

PHOTOSENSITIZED FORMATION OF HYDROGEN PEROXIDE IN STRONGLY ALKALINE METHANOLIC SOLUTIONS

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Metal-free phthalocyanine as well as eosine act as photosensitizers of a fast autoxidation of methanol in strongly alkaline solution during which hydrogen peroxide accumulates. The rate of formation of hydrogen peroxide further increases if the reaction takes place in the vicinity of an electrode on which hydrogen peroxide and phthalocyanine are oxidized. Irradiation of such electrode gives rise to a strong photoeffect.

In photosensitized autoxidations of aliphatic alcohols in non-alkaline media hydrogen peroxide appears as one of the reaction products in various proportions besides the corresponding aldehydes or ketones and acids. This was observed, *e.g.*, in benzophenone-sensitized reactions¹ or with anthraquinone-2-sodium² and -2,6-disodium³ sulphonates as sensitizers. In the eosine-sensitized autoxidation of methanol only formaldehyde was obtained as the oxidation product⁴. The simple oxidation of methanol in strongly alkaline solution follows an unusual path, as the first oxidation product, formaldehyde, reacts fast and quantitatively with hydrogen peroxide yielding molecular hydrogen and formate. Although this reaction attracted the attention of many authors⁵⁻⁸, nobody as yet has tried to initiate it by visible light. In course of our study of photoelectrochemical behaviour of phthalocyanines we found that photosensitized oxidation of methanol by oxygen was the cause of a marked photoeffect observed when the dropping mercury electrode (D.M.E.) was irradiated in strongly alkaline methanolic solutions of metal-free phthalocyanine.

EXPERIMENTAL

All solutions were prepared from analytical grade purity reagents. The experiments were carried out in a glass cell with a plane window through which the light was passed. The cell was provided with inlet and outlet tubes for gas; the D.M.E. and a tube connection to the aqueous saturated calomel electrode could be introduced to the cell through the stopper. A high pressure xenon lamp XBO 200 Narva (Berlin) served as light source. Absorption spectra were recorded with the Unicam SP. 800 spectrophotometer, and polarographic measurements were carried out with the polarograph LP 60 of Laboratorní přístroje, Prague.

RESULTS AND DISCUSSION

The solution, mostly of 10^{-5} M metal-free phthalocyanine in 0.1M-LiOH in methanol, was irradiated by light of constant intensity, and the production and accumulation of H_2O_2 was followed by d.c. polarography. The absorption spectrum of phthalocyanine remained unchanged by the photoreaction indicating that no bleaching of the sensitizer took place.

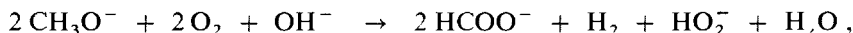
The reaction appeared to be highly sensitive to the presence of oxygen. The solution was deaerated by a stream of pure nitrogen which passed through a column of the BTS catalyst (BASF) to remove traces of oxygen before entering the cell. In this way after 1 hour of deaeration the concentration of oxygen in the solution was decreased to a value below 10^{-5} M, as on the polarographic curve no oxygen reduction was apparent. During the polarographic measurement nitrogen was passed above the solution. However, with the oxygen concentration kept as low as that, on switching on the light the production of H_2O_2 in the solution began immediately and within 100 minutes of irradiation its concentration built up to $6 \cdot 10^{-4}$ M. Equal concentration of H_2O_2 was reached after mere 5 minutes of irradiation when the solution was saturated by pure oxygen under atmospheric pressure. The rate of accumulation of hydrogen peroxide slows down with time, until its concentration reaches a limiting value which depends on the experimental conditions; in our experiments it was between 10^{-3} and 10^{-2} M. The concentration of OH^- ions plays an important role in the reaction: in a solution containing 0.01M-LiOH + 0.09M-LiCl the rate of production of H_2O_2 is by an order of magnitude less than in 0.1M-LiOH, and in a solution of 0.001M-LiOH + 0.099M-LiCl no hydrogen peroxide appears, even after prolonged irradiation.

If eosine is used instead of phthalocyanine in the same molar concentration, the photoreaction proceeds in the same way and at a comparable rate.

When the beam of light is focussed on the surface of the D.M.E. dipping in the solution near the cell wall to minimize the loss of light intensity by absorption, an especially intensive production of H_2O_2 takes place in the vicinity of the electrode if the electrode is polarized in the potential range 0 to -0.25 V vs S.C.E. Under such conditions at the electrode hydrogen peroxide is oxidized to oxygen which is again immediately consumed in the photoreaction. Phthalocyanine PcH_2 , in alkaline solutions in the form of its anion⁹ Pc^{2-} , is also electrooxidized in that potential range: on the polarogram it gives a small, apparently adsorption-controlled oxidation wave. An electro-oxidation product is presumably identical with a product of the photoreaction of Pc^{2-} , since when oxygen is passed through non-irradiated solution around the D.M.E. to which potential of oxidation of Pc^{2-} is applied, the formation of H_2O_2 is shown on the polarogram. This product is possibly the species Pc^\cdot generated either in the reaction of the triplet with the ground state Pc^{2-} (the D—D mechanism¹⁰) at low oxygen concentrations, or, to a small extent, by electron

transfer from the triplet Pc^{2-} to oxygen at high oxygen concentrations where the main product is the singlet oxygen¹¹. Judging by an analogous reaction with chlorophyll¹², the anion radical $Pc^{\cdot-}$ is likely to react with methanol forming methanol radical. Thus at the irradiated D.M.E. in the given potential range there are simultaneously generated the reaction component, O_2 , as well as an active form of the catalyst, $Pc^{\cdot-}$, and hence the high rate of the photoreaction near the electrode. Eosine shows no electrooxidation at the D.M.E., and also the irradiation of the electrode has a considerably weaker effect on the increase of the reaction rate, due only to the regeneration of oxygen by electrooxidation of hydrogen peroxide. However, in solution of either of the sensitizers, when the electrode polarized between 0 and -0.25 V vs S.C.E. is exposed to light, an immediate increase of current to a constant value ensues which disappears on cutting off the irradiation.

Once the methanol radical is produced the mechanism of the autoxidation proper proceeds presumably by its combination with oxygen to the hydroperoxy radical which at low oxygen concentration reacts with another methanol radical to form dioxymethylperoxide^{6,13}, or at high oxygen concentration dimerizes to a short-lived tetroxide¹⁴⁻¹⁶. These species then decompose in a solution-assisted process into the final products. The great enhancing effect of alkalinity of the solution on the reaction rate can be explained by the acceleration of the decomposition of dioxymethyl peroxide which had been described before^{6,8}. Although the occurrence of several side reactions has to be taken into account, according to the present results the main overall reaction is given by the equation



in agreement with the literature data. The actual yield of hydrogen peroxide is probably partly due to disproportionation of the $\text{O}_2^{\cdot-}$ radical anions¹⁷ formed in course of the photoreaction of the sensitizer.

When sufficient amount of hydrogen peroxide accumulates, it enters itself into reactions with the triplet state of the sensitizer¹⁸, and thereby its steady-state concentration is determined.

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