Asian Journal of Chemistry Vol. 1, No. 4 (1989), 356-361

Dye-sensitised Photo-dimerisation of Mandelic Acid by Singlet Oxygen

SURESH C. AMETA,* (MRS.) P. B. PUNJABI AND (MISS) NEETA MANGAL

Department of Chemistry
Sukhadia University
Udaipur-313 001, India

and

P. K. JAIN AND (MRS.) SHASHI K. AGARWAL

Department of Chemistry
M.L.V. Government College
Bhilwara-311 001, India

Dye-sensitized photo-dimerisation of mandelic acid has been carried out. The product has been isolated and characterized. The participation of singlet oxygen as the active species has also been confirmed. A tentative mechanism for the photo-dimerisation of mandelic acid by singlet oxygen has been proposed.

INTRODUCTION

A great deal of literature survey reveals that α-hydroxy acids play an important role in biological processes. These acids undergo oxidation with different oxidising agents, e.g. *p*-methyl-mandelic acid is converted to terephthalaldehyde tetraacetate by chromyl acetate in acetic anhydride.[1] α-Hydroxy acids are oxidized by permanganate to give two sets of products. In basic solution, the keto acids are the principal products although these can be subjected to further oxidation.[2-4] Mandelic acid is oxidized to phenyl-glyoxylic acid by alkaline permanganate in good yield.[5]

Oxidative decarboxylation of mandelic acid occurs to a great extent in acid permanganate producing benzaldehyde and carbon dioxide. Lead tetraacetate oxidation of α-hydroxy acids has also been studied.[6-10] A variety of the reaction paths can be written, obvious one involves coordination of the hydroxyl group to the lead atom, followed by loss of CO_2. Pink and Steward[11,12] have carried out oxidative decarboxylation of α-hydroxy acids by bromine in presence of Ag^+ ions in neutral, acidic and alkaline medium. Oxidation of hydroxy acids by bromine, catalyzed by Mn(III), has also been investigated.[13]

Although the oxidation of hydroxy acids is well studied but it is evident that dye sensitized photo-chemical reactions of α-hydroxy acids received negligible attention and therefore, the present work was undertaken.

EXPERIMENTAL

The purity of the mandelic acid was checked by their melting points and thin layer chromatograhy. Different sensitizers like methylene blue (CI 52015 Aldrich), eosin-Y (CI 45380, BDH), rose bengal (CI 45440, Aldrich), thionine (CI 52000 Riedel) and riboflavin (LC) were used for generating singlet oxygen. The solvents were distilled before use. Doubly distilled water was used to prepare all solutions.

A 200W tungsten lamp (Sylvania) was used for irradiation purpose. An oxygen gas cylinder was used for passing oxygen gas in the reaction mixture.

Infra-red spectra were scanned on Perkin-Elmer Grating 377 Spectrophotometer. Ultra-violet spectra were recorded on Beckmann 26, spectrophotometer, NMR was recorded with 90 MHz FT-FX 600 JEOL and mass spectra were recorded on a JEOL 200 data system.

2.0 gm of mandelic acid was dissolved in 30 ml of doubly distilled water. 1 ml solution of methylene blue (4.3×10^{-3}M) was added to it, so that the concentration of the methylene blue in the reaction mixture was 1.43×10^{-4}M. The solution was then irradiated with a tungsten lamp kept at a distance of 20 cms from the lower surface of the reaction flask. Oxygen gas was continuously bubbled through the solution. The progress of the reaction was followed by regular TLC analysis. The solvent system used was benzene : acetic acid : water = 2 : 2 : 1 (v/v). After 20 minutes of irradiation, it was found that TLC of the solution gave two spots, one corresponding to mandelic acid and another corresponding to the product. The irradiation was stopped when TLC plate showed single spot corresponding to the product only. The solution was decolourized with activated animal charcoal and the decolourized solution was left for evaporation. A solid was obtained which was crystallized from alcohol (m.pt. 250–252°C).

Elemental analysis—Found: C = 71.1%, H = 5.18%; Calcd: C = 71.8%, H = 5.04%.

UV λ_{max} (Ethanol), 206, 212 and 261 nm.

IR ν_{KBr}. 3042(s), 2994(s), 1698(s), 1523(m), 1460(m), 1393(s), 1323(s), 1277(m), 1212(m), 1177(w), 1154(s), 1067(m), 972(s), 796(m), 755(s), 670(s), 580(m), 560(s), 428(m) cm^{-1}.

NMR $CDCl_3(\tau)$: 8.76 (triplet, 6H), 5.84 (quartet, 4H), 4.64 (singlet, 2H), 2.73 (singlet, 10H).

MASS (m/e), 70 eV: 326 (3.47%), 311 (2.46%), 299 (6.58%), 297 (1.90%), 281 (100.0%), 253 (2.08%), 252 (9.26%), 239 (1.26%), 163 (1.40%), 148 (2.22%), 134 (0.97%), 118 (0.68%), 27 (20.78%), 74 (2.36%), 73 (4.15%), 45 (7.23%), 29 (19.47%) and 15 (3.56%).

The effect of solvents on the photo-dimerisation of product was determined. The results are reported in Table 1.

TABLE 1

EFFECT OF SOLVENTS

[Methylene blue] = 1.43×10^{-4}M Time of irradiation = 40.0 min.

Solvent	Life time[14-15] (μS)	Yield of the product (%)
Water	2	27.0
Acetone	42	48.0
Dioxane	32	41.0
Pyridine	17	33.0
Ethanol	19	38.0
Methanol	11	31.0

Keeping all other factors similar, photo-dimerisation of mandelic acid was carried out in presence of various sensitizers. Effect of the triplet energy of various sensitizers on the yield of photoproduct are reported in Table 2.

TABLE 2

EFFECT OF TRIPLET ENERGIES

[Dye] = 1.43×10^{-4}M Time of irradiation = 40.0 min.

Sensitizer	Triplet of energy[16-18] (Kcal mol^{-1})	Yield of the product (%)
Methylene	34.0	27.0
Eosin-Y	43.2–46.0	22.0
Rose bengal	37.5–42.2	24.0
Thionine	48.0	18.0
Riboflavin	57.8	13.0

The participation of singlet oxygen in the photo-dimerisation of mandelic acid was confirmed by carrying out the reaction in the presence of different singlet oxygen scavengers. The yield of photo-product in the presence of scavengers are reported in Table 3.

TABLE 3

EFFECT OF SINGLET OXYGEN SCAVENGERS

[Methylene blue] = $1.43 \times 10\text{-}4$M Time of irradiation = 40.0 min.

[Scavenger] = 1.0×10^{-d}M

Scavengers[19-23]	Yield of the product (%)
—	27.0
Nickel chloride	0.6
Cobalt chloride	0.4
β-carotene	Nil
DABCO	0.2
α-Tocopherol	Nil

RESULTS AND DISCUSSION

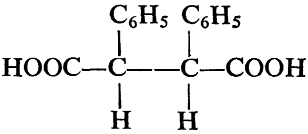
The absorption band at 212 nm is characteristic of the presence of a carboxylic group in the compound whereas the bands at 206 and 261 nm are due to the aromatic ring system.

The band at 3042 cm^{-1} is due to C-H stretching vibration in phenyl ring. The band at 2994 cm^{-1} indicates aliphatic C-H stretching. The bands at 1460 and 1393 cm^{-1} are due to simple aliphatic C-H bending vibrations. The absorption band at 1212 cm^{-1} may be assigned to C-COOH stretching whereas the band at 1177 cm^{-1} shows C-COOH bending. The band at 1698 cm^{-1} indicates the presence of carboxylic group in the compound, whereas the band at 670 cm^{-1} shows C-C-C skeletal deformation.

The triplet at 8.76 τ and quartet at 5.84 τ indicates the presence of methyl and methylene protons in the molecule. The singlet 4.64 τ shows the presence of methane protons. Whereas the broad singlet at 2.73 τ is characteristic of a monosubstituted phenyl ring.

The molecular ion peak of the diethyl ester of the product was obtained at m/e = 325, but relatively of low intensity. The fragments at m/e 311, 297 are due to the loss of $-CH_3$ and $-CH_2CH_3$ respectively whereas a fragment of m/e = 27 give rise to the peak at m/e = 299. The base peak is observed at m/e = 281 and is probably due to $[M\text{-}OCH_2CH_3]^+$ fragment. The fragment at m/e = 253 and 252 may be assigned to $[M\text{-}73]^+$ and $[M\text{-}74]^+$, respectively. A fragment of m/e = 77 is characteristic of the presence of a phenyl ring in the molecule. The fragments at m/e = 73, 45, 29 and 15 are due to the fragments $[CH_2COOCH_2CH_3]^+$, $[COOCH_2CH_3]^+$, $[OCH_2CH_3]^+$, $[CH_2CH_3]^+$ and $[CH_3]^+$ respectively.

Thus on the basis of analytical and spectral data the products have been assigned the following structure.



$$\mathrm{HOOC{-}\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle C_6H_5}{\overset{|}{C}}}}{-}{-}\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle C_6H_5}{\overset{|}{C}}}}{-}COOH}$$

On the basis of these observations, a tentative mechanism has been proposed.

Hydroxyl radical abstraction by singlet oxygen will result into the generation of species $HO_2^{\cdot}$ which is commonly known. It may have two alternative pathways:

(i) Singlet oxygen may be directly converted to ground state oxygen i.e.

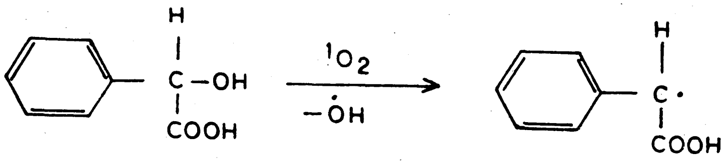
$$2\,\dot{O}H + 2\,{}^{1}O_2 \rightarrow 2\,HO_2^{\cdot} + {}^{3}O_2$$

(ii) It may be converted to ground state oxygen via an intermediate unstable radical $HO_3^{\bullet}$

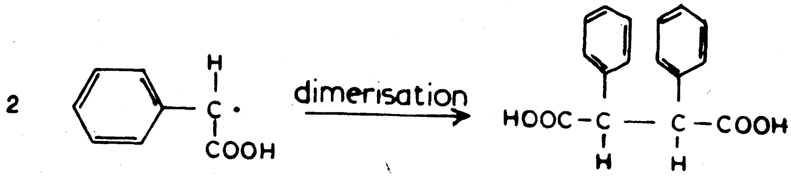
$$\dot{O}H + {}^1O_2 \rightarrow HO_3^{\bullet}$$

$$2\,HO_3^{\bullet} \rightarrow 2\,HO_2^{\bullet} + {}^3O_2$$

Thus on the basis of available experimental data a mechanism for the formation of dl-diphenyl succinic acid (II) from mandelic acid (I) may be explained as:



(I)



(II)

REFERENCES

1. L. Dyksterhuis and D. E. A. Rivett, *J. S. African Chem. Inst.*, **15**, 20 (1962).
2. G. V. Bakore, R. Shanker and U. Goyal, *Indian J. Chem.*, **1**, 331 (1963).
3. G. V. Bakore and R. Dayal, *Curr. Sci. (India)*, **28**, 279 (1959).
4. Y. K. Gupta and R. Dutta, *Proc. Natl. Acad.*, **28A**, 236 (1959).
5. C. D. Hurd and R. W. McNamee, *Org. Synth. Coll.*, **1**, 244 (1941).
6. R. Criegee, *Ann.*, **481**, 275 (1930).
7. R. Criegee, E. Buchner and W. Walther, *Ber.*, **73**, 571 (1949).
8. R. Criegee and H. Zogel, *Chem. Ber.*, **84**, 215 (1951).
9. R. Criegee, *Angew. Chem.*, **70**, 173 (1958).
10. E. Baer, R. Grosheintz and H. O. L. Discher, *J. Amer. Chem. Soc.*, **61**, 2607 (1939).
11. J. M. Pink, *Can. J. Chem.*, **48**, 1169 (1970).
12. J. M. Pink and R. Stewart, *Can. J. Chem.*, **49**, 654 (1971).
13. N. N. Kotia, Ph.D. Thesis, Univ. of Raj., Jaipur, India (1964).
14. D. R. Brewer, Ph.D. Thesis, Georgetown University, USA (1974).
15. R. H. Young, D. Brewer and R. A. Keller, *J. Amer. Chem. Soc.*, **95**, 375 (1973).

16. D. R. Kearns, *Photochem. Photobiol.*, **10**, 215 (1969).
17. K. Eskins, *Photochem. Photobiol.*, **20**, 609 (1979).
18. W. Adams, *Chemiker-Zritung*, **99**, 144 (1975).
19. D. J. Carlsson, G. D. Mendenhall, T., Suprunchuk and D. M. Wiles, *J. Amer. Chem. Soc.*, **94**, 8960 (1972).
20. D. J. Carlson, T. Suprunchuk and D. M. Wiles, *Can. J. Chem.*, **52**, 3728 (1974).
21. C. S. Poote and R. W. Denny, *J. Amer. Chem. Soc.*, **90**, 6533 (1968).
22. K. Gollnick and J. H. E. Lindner, *Tetrahedron Lett.*, 1903 (1973).
23. W. F. Smith (Jr.), *J. Amer. Chem. Soc.*, **94**, 186 (1972).

[*Received*: 21 December 1988; *Accepted*: 22 May 1989]. AJC—57