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Study Photo oxidation of Salicylic Acid by Titanium Oxide.

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ABSTRACT
Photo catalysis has received enormous attention in last few decades because of its potential application in environmental treatment and fine chemical synthesis. Organic pollutants in wasted can be easily degraded in to carbon dioxide and water molecules. Similarly, under dry organic solvent or controlled pH, irradiation time, by using visible or UV light etc., the compound may also be selectively oxidized into fine chemical products in place of complete mineralization.[1-5] Titanium dioxide as a semiconductor photo catalyst has been intensively investigated since Fujishima and Honda studied the photo catalytically splitting of water on TiO_2 electrodes in 1972.[1] TiO_2 also, as its non-toxicity, long range photo stability, and high activity, has been widely utilized in mineralizing toxic and non-biodegradable environmental contaminants as well as in the various organic synthesis. Salicylic acid as a medication is used most commonly to help remove our outer layer of the skin.[10] So that, it is used to treat warts, acne, psoriasis, ringworm, dandruff, and ichthyosis.[10][11] As with other hydroxy acids, salicylic acid is also a beta hydroxyl acid and a key ingredient in many skincare products for the treatment of seborrhoeic dermatitis, acne, corns, psoriasis, keratosis pilaris, calluses, acanthosis nigricans, ichthyosis and warts.[12] Salicylic acid is also used as a very good food preservative, an antibacterial and antiseptic.[16] As a food additive[16-18], TiO_2 (titanium dioxide) is approved its utility in various countries like EU, USA , New Zealand and Australia; it is listed by INS number 270 or E number E-270. It is therefore planed to investigate photo-degradation of salicylic acid by semiconductors. Hence, this part of work may help to arouse the interdisciplinary interest in the side effects of photoproducts, where these are being used.
Keywords: *Semiconductor, Titanium dioxide, Photo-oxidation, Sodium Salt of Salicylic acid.*

I. INTRODUCTION

Titanium dioxide (TiO_2), as a semiconductor photo catalyst has been intensively investigated since Fujishima and Honda studied the photo catalytic splitting of water on TiO_2 electrodes in 1972.[1] Since then, many research efforts have been performed in understanding the fundamental processes and in enhancing the photo catalytic efficiency of TiO_2. Titanium dioxide is when exposed to UV light, electrons in the uppermost valence band will jump to the conduction band and create conduction band electrons and valence band holes. In most instances, the valence band holes and conduction band electrons simply recombine liberating heat or light, a process known as recombination. Recombination is responsible for the low quantum yields.[2-4] Photoelectron trapping has long been regarded as an effective mechanism to reduce the charge recombination on semiconductor photo catalysts. Many successful efforts have made to enhance the catalytic efficiency of TiO_2 by doping with metals (like Ag) and various non metal doping agents like N, P, S.[5-7]

The presence of pharmaceuticals, personal care products (PPCPs) and other hazards in surface water is an emerging environmental issue and provides a new challenge to drinking water, wastewater, and water reuse treatment system.[8-11] These discharged could persist in environmental waters for a long time and accumulate in various organisms of the food chain[12], which may adversely affect the environmental ecosystems.

Salicylic acid is a phenolic acid which is a lipophilic monohydroxybenzoic acid, and belongs to the category of beta hydroxy acid(BHA). It has the formula $C_7H_6O_3$. This colorless crystalline organic acid is widely used in organic synthesis and functions as a plant hormone. Its water solubility is 2.48 grams per litre at 20^0 temperatures. It is derived from the metabolism of salicin. In addition to serving as an important active metabolite of aspirin (*acetylsalicylic acid*), which acts in part as a prodrug to salicylic acid, it is probably best known for its use as a key ingredient in topical anti-acneproducts. The salts and esters of salicylic acid are known as salicylates. It is on the WHO Model List of Essential Medicines, the most important medications needed in a basic health system.[13]

Salicylic acid as a medication is used most commonly to help remove the outer layer of our skin.[10] As such, it is used to treat warts, psoriasis, dandruff, acne, ringworm, and ichthyosis.[14,15] As with other hydroxy acids, salicylic acid is a key ingredient in many skincare products for the treatment of seborrhoeic dermatitis, acne, psoriasis, calluses, corns, keratosis pilaris, acanthosis nigricans, ichthyosis and warts.[16]

Some people are hypersensitive to salicylic acid and related compounds. As a topical agent and as a beta-hydroxy acid (and unlike alpha-hydroxy acids), salicylic acid is capable of penetrating and breaking down fats and lipids, causing moderate chemical burns of the skin at very high concentrations. It is veru important to note that it may damage the lining of pores if the solvent is alcohol, acetone or an oil. Counter limits are set at 2% for topical preparations expected for the face and 3% for those expected to be washed off, such as acne cleansers or shampoo. According to a study, 17% and 27% salicylic acid, which is sold for wart removal, should not be applied to the face and should not be used for acne treatment. Even for wart removal, such a solution should be applied once or twice a day more frequent use may lead to an increase in side-effects without an increase in efficacy.[20] Salicylic acid occurs in plants as free salicylic acid and its carboxylated esters and phenolic glycosides. In several studies suggest that humans metabolize salicylic acid in measurable quantities from these plants.[21] Salicylic acid is considered as a frequent pollutant in wastewaters of several industries.[22]

Salicylic acid is used in the production of other pharmaceuticals, including4-aminosalicylic acid, sandulpiride, and landetimide (via Salethamide). Salicylic acid was one of the original starting materials for making acetylsalicylic acid (aspirin) in 1897.[17] Salicylic acid is also used as a food preservative, a bactericidal and an antiseptic.[16] As a food additive[19,20], TiO_2 (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. It is therefore planed to investigate photo-degradation of salicylic acid by semiconductors specially with TiO_2. Hence, this part of reported work may help to arouse the interdisciplinary interest in the side effects of photoproducts, where these are being used.

In the present part of study, it is planned to investigate photo-oxidation of salicylic acid (2-hydroxyl-benzoic acid) by semiconductor sensitized in visible lig ht which undergoes complete mineralization. Titanium dioxide is when exposed to UV light; electrons in the uppermost valence band will jump to the conduction band and create conduction band electrons and valence band holes. In most instances, the valence band holes and conduction band electrons simply recombine liberating heat or light, a process known as recombination. Recombination is responsible for the low quantum yield

II. EXPERIMENTAL

The organic compounds i.e. Salicylic acid, Silica gel-G, Resublimed Iodine (sm), ninhydrin, 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 2×200 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, pH meter (Eutech pH 510),conductivity meter (Systronic), spectrophotometer (Systronic) and I.R. spectrometer (Perkin-Elmer Grating-377) was used.

The Salicylic acid solutions is prepared in water as the required concentrations as mentioned in the Tables**.** The required concentration of semiconductor and mixed semiconductors has been added to the reaction mixture as per requirement for heterogeneous photo catalytic 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 ninhydrin 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 by preparing appropriate 2, 4-DNP derivatives and also were identified by melting point of derivative, spectrophotometer, IR-spectrometer, NMR-spectrometer.

The optimum yield of obtained 2, 4-DNP [with 0.50gm and 84 ml HCl in 500 ml aqueous solution] was measured by using spectrophotometers (colourimeter) and conductivity meter. Various probable variations like the role of different semiconductors, mixed semiconductors, visible and UV-light etc., were studied. Some sets of experiments are also made in controlled conditions such as in absence of UV or visible light, semiconductors and stirring etc.

III. RESULTS AND DISCUSSION

1. The effect of substrate

Effect of amount of substrate on the oxidation of Salicylic acid was studied at different concentrations varying from 1.38×10^{-2} M to 1.73×10^{-2} M at fixed amount TiO_2 (1.66×10^{-2} M). The total volume of reaction mixture is 50 ml and the results are reported in the Table 1 and shown in Plot 1.

Table 1

1. Solvent : Water
2. TiO_2 : 1.66×10^{-2} M (1.33 g/L)
3. Irradiation time : 120 min
4. Visible light : 2 × 200 W Tungsten lamps

S. No.	Conc. Of Substrate (Salicylic acid)	Percent yield of product (1,4-Benzoquinone-2 carboxylate)
1	1.38×10^{-2}	5%
2	1.43×10^{-2}	9%
3	1.48×10^{-2}	11%
4	1.53×10^{-2}	14%
5	1.58×10^{-2}	17%
6	1.63×10^{-2}	19%
7	1.68×10^{-2}	23%
8	1.73×10^{-2}	26%

Plot -1 The effect of substrate

2. The effect of photo catalyst

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 Table 2 and shown in Plot 2.

1. Solvent : Water
2. Salicylic acid : 1.44×10^{-2} M (2.00 gm/Lt)
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 (1,4-Benzoquinone-2 carboxylate)
1	1.66×10^{-2}	8%
2	2.50×10^{-2}	11%
3	3.34×10^{-2}	13%
4	4.18×10^{-2}	17%
5	5.02×10^{-2}	20%
6	5.85×10^{-2}	22%
7	6.69×10^{-2}	25%
8	7.53×10^{-2}	27%

Plot 2 The effect of photocatalyst

3. 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 Table 3 and shown in Plot 3

1. Solvent : Water
2. TiO_2 : 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 (Salicylic acid)	Percent yield of product (In visible light)	Percent yield of product (In UV light)
1	1.38×10^{-2}	5%	18%
2	1.43×10^{-2}	9%	25%
3	1.48×10^{-2}	11%	31%
4	1.53×10^{-2}	14%	39%
5	1.58×10^{-2}	17%	46%
6	1.63×10^{-2}	19%	53%
7	1.68×10^{-2}	23%	60%
8	1.73×10^{-2}	26%	66%

Plot 3 The effect of light

4. 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 Table 4 and shown in Plot 4

1. Solvent : Water
2. Salicylic acid : 1.44×10^{-2} M (2.00 gm/lt)
3. Irradiation Time : 120 min.
4. Visible Light : 2 × 200 W Tungsten Lamps.

Table 4

S. No.	Photocatalyst	Band gap (eV)	Wavelength (nm)	Yield of Photoproduct
1	Fe_2O_3	2.2	564	10%
2	CdS	2.4	516	13%
3	WO_3	2.6	477	07%
4	TiO_2	3.1	400	11%
5	ZnO	3.2	388	03%
6	SnO_2	3.5	354	08%
7	ZnS	3.6	345	04%

Plot 4. The effect of nature of photocatalyst

The effect of amount of on the oxidation of Salicylic acid was studied by using variable amount of substrate, as reported in Table 1 and Plot 1. The efficiency was highest at maximum 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 Salicylic acid was investigated employing different concentrations of the TiO_2 as reported in Table 2 and Plot 2. It was observed that the yield of photo-product increasing with increasing catalyst level up to 7.53×10^{-2} 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 7.53×10^{-2} M, addition of photocatalyst do not affect the yield of product because of the fact that after this limiting amount, the surface at the bottom of the reaction vessel become completely covered with photocatalyst. Now increase in the amount of photocatalyst will only increase the thickness of the layer at the bottom and this limit depends on the safe of the bottom of vessel. Keeping all the factors identical the effect of the nature of photocatalyst on the photo-oxidation of Salicylic acid was studied by using visible and UV light as shown in the Table 3 and Plot 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 as more yield in UV light.

Titanium dioxide (TiO_2) 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. Fe_2O_3, CdS, WO_3 (having low band gap than TiO_2 semiconductor) on the TiO_2 catalyst photocatalytic reactions have also been studied. TiO_2 is the most frequently used photo catalyst 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 WO_3 has been investigated as a potential photo catalyst, but it is generally less active catalytically than TiO_2. However, these can be combined (Doping) with other semiconductors including TiO_2 to achieve greater photo catalytic efficiency or stability. Keeping all the factors identical the effect of the nature of photocatalyst on the photo-oxidation of Salicylic acid was studied by using different photocatalysts as shown in the Table 4 and Plot 4

It is now well established that the photocatalytic oxidation of several organic compounds by optically excited semiconductor oxides is thermodynamically allowed at room temperature in presence of oxygen. On the basis of analytical, chemical and spectral data the product was characterized 1,4-Benzoquinone-2 carboxylate.

After completion of photocatalytic reaction the photoproduct was characterized by usual qualitative tests treatment with (1) Semicarbeazide, (2) Hydroxylamine hydrochloride, (3) 2, 4-Dinitrophenyl phenyl hydrazones (M. Pt. 113ºC) shows that photoproduct is 1,4-Benzoquinone-2-carboxylic acid. IR analysis show two moderately intense peaks at 1633 cm^{-1}(C=O stretching) and 2892 cm^{-1} (C-H 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 OH group in the 2, 4-DNP of photoproduct. The confirmatory test for 1,4-Benzoquinone-2-carboxylic acid are very general laboratory methods are available. Its Ca salts also formed to identify.

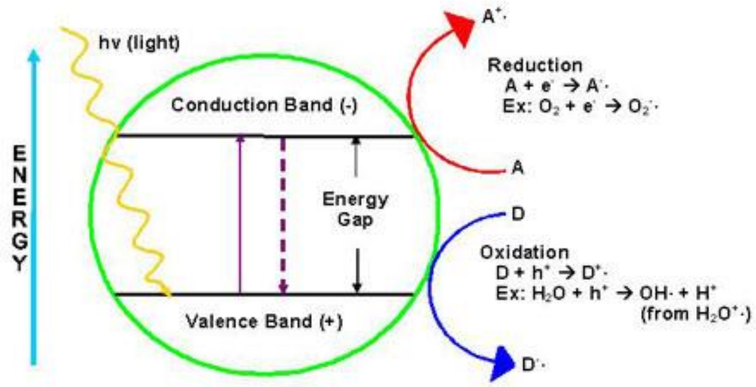
MECHANISM

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

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:

$TiO_2 + h\nu \rightarrow (h - e)$ Excitation …(1)

$(h - e) \rightarrow h^+ + e^-$ Separation …(2)



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 Gamma hydroxyvaleric 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:

$h^+ + OH^-_{(s)} \rightarrow OH^\bullet$ … (3)

$e^- + O_2\,(abs) \rightarrow O_2^{\bullet -}\,(abs)$ …(4)

The formed $OH^{\bullet}$ radicals are reacted with adsorbed on the surface, is reacted with the malic acid water to generate Gamma hydroxyvaleric acid radical and water molecule, as follows:

$Y\text{-}OH + OH^{\bullet} \rightarrow Y^{\bullet}\text{-}OH + H_2O$ …(5)

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:

$O_2^{\bullet-}\ (abs) + H_2O \rightarrow OH^-_{(s)} + HO_2^{\bullet}$ …(6)

Gamma ketovaleric acid formed according the following steps:

$Y^{\bullet}\text{-}OH + HO_2^{\bullet} \rightarrow Y(O) + H_2O_2$ ...(7)

IV. CONCLUSION AND SUGGETIONS

The work reported is only the study of sensitized photocatalytic action of TiO_2 on Salicylic acid as dilute solution in the presence of light and air. This study may have importance to attract the attentions of the researchers about the causes of the probable side effects of the photoproducts and this may arose a common field of interest for the relevant researchers like pharmacists as well as the chemists.

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