We have shown that the decarboxylation of pyruvic acid in deoxygenated solvents does not involve Type 1 cleavage but occurs via a bimolecular electron transfer reaction.[12]

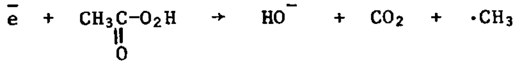


$$(CH_3COCO_2H)^* + CH_3COCO_2H \rightarrow CH_3\!-\!\underset{O^-}{\underset{|}{\dot{C}}}O_2H + CH_3\dot{C}O + H^+ + CO_2$$

In the presence of oxygen at a concentration approximately that of the acid, electron transfer to oxygen may also occur:-

$$(CH_3COCO_2H)^* + O_2 \rightarrow CH_3\dot{C}O + CO_2 + H^+ + O_2^{\overline{\cdot}}$$

The acetyl radicals generated in these processes can be scavenged by oxygen to give per-acetic acid. The pyruvate radical anion should be oxidised by oxygen to give the superoxide anion, and the later species may well participate in the photo-oxidative degradation.[13] It is also possible that per-acetic acid may suffer further degradation by reduction with an electron derived from either the excited pyruvic acid or the pyruvate radical anion.

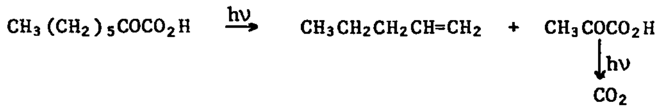


$$\bar{e} + CH_3\underset{O}{\underset{\|}{C}}\!-\!O_2H \rightarrow HO^- + CO_2 + \cdot CH_3$$

It is interesting to note that α-oxo-carboxylic acids which undergo the Type II reaction give good yields of carbon dioxide. In the case of α-oxo-octanoic acid the presence of oxygen had little effect on the yield of pent-1-ene and therefore the oxygen does not appear to be reacting with the intermediate 1,4-biradical[14].

In all probability the carbon dioxide generated in these reactions is coming from the pyruvic acid generated in the Type II reaction.

e.g.



$$\mathrm{CH_3(CH_2)_5COCO_2H} \xrightarrow{h\nu} \mathrm{CH_3CH_2CH_2CH{=}CH_2} + \begin{array}{c}\mathrm{CH_3COCO_2H}\\ \downarrow h\nu \\ \mathrm{CO_2}\end{array}$$

Acknowledgements

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8. Loss of carbon dioxide under degassed conditions.
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TABLE 1

YIELDS OF CARBON DIOXIDE FROM THE DIRECT IRRADIATION[(a)] OF PYRUVIC ACID (10^{-2}M) UNDER OXYGEN, IN VARIOUS SOLVENTS

Solvent	Yields (%) of carbon dioxide
Acetone	101
Acetonitrile	73.1
Benzene	46.5$^{(b)}$
t-Butanol	76.3
Chloroform	52.4
Dimethylformamide	85.3
Ethanol	23.6
Methanol	32.5$^{(b)}$
Water	62.1

(a) 3 hour irradiation
(b) 6 hour irradiation

TABLE 2

YIELDS OF CARBON DIOXIDE FROM THE DIRECT IRRADIATION OF α-OXO-CARBOXYLIC ACIDS (10^{-2}M) UNDER OXYGEN (A) IN METHANOL, AND (B) IN ACETONITRILE

α-OXO-CARBOXYLIC ACID (10^{-2}M)	YIELD (%) OF CARBON DIOXIDE			
	A. O_2/CH_3OH		B. O_2/CH_3CN	
	6h	20h	6h	21h
PYRUVIC ACID	32.5	57.9	141.3	160.0
α-OXO-BUTYRIC ACID	41.4	61.2	148.6	156.4
α-OXO-GLUTARIC ACID	52.4	72.7	123.0	140.5
3,3-DIMETHYL-2-OXO-BUTYRIC ACID	32.9	61.3	145.6	189.0
α-OXO-VALERIC ACID	45.3	78.4	112.9	154.5
α-OXO-PIMELIC ACID	46.5	94.8	98.9	133.8

TABLE 3

SOLVENT ISOTOPE EFFECT UPON THE YIELD OF CARBON DIOXIDE FROM THE DIRECT IRRADIATION(a) OF α-OXO-CARBOXYLIC ACIDS IN OXYGENATED SOLUTION

α-OXO-CARBOXYLIC ACID (10^{-2}M)	SOLVENT	Yield (%) of carbon dioxide	Isotope effect
Pyruvic Acid	Deuteriochloroform	76.75	1.4
Pyruvic Acid	Chloroform	54.81	
α-oxoglutaric acid	Acetonitrile /D_2O (1:24)	66.59	1.2
α-oxoglutaric acid	Acetonitrile/H_2O (1:24)	54.82	

(a) in each case the irradiation time was 3h.

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