Photo-induced Catalytic Reactions of Alcohols on Zinc Oxide Suspensions in Cyclohexane: Oscillation in the Concentration of Hydrogen Peroxide Formed

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The concentration of peroxide formed during the photoinduced catalytic reactions of alcohols on zinc oxide in cyclohexane oscillate in a wave-like manner with time. Nitrogen containing compounds like amides and amines have a marked effect on this periodicity. Possible causes of this behaviour are examined.

It has been established that when suspensions of zinc oxide in water or hydroxylic media like alcohols at room temperature are subjected to 365 nm radiation, photoinduced catalytic reactions occur. Hydrogen peroxide is one of the products. The photo reactions of alcohols in irradiated suspensions of ZnO in various solvent media have been investigated in detail in this laboratory. The observations in cyclohexane media are presented here.

Alcohols like benzyl alcohol and benzhydrol were photooxidized in suspensions of zinc oxide. In all solvents except cyclohexane the concentration of peroxide increased with time to reach a steady value. In a paraffinic solvent like cyclohexane the yield of peroxide showed a strange trend. The concentration of peroxide reached a maximum value and then decreased to a minimum value and continued to go through the cycle of rise and fall with progress of time (Figs. 1 and 2). There was a periodicity in this behaviour. As the concentration of the alcohol was increased this behaviour disappeared. For each alcohol there is a concentration range within which alone this behaviour is observed.

Addition of amides like formamide, acetamide and N,N-diethylformamide (N,N-DEF) to the system, before the commencement of irradiation had a profound influence on the oscillation. The concentration of peroxide formed at the peak of the wave was lowered and the peaks appeared earlier than when the amides were not present (Fig. 3). Of the amides, N,N-DEF was the most effective in reducing the yield of peroxide. Infrared spectral studies showed that the amides, which influence the oscilla-

References
Fig. 1 — Effect of varying [benzyl alcohol] on the formation of H₂O₂

Fig. 2 — Effect of varying [benzhydrol] on the formation of H₂O₂

Fig. 3 — Effect of added amides on the photocatalyzed reactions of benzyl alcohol

Fig. 4 — Effect of addition of N,N-diethyl formamide (N,N-DEF) during the course of reaction

When the amide was added at a time when the yield of peroxide had reached a higher value than at the trough of the curve, there was a rapid fall in its concentration with time of irradiation. But when the addition was made at times corresponding to yields of peroxide lower than at the trough of the curve, the peroxide yield increased slightly with time of irradiation (Fig. 4).

When aniline, diphenylamine or a free radical scavenger like 2,6-ditertiarbutyl-4-methylphenol (DMP) was added initially to the system, the oscillation in the formation of peroxide was not observed. This might be due to the fact that in the presence of these reagents the concentration of peroxide that can be attained is much below the critical concentration required for noticeable
This occurs when the concentration of peroxide reaches the minimum. When OH⁻ and H⁺ are destroyed the concentration of peroxide can again increase. If the concentration of alcohol is increased or if alcohol is the solvent itself, all the sites can be occupied by alcohol and fewer sites may be available for the released hydrogen atom. In such a case H⁺ is removed as HO₂⁻. The maxima and minima would not occur. In fact it is interesting to note the absence of maxima and minima when alcohol concentration is high. Amides form a surface complex with irradiated ZnO (IR studies). This would cause depletion of vacant sites.

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References

Lithium Isotope Effects in Ion-exchange Equilibria in Mixed Solvents

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Lithium isotope effects in cation-exchange equilibria on Dowex 50W × 8 resin have been investigated in 76% (w/w) methanol-water, 44.2% (w/w) acetone-water, 52.8% (w/w) DMSO-water and 20.7% (w/w) isopropanol-water mixtures by the breakthrough technique using lithium acetate or lithium chloride feed solutions. The single stage separation factor (αₗ) increases appreciably in MeOH-H₂O mixture, remains unchanged in acetone-water and DMSO-H₂O mixtures and decreases in isopropanol-water as compared to the value in aqueous medium. αₗ values for the mixed solvent systems have been interpreted in terms of the differences in the state of solvation of Li⁺ ions in the solution and in the resin phase taking into consideration the solvent fractionation effects exhibited by the resin in mixed solvent systems.

THE single stage separation factors for lithium isotopes (αₗ) in ion-exchange equilibria on polystyrene sulphon acid type ion-exchange resins (Eq. 1)

\[ ^{6}\text{Li}^{+} + ^{7}\text{LiR} \rightleftharpoons ^{7}\text{Li}^{+} + ^{6}\text{LiR} \]  

... (1)

are small in aqueous systems. The effect of mixed solvents in these systems has also been investigated by a few workers; however their observations differ. The isotope effects, in aqueous medium, have been explained by Lee and Begun in terms of