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Photocatalyzed Oxidation of Triphenyl Derivatives of P, As, Sb & Bi and Reduction of Their Oxides

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Introduction

Heterogeneous photocatalysis provides the means not only for utilizing solar energy but also for new synthetic routes[1,2] and pathways of degradation of industrial wastes.[3] Particulate semiconductors suspended in solution or metal-doped semiconductors[2] such as TiO_2, CdS, ZnO, Fe_2O_3, WO_3, Pt/TiO_2, Ag/TiO_2, colloidal TiO_2, etc., have attracted the attention of many chemists as several reactions which are inaccessible by other means may be accomplished through heterogeneous photocatalysis. For instance the formidable reduction of sulfonyl group in aryl methyl sulfones has been achieved by us smoothly on the surface of irradiated TiO_2.[4]

TiO_2 is widely used as the semiconductor phtotocatalyst in many organic reactions due to its nontoxic nature, chemical stability, availability, and capability of repeated use without substantial loss of catalytic activity.[2] Irradiation of TiO_2 using low energy UV radiation (λ >350 nm) induces the formation of an electron-hole pair (e^-−h^+). The electron is promoted from the valence band to the conduction band readily available for transference while the positive equivalent, the hole (h^+) in the valence band, is ready to accept the electron from the substrate.[5] The substrate that receives the electron from the semiconductor would be reduced whereas that which donates the electron to the semiconductor is oxidized.

Though semiconductor-photoinduced oxidation of several organic compounds has been studied,[2] there are only a few reports of photosensitized reductions such as reduction of aldehydes and ketones,[6] nitroaromatics,[7] and aryl methyl sulfones.[4] The limited success of organic reductions on semiconductor surfaces may be attributed to the modestly negative potential of electrons at the conduction band of the semiconductor and the ease of oxygen reduction by electrons.[5]

To the best of our knowledge there appears to be no report on the photocatalyzed oxidation of organo-group VA compounds, Ar_3M, and herein we present our results on the TiO_2-sensitized photooxidation of triphenylphosphine, tri-*p*-tolylarsine, triphenylstibine, and triphenylbismuthine.

Though triphenylphosphine has been extensively employed as a deoxygenating agent,[8] not much attention has been paid to the reduction of the oxide. Only a few attempts have been made to reduce the oxides, Ar_3MO.[9] Handa et al.[10] reduced Ph_3PO to Ph_3P using the SmI_2−THF−HMPA system. Our report here includes deoxygenation of Ar_3MO on the surface of illuminated TiO_2 in an organic solvent in the presence of triethylamine (TEA).

Results and Discussion

Oxidation. Triphenylphosphine and triphenylstibine have been oxidized to their corresponding oxides in yields >75% in 30 min in methanol (Table 1). The oxidation product of triphenylstibine was found to be a polymer having high mp (>280 °C) in accordance with the previous report.[12] On the other hand, triphenylbismuthine and tri-*p*-tolylarsine were oxygenated to the extent of 50−65%. However, the yield of the oxygenated product increased with longer irradiation time.

By considering the yield of the oxide at 30 min, the relative order of reactivity is found to be $Ph_3P > Ph_3Sb > (p\text{-}CH_3C_6H_4)_3As > Ph_3Bi$. During our extensive studies on the mechanism of oxidation of Ar_3M by isostructural and isoelctronic oxidants peroxodisulfate[13] and peroxodiphosphate,[12] we observed the same order of reactivity.

We propose the following mechanism for the photocatalyzed oxidation of Ar_3MO, analogous to the oxidation of organic sulfides.[14]

$$\mathrm{TiO_2} \xrightarrow{h\nu} \mathrm{TiO_2(h^+)} + \mathrm{e^-}$$

$$\mathrm{O_2} + \mathrm{e^-} \rightarrow \mathrm{O_2^{\bullet -}}$$

$$\mathrm{Ar_3M} + \mathrm{TiO_2(h^+)} \rightarrow \mathrm{Ar_3M^{\bullet +}} + \mathrm{TiO_2}$$

$$\mathrm{Ar_3M^{\bullet +}} + \mathrm{O_2^{\bullet -}} \rightarrow [\mathrm{Ar_3M^+OO^-}] \xrightarrow{\mathrm{Ar_3M}} 2\mathrm{Ar_3MO}$$

While the photocatalyzed oxidation of Ar_3As and Ar_3Bi yields 14% and 16% of other products in 30 min, these products decrease with a longer period of irradiation, implying that they have been converted to Ar_3MO. One possible explanation is that in these cases, the miscellaneous products may contain a major amount of Ar_2MO_2Ar which may decompose on prolonged irradiation to give Ar_3MO. Though we are investigating this aspect in detail, in the photolysis of Ph_3Sb in the presence of oxygen in benzene, the formation of Ph_2SbO_2Ph has been postulated.[15]

Reduction. Photolysis of a solution of Ar_3MO in an organic solvent purged with nitrogen in the absence of either TiO_2 or TEA or both has not resulted in any reduced product. Only in the presence of both photocatalyst and TEA, the deoxygenated products have been obtained (Table 2). TEA functions as a sacrificial electron donor which prevents electron-hole recombination process by trapping the hole (h^+) effectively.[2] While 4 h

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Table 1. Photooxidation[a] of Triaryl Group VA Compounds (Ar_3M) on TiO_2 in Methanol

substrate		irr time	product mixture (%)[b]		
Ar	M	(min)	Ar_3M	Ar_3MO	X[c]
phenyl	P	15	16	75	9
phenyl	P	30	9	82	9
phenyl	Sb	30	15	77[d]	8
p-tolyl	As	30	22	64	14
phenyl	Bi	30	32	52	16
p-tolyl	As	90	15	74	11
phenyl	Bi	120	21	74	5

[a] Irradiated using 350 nm/400 W annular reactor. Catalyst (TiO_2): 1%. Solvent: 15 mL, oxygen-saturated. [b] GC analysis results. Error limit: ±5%. [c] Other products including diaryl derivatives. [d] The oxidation product was a polymer.[12]

Table 2. TiO_2-Photosensitized[a] Deoxygenation of Triaryl Group VA Oxides (Ar_3MO) in the Presence of Triethylamine

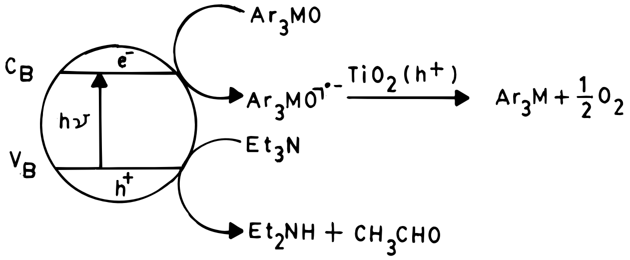
substrate		irr		product mixture (%)[b]		
Ar	M	time	solvent	Ar_3M	Ar_3MO	X[c]
phenyl	P	4 h	MeOH	25	57	18
phenyl	Sb	4 h	MeOH	19	69	12
p-tolyl	As	4 h	MeOH	25	56	19
phenyl	Bi	4 h	MeOH	36	46	18
phenyl	Bi	30 min	DMF	35	46	19
p-tolyl	As	30 min	DMF	26	55	19
phenyl	Sb	30 min	DMF	20	68	12
phenyl	P	30 min	DMF	24	57	19

[a] Irradiated using 350 nm/400 W immersion reactor. Catalyst (TiO_2): 1%. TEA: 0.5%. Solvent: 200 mL. Nitrogen purging for 45 min. [b] GC analysis results. Error limit: ±5%. [c] Other products including diaryl derivatives.

of irradition of Ar_3MO in methanol yields about 20−30% of deoxygenated product, it is interesting to note that the same result is accomplished in DMF in 30 min (Table 2). It may be due to the electron-donating capacity of DMF and the availability of more electrons for reduction.[16] The sacrificial electron donor TEA has been converted to diethylamine and acetaldehyde as reported in the reduction of organic substrates by illuminated CdS in the presence of TEA.[16]

On the basis of the experimental results, we propose a plausible mechanism as shown in Scheme 1 for the photoinduced reduction of Ar_3MO in the presence of TEA on TiO_2. The formation of oxygen has been confirmed by GC analysis of the evolved gas.

Scheme 1. Plausible Mechanism of the Photoinduced Reduction of Ar_3MO (M = P, As, Sb, or Bi) in the Presence of TEA on TiO_2



Experimental Section

Triphenylphosphine (Riedel, pyrosynth), triphenylstibine (Aldrich), and triphenylbismuthine (Aldrich) were recrystallized from ethanol. Tri-*p*-tolylarsine was prepared by reported methods.[11] Hydrogen peroxide oxidation of the above subtrates yielded the oxides.[12] TiO_2 (anatase, Aldrich, 99.9%) was used as the photocatalyst. All the solvents employed were AR/HPLC grade. The commercial BDH sample of triethylamine was purified by distillation.

Oxidation. One millimolar solution of Ar_3M in methanol (15 mL) containig suspended TiO_2 (0.15 g) was saturated with oxygen and irradiated with a 400 W medium pressure mercury vapor lamp ($\lambda > 350$ nm) in an annular reactor with water filter.

Reduction. Reduction of Ar_3MO (1 mM) was performed in presence of TEA (0.5 M) using 2 g of TiO_2 suspended in methanol or acetonitrile (200 mL). An immersion type reactor with a medium pressure mercury vapor lamp (400 W, 350 nm) with a water filter was employed here, and the reaction mixture was continuously stirred using a magnetic stirrer. Before irradiation, the solution was purged with nitrogen for 45 min.

Product Analysis. The reaction mixture, after removing the catalyst by centrifugation followed by filtration, was analyzed by gas chromatograph (NETEL, India) fitted with Dexil 300 GC column and FID.

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