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The Study Of Semiconductor Oxide/H₂O₂/UV System As A Photocatalytic System For Deoximation: The Effect Of Some Operational Parameters

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ABSTRACT

In this report titanium dioxide(anatase and rutile) and zinc oxide as semiconductor oxides are used as photocatalysts while hydrogen peroxide is auxilary oxidant. A variety of oximes were converted to their carbonyl compounds in the present of photocatalysts with hydrogenperoxide under UV-irradiation by 400W high pressure mercury lamp. The observed results revealed that the order of photocatalytic activity for deoximation was ZnO>TiO₂(rutile)> TiO₂(anatase) The effect of some other physicochemical parameters such as amount of photocatalyst, solvent and time of irradiation were studied. The carbonyl compounds were regenerated from the related oximes after 14-22h. The results showed the photostability of this type of compounds. © 2007 Trade Science Inc. - INDIA

INTRODUCTION

The cleavage of oximes to regenerate aldehydes and ketones is an important reaction because, the oximes serve as efficient protective groups for aldehydes and ketones and extensively used for the purification and characterization of carbonyl compounds. Several methods have been reported for deoximations. Among these are; chromium trioxide[1], 3-carboxy-pyridiniumchlorochromate[2], sodium perborate[3], peroxymonosulphate ion[4], tert-butyl hydrogenperoxide[5], ammonium persulphate-alumina using microwave[6], dess-martin periodinane[7], l-benzyl-4-aza-1-azoniabicyclo[2.2.2]octane periodate[8], microwave assisted sodium periodate supported on silica[9], KMnO₄-dicyclohexyl-18-crown-6[10,11], tungstate sulfuric acid (TSA)/ NaNO₂ or KMnO₄[12,13], N-bromophthalimide[14], supported quinolinium fluoro-

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chromat[15], HIO_3/SiO_2[16], tert-butyl hypo-iodite[17], TiO_2/O_2[18].

Classically, the recovery of the parent carbonyl compounds from the oximes involves hydrolytic cleavage which removes the hydroxylamine from equilibrium[19-29]. However, many of these existing methods either employ highly toxic reagents or give further oxidation of liberated aldehydes into their carboxylic acids. Therefore, careful controlling of reaction temperature and the quantity of oxidants are necessary.

Recently, the potentiality of heterogeneous photocatalysis in chemistry is a well-established procedure[30]. The strong oxidizing power of the photo-generated holes of semiconductors(large band gap material), the chemical inertness and resistance to both photocorrosion and decomposition reactions which plague other band gap materials(e.g., Si, Ga, As, GaP, Inp, CdS, etc.), low cost and wide availability in addition to the nontioxicity of TiO_2(anatase and rutile) and zinc oxide have made them as superior photocatalysts[31]. Several articles and reviews have been written on the use of semiconductor oxides as photocatalyst[30, 31, 32-35].

The possibility of using the semiconductor/liquid junction as a site for light-stimulated redox reactions has provided a simple conceptual framework for extensive progress toward efficient oxidation reaction[36]. In continuation of our ongoing program to develop synthetic protocols utilizing in thermal[12-13] and photochemical conditions[37-42], we wish to report herein investigation of a heterogeneous photocatalysis method for regeneration of carbonyl compounds from oximes using titanium dioxide(rutile and anatase) and zinc oxide as photocatalysts with H_2O_2 as running oxidant under UV-irradiation.

MATERIAL AND METHOD

Reagents

Chemicals were purchased from Merck, Fluka, Aldrich chemical companies. Oximes were prepared from the corresponding carbonyl compounds according to the reported procedure. The reactions were monitored by thin layer chromatography(TLC). The products were isolated and identified by comparison of their physical and spectral data with authentic samples.

Instruments

IR spectra were recorded on FT-IR JASCO-680 instrument model. ^{1}H NMR data were obtained on 300MHz DPX-Brucker model. Melting point of compounds was measured on BI-Barnstead Electrothermal. A Sigma 301 model of centrifuge was used for separation of photocatalysts from solution.

General procedure for the regeneration of carbonyl compounds from oximes in aqueous acetonitrile solvent
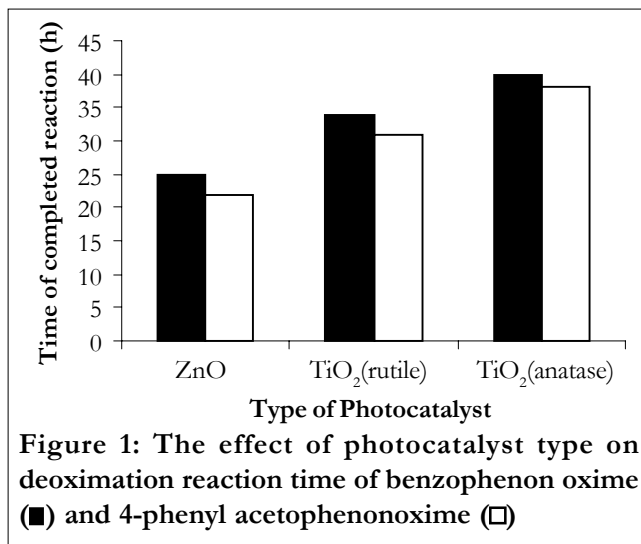
Zinc oxide(50mg, ZnO) was added to a solution containing oxime(0.5mmol) in 20mL aqueous acetonitrile(20%) and hydrogen peroxide(2mmol), then the mixture was stirred at room temperature under irradiation of UV light (400W high pressure mercury lamp) for the appropriate time(14-22h). The progress of the reaction was monitored by TLC. After completion of the reaction as monitored by TLC(n-hexane: ethylacetate), the zinc oxide was separated by centrifuge. Evaporation of the solvent followed by chromatography on a silica-gel plate afforded the pure products in 75%-95% yields (TABLE 1).

RESULTS AND DISCUSSION

Our investigation during the controlled reactions showed to us: (a) UV irradiation is necessary for the effective progress of the deoximation reactions (b) without the selected oxidant, the deoximation reactions were not done considerably even with prolonged reaction times. With this preliminary results, the optimization of important operational parameters were performed.
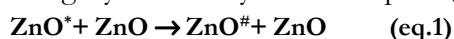
The type of photocatalyst

For this purpose the amount of 20mg of TiO_2(anatase or rutile) and zinc oxide were used for photocatalytic conversion of 0.1mmol of benzophenonoxime or 4-phenylacetophenonoxime in aqueous acetonitrile with 0.4 mmol hydrogen peroxide under irradiation. The time required for completion of the deoximation was used for comparison of the photocatalytic activity of semiconductor oxides. As shown in figure 1, zinc oxide>titanium dioxide(rutile) >titanium dioxide(anatase) completed the deoximation, respectively. The shorter reaction times and easily centrifugation are two practical advantages for

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Figure 1: The effect of photocatalyst type on deoximation reaction time of benzophenon oxime (■) and 4-phenyl acetophenonoxime (□)

Figure 2: The effects of photocatalyst amounts of zinc oxide on completion of the reaction on two oxime as typical substrate.

zinc oxide with respect to titanim dioxide specially for anatase form of it. It seems the higher quantum yields and slower recombination of photogenerated electron/ hole couples of it are responsible to this better photocatalytic activity of ZnO.

The amount of photocatalyst

After choice of the better photocatalyst, the optimum amount of it on photocatalytic oxidation of titled compounds was investigated. To obtain the optimum amount of ZnO, two photocatalytic oxidative deoximation were runned on the oximes of entries 1 and 9 as typical oximes using various amounts of ZnO. As shown in figure 2, oxidation times of the selected compounds were decreased by increasing the photocatalyst amounts, then reached the lowest time of completion of the deoximation and finally remained at constant value of 50mg. It is interesting to note that this phenomenon has been observed previously in other photocatalytic reaction. This can be rationalized in terms of availability of active sites on ZnO surface and the light penetration of photoactivating light into the suspension. The availability of active sites increases with the suspension of photocatalyst loading, but the light penetration and hence the photoactivated volume of the suspension shrinks. Moreover, the increase in the time of oxidation(figure 2, oxime of entry 1 and 9) at higher photocatalyst loading may be due to deactivation of activated molecules by collision with ground state molecules. Shielding by ZnO may also take place(eq.1):
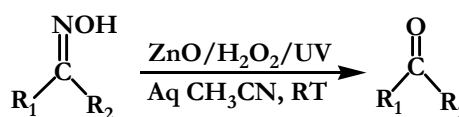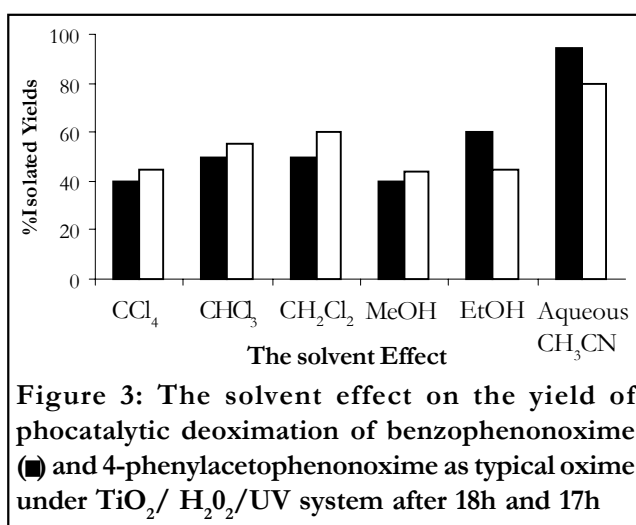
$$ZnO^* + ZnO \rightarrow ZnO^\# + ZnO \qquad (eq.1)$$

Where ZnO^* is the ZnO with active species
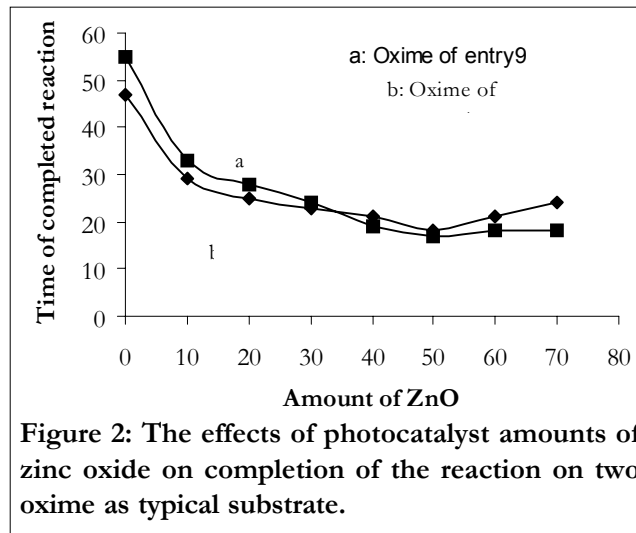
adsorbed on its surface and $ZnO^\#$ is the deactivated form of ZnO[37-46].

The type of solvent

The solvent plays a crucial role on reaction course. As shown in figure 3 from our findings on photocatalytic deoximation of benzophenonoxime and 4-phenylacetophenonoxime as typical substrates in various solvents such as carbon tetrachloride, chloroform, dichloromethane, methanol, ethanol and aqueous acetonitrile(20%), We found that aqueous acetonitrile was to be the best media for photocatalytic deoximation in our conditions. In general, it is

Figure 3: The solvent effect on the yield of phocatalytic deoximation of benzophenonoxime (■) and 4-phenylacetophenonoxime as typical oxime under TiO₂/ H₂0₂/UV system after 18h and 17h
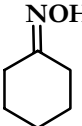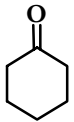

SCHEME 1

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TABLE 1: Photocatalytic regeneration of carbonyl compounds from oximes at room temperature using ZnO/H_2O_2/UV system in aqueous acetonitrile (20%)

Entry	Substrate	Product[a]	Time/h	Yield (%)[b]
1	(benzophenone oxime)	(benzophenone)	18	94
2	C_6H_5–C(=NOH)–CH_3	C_6H_5–C(=O)–CH_3	15	91
3	(fluorenone oxime)	(fluorenone)	17	95
4	H_3C–furan–C(=NOH)–CH_3	H_3C–furan–C(=O)–CH_3	14	75
5	(1-tetralone oxime)	(1-tetralone)	18	90
6	Cl–C_6H_4–C(=NOH)–CH_3	Cl–C_6H_4–C(=O)–CH_3	17	92
7	Br–C_6H_4–C(=NOH)–CH_3	Br–C_6H_4–C(=O)–CH_3	15	70
8	(1-indanone oxime)	(1-indanone)	15	85
9	biphenyl–C(=NOH)–CH_3	biphenyl–C(=O)–CH_3	17	80
10	CH=NOH, NO_2	CH=O, NO_2	19	75
11	CH=NOH, OMe	CH=O, OMe	14	85
12	CH=NOH, OMe	CH=O, OMe	15	82

well-known that the photocatalytic reactions in aqueous solution proceed mainly by the contributions of active oxygen species, such as ˙OH, $O_2^{˙-}$ and HO_2˙.

These species are formed by interaction of e⁻ representing photoinduced conduction band electrons and photoinduced valence band holes with O_2 or other

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TABLE 1 Continued

Entry	Substrate	Product[a]	Time/h	Yield (%)[b]
13	NOH (cyclohexanone oxime)	O (cyclohexanone)	20	84
14	NOH ‖ n-C$_7$H$_{15}$-CH	O ‖ n-C$_7$H$_{15}$-CH	22	75

SCHEME 2

oxidants such as hydrogen peroxide in aqueous solution. Since, the reaction ability of ·OH radicals is high enough to attack any organic molecules, it has been assigned as a key species in the oxidation mechanism of many hazardous chemical compounds. But for the non-destructive oxidation of organic compounds acetonitrile is the best solvent because itself don't involve in the photochemical reactions. For accelerating the reaction aqueous acetonitrile was used instead of pure acetonitrile. Other solvents such as alcohol, dichloromethane, chloroform and carbon tetrachloride with entrance in the reaction lower the efficiency of the oxidation reaction. Methanol and ethanol consume oxidant species to undergo oxidation themselves, therefore decrease effective oxidation of the oximes. All experiments were performed at room temperature.

In obtained optimum conditions the photocatalytic reactions (SCHEME 1) proceed efficiently in high yields. To the best of our knowledge this is the first report of the regeneration of aldehydes and ketones from oximes using ZnO/H_2O_2 system.

The results are summarized in TABLE 1. As shown in TABLE 1 electron withdrawing substituents have longer reaction time than electron donor substituents due to resistance to oxidation probably because of unstable intermediate of them during the progress of

the reactions. Also aliphatic oxime are deoximated in longer reaction time with respect to benzylic oximes because of stability of benzylic intermediate formed during the deoximation of benzylic oximes. SCHEME 2 shows brief summary of photo-deximation mechanism, in this way that under irradiation, photocatalyst is excited and electron/hole(h$^+$) couples are formed. Both electrons and holes produce active species (OH$^-$, OH·, HOO·) during the oxidation or reduction of H_2O_2 that they attack to oxidize the oximes sequently to corresponding carbonyl compounds.

CONCLUSION

In this paper we investigated utility of a photocatalytic system including photocatalyst/H_2O_2 for photodeoximation of some oxime compounds in various solvents. The carbonyl compounds were regenerated from the related oximes in the presence of $ZnO(50mg)/H_2O_2$ in aqueous acetonitrile in good to excellent yields in 14-22 hours. The oximes showed relatively good photostability under irradiation conditions.

ACKNOWLEDGMENT

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