Amines are used as sacrificial single-electron donors in many photoinduced redox studies. A set of experiments simultaneously to compare the results.

The intensity of sunlight is overcome by carrying out a set of experiments simultaneously to compare the results. The yield of the product is higher with illumination at 254 rather than at 365 nm. Electron donors enhance photocatalysis and singlet oxygen quencher fails to inhibit catalysis. Photocatalysis occurs in protic as well as aprotic solvents. The mechanism of photocatalysis is discussed and the product formation analysed using a kinetic model.

Photocatalytic processes over semiconductor powders continue to receive considerable interest from the standpoint of solar energy utilization, but only a few studies involve natural sunlight, which are preliminary. TiO$_2$ and ZnO are the most widely used photocatalysts, but they require UV light for activation; solar UV light reaching the earth surface is relatively small (ca. 3–5%). Use of dye-sensitizers improves the performance of the photocatalyst and extends its light-absorption capacity to the visible portion of the solar spectrum. However, the problem in chemical transformations is the cost and reuse; dye-sensitizers are only adsorbed over the photocatalyst. The bandgap energy of cadmium oxide (CdO) is 2.1 eV and can be activated only adsorbed over the photocatalyst. Photocatalysis also was carried out in a micro photoreactor (HMI SL W6, supplied by Heber Scientific) fitted with a 6 W, 254 nm, low-pressure mercury lamp and a 6 W, 365 nm mercury lamp. Quartz and borosilicate glass tubes were used for 254 and 365 nm lamps respectively.

The light intensity ($I_0$) was determined by ferrioxalate actinometry.

The volume of the reaction solution was always maintained as 25 ml in the multilamp photoreactor and 10 ml in the micro reactor. Air was bubbled through the reaction solution that effectively stirs the solution and keeps the suspended catalyst under constant motion. Absorbance was measured at 375 nm after centrifuging the catalyst and diluting the solution five times to keep the absorbance within the limits of the Beer–Lambert law.

Solar photocatalysis of aniline in ethanol on CdO yields azobenzene as the only product. The GC-mass, IR and UV–Vis spectra of the extracted solid product are identical with those of trans-azobenzene (Fluka).

In both solar and UV photocatalysis, the UV–Vis spectra of the reaction solution recorded during the progress of the reaction are similar (Figure 1; $\lambda_{max}$ = 375 nm), but not identical with that of the extracted solid product ($\lambda_{max}$ = 434 nm). This is because of the formation of both cis and trans-azobenzzenes during the course of the reaction, and the unstable cis form ($Z$) transforms to the trans form ($E$) slowly on standing. The UV–Vis spectrum of the irradiated reaction solution allowed to stand for a few days in dark is identical with that of the authentic trans-azobenzene,

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Cadmium oxide (CdO) photocatalyses the oxidation of aniline to azobenzene and shows sustainable catalytic activity. The reaction in ethanol was studied with natural sunlight and UV irradiation (365 nm) as a function of aniline, catalyst loading, airflow rate, solvent composition, etc. The effects on the rate of solar oxidation are similar to those with UV light. The problem of fluctuation of sunlight intensity is overcome by carrying out a set of experiments simultaneously to compare the results.

The solar photocatalysed oxidations were made from 10.30 a.m. to 12.30 p.m. during summer (March–July) under clear sky. The intensity of solar radiation was measured using Global pyranometer, MCPT, supplied by Industrial Meters, Mumbai. Fresh solutions of aniline of desired concentrations were taken in wide cylindrical glass vessels of uniform diameter and appropriate height; the catalyst powder covered the entire bottom of the vessel. Air was bubbled using a micro pump without disturbing the catalyst bed. The volume of the reaction solution was kept as 25 ml and the loss of solvent due to evaporation was compensated periodically. One millilitre of the reaction solution was withdrawn at regular intervals, diluted five times and the absorbance measured at 375 nm using Hitachi U-2001 UV–Vis spectrophotometer.

Photocatalytic studies with UV light were carried out in a multilamp photoreactor (HMI MP88, supplied by Heber Scientific, Chennai) fitted with eight 8 W mercury UV lamps of wavelength 365 nm (Sankyo Denki, Japan) and highly polished anodized aluminum reflector; the sample was placed at the centre. Four cooling fans at the bottom of the reactor dissipate the generated heat. The reaction vessel was a borosilicate glass tube of 15 mm inner diameter. Photooxidation was also carried out in a micro photoreactor (HMI SL W6, supplied by Heber Scientific) fitted with a 6 W, 254 nm, low-pressure mercury lamp and a 6 W, 365 nm mercury lamp. Quartz and borosilicate glass tubes were used for 254 and 365 nm lamps respectively.

The light intensity ($I_0$) was determined by ferrioxalate actinometry.

The volume of the reaction solution was always maintained as 25 ml in the multilamp photoreactor and 10 ml in the micro reactor. Air was bubbled through the reaction solution that effectively stirs the solution and keeps the suspended catalyst under constant motion. Absorbance was measured at 375 nm after centrifuging the catalyst and diluting the solution five times to keep the absorbance within the limits of the Beer–Lambert law.

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confirming the slow transformation of the unstable cis form to trans form. For a solution of cis and trans-azo-benzenes,

\[
\begin{align*}
[E] &= \frac{\text{abs}_{281}(E_{281}) - \text{abs}_{433}(E_{281})}{(E_{281}) - (E_{433})} \\
[Z] &= \frac{\text{abs}_{281}(E_{433}) - \text{abs}_{433}(E_{281})}{(E_{281}) - (E_{433})}
\end{align*}
\]

where \(e\) is the corresponding molar extinction coefficient.

Calculation of the ratio \([E]/[Z]\) using the above equations,

\[
\text{The experimentally determined } E_{E_{433}} \text{ and } E_{E_{281}}, \text{ the reported } E_{Z_{433}} \text{ and } E_{Z_{281}} \text{ and the measured absorbance of the reaction solution at 433 and 281 nm at different periods of the reaction shows that the ratio remains practically the same (1.86) during the course of photooxidation. The total concentration of azobenzene, } (\langle E \rangle + \langle Z \rangle) = \text{abs}_{375}\{1 + (\langle E \rangle/\langle Z \rangle)\}/(\langle Z_{375} \rangle + \text{abs}_{375}(\langle E \rangle/\langle Z \rangle)); \text{ } E_{E_{375}} \text{ was determined experimentally and } E_{Z_{375}} \text{ calculated from the measured abs}_{375}; \text{ abs}_{375} = (\langle E_{375} \rangle + \text{abs}_{375}(\langle E \rangle/\langle Z \rangle))\langle Z \rangle).
\]

The measurement of solar radiation shows fluctuation of sunlight intensity (530 ± 40 W m\(^{-2}\)) during the course of photooxidation, even under clear sky. Now, identical sunlight intensity was maintained for a set of photooxidation experiments of different reaction conditions by performing the experiments simultaneously, thus making possible the comparison of the solar results. The solar photooxidation results are reproducible. For example, Figure 2 is the linear increase of absorbance of the reaction solution with reaction time; one set of experiments was conducted in ethanol and benzene side by side on one day and the other set similarly on another day. The ratio of the slopes of the absorbance–time profiles of the reactions in ethanol and benzene remains the same (1.5), although the experiments were conducted on different days, obviously under different sunlight intensities. This reproducibility is not surprising, as the fluctuation of sunlight intensity is identical in test and control (standard) experiments and the ratio turns out to be independent of fluctuation of intensity. Further, the results of a pair of experiments performed simultaneously confirm the reproducibility of the rates of solar photocatalysis. Figure 3 presents the solar photoformation of azobenzene...
in ethanol under identical conditions and carried out simultaneously. The ratio of the rates obtained from the linear plots is unity (1.04).

The influence of various factors on the solar photocatalysis in ethanol was examined by carrying out the given set of experiments simultaneously; data in each figure correspond to a set of photocatalytic experiments conducted simultaneously. The least squares slope of the linear plot of [azo-benzene] versus time (e.g. Figure 3) yields the rate of formation of azobenzene. Experiments at different concentrations of aniline show that the reaction rate increases with [aniline] (Figure 4) and the variation conforms to the Langmuir–Hinshelwood model. The double reciprocal plot of rate versus [aniline] yields a straight line with a positive y-intercept. The variation in the amount of CdO spread at the bottom of the reaction vessel (catalytic bed) does not lead to any appreciable change in the photocatalysis rate (Figure 5); the bottom of the cylindrical reaction vessel was fully covered by the catalyst in all the cases and increase in the amount of CdO does not lead to increase in the area of the catalyst bed, but only results in increased thickness of the CdO bed. In the absence of the photocatalyst, the reaction is an uncatalysed one and hence the small rate. The photoformation of azobenzene increases linearly with the apparent area of the catalyst bed (Figure 6). Study of the photooxidation as a function of airflow rate reveals enhancement of photocatalysis by oxygen (Figure 7). The variation of reaction rate with airflow rate indicates Langmuir–Hinshelwood kinetics and the linear double reciprocal plot of reaction rate versus airflow rate confirms the same. The reaction was also studied without bubbling air, but the solution was not deaerated. The dissolved oxygen itself brings in the oxidation, but the photocatalysis is weak. The reaction does not occur in dark. The photocatalyst does not lose its catalytic activity on repeated use. Reuse of the photocatalyst yields identical results. Addition of water to the reaction medium slows down the reaction (Figure 8).

Electron donors like triphenylphosphine (TPP), hydroquinone (HQ), diphenylamine (DPA) and triethylamine (TEA), enhance the photoformation of azobenzene. Addition of 0.287 M TEA to the reaction solution increases the azobenzene formation rate by ca. 165% (the reaction conditions as in Figure 9). Variation of the enhanced photoformation rate with [TPP], [HQ] and [DPA] (Figure 9) reveals the Langmuir–Hinshelwood kinetics, and the linear double reciprocal plots of the enhanced rate versus [TPP], [HQ] and [DPA] confirm the same. Use of sacrificial electron donors leads to hole-trapping, resulting in enhanced photocatalysis. Both anionic and cationic surfactants enhance the photocatalysis; addition of aerosol OT (sodium bis-2-ethylhexyl sulphonate, 0.0225 M), sodium laureyl

![Figure 4](image4.png)

Figure 4. Azobenzene formation in ethanol on CdO at different [aniline]; weight of CdO = 1.0 g, volume of reaction solution = 25 ml, airflow rate = 4.75 (solar), 7.8 (UV) ml s\(^{-1}\); solar: CdO bed = 12.5 cm\(^2\); UV: \(\lambda = 365\) nm, \(I_0 = 2.46 \times 10^{-5}\) einstein l\(^{-1}\) s\(^{-1}\).

![Figure 5](image5.png)

Figure 5. Azobenzene formation in ethanol at different amounts of CdO loading; [aniline] = 0.113 M, volume of reaction solution = 25 ml, airflow rate = 4.75 (solar), 7.8 (UV) ml s\(^{-1}\); solar: CdO bed = 12.5 cm\(^2\); UV: \(\lambda = 365\) nm, \(I_0 = 2.46 \times 10^{-5}\) einstein l\(^{-1}\) s\(^{-1}\).

![Figure 6](image6.png)

Figure 6. Azobenzene formation (solar) in ethanol at varying areas of CdO bed; [aniline] = 0.113 M, weight of CdO = 1.0 g, volume of reaction solution = 25 ml, airflow rate = 4.75 ml s\(^{-1}\).
sulphate (SLS, 0.0347 M) and cetyltrimethylammonium bromide (CTAB, 0.0274 M) to the reaction solution (conditions as in Figure 9) increases the photoformation rate by 21, 127 and 83% respectively. Vinyl monomers like acrylonitrile (0.608 M) and acrylamide (0.141 M) neither suppress the photocatalysis nor undergo polymerization, indicating the absence of free radicals in the reaction solution during the course of photocatalysis.

CdO photocatalyses the oxidation in n-butanol, t-butanol, propane-1,2-diol, 2-butoxyethanol, ethyl methyl ketone, acetic acid, dimethylformamide, acetonitrile, ethyl acetate, 1,4-dioxane, benzene, toluene, chlorobenzene, nitrobenzene, n-hexane, chloroform and carbon tetrachloride, besides ethanol as seen from the UV–Vis spectra of the reaction solutions at different illumination times ([PhNH$_2$] = 0.113 M, CdO suspended = 1.0 g, airflow rate = 7.8 ml s$^{-1}$, $\lambda = 365$ nm, $I_0 = 2.46 \times 10^{-5}$ einstein l$^{-1}$ s$^{-1}$, volume of reaction solution = 25 ml).

The photocatalysed oxidation of aniline in ethanol in the presence of air on CdO was studied using a multilamp photoreactor with mercury UV lamps of wavelength 365 nm. Linear increase of azobenzene concentration with illumination time yields the photochemical formation rate (e.g. Figure 3) and the rates are reproducible to ±6%. Rate measurements at different [aniline] show increase in the oxidation rate with [aniline] (Figure 4) and the increase is

![Figure 7](image7.png)  
**Figure 7.** Azobenzene formation in ethanol on CdO at different airflow rates: [aniline] = 0.113 M, weight of CdO = 1.0 g, volume of reaction solution = 25 ml; solar: CdO bed = 12.5 cm$^2$; UV: $\lambda = 365$ nm, $I_0 = 2.46 \times 10^{-5}$ einstein l$^{-1}$ s$^{-1}$.

![Figure 8](image8.png)  
**Figure 8.** Azobenzene formation on CdO in aq. EtOH; [aniline] = 0.113 M, weight of CdO = 1.0 g, airflow rate = 7.8 ml s$^{-1}$, $\lambda = 365$ nm, $I_0 = 2.46 \times 10^{-5}$ einstein l$^{-1}$ s$^{-1}$.

![Figure 9](image9.png)  
**Figure 9.** Azobenzene formation in ethanol on CdO in the presence of electron donors (ED); [aniline] = 0.113 M, weight of CdO = 1.0 g, volume of reaction solution = 25 ml, airflow rate = 4.75 (solar), 7.8 (UV) ml s$^{-1}$; solar: CdO bed = 12.5 cm$^2$; UV: $\lambda = 365$ nm, $I_0 = 2.46 \times 10^{-5}$ einstein l$^{-1}$ s$^{-1}$.

![Figure 10](image10.png)  
**Figure 10.** Azobenzene formation in ethanol on CdO at different light intensities; [aniline] = 0.113 M, CdO suspended = 1.0 g, airflow rate = 7.8 ml s$^{-1}$, $\lambda = 365$ nm, volume of reaction solution = 25 ml.
according to the Langmuir–Hinshelwood kinetics. Increase in the amount of CdO suspended in the reaction medium leads to increased azobenzene formation, but the rate reaches a limit at high catalyst loading (Figure 5). Study of the photooxidation as a function of airflow rate reveals enhancement of photocatalysis by oxygen and the variation of the reaction rate with flow rate conforms to the Langmuir–Hinshelwood kinetics (Figure 7). The reaction was also studied without bubbling air, but the solution was not deoxygenated. The dissolved oxygen itself brings in the oxidation, but the photocatalysis is slow.

The photooxidation was examined as function of light intensity. Oxidation was carried out on two, four and eight lamps; the angles sustained by the adjacent lamps at the sample are 180, 90 and 45° respectively. Figure 10 presents the variation of rate with light intensity. The reaction does not occur in dark. Investigation of photocatalysis using a 6 W, 365 nm mercury lamp (I₀ = 1.81 × 10⁵ einstein 1⁻¹ s⁻¹) and a 6 W, 254 nm, low-pressure mercury lamp (I₀ = 5.22 × 10⁶ einstein 1⁻¹ s⁻¹) separately in the micro reactor under identical conditions reveals that high-energy radiation is more effective in bringing out the photocatalysis. Azobenzene formed in 10 min on illumination at 365 and 254 nm is 95 and 363 μM respectively, ([aniline] = 0.113 M, CdO suspended = 0.2 g, airflow rate = 7.8 ml s⁻¹, volume of reaction solution = 10 ml). The metal oxide does not lose its photocatalytic activity on illumination. Reuse of the catalyst reveals sustainable photocatalytic efficiency. Addition of water to the reaction solution suppresses the photocatalysis (Figure 8).

Electron donors like TPP, HQ, DPA and TEA enhance azobenzene formation. Variation in the enhanced photooxidation rate with [TPP], [HQ] and [DPA] suggests Langmuir–Hinshelwood kinetics (Figure 9). Addition of TEA (0.287 M) to the reaction mixture doubles the rate of azobenzene formation. Aerosol OT (0.0225 M), SLS (0.0347 M) and CTAB (0.0274 M) enhance photocatalysis with UV light by 82, 67 and 16% respectively. Also, vinyl monomers like acrylonitrile (0.608 M) and acrylamide (0.141 M) fail to inhibit the photocatalysis, nor do they polymerize. Azide ion (0.154 M), a singlet oxygen quencher, fails to suppress the formation of azobenzene, indicating the absence of involvement of singlet oxygen in photocatalysis (conditions as in Figure 9).

Photooxidation on CdO surfaces with UV light also occurs in n-butanol, t-butanol, propane-1,2-diol, 2-butoxyethanol, ethyl methyl ketone, acetic acid, dimethylformamide, acetonitrile, ethyl acetate, 1,4-dioxane, benzene, toluene, chlorobenzene, nitrobenzene, n-hexane, chloroform and carbon tetrachloride, as shown by the UV–Vis spectra of the reaction solutions at different illumination times.

The bandgap energy of CdO is 2.1 eV. Illumination of the semiconductor with light of energy greater than the bandgap leads to bandgap excitation of the semiconductor, resulting in the creation of electron–hole pairs; holes in the valence band and electrons in the conductance band. Since the recombination of photogenerated electron–hole pairs in semiconductors is so rapid (occurring in a picosecond timescale), for an effective photocatalysis the reactants are to be adsorbed on the photocatalyst. The hole reacts with adsorbed aniline molecule to form aniline radical-cation (PhNH₂⁺). In the presence of oxygen, transfer to the adsorbed oxygen molecule resulting in highly active superoxide radical-anion, O₂⁻, effectively removes the electron. The reaction of aniline radical-cation with superoxide radical-anion results in nitrosobenzene. Condensation of nitrosobenzene with aniline, present in large excess, yields azobenzene.

\[
SC + hv \rightarrow h_{(vb)}^\bullet + e_{(cb)}^\bullet
\]
\[
\text{PhNH}_2\text{(ads)} + h_{(vb)}^\bullet \rightarrow \text{PhNH}_2^+
\]
\[
\text{O}_2\text{(ads)} + e_{(cb)}^\bullet \rightarrow \text{O}_2^-
\]
\[
\text{PhNH}_2^+ + \text{O}_2^- \rightarrow \text{PhNO} + \text{H}_2\text{O}
\]

Ethanol may undergo oxidation in the presence of an illuminated semiconductor and generation of radicals is possible. If the photooxidation of aniline were due to the radicals generated from solvent ethanol, contrary to the experimental observations, azobenzene formation should not depend on [aniline]. The photogenerated radicals are short-lived and react almost instantaneously, demanding non-dependence of the reaction rate on [aniline]. Also, the oxidation occurs in a number of organic solvents.

The kinetic law that governs heterogeneous photocatalysed reaction in a continuously stirred tank reactor is,

\[
\text{Rate} = k_1K_1SI_0C[\text{PhNH}_2]\gamma(1 + K_1[\text{PhNH}_2])(1 + K_2\gamma),
\]

where \(K_1\) and \(K_2\) are the adsorption coefficients of aniline and oxygen on CdO, \(k\) is the specific rate of oxidation of aniline, \(S\) is the specific surface area of CdO, \(C\) is the amount of CdO suspended per litre and \(I_0\) is the light intensity in einstein 1⁻¹ s⁻¹. The linear double reciprocal plots of rate of azobenzene formation versus (i) [PhNH₂] and (ii) airflow rate are in agreement with the kinetic law and afford the adsorption coefficients as \(K_1 = 23\ \text{mol}^{-1}\), \(K_2 = 0.08\ \text{ml}^{-1}\) s⁻¹; \(k = 20\ \mu\text{mol} 1\ \text{m}^2\ \text{einsteins}^{-1}\). The data-fit to the curves (Figures 4 and 7), drawn according to the above kinetic law using a computer program, supports the rate equation. However, the rate of photocatalysis fails to vary linearly with the amount of CdO suspended. This is because of the high catalyst loading. At high catalyst loading, the surface area of the catalyst exposed to illumination does not commensurate with the weight of the catalyst. The amount of CdO employed is beyond the critical amount corresponding to the volume of the reaction solution and reaction vessel; the whole amount of CdO is
not exposed to illumination. Photocatalysis lacks linear dependence on illumination intensity; less than first power dependence on illumination intensity. Photocatalysis lacks linear dependence on illumination intensity.


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**Angiotensin-converting enzyme insertion/deletion genotype is associated with premature coronary artery disease in Indian population**

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The insertion/deletion polymorphism of angiotensin-converting enzyme (ACE) gene has been implicated in the pathogenesis of cardiovascular diseases. However, the precise association between them remains unclear. The objective of the present study was to find the influence of angiotensin-converting enzyme (insertion/deletion) polymorphism on cardiovascular diseases. We genotyped the Alu insertion/deletion of the ACE gene in 434 patients and 500 control subjects. Information on severity of vessel disease, clinical status, age, smoking and alcohol status, lipid profile and body mass index was also collected. The present study indicated a significant association of coronary artery diseases (CADs) with Alu ACE insertion/deletion polymorphism, located in the intron 16 region of the ACE gene. Thus, we identified a clinical subgroup of CAD patients, characterized with triple vessel defect and most often associated with diabetes.

ANGIOTENSIN-converting enzyme (EC 3.4.15.1; dipetidyl carboxypeptidase) is a zinc metallopeptidase which cleaves the C-terminal dipeptide (His-Leu) from angiotensin I and generates a vasoconstrictor¹, angiotensin II. Through protease activity it also inactivates bradykinin, which is a potent vasodilator. Due to its role in the renin-angiotensin—aldosterone system, human vascular tone and blood salt/water balance have been maintained. The gene for angiotensin converting enzyme (ACE) has been mapped to chromosome 17q23 and comprises 26 exons and 25 introns²-³. The activity of ACE was strongly influenced by a quantitative trait locus which is in linkage disequilibrium with the Alu insertion/deletion (I/D) marker⁴-⁷ in intron 16. A relationship between D-allele dose and enzymatic levels was established for both circulating and cellular ACE⁸-¹⁳. Numerous studies reported association of D-allele with cardiovascular diseases¹⁴-¹⁷, in addition to the diseases like non-insulin-dependent diabetes mellitus, nephropathy¹⁸-²⁰, knee osteoarthritis²¹ and breast cancer²²,²³. However, this association was not observed in all the studies²⁴-²⁹. Thus, there has been a considerable controversy over the association of ACE (I/D) polymorphism and disease status. Also, the influence of the

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