



STUDY OF SEMICONDUCTOR PHOTOCATALYSED OXIDATION OF TARTRONIC ACID USED AS COSMETIC AND HYPOGLYCEMIC ACTION.

Pushkar Raj Meena*

H.O.D. Chemistry, S.P.S.B. Govt. College-Shahpura, Bhilwara (Raj.)-India.

Corresponding Author: Pushkar Raj Meena

H.O.D. Chemistry, S.P.S.B. Govt. College-Shahpura, Bhilwara (Raj.)-India.

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ABSTRACT

Heterogeneous catalysts have become a crucial part of many industrial activities, such as organic synthesis, oil refining, and pollution control.^[1-5] TiO₂ has proven to be one of the promising *n*-type semiconductors due to its wide band gap (3.2 eV) under ultraviolet light.^[6-8] TiO₂ also, due to its non-toxicity, long term photo stability, and high effectiveness, has been widely utilized in mineralizing toxic and non-biodegradable environmental contaminants as well as the novel organic synthesis.^[9,10] Tartronic acid is much more efficient at removing dissolved oxygen than the conventional treatments, without increasing the corrosivity of the system.^[11] Tartronic acid can be found in potato, a potential biomarker for the consumption of these food products.^[12] As a food additive^[16-18], TiO₂ (titanium dioxide) is approved for use in various countries like EU, USA, Australia and New Zealand; it is listed by INS number 270 or E number E-270. In the present part of study, it is planned to investigate photo-oxidation of tartronic acid (hydroxyl-propandioic acid) by semiconductor sensitized in visible light and the photoproduct was mesoxalic acid. From the fact that the use of insulin in combination with mesoxalic acid produced more marked effect, it is presumed this drug enhances the activity of insulin. These hydroxyacids can be able to reverse some of the damage caused by photo aging, but at the same time they make the skin more susceptible to photo aging. Several aspects concerning the mechanism of action of alpha hydroxyacids are still unknown. The toxic nature of photoproduct and safety parameter is still unknown of mesoxalic acid. It is therefore planned to investigate photo-oxidation of tartronic acid by semiconductors. Hence, this part of reported work may help to arouse the interdisciplinary interest about the side effects of photoproducts, where these are being used.

KEYWORDS: Semiconductor, Titanium dioxide, Photo-oxidation, Tartronic acid, mesoxalic acid.

INTRODUCTION

The catalysis industry is a billion-dollar industry that accounts for the manufacture of 60% of all the chemicals that are being used for most chemical processes. Some of the products derived from catalytic processes include polymers, plastics, pharmaceuticals, and detergents. After decades of research, systematic information on the catalytic properties of many catalysts has been established and accumulated. Heterogeneous catalysts have become a crucial part of many industrial activities, such as organic synthesis, oil refining, and pollution control.^[1-5] TiO₂ has proven to be one of the promising *n*-type semiconductors due to its wide band gap (3.2 eV) under ultraviolet light.^[6-8] Titanium dioxide has been intensively investigated as a semiconductor photocatalyst since Fujishima^[1] and Honda discovered the photocatalytic splitting of water on TiO₂ electrodes in 1972¹. Recently, the application of TiO₂ photocatalysts has mainly been focused on the decomposing toxic and hazardous organic pollutants in contaminated air and water, which is of great importance for the environmental protection.^[9] TiO₂ also, due to its non-toxicity, long term photo stability, and high

effectiveness, has been widely utilized in mineralizing toxic and non-biodegradable environmental contaminants as well as the novel organic synthesis.^[10]

Tartronic acid can be found in potato, which makes the hydroxyl propandioic acid a potential biomarker for consumption of this food product. The photoproduct of this reported study is mesoxalic acid (ketomalonic acid). Mesoxalic acid was prepared by oxidative dehydrogenation of tartronic acid with air in aqueous solution on carbon supported platinum-bismuth catalyst. The results obtained for this reaction and for analogous catalytic oxidation of glyceric acid to hydroxypyruvic acid, and lactic acid to pyruvic acid, enabled a general mechanism to be proposed for selective oxidation of α -hydroxyacids to ketoacids.^[11,12]

As a highly functionalized molecule, mesoxalic acid has potential use as a complexion agent and as a precursor in organic synthesis, but its present high cost limits application. Tartronic acid is much more efficient at removing dissolved oxygen than the conventional treatments, which include erythorbic acid and

hydroquinone; without increasing the corrosivity of the system. The calculations show the greatly improved efficiency of tartronic acid over erythorbic acid when dosed in equivalent amounts. Efficient operation of boilers and other steam-run equipment requires chemical treatment of feed water to control corrosion. Corrosion in such systems generally arises as a result of oxygen attack of steel in water supply equipment, pre-boiler systems, boilers, and condensate return lines.

Since the discovery of insulin, various new compounds having hypoglycemic action other than the pancreatic hormone has been reported. In 1922 Collip,^[13] reported *Glucokinin* and in 1927 Allen^[14] *Myrtillin*, both of which are extracted from plants or yeast, and have hypoglycemic action. From the fact that the use of insulin in combination with meso-oxalic acid produced more marked effect, it is presumed this drug enhances the activity of insulin. However, the fact this drug used together with insulin in the tests with the depancreatized dog produced little effect leads us to believe this drug does not aid the activity of insulin itself. Furthermore, it is assumed the presence of pancreas is essential.

Alpha hydroxyacids is due to their excellent capability to penetrate skin, it is being used in a variety of skin care products and peeling agents^[15] including moisturizers, cleansers, eye cream, sunscreen and foundations etc., simultaneously the titanium oxide, zinc oxides etc. are used as the base for these materials. These hydroxyacids can be able to reverse some of the damage caused by photo aging, but at the same time they make the skin more susceptible to photo aging. As a food additive^[16-18], TiO₂ (titanium dioxide) is approved for use in various countries like EU, USA, Australia and New Zealand; it is listed by INS number 270 or E number E-270.

Several aspects concerning the mechanism of action of alpha hydroxyacids are still unknown. The toxic nature of photoproduct and safety parameter is still unknown of mesoxalic acid. It is therefore planned to investigate photo-oxidation of tartronic acid by semiconductors. Hence, this part of reported work may help to arouse the interdisciplinary interest about the side effects of photoproducts, where these are being used as cosmetic, wine and food industries.

EXPERIMENTAL

The organic compounds i.e. Tartronic acid (Fluka), Silica gel-G, Resublimed Iodine (sm), ninhydrine, titanium oxide, tungsten oxide, iron oxide, zinc oxide, cadmium sulphide, stannic oxide, copper oxide, some other semiconductors and other analytical chemicals. UV chamber with UV tube 30 W (Philips), spectrophotometer (Systronic), spectrometer (Systronic), tungsten filament lamps 2 x 200 W (Philips) for visible light, 450 W Hg-arc lamp, water shell to filter out IR radiations and to avoid any thermal reaction, necessary glass wares, thin layer chromatography and paper chromatography kits for to determine the progress of

reaction, conductivity meter (Systronic) to determine the optimum yields of photoproducts, pH meter (Eutech pH 510), spectrophotometer (Systronic) and I.R. spectrometer (Perkin-Elmer Grating-377) was used.

The tartronic acid solutions are prepared in water and acetonitrile solvent as the required concentrations as mentioned in the Table 3.1. The required concentration of semiconductor or mixed semiconductors has been added to the reaction mixture for heterogeneous photocatalytic reactions. Variations were made to obtain the optimum yield of photoproducts.

The progress of reaction was monitored by running thin layer chromatography at different time intervals, where silica gel-G was used as an adsorbent and ninhydrine or resublimed iodine (sm) chamber was used as eluent for spot test detection. For colorless spot detection a slide spot detector; UV chamber (Chino's) was used. At the end of reaction or the process the photoproducts has been isolated as its salts and by preparing appropriate derivatives were identified by spectrophotometer, IR-spectrometer, NMR-spectrometer. The optimum yield of obtained 2, 4-DNP [with 0.50 g and 84 mL HCl in 500 mL aqueous solution] was measured by using spectrophotometers and conductivity meter. Various probable variations like the role of different semiconductors, mixed semiconductors, visible and UV-light etc., was studied. Some sets of experiments are also made in controlled conditions such as in absence of UV or visible light, semiconductors and stirring etc.

RESULTS AND DISCUSSION

The effect of substrate

The effect of amount of substrate on the oxidation of tartronic acid was studied at different concentrations varying from 1.25×10^{-2} M to 4.16×10^{-2} M at fixed amount TiO₂ (1.66×10^{-2} M). The total volume of reaction mixture is 50 mL and the results are reported in the following Table 1 and shown in Figure 1.

1. Solvent: Water
2. TiO₂: 1.66×10^{-2} M (1.33 g/L)
3. Irradiation time: 120 min
4. Visible light: 2 x 200 W Tungsten lamps.

Table 1.

S. No.	Conc. Of Substrate (Tartronic acid)	Percent yield of product (Mesoxalic acid)
1	1.25×10^{-2} M	17.5%
2	2.22×10^{-2} M	18.9%
3	2.77×10^{-2} M	21.3%
4	3.33×10^{-2} M	24.7%
5	3.88×10^{-2} M	28.8%
6	4.44×10^{-2} M	33.2%
7	4.99×10^{-2} M	36.4%
8	5.55×10^{-2} M	40.6%

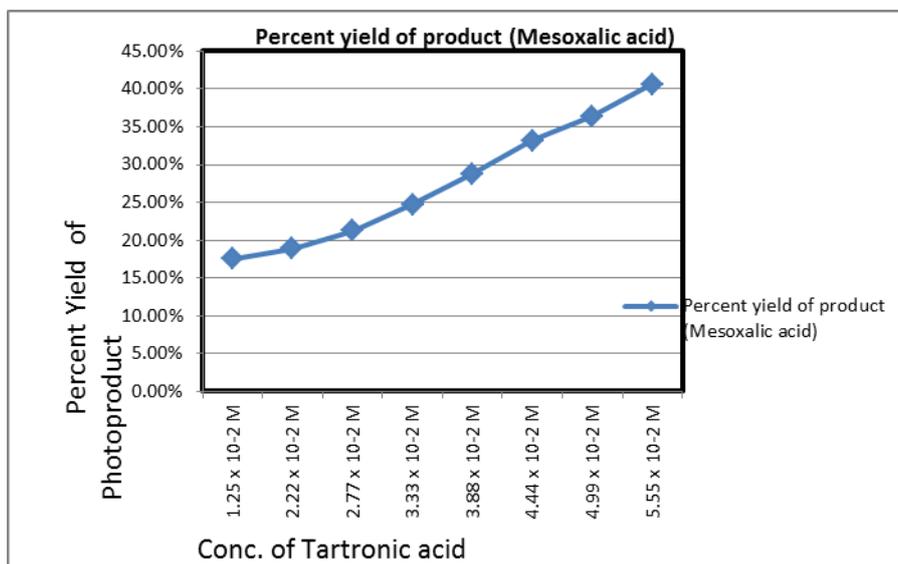


Fig 1: The effect of lactic acid concentration.

The effect of photocatalyst

Keeping all other factors identical the effect of amount of TiO_2 has also been observed. The total volume of reaction mixture is 50 mL and the results are reported in the following Table 2 and shown in Fig. 2.

1. Solvent: Water
2. Tartronic acid, 3.33×10^{-2} M (3.00 g/L)
3. Irradiation time: 120 min
4. Visible light: 2×200 W Tungsten lamps

Table 2.

S. No.	Conc. Of Photocatalyst (TiO_2)	Percent yield of product (Pyruvic acid)
1	1.66×10^{-2} M	17.3%
2	2.50×10^{-2} M	23.1%
3	3.34×10^{-2} M	27.9%
4	4.18×10^{-2} M	35.5%
5	5.02×10^{-2} M	40.2%
6	5.85×10^{-2} M	41.1%
7	6.69×10^{-2} M	41.7%
8	7.53×10^{-2} M	42.2%

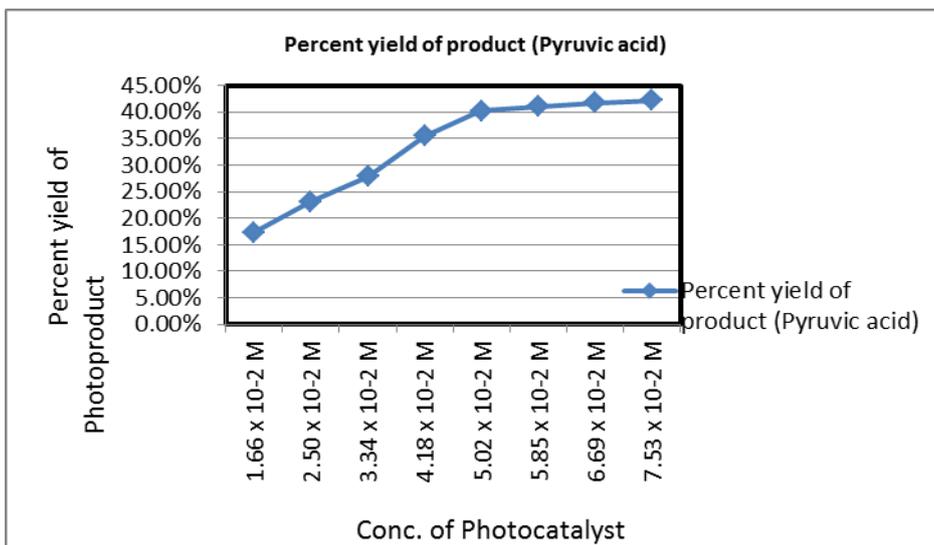


Fig. 2: Percent yield of product (Mesoxalic acid).

The effect of type of radiations

The effect of type of radiations on photocatalytic reaction was studied in visible light and ultraviolet light keeping all other factors identical. The total volume of reaction mixture is 50 mL and the results are reported in the following Table.3 and shown in Fig. 3.

1. Solvent: Water
2. TiO₂: 1.66 × 10⁻² M (1.33 g/L)
3. Irradiation time: 120 min
4. Visible light: 2 × 200 W Tungsten lamps
5. UV Light: UV Chamber 30 W (Philips Tube)

Table 3,

S. No.	Conc. Of Substrate (Tartronic acid)	Percent yield of product (In visible light)	Percent yield of product (In UV light)
1	1.25 x 10 ⁻² M	17.5%	6.4%
2	2.22 x 10 ⁻² M	18.9%	8.1%
3	2.77 x 10 ⁻² M	21.3%	10.0%
4	3.33 x 10 ⁻² M	24.7%	13.3%
5	3.88 x 10 ⁻² M	28.8%	17.2%
6	4.44 x 10 ⁻² M	33.2%	19.4%
7	4.99 x 10 ⁻² M	36.4%	22.1%
8	5.55 x 10 ⁻² M	40.6%	23.9%

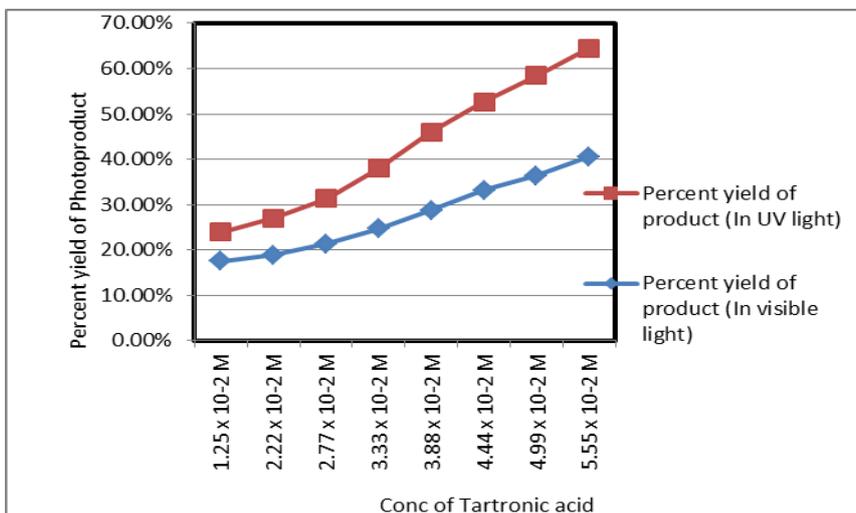


Fig. 3: The effect of UV and Visible light.

The effect of nature of photocatalyst

The effect of the nature of photocatalyst on photocatalytic reaction was studied by different photocatalysts, which are Ferric oxide, Cadmium sulphide, Tungsten oxide, Titanium oxide, Stannic oxide and Zinc sulphide. The total volume of reaction mixture is 50 mL and the results are reported in the following

Table 4 and shown in Fig. 4.

1. Solvent: Water
2. Tartronic Acid: $5.259 \times 10^{-2} \text{M}$
3. Irradiation Time: 120 min.
4. Visible Light: $2 \times 200 \text{ W}$ Tungsten Lamps.

Table 2.4.

S. No.	Photocatalyst	Band gap (eV)	Wavelength (nm)	Yield of Photoproduct
1	Fe ₂ O ₃	2.2	564	25.8%
2	CdS	2.4	516	45.0%
3	WO ₃	2.6	477	51.4%
4	TiO ₂	3.1	400	40.6%
5	ZnO	3.2	388	22.5%
6	SnO ₂	3.5	354	48.5%
7	ZnS	3.6	345	55.7%

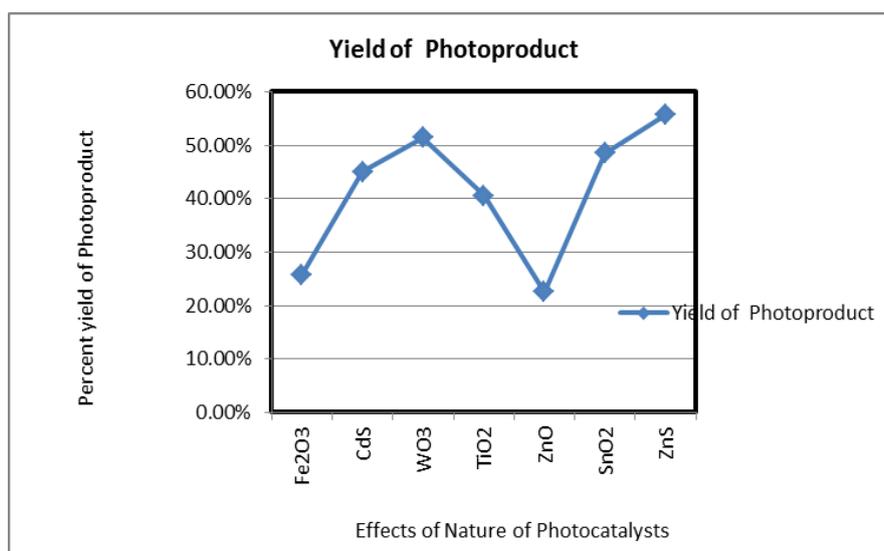


Fig. 2.4: Percent yield of product

Fig. 4: The effect of nature of photocatalyst.

The effect of amount of on the oxidation of tartronic acid was studied by using variable amount of substrate, as reported in Table 1 and Fig. 1. The highest efficiency was observed at optimum concentration. It may be explained on the basis that as the concentration of substrate increases, more substrate molecules are available for photocatalytic reaction and hence an enhancement on the rate was observed with increasing concentration of substrate.

The amount of photocatalyst on oxidation of tartronic acid was investigated employing different concentrations of the TiO₂ as reported in Table 2 and Fig. 2. It was observed that the yield of photo-product increasing with increasing catalyst level up to $5.02 \times 10^{-2} \text{M}$ and beyond this, the yield of photo-product is constant. This observation may be explained on the basis that on the initial stage, even a small addition of photocatalyst will increase the yield of photoproduct as the surface area of

photocatalyst increases, but after a certain amount $5.02 \times 10^{-2} \text{M}$, addition of photocatalyst do not affect the yield of product because of the fact that at this limiting amount, the surface at the bottom of the reaction vessel become completely covered with photocatalyst and this observation has seen as, if the air is passed and magnetic stirrer is used during the exposer to the reaction mixture decreased the amount of photoproduct. Hence increase in the amount of photocatalyst will only increase the thickness of the layer at the bottom. Keeping all the factors identical the effect of the nature of photocatalyst on the photo-oxidation of tartronic acid was studied by using different photocatalysts as shown in the Table 3 and Fig. 3. As we know that the low band gap is more suitable for visible light and this property quite resembles the observed data as the table reported. It may also be happen that in UV light the there may any different major photoproduct produces.

Keeping all the factors identical the effect of the nature of photocatalyst on the photo-oxidation of tartronic acid

was studied by using different photocatalysts as shown in the Table 4 and Fig. 4. The maximum amount observed by ZnS and the minimum amount observed by Fe₂O₃ photocatalyst. This may be due to the reaction may proceed towards the complete mineralization or giving some other photoproducts in such cases.

As we know that titanium dioxide (TiO₂) is the most common photocatalyst and comparably little research has been conducted on zinc oxide, ZnO, which could be a viable alternative for some applications. The effect of other semiconductor particle e.g. Fe₂O₃, CdS, WO₃ (having low band gap than TiO₂ semiconductor) on the TiO₂ catalyst photocatalytic reactions have also been studied. TiO₂ is the most frequently used photocatalyst because of its photo stability and low cost, combined with its biological and chemical inertness and resistant to photo and chemical corrosion. On the other hand, binary metal sulfide semiconductors such as CdS and PbS are regarded as insufficiently stable for catalysis and are toxic. ZnO is also unstable in illuminated aqueous solutions while WO₃ has been investigated as a potential photocatalyst, but it is generally less active catalytically than TiO₂. However, these can be combined with other semiconductors including TiO₂ to achieve greater photocatalytic efficiency or stability. It is now well established that the photocatalytic oxidation of several organic compounds by optically excited semiconductor oxides is thermodynamically allowed in presence of oxygen at room temperature. On the basis of analytical, chemical and spectral data the product was characterized as mesoxalic acid.

After completion of photocatalytic reaction the photoproduct was characterized by usual qualitative tests: treatment with (1) Semicarbazide, (2) Hydroxylamine hydrochloride, (3) 2, 4-Dinitrophenyl phenyl hydrazones (M. Pt. 202°C) shows that photoproduct is mesoxalic acid. IR analysis shows two moderately intense peaks at 2909 cm⁻¹ and 2881 cm⁻¹ (C-H stretching) and peak at 1728 cm⁻¹ (C=O stretching) confirms the presence of ketonic group in the 2,4-DNP of photoproduct. Absence of signal peaks at around 3200 cm⁻¹ and at 1015-1050 cm⁻¹ confirms the absence of alcoholic group in the 2, 4-DNP of photoproduct. The confirmatory test for mesoxalic acid is carried out as following method:

Test for mesoxalic acid

Since the general tests are employed to identify the pyruvic acid. Special test is done as follows.

To 0.5 mL of solution containing carbonyl acid + 0.5 mL water + 0.5 mL of 0.2% FeCl₃.6H₂O + 3% of cysteine hydrochloride + 3 mL of 3N-HCl. The test tube is now immersed in a bath of ice and water, and 0.5 mL of freshly prepared 0.1% solution of alpha-methylindole is added. After being shaken, the tubes, still in bath, kept 24 hrs in refrigerator. A light pink color appears which nearly reaches its maximal intensity in 24 hours. Tartronic acid gives orange color (480 nm). Optimum yield may be

measured by optical density at 480 nm vs. time of irradiation. This is very accurate and well recognizes chemical test for hydroxy acids.^[39,40]

Separation of 2, 4-DNP (Test for Ketoacids)

A visible precipitate may or may not appear, according to the amount of hydrazone substances present. The whole is now shaken with 20 mL of ethyl acetate in a glass stopper 50 mL separating funnel. After separation, the aqueous layer, which is nearly colorless, is extracted with further 10 mL of ethyl acetate; as soon as the aqueous layer is colorless, as usually is the case after two extractions, it is discarded. The united ethyl acetate extracts now contain all the unchanged 2, 4-dinitrophenyl hydrazine together with the hydrazones which have been formed. The liquid is also acid, owing to the extraction of certain amount of hydrochloric acid; these must be neutralized by shaking with solid calcium carbonate (1, 2). The solution is decanted into a glass evaporating basin, washing the calcium carbonate with further ethyl acetate until it is colorless. The washing is added to the main bulk of fluid. The substances in solution must now be transferred to toluene (3). This is accomplished by evaporating the contents of the dish on a water bath to 1-2 mL and then, after removal from the bath, adding about 20 mL of toluene. The slightly cloudy yellow solution is again transferred to the separating funnel and is thoroughly shaken with 5 mL of cold 25% sodium carbonate solution (4). If mesoxalic acid was originally present its hydrazones dissolve in the aqueous layer, coloring it brown. This extraction is repeated with fresh Na₂CO₃ solution until the latter remains colorless; two or three repetitions usually sufficient. The united sodium carbonate layers are now acidified by adding concentrated HCl drop by drop. The 2, 4-DNP of mesoxalic acid is precipitated and lemon-yellow suspension results. This is extracted in a separating funnel with successive 10 mL portions of ethyl acetate until the aqueous layer is colorless (5). It is now usually to employ more than 20 mL of ethyl acetate to achieve this. The ethyl acetate solution now contains all the mesoxalic acid hydrazone which was present, and is evaporated to dryness in a glass basin on a water bath. The yellow residue is dissolved when cooled in 5% alcoholic KOH (6), giving a deep red solution, which is made up in a graduated vessel with further alcoholic KOH to a volume such that the color is suitable for reading in colorimeter. In practice it is found that the total volume at this stage should be about 50 mL for every mg of mesoxalic acid that was originally present in the reaction mixture.

- (1) If neutralization be omitted, the subsequent heating of the solution leads to the formation of small quantities of compounds other than the mesoxalic acid derivative, which are extracted by the sodium carbonate, coloring it brown, and which are afterwards precipitated upon acidification, giving a reddish color in the final treatment with alcoholic potash. When the neutralization is properly carried

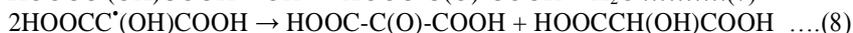
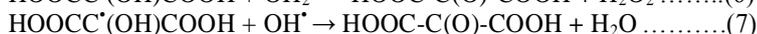
out, the sodium carbonate always remains colorless in blank determinations, i.e. when no mesoxalic acid is present.

- (2) It was that first the practice of neutralize the acid solution before extracting with ethyl acetate, but if this be done it is found that extraction has to be repeated a much larger number of times before the aqueous layer is colorless.
- (3) The solubility of mesoxalic acid derivative in ethyl acetate is so great that it is not completely removed by sodium carbonate solution. Moreover, shaking the ethyl acetate solution with sodium carbonate solution to lead to a small amount of saponification, with the result that separation into layers is imperfect. The substitution of toluene for the ethyl acetate overcome both of these difficulties, but it cannot be used for extraction at the outset because the hydrazine and hydrazones are not sufficiently soluble in to render the process efficient.
- (4) The toluene extract and the sodium carbonate solution must both be at room temperature. Warm Na_2CO_3 react with other 2, 4-DNPs besides that of mesoxalic acid.
- (5) A good deal of care must be taken at this stage that the effervescence produced by the librated CO_2 does not lead to loss by splashing.

Mechanism

On the basis of results and discussion the following tentative mechanistic part has discussed for photocatalytic oxidation of tartronic acid, with collaborating the results already reported for other studied compounds.

Mesoxalic acid formed according the following steps



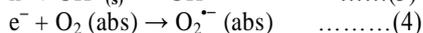
The whole process can be summarized in the following Fig. 5.

By the observations of photoproducts, it is very important to discuss the characteristic and nature (specially the toxic natures) of photoproduct as the photo reactants are being used in chemical peels, a variety of skin care products including moisturizers, cleansers, eye cream, sunscreen and foundations etc. The U.S. Food and Drug Administration¹⁰ permits up to 1% TiO_2 as an inactive ingredient in food products. While there is no known health effects associated with the use of TiO_2 , a recent study found that 3-6 year old children are the most affected group of people that consume TiO_2 particles from food products. So that the probable side effects of the photoproducts may be the common field of interest for the relevant researchers like dermatologists, pharmacists as well as the chemists. Similarly the side effects of food materials and wine-hangover may be due these type of oxidative products as the mesoxalic acid may further oxidized into other compounds. The

With respect to a semiconductor oxide such as TiO_2 , photocatalytic reactions are initiated by the absorption of illumination with energy equal to or greater than the band gap of the semiconductor. When the suspension of titanium oxide irradiated with visible light electron will be promoted from valence band to conduction band leaving a positive hole in the valence band.

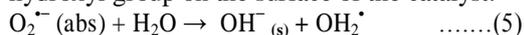


It was explained before, that the surface of TiO_2 with high surface area retains subsets of hydroxyls, where the net surface density is 4-5 hydroxyl per nm. In addition, suspension of TiO_2 in solution of tartronic acid gives a surface hydroxide ion as locations for primary photo-oxidation processes. Photo holes are trapped by surface hydroxyl groups, whereas electrons are trapped by adsorbed oxygen.



The formed radicals are reacted with adsorbed on the surface, is reacted with the tartronic acid to form a radical and releases a water molecule,
 $\text{HOOCCH}(\text{OH})\text{COOH} + \text{OH}^* \rightarrow \text{HOOC-C}^*(\text{O})\text{-COOH} + \text{H}_2\text{O}$

The formed radicals are reacted with adsorbed on the surface, is reacted with the formed water to regenerate hydroxyl group on the surface of the catalyst:



mechanistic part of the photochemical transformations is also helpful for chemists to understand more about these new advanced oxidation processes. Hence, this part of reported work may help to arouse the interdisciplinary interest about the side effects of photoproducts, where these are being used.

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