Effect of Some Amides & Amines on the Photocatalysed Reaction of Benzyl Alcohol on Zinc Oxide

E. P. YESODHARAN, V. RAMAKRISHNAN & J. C. KURIACOSE*

Department of Chemistry, Indian Institute of Technology, Madras 600036

Nitrogen containing compounds like amides and amines strongly inhibit the photocatalysed reactions of alcohols on zinc oxide. The amides form stable surface complexes with zinc oxide which may be responsible for the inactivation while the amines trap the free radicals responsible for the propagation of the reaction. Based on these observations it is proposed that there are two distinct processes in the photocatalysed reactions; the heterogeneous process, taking place on the surface of the catalyst, which initiates the reaction and the homogeneous process which propagates the reaction. A mechanism consistent with the observations is proposed and discussed.

THE mechanism of photocatalysed reactions of alcohols on oxide catalysts has not been extensively investigated. It is known that the dehydrogenation of isopropanol on irradiated zinc oxide proceeds through free radicals[1,2]. Detailed studies on this system revealed that oxygen is essential for the process[3]. The reaction rate was enhanced by increase in polarity of the solvent[3]. However, the reaction is found to proceed very slowly in solvents like formamide in spite of their higher dielectric constants. Hence a detailed investigation of the effect of various amides and other nitrogen containing compounds like amines on the photocatalysed reactions is undertaken employing the photodehydrogenation of benzyl alcohol as the test reaction. Results are presented in terms of the hydrogen peroxide formed in presence of various nitrogen containing compounds. The present work is chiefly concerned with the production of H_2O_2 from hydrogen containing compounds because of its importance as a possible means of storing solar energy in the form of chemical energy[4].

Materials and Methods

A Hanovia high pressure quartz mercury arc was used as the light source. Radiations above 3800 Å are not absorbed by ZnO as is revealed by its reflectance spectrum. The lamp is mounted horizontally above a mechanical shaker and provided with an aluminium foil shade to reflect the light downwards. The intensity of the lamp was measured by benzophenone-benzhydrol actinometry[5] and found to be 2.5×10^{-6} einsteins litre^{-1} sec^{-1}. The reaction vessel consisted of a pyrex tube with an opening for introducing the solids and liquids and a small side tube for bubbling gases. This was provided with an outer jacket through which water at the desired temperature was circulated. Catalyst (0.35 g), observed to be the critical amount, and the liquid (30 ml) under investigation were taken

in the reaction vessel which was then clamped to the platform of the mechanical shaker and shaken throughout the experiments. Samples were removed from the tube at various intervals and analysed. H_2O_2 was estimated by iodometry[1]. Other products have been identified as benzaldehyde and toluene by gas chromatography.

All the chemicals were purified by standard methods. The purity was confirmed by gas chromatography in the case of liquids and by melting points in the case of solids.

Infrared spectra were recorded either in thin films in the case of liquid or in KBr matrix in the case of solids on a Perkin-Elmer 257 spectrometer.

Results and Discussion

The reactions of benzyl alcohol on a zinc oxide catalyst irradiated at 3650 Å were carried out in acetonitrile solvent. The reaction does not proceed when the sample is irradiated in the absence of oxygen and also when treated with oxygen in the absence of irradiation, suggesting that both light and oxygen are essential for the reaction[3,6]. Under identical conditions of irradiation and oxygen concentration the reaction is very slow in an amide solvent. A few observations were made with the amides present in the system as another solute. The effect of various concentrations of formamide on the reaction is shown in Fig. 1. It is seen that the rate of formation of H_2O_2 is not affected by formamide at lower concentrations ($< 0.2M$). At concentrations of the amide $> 0.5M$ the inhibition reaches a limiting value. Substitution of hydrogen on the nitrogen atom by electron releasing groups like $-CH_3$, $-C_2H_5$, etc., enhances the efficiency of inhibition while groups like $-C_6H_5$ which are electron withdrawing lower the efficiency. The effect of hydrogen attached to the carbon on the inhibition was also studied. Acetamide is slightly more effective than formamide while benzamide and urea do not have any significant effect. A comparative study of the effect of various amides on the reactions of benzyl alcohol is given in Fig. 2.

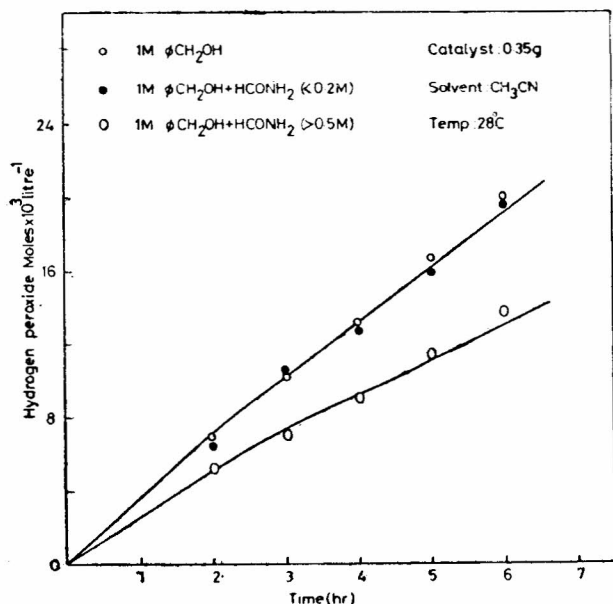*Author to whom all correspondence should be addressed.

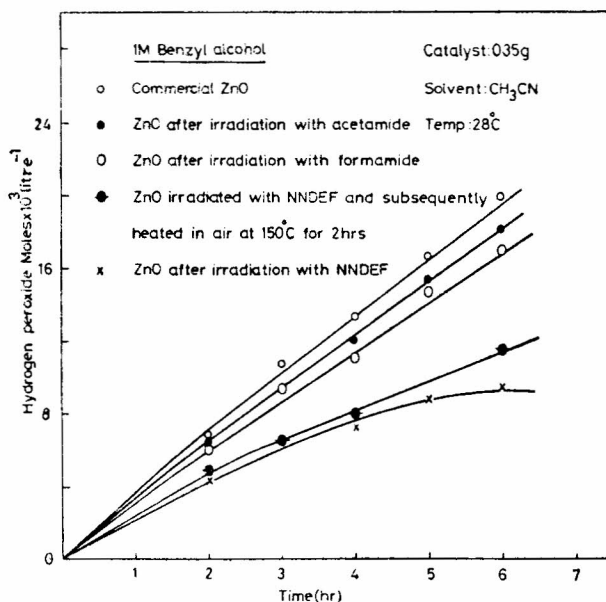Fig. 1 — Effect of formamide on the photoreaction of benzyl alcohol on ZnO

Fig. 2 — Effect of different amides on the photoreaction of benzyl alcohol on ZnO

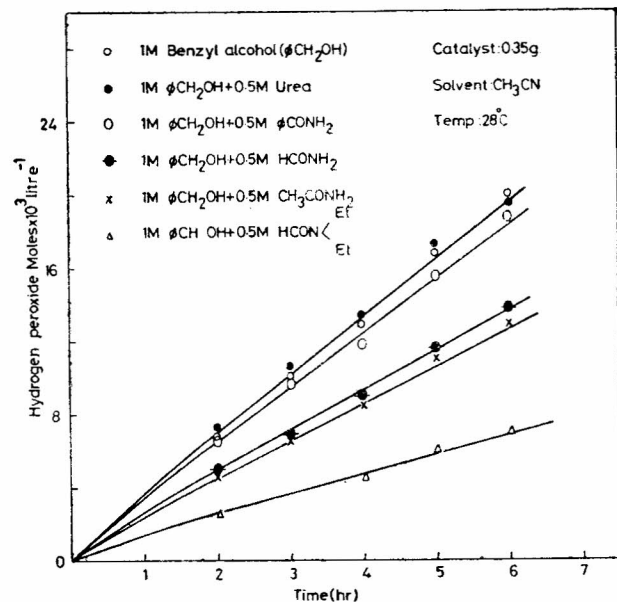Fig. 3 — Effect of preirradiation of ZnO in the presence of amides on the photocatalytic activity

TABLE 1 — C=O STRETCHING VIBRATIONS IN VARIOUS AMIDES IN THE PURE STATE AND OF A ZINC OXIDE SAMPLE IRRADIATED IN THE PRESENCE OF AMIDES

Amide	Pure amide (cm^{-1})	Amide over ZnO (irradiated) (cm^{-1})
Formamide	1650	1610
N,N-Dimethylformamide	1645	1585
N,N-Diethylformamide	1660	1620
Acetamide	1690	1660
Benzamide	1670	1670
N,N-Diphenylformamide	1670	1670

This inhibition by amide can be due to its effect either on the process at the surface of zinc oxide or on that in the homogeneous liquid phase. To see which of these possibilities is more likely a few observations were made with samples of zinc oxide which were soaked in the amides, irradiated, filtered and then used for the reactions. If the amides are affecting the surface activity of the catalyst the rate of reaction would be expected to be less in this case. The results presented in Fig. 3 suggest that the pretreated catalyst is less active than the fresh sample. It is also not just the removal of adsorbed oxygen since this sample of zinc oxide could not

regain its original activity even on treatment with oxygen at 100° for 1 hr. This shows conclusively that due to the irradiation of zinc oxide in contact with the amides a permanent charge is brought about in the zinc oxide.

Infrared spectra of zinc oxide samples, which were irradiated in the presence of amides showed that the amides remain strongly adsorbed on the zinc oxide surface. When compared with the spectra of pure amides, it is seen that except in the case of urea, benzamide and N,N-diphenylformamide the $\nu C=O$ is lower for the amides adsorbed on the surface (Table 1). Other frequencies are all identical for the pure as well as the adsorbed amides. This shows that the amides form complexes with zinc oxide through the oxygen of C=O. On irradiation of zinc oxide some of the electrons are promoted from the valence band to the conduction band and are taken up by the adsorbed oxygen resulting in O_2^-. Now the zinc oxide is left electron deficient and the amides get strongly adsorbed or bonded by donating electrons through the oxygen.

The spectrum of zinc oxide sample irradiated in the presence of urea shows that urea does not get adsorbed at all. But other amides even without

irradiation get weakly adsorbed. If the ZnO samples are not irradiated in contact with the amides the spectral bands disappear completely on washing the ZnO with the solvent while this is not the case with the irradiated samples. The inability of benzamide and urea to form complexes and their inefficiency to inhibit the reaction concerned, suggest a correlation between the two processes. The efficiency of each amide as an inhibitor can be seen from the data in Table 2.

The effect of dielectric constant of the medium on the inhibition by amides was tested by carrying out reactions in a nonpolar solvent like cyclohexane. The results are plotted in Fig. 4. Previous studies[2] have shown that the amount of H_2O_2 formed in cyclohexane increases and then decreases and again increases with time of irradiation. This oscillation in the concentration of H_2O_2 is there even in the presence of amides, but to a lesser extent. (The role of inhibitors on the phenomenon of oscillation will be dealt with in detail in a separate paper.) However, the extent of inhibition is less compared to that in acetonitrile. This supports the suggestion that the inhibition involves a polar intermediate or the transfer of electrons since a polar solvent enhances the process.

Infrared studies of nitrogenous residues by Markham et al.[7,8] revealed that formamide in water, when irradiated over zinc oxide, gives rise to a cyanate species which remains strongly adsorbed on the surface and causes the inhibition. In the studies reported here, with acetonitrile as the solvent, all the bands characteristic of the amide under consideration were present on the zinc oxide even after irradiation, except the shift in $\nu C=O$. Hence it is the amide itself by forming a complex with zinc oxide and not any species formed from it that is responsible for the observed inhibition in acetonitrile. The amides exclude the alcohol molecules from interacting with most of the zinc oxide surface. A part of the surface may still be left behind unoccupied by the amide, as is evident from the low but significant rate of reaction even in its presence. This is further confirmed by the observations presented in Fig. 5 which show the effect of addition of amides to the system during the course of the reaction. It is expected that the reaction should change to a lower rate of conversion from the point of addition since the amides should be capable

of displacing the alcohol from the surface. The experimental findings also agree with this assumption.

The donation of electrons by the amides and hence the complex formation will be facilitated by the presence of electron releasing groups either on the nitrogen or on the C of the $C=O$. This will explain the high inhibiting efficiency of diethylformamide. In this case the complex formed may be of the type (I).
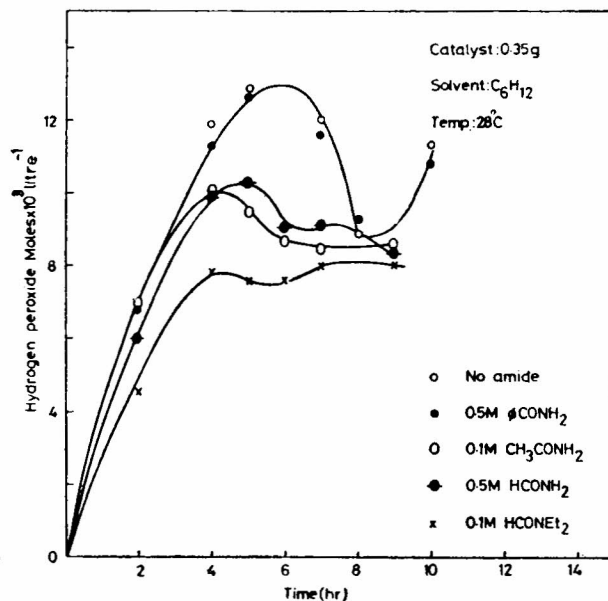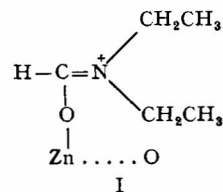
$$H-C=\overset{+}{N}\begin{matrix} CH_2CH_3 \\ CH_2CH_3 \end{matrix}$$
$$\begin{matrix} | \\ O \\ | \\ Zn \ldots O \end{matrix}$$

I

Fig. 4 — Effect of different amides on the photoreaction of benzyl alcohol in the presence of cyclohexane
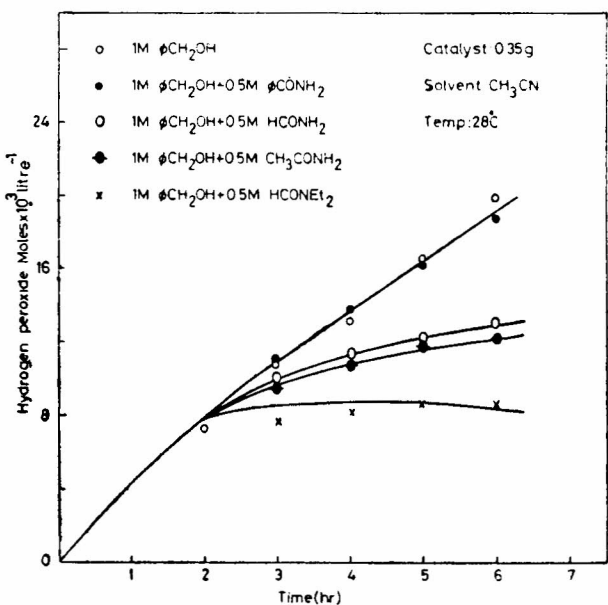
Fig. 5 — Effect of the addition of different amides during the course of the photoreaction of benzyl alcohol (addition after 2 hr)

TABLE 2 — AMOUNT OF H_2O_2 FORMED AT THE END OF 4 HOURS OF IRRADIATION IN THE PRESENCE OF VARIOUS AMIDES

(Weight of ZnO = 0.35 g; solvent: CH_3CN; temp.: 28°; vol. of solution: 30 ml; concentration of the amide: 0.5M)

Amide	Amount of H_2O_2 formed (mmole litre⁻¹)
Nil	13.5
N,N-Diphenylformamide	13.2
Urea	14.0
Benzamide	11.5
Formamide	8.7
Acetamide	8.0
N,N-Diethylformamide	3.8

Due to steric factors, one molecule of the amide itself may make many active sites on zinc oxide inaccessible to the alcohol. However, in benzamide and N,N-diphenylformamide, due to structural factors, the electrons are not that easily available for coordination with the catalyst and hence its inefficiency.

To see whether the inhibition is characteristic of all nitrogenous compounds or of only those containing —C=O groups a few observations were made in the presence of amines. The results obtained in the presence of various amines, in acetonitrile are plotted in Fig. 6. The amount of H_2O_2 formed in the presence of 3,5-ditertiarybutyl-4-methylphenol (DMP) is also plotted. The very much lower rate in the presence of this well known free radical inhibitor shows that the reaction proceeds through free radicals. The effect of all the amines remain the same irrespective of their structure suggesting that the mechanism of inhibition is similar. Diphenylamine (DPA) which is one of the inhibitors used here is a well known inhibitor for heterogeneously initiated liquid phase oxidation of hydrocarbons[9] which proceed through free radicals. Hence the inhibition by all the amines may be by quenching the free radicals that are responsible for the reaction and not by affecting the activity of zinc oxide. This is confirmed by the observation that zinc oxide samples irradiated with the amines, filtered and then used for the reaction are as active as pure zinc oxide. Amines have been reported to act as poisons on oxide surfaces[10]. But from infrared spectral data it is seen that the amines fail to get adsorbed on zinc oxide, in the presence of the alcohol (the spectra were identical for the zinc oxide samples irradiated with and without the amines) and hence the inhibition is due neither to the poisoning of the 'surface nor to any complex formation. Table 3 summarizes the results in the presence of various amines.

TABLE 3 — AMOUNT OF H_2O_2 FORMED AT THE END OF 4 HOURS OF IRRADIATION IN THE PRESENCE OF VARIOUS AMINES

(Weight of ZnO=0·35 g; solvent: CH_3CN; temp.: 28°; vol. of solution: 30 ml; concentration of the amine: 0·1M)

Amine	Amount of H_2O_2 (mmole litre^{-1})
Nil	13·5
Aniline	6·5
N-Methylaniline	6·1
Diphenylamine	6·1

However, higher concentrations of these amines could not be used, since they themselves undergo photoreaction to give different products. For example, aniline gives azobenzene (detected spectrophotometrically) while N,N-dimethylaniline (not used here because of its high reactivity) gives crystal violet.

In order to investigate the effect of dielectric constant of the medium on the nature as well as the extent of inhibition by the amines a few experiments were carried out in a nonpolar solvent like cyclohexane. The extent of inhibition by all the amines is more or less the same (Fig. 7). But DMP which was a more efficient inhibitor than the amines in acetonitrile is only as effective as the latter in cyclohexane. The oscillation in the concentration of H_2O_2 is also suppressed by the amines. This might be due to the fact that the amount of H_2O_2 formed in the presence of amines is much less than the optimum concentration required for the oscillation[11]. Also the extent of inhibition is not much different in the two solvents and hence it is unlikely that it is a process involving transfer of electrons or charged species.

Fig. 6 — Effect of different amines and 3,5-di-t-butyl-4-methylphenol (DMP) on the photoreaction of benzyl alcohol on ZnO

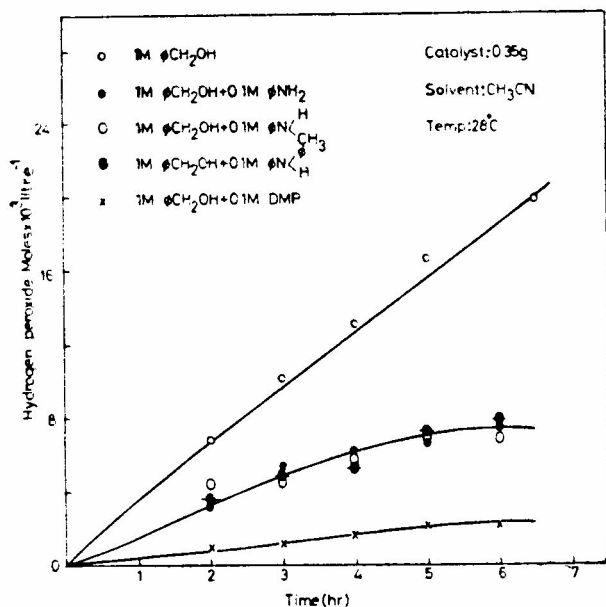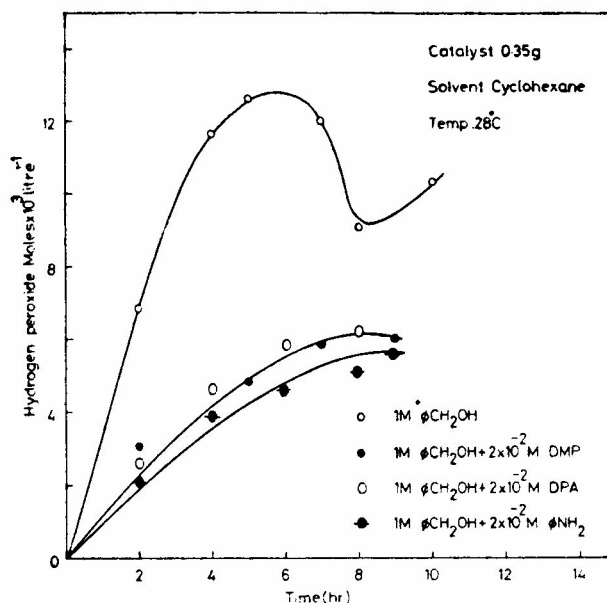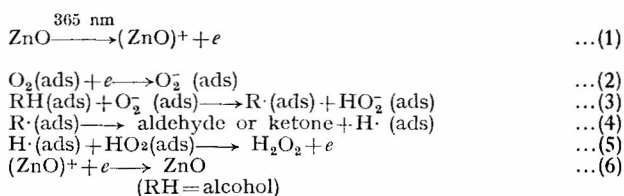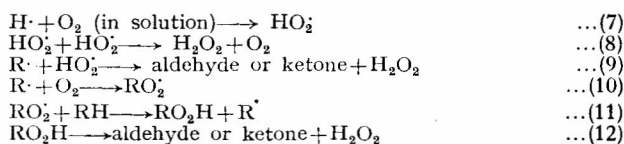Fig. 7 — Effect of different amines and DMP on the photoreaction of benzyl alcohol on ZnO in cyclohexane

Surface reaction

$$ZnO \xrightarrow{365 \text{ nm}} (ZnO)^+ + e \qquad \ldots(1)$$

$$O_2(ads) + e \longrightarrow O_2^-(ads) \qquad \ldots(2)$$
$$RH(ads) + O_2^-(ads) \longrightarrow R \cdot (ads) + HO_2^-(ads) \qquad \ldots(3)$$
$$R \cdot (ads) \longrightarrow \text{aldehyde or ketone} + H \cdot (ads) \qquad \ldots(4)$$
$$H \cdot (ads) + HO_2(ads) \longrightarrow H_2O_2 + e \qquad \ldots(5)$$
$$(ZnO)^+ + e \longrightarrow ZnO \qquad \ldots(6)$$
$$(RH = \text{alcohol})$$

Homogeneous reaction

$$H \cdot + O_2 \text{ (in solution)} \longrightarrow HO_2 \qquad \ldots(7)$$
$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \qquad \ldots(8)$$
$$R \cdot + HO_2 \longrightarrow \text{aldehyde or ketone} + H_2O_2 \qquad \ldots(9)$$
$$R \cdot + O_2 \longrightarrow RO_2 \qquad \ldots(10)$$
$$RO_2 + RH \longrightarrow RO_2H + R \qquad \ldots(11)$$
$$RO_2H \longrightarrow \text{aldehyde or ketone} + H_2O_2 \qquad \ldots(12)$$
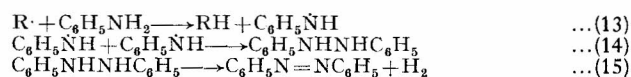
Scheme 1

In the light of these observations a mechanism, shown in Scheme 1 can be proposed for the photocatalysed reactions of alcohols on zinc oxide.

Adsorbed oxygen may be responsible for the surface processes, which is the initiating step, while dissolved oxygen is responsible for the propagation of the reaction. The observation that in deaerated solutions as well as on zinc oxide deprived of any adsorbed oxygen, the reaction is very slow[3] confirms the necessity of both types of oxygen species.

The amides inhibit the reaction by interacting with the catalyst surface and thus the initiation reaction which is exclusively heterogeneous in nature is suppressed. The small extent of reaction may be either due to the incomplete coverage of the zinc oxide surface by the amides or due to the low efficiency of the zinc oxide-amide complex as a photocatalyst. The amines probably interact with the radicals in the homogeneous phase either producing undesired products or changing the course of the reaction. For example, in the presence of aniline the reaction may proceed as shown in Scheme 2,

$$R \cdot + C_6H_5NH_2 \longrightarrow RH + C_6H_5\dot{N}H \qquad \ldots(13)$$
$$C_6H_5\dot{N}H + C_6H_5\dot{N}H \longrightarrow C_6H_5NHNHC_6H_5 \qquad \ldots(14)$$
$$C_6H_5NHNHC_6H_5 \longrightarrow C_6H_5N = NC_6H_5 + H_2 \qquad \ldots(15)$$

Scheme 2

resulting in azobenzene and not the aldehyde from the alcohol as expected.

The results for the formation of H_2O_2 in the presence of amides, amines and a combination of the two are given in Table 4.

TABLE 4 — AMOUNT OF H_2O_2 FORMED AT THE END OF 4 HOURS OF IRRADIATION IN THE PRESENCE OF ANILINE, N,N-DIETHYLFORMAMIDE AND A COMBINATION OF THE TWO

(Weight of ZnO = 0·35 g; solvent: CH_3CN; temp. 28°C; vol. of solution: 30 ml)

Nitrogen containing compound	Amount of H_2O_2 (mmole litre^{-1})
Nil	13·5
N,N-Diethylformamide (DEF) (0·5M)	3·8
Aniline (0·1M)	6·5
DEF (0·5M) + Aniline (0·1M)	0·5

The suggestion that the amides and the amines act as inhibitors by influencing two different processes is further supported by the observation that a mixture of N,N-diethylformamide and aniline could inhibit the reaction almost completely, which either of them could not do independently.

Acknowledgement

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