PHOTOCHEMICAL HYDROXYLATION OF SALICYLIC ACID BY HYDROGEN PEROXIDE. PHOTOCATALYTIC EFFECT OF Fe(III)

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Received May 18, 1983
Accepted November 14, 1983

The rate and quantum yields of photoinitiated hydroxylation of salicylic acid by hydrogen peroxide can be increased substantially by adding Fe(III) compounds to the reaction mixture. The UV radiation reduces the catalytically inactive Fe(III) to catalytically active Fe(II) during the reaction, thereby continuously producing the Fenton reagent.

We have shown recently [1, 2] that the photolysis of hydrogen peroxide is catalyzed by transition metal ions. The photocatalytic effect of Fe(III) has been explained in terms of photochemical reduction of Fe(III) to Fe(II), the latter catalyzing the thermal decomposition of hydrogen peroxide. It will now be of interest to examine whether the photocatalytic effects of transition metal ions may also be helpful in accelerating oxidation or hydroxylation of organic compounds by hydrogen peroxide.

It is well known that hydrogen peroxide containing added ferrous ions (Fenton's reagent) [3] effectively oxidizes or hydroxylates a number of organic compounds [4]. Typical of such reactions is the hydroxylation of salicylic acid [5]. In this paper, we shall demonstrate that salicylic acid can be hydroxylated effectively by hydrogen peroxide in a photochemical way if the reaction mixture contains ferric ions.

EXPERIMENTAL

The reaction was carried out in a thermostated quartz cell irradiated with the whole spectrum of a Phillips 93110 E medium pressure mercury lamp. The course of the reaction was followed spectrophotometrically. The UV absorption spectrum of the reaction mixture was recorded at regular times.
intervals on SP 800 B (Unicam, Cambridge) and Specord UV-VIS (Carl Zeiss, Jena) spectrophotometers.

In the determination of quantum yields, the initiating radiation was monochromatized by a UV KS IF 300 metal interference filter (Carl Zeiss, Jena), which transmits primarily the 297 nm, 303 nm and 313 nm lines of the medium pressure mercury lamp spectrum.

The method used to determine quantum yields was as follows. After irradiating the reaction mixture for a given time, the amount of product was determined. A reference run was always made to test the rate of the thermal reaction. In the next experiment an actinometric solution of 0.006 M ferrioxalate was used instead of the reaction mixture, and the light flux intensity was determined [6]. Since the geometry in the radiation intensity measurements was the same as in measuring the rate of photoinitiated reaction and the light flux did not change with time, it was assumed that the light flux incident upon the reaction cell in the photochemical reaction was the same as in actinometry.

From UV absorption spectrum of the reaction solution it is possible to show that the lines of the initiating radiation were effectively absorbed by the reaction solution, namely 95.5%, 94.4% and 77.1% for 297 nm, 303 nm and 313 nm, respectively. As the reaction mechanism has not yet been completely resolved, a question remains as to which of the reaction solution components are photochemically active, i.e. with respect to which of them the quantum yield values should be calculated. The quantum yields listed in Table 2 refer to the total amount of radiation absorbed in the reaction system. The effect of added EDTA in acting as an internal filter is discussed in the following section.

The product of the photoinitiated hydroxylation of salicylic acid was isolated as described by Grinstead [5]. Unreacted salicylic acid was separated from acidified reaction mixture by extraction with chloroform. Subsequent extraction with diethyl ether and evaporation yielded the product of the photoinitiated hydroxylation. This product was dissolved in water, and its absorption spectrum was recorded. Comparison with the spectra of 2,3-, 2,4-, and 2,5-dihydroxybenzoic acids [7] showed that the predominant product of the photoinitiated hydroxylation was 2,5-dihydroxybenzoic acid.

RESULTS AND DISCUSSION

The change in the UV absorption spectrum of a solution of salicylic acid and hydrogen peroxide on irradiating with ultraviolet light is shown in Fig. 1.