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Photolysis of Aromatic Compounds in Water in the Presence of Hydrogen Peroxide[1]

M. Mansour

Gesellschaft für Strahlen- und Umweltforschung mbH München, Institut für Ökologische Chemie, D-8050 Freising-Attaching, Federal Republic of Germany

Hydroxylation of aromatic compounds in the liquid phase can be accomplished with Fenton's reagent (Walling 1975), the Undenfriend system (Undenfriend et al. 1954), the Haber-Weiss reaction (Weinstein et al. 1979), sensitized and unsensitized photolysis of hydrogen peroxide (Omura et al. 1968; Schenk 1957), as well as inorganic peroxides (Olah et al. 1978). With several classes of compounds the hydroxylation is surprisingly selective and is faster in the presence of molecular oxygen than in its absence. Thus, on sensitized photolysis of hydrogen peroxide, benzene yields phenol and biphenyl as main products along with smaller amounts of pyrocatechol (Stein et al. 1950), OH-radicals are present in the reaction.

Photochemical processes in the liquid phase may proceed via direct photolysis as well as via secondary reactions with reactive species of oxygen such as OH-radicals, ozone and peroxy radicals (Mill et al. 1980). The photolysis of hydrogen peroxide in aqueous solution with wavelengths in the sunlight region ($\lambda \geqslant 290$ nm) produces OH-radicals, which are known to react with a large number of environmental chemicals (Foster et al. 1974). Because of their high electronegativity, OH-radicals are very reactive oxidizing species and commonly play the dominant role in the degradation of organic chemicals in both the gas and the liquid phases (Gorse et al. 1972).

It was our intention to obtain the most precise information possible about the reactivity of certain aromatic compounds with OH-radicals generated in aqueous solution by photolysis of hydrogen peroxide. By extrapolation, the decrease in concentration on irradiation with sunlight can serve as a simple measure of the degradability of a compound. The characterization of the intermediates was not the main goal of this work.

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1) Dedicated to Professor Friedhelm Korte on the occasion of his 60th birthday

MATERIALS AND METHODS

30% hydrogen peroxide and UV-light of wavelengths greater than 290 nm were used in the present work. The only waters used were tap water and distilled water.

The experiments were conducted in a thermostated glass cylinder. To improve mixing the reaction solution was flushed with a stream of nitrogen. A Philips HPK 125 W lamp giving $17 \cdot 10^{-3}$ mole quanta per hour was employed. The lamp was surrounded by a Pyrex cooling jacket which was immersed to about 95% of its length in the reaction solution, and was cooled to 20 - 25° C. The solution was stirred by a magnetic stirrer. Hydrogen peroxide concentrations were measured spectrophotometrically and titrimetrically (Vogel 1955). We used a Pye Unicam SP8-100 spectrophotometer to determine the absorption coefficient for aromatic compounds. The conditions were: λ 320 - 250 nm, quartz cell 1 cm wide, band widht 1,2 nm.

Our experience has shown that the individual compounds could be analysed by direct injection of the water sample into the gas chromatographs without a sample work-up if the concentration is high enough. In many cases, however, enrichment was performed by extraction with suitable solvents.

A gas chromatograph (Carlo Erba Fractovap 2450) equipped with a flame ionisation detector and coupled to a 1 mV recorder (Linseis L 6501) with an electronic integrator (Hewlett Packard 3881 A) was employed. The columns used were 2m x 3mm ID. Glass columns packed with Tenax GC 60/80 mesh Gas-Chrom for the determination of methanol, allyl alcohol, benzene and toluene and 1% SP 1240 deactivated for acidic compounds on 80/100 Supelcoport for the determination of p-cresol and phenol. 3% SE-30 was used for dimethyl phthalate. The carrier gas was nitrogen (GC grade) at a flow rate of 30 mL/min. Quantification was based on external standards using the authentic compounds in the analytical solvent. The column temperature was programmed from 80 to 220° C at 6° C/min., with the flame ionization detector at 250° C.

All solvents were analytical reagent quality and were obtained from E. Merck, D-6100 Darmstadt, F.R.G.; hydrogen peroxide (30%) was obtained from Fluka, D-7910 Neu-Ulm, F.R.G.; dimethyl phthalate and p-cresol, both from Fluka, Ch-9490 Buchs, Switzerland, were of the highest available purity (99%). The standards were prepared by dissolving the substance in 15 mL water and mixed well to give concentrations of 0,06 and 0,03 mg/mL. A standard curve was obtained by analysing the solutions.

For the dark reaction a solution of 100 mL distilled water at pH 4,5 of p-cresol (2,1 g) and H_2O_2 (0,53 mL) was allowed to stand in the dark, purged with N_2, for 24 hours. The reaction mixture was extracted twice with 50 mL cyclohexane; the extract was concentrated to 0,5 mL and analysed by gas chromatography. The analysis indicated 86 - 94% of the p-cresol remained unreacted. Similar reactions in the dark at pH 2,5 and pH 8,9 showed 89% and 84% of the p-cresol, respectively, to remain. All the analyses were carried in triplicate.

RESULTS AND DISCUSSION

Chemical processes in water can be treated analogously to those in the atmosphere. Chemicals introduced into the environment by human activities can cause ecological effects in manifold ways. Their lifetime in the compartments like air, soil and water can be determined by chemical processes. Persistent substances present difficult problems during effluent treatment, because they are slow biodegradable and can not be satisfactorily removed by the physical and chemical methods commonly used. Photodegradation in water under certain circumstances can give us informations and data on mobility, dissipation and accumulation of the substance in the environment. It is well established that hydrogen peroxide and ozone, in water irradiated by UV-light, are especially suitable for decomposing environmental chemicals (Draper et al. 1981). It is also known that OH-radicals are very reactive towards organic chemicals in water and the atmosphere (Calvert et al. 1966). They possess a great affinity for electrons and react with a variety of chemical classes by abstraction of a hydrogen atom or by addition to a carbon-carbon double bond to form water and an alkyl radical. A comparison of OH with OR and ozone shows OH to be the most effective (Hoigné et al. 1977). Decomposition of H_2O_2 into radicals is effected by light and is faster at higher pH values. The rate of decomposition of H_2O_2 into OH radicals thus depends on pH and on the nature and concentration of impurities in the water (Fig. 1). We have investigated the effect of H_2O_2 on the oxidation of benzene and determined the rate and the product distribution accurately. The decomposition rates of H_2O_2 were greater than those of benzene. Thus, the observed variations in the rate of decomposition of H_2O_2 with its concentration shows the presence of a hydrogen peroxide decomposition system that is initiated by OH or other radicals formed by decomposition of the substrate (Fig. 2). The concentration of H_2O_2 altered only little during the early stages of the reaction, so it may be considered to be constant in this first phase, while the second reaction phase proceeds faster as the initial ratio of substrate to hydrogen peroxide increases.

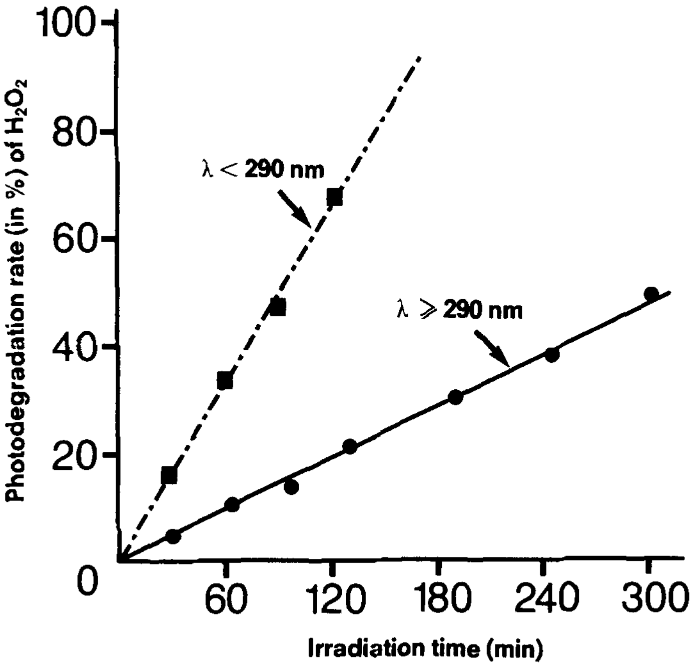

Fig. 1: Photodecomposition of 0,532 mole H_2O_2 in 1000 mL aqueous solution at 25° C

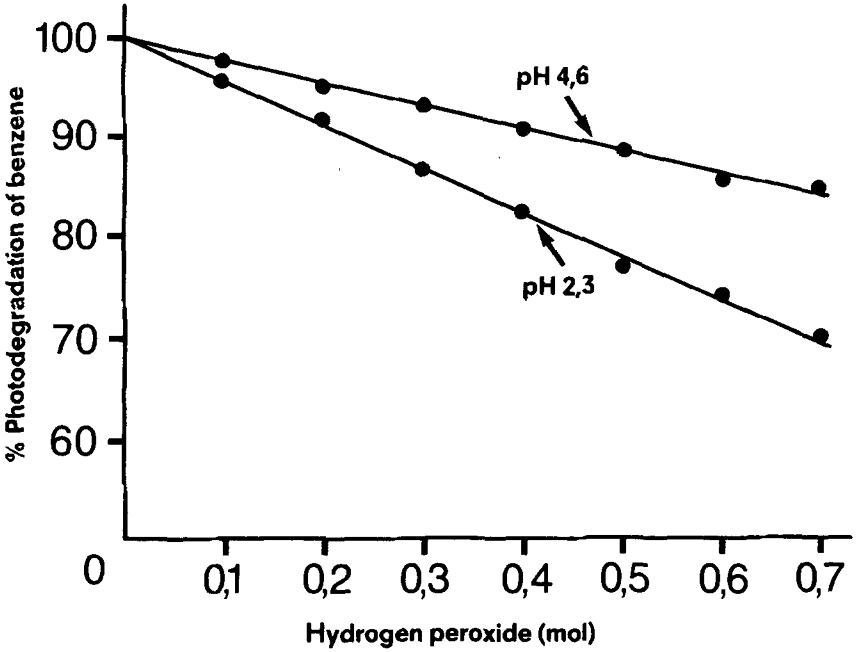

Fig. 2: Photodegradation rate of $9,2 \cdot 10^{-5}$ M Benzene solutions at pH 4,6 and pH 2,3 under $\lambda > 290$ nm in distilled water after 3 hours

At approximately equal initial substrate and H_2O_2 concentrations the reaction slows progressively with time. Higher concentrations of H_2O_2 also cause the reaction to slow down. At pH 3,9 the H_2O_2 decomposition and the oxidation of organic compounds take place quickly (Fig. 3).

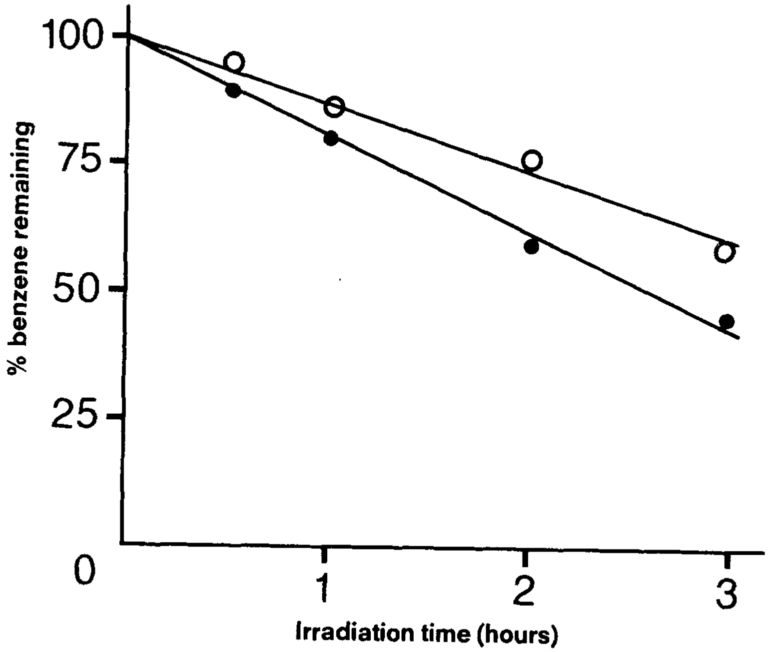

Fig. 3: Photodegradation of 2,45 · 10^{-5} M Benzene in the presence of 0,53 mL H_2O_2 in 1000 mL distilled water (O) and tap water (●) under $\lambda > 290$ nm

At pH 2,5 the H_2O_2 reaction rate depends on the organic substrate and its behavior in aqueous solution. The influence of oxygen and nitrogen on the decomposition was investigated and it was found that increasing concentrations of oxygen accelerate the H_2O_2 breakdown in comparison with rates after flushing with nitrogen. In order to test whether the OH radicals and other oxygen species can react with model compounds, we held a constant number of parameters: reaction time, molar ratio of H_2O_2 to substrate and temperature (Tab. 1). The highly chlorinated compounds PCB and cyclodiene insecticides react at slightly different rates (Mansour et al. 1983). The present investigation support the conception that UV causes changes in the chemical compounds in the presence of OH radicals and may play an important role in the disappearence of the substances in aquatic environment. Our investigation suggest that

Table 1. Photooxidation of organic compounds in aqueous hydrogen peroxide with ultra violet light

Substrate	concentration of substrate mg/200 mL	concentration of hydrogen (mole/L)	photo-reaction time (min)	substrate disappearence*% λ <290 nm	λ >290 nm	initial pH
Methanol	2,15	0,53	180	38,5	10,75	5,3
Allyl-alcohol	2,70	0,49	180	41,8	14,85	5,9
Benzene	1,17	0,57	240	58,6	25,4	6,3
Toluene	1,80	0,62	300	45,4	18,2	6,5
p-Cresole	3,50	0,51	300	60,3	22,3	5,2
Phenol	2,80	0,42	180	49,7	21,5	5,9
Dimethyl-phthalate	2,87	0,45	300	25,4	7,4	6,7

* Calculations based on triplicate analyses. Reproducibility was ± 0,25%.

some compounds can be detoxified by hydroxylation. Kinetic studies of these experiments and identification of photoproducts are in progress. The results shall be published elsewhere.

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