

**DYE-SENSITIZED PHOTOOXYGENATION OF
MALEIC AND FUMARIC ACIDS
BY SINGLET OXYGEN**

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الخلاصة :

دُرِسَ التفاعل الضوئي الحساس للصبغة لكل من حمض المالك والفيوماريك مع الأوكسجين . وفُصِّلَت النواتج وعُرِّفَت بأنها حمض (الترتاريك) بالصورة (يميني - يساري) الدوران في حالة حمض المالك ، والصورة (ميزو) في حالة حمض الفيوماريك . وتَمَّ التأكد من المشاركة النشطة للأوكسجين المفرد الترابط لكامل الأوكسدة . وفي الوقت نفسه تَمَّ اقتراح خط سير مؤقت للتفاعل الضوئي لكل من حمض المالك والفيوماريك مع الاكسجين أحادي الترابط .

ABSTRACT

Dye-sensitized photooxygenation of maleic and fumaric acids gives products isolated and characterized as dl- and *meso*-tartaric acids in the case of maleic and fumaric acids, respectively. The participation of singlet oxygen as the active oxidizing species has also been confirmed. Tentative mechanisms for the photooxygenation of maleic and fumaric acids by singlet oxygen have been proposed.

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INTRODUCTION

Maleic and fumaric acids are important biological substrates as these are involved in the tricarboxylic acid and urea cycles in living beings. It has been reported that maleic acid can be oxidized to *meso*-tartaric acid by treating it with either potassium permanganate or sodium chlorate and osmium tetroxide, whereas fumaric acid yields *dl*-tartaric acid [1–3]. On the other hand, maleic and fumaric acids yield *recemic* and *meso*-tartaric acid, respectively, on *per-acid* oxidation [3]. The oxidation of maleic and fumaric acids has been investigated by Jakey *et al.* [4–7] in detail from the kinetic point of view. An extensive literature survey reveals that dye-sensitized photooxygenation of unsaturated dicarboxylic acid has received little [8] attention and, therefore, the present work was undertaken.

EXPERIMENTAL

The purity of the maleic and fumaric acids was ascertained by their melting points and thin layer chromatography. The solvents were distilled before use. 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. Doubly distilled water was used to prepare all solutions.

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

Ultraviolet spectra were recorded on a Beckmann 26 Spectrophotometer. Infrared spectra were scanned on a Perkin–Elmer Grating-377 Spectrophotometer. NMR spectra were recorded with 90 MHz FT-FX 600 JEOL and mass spectra were recorded on a JEOL 200 data system.

0.2 gm of maleic and fumaric acids were dissolved in doubly distilled water (30 ml) in two reaction flasks separately so that the concentration of the substrate was 5.76×10^{-2} M in reaction mixture. 1 ml solution of methylene blue (4.3×10^{-3} M) was added to these solutions, so that the concentration of the methylene blue in the reaction mixtures was 1.43×10^{-4} M. The solutions were then irradiated

with a tungsten lamp kept at a distance of 20 cm from the lower surface of the reaction flasks. The overall spectral range of the tungsten lamp was used. A water filter was used to cut off IR radiation. Oxygen gas was continuously bubbled through the solutions. The solvent system used for maleic acid was ethyl acetate: acetic acid: water at 3:1:1 (v/v) and that for fumaric acid was *n*-butanol: formic acid: water at 10:2:15 (v/v). No solid products were separated from the solutions during the reaction. However, after half an hour of irradiation, it was found that TLC of both solutions, *i.e.* maleic and fumaric acid respectively, gave two spots, one corresponding to the original substance and another corresponding to the product. The reaction was allowed to proceed to completion. The irradiation was stopped, when TLC analyses showed a single spot corresponding to product only. The solution was then decolorized with activated animal charcoal and the decolorized solutions were left for evaporation. The solid products so obtained, were crystallized from water (m.p. of the products of maleic and fumaric acids are 206° and 140°C respectively).

Elemental analysis: *Found*: C = 31.96%; H = 4.01%; and *calculated*: C = 32.10%; H = 3.98%. UV: λ_{\max} (Ethanol): 209 nm (ϵ 30). IR: ν_{KBr} 3590–3520(s), 3180(s), 2988(s), 1770(s), 1770(s), 1580(w), 1520(m), 1462(m), 1390(s), 1325(s), 1275(s), 1215(m), 1180(w), 1155(s), 1140(s), 1070(m), 972(s), 830(m), 796(m), 492(w), 670(s), 580(m), 560(s), and 424(m) cm^{-1} .

As the products were non-volatile, their diethyl esters were prepared for NMR and mass spectra. The esters were prepared by the usual method (ion exchange resin catalyst method) [9].

NMR: (diethyl ester of the product); 8.70 (triplet; 6H), 5.78 (quartet; 4H), 5.04 (broad singlet; 2H), and 4.42 (broad singlet; 2H).

Mass spectrum: *m/e*, 70 eV (diethyl ester of the product); 206 (9.26%), 191 (2.16%), 189 (2.20%), 188 (100.0%), 177 (1.40%), 170 (1.25%), 161 (20.84%), 133 (7.06%), 132 (6.72%), 103 (40.68%), 87 (0.98%), 74 (4.68%), 73 (6.72%), 45 (9.26%), 29 (38.12%), and 15 (6.10%).

The effect of the nature of the solvent on photo-oxidation of maleic and fumaric acids was investigated

in various solvents such as acetone, dioxane, pyridine, ethanol, and methanol. However, the amount of the substrate could not be kept constant as the solubility is less in other solvents and, therefore, the relative yield of the product was determined in these cases. The results are reported in Table 1.

Table 1. Effect of Solvent.

[Methylene blue] = 1.43×10^{-4} M			
Solvent	Lifetime of singlet oxygen [10, 11] (μ s)	Yield of the product (%)	
		dl-Tartaric acid	meso-Tartaric acid
Water	2.0	20.0	17.0
Acetone	42.0	55.0	45.0
Dioxane	32.0	40.0	39.0
Pyridine	17.0	60.0	50.0
Ethanol	19.0	37.0	33.0
Methanol	11.0	30.0	26.0

Since there is a negative correlation between the dielectric constant of solvents and life time of $^1\text{O}_2$, lifetime of singlet oxygen is more in nonpolar solvents. The more yield of product in nonpolar solvents may be attributed to the greater lifetime of $^1\text{O}_2$ in these solvents.

Keeping all other factors identical, dye-sensitized photooxidation of maleic and fumaric acids has also been carried out in the presence of various sensitizers. The effect of the triplet energies of the sensitizers has been observed on the yield of the products and the results are reported in Table 2.

Dye-sensitized photooxidation of maleic and fumaric acids have also been carried out in presence of various singlet oxygen scavengers and the results are reported in Table 3.

RESULTS AND DISCUSSION

The electronic absorption band at 209 nm (with low intensity) is characteristic of the presence of a carboxylic group in the compound.

A broad band at $3590\text{--}3520\text{ cm}^{-1}$ is due to O–H stretching vibrations whereas the band at 1325 cm^{-1} is due to O–H bending vibrations. The band at 2998, 1462, and 1390 cm^{-1} are due to simple aliphatic C–H stretching and bending vibrations. The absorption band at 1215 cm^{-1} may be attributed to C–COOH stretching whereas the band at 1180 cm^{-1} indicates C–COOH bending. The presence of a band at 1700 cm^{-1} indicates the presence of a saturated aliphatic carboxylic group in the component, C–C–C skeletal deformation is clearly indicated by the band at 670 cm^{-1} .

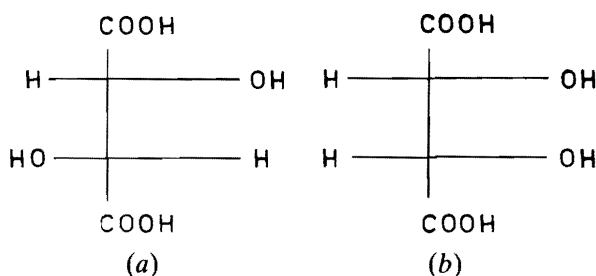
The triplet at 8.70τ and a quartet at 5.78τ are due to methyl and methylene protons, respectively as the NMR of diethyl ester of the product was recorded. The broad singlets at 5.04 and 4.42τ may be assigned to the methine and hydroxy protons, respectively.

The molecular ion peak of the diethyl ester of the product was obtained at $m/e = 206$. It loses methyl and ethyl groups to give fragments at $m/e = 191$ and 177 , respectively, $m/e = 189$ and 188 may be due to the removal of hydroxyl radical and water molecule which indicates the presence of a hydroxyl group in the molecule. The fragment with $m/e = 170$ may be attributed to the removal of the presence of two hydroxy groups on adjacent carbon atoms. The fragments at $m/e = 87, 73, 45, 29,$ and 15 may be due to $[\text{CH}_2\text{COOCH}_2\text{CH}_3]^+$, $[\text{COOCH}_2\text{CH}_3]^+$, $[\text{OCH}_2\text{CH}_3]^+$, $[\text{CH}_2\text{CH}_3]^+$, and $[\text{CH}_3]^+$, respectively. Thus, on the bases of comparison of the analytical and spectral data of the products with that of dl- and meso- tartaric acids the following structures (a) and (b) have been assigned to the products from maleic

Table 2. Effect of Triplet Energies of Sensitizers.

[Dye] = 1.43×10^{-4} M		Solvent: Water	
Sensitizer	Triplet energy [12–14] (kcal mol^{-1})	Yield of the product (%)	
		dl-Tartaric acid	meso-Tartaric acid
Methylene blue	34.0	20.0	17.0
Eosin-Y	43.2–46.0	15.0	11.0
Rose Bengal	37.5–42.2	17.0	14.0
Thionine	48.0	9.0	7.0
Riboflavin	57.8	5.0	3.0

and fumaric acids, respectively. The quantum yields for the photooxygenation of maleic and fumaric acid by singlet oxygen were 0.24 and 0.20, respectively.

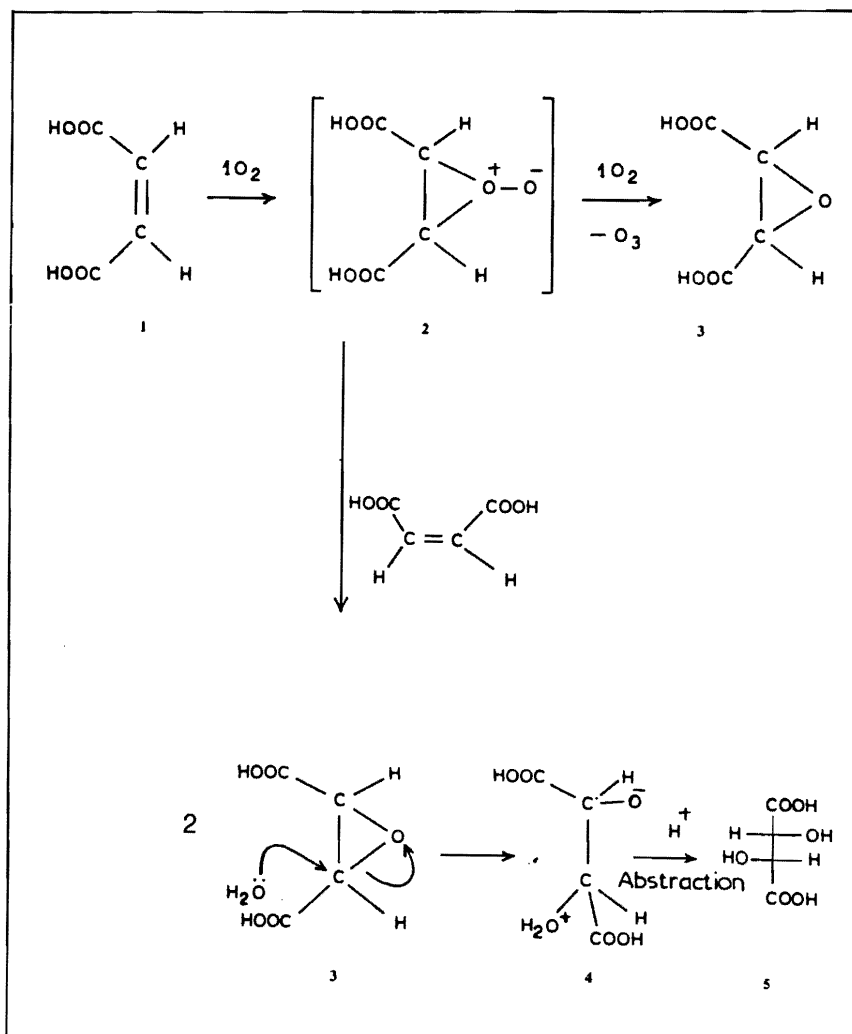


One difference was found in the case of the product of maleic and fumaric acids is that the m.p. of *p*-nitrobenzyl ester derivative of product of maleic acid was found to be 146° while that of fumaric acid was 93°.

The following tentative mechanisms have been proposed for the dye-sensitized photooxidation of maleic and fumaric acids by singlet oxygen.

The first step involves the formation of a zwitterionic perepoxide intermediate **2** from maleic acid **1** which may, then leads to the formation of epoxide **3** following one of the two paths: (a) **2** may react further with singlet oxygen to give epoxide and ozone or (b) **2** may react with another molecule of maleic acid to give two molecules of epoxide. As it will not be easier for the water molecule to attack from the side of epoxide ring due to steric hindrance, the water molecule may attack on epoxide from the other side giving **4**. Then a proton migration in **4** will give rise to the racemic form of tartaric acid **5**.

The formation of epoxide *via* perepoxide has also been reported by earlier workers [20-23] (Scheme 1).

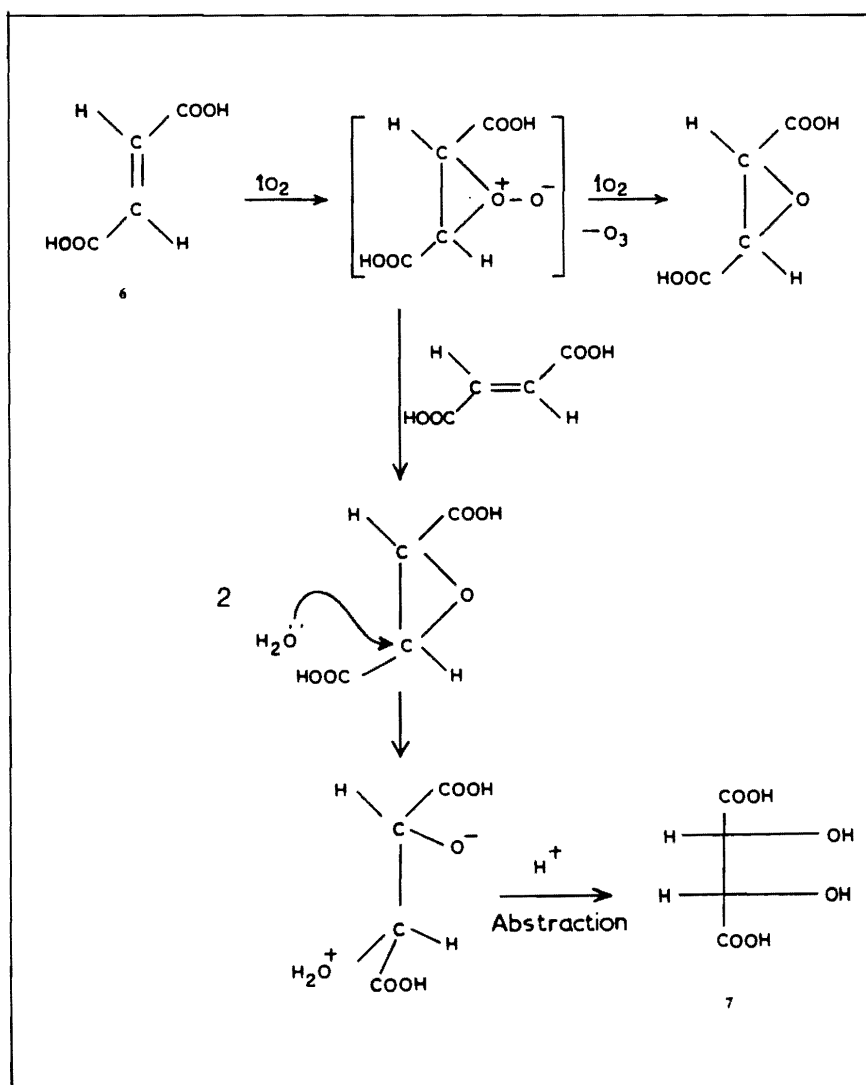


Scheme 1.

Table 3. Effect of Singlet Oxygen Scavengers.

Scavenger [15-19]	Yield of the product (%)	
	dl-Tartaric acid	meso-Tartaric acid
—	20.0	17.0
Nickel chloride	0.9	0.6
Cobalt chloride	0.7	0.4
β-Carotene	Nil	Nil
DABCO	0.3	0.1
α-Tocopherol	0.2	Nil

Similarly, formation of *meso*-tartaric acid **7** has been proposed from fumaric acid as in Scheme 2.



Scheme 2.

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