BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 289—291 (1969)

Effect of Ultrasonic Waves on Eriochrome Black T

Sheo PRAKASH and S. K. JAIN

Chemical Laboratories, University of Allahabad, Allahabad, India

(Received March 30, 1968)

Ultrasonic waves of high frequency (1 Mc/sec) have been employed to study the effects on the dilute aqueous solution of Eriochrome Black T. The deaeration of the solution by nitrogen does not greatly affect the rate of decolourization. The process is irreversible and the kinetic study shows it to be unimolecular. Oxidation and subsequent destruction of the dye molecule has been found to be the cause of the fading of the dye solution.

The decolourization of dyes by ultrasonic waves has been reported by Olson and Garden,[1] Azami and Hinohara[2] and Prakash and Prakash.[3–6] The aqueous solutions of various dyes have been found to be decolourized when subjected to the action of light, X-rays and γ-rays. The present paper describes the effect of ultrasonic waves on an aqueous solution of Eriohcrome Black T (abbreviated as EBT).

Experimental

Mullard's high frequency generator type E-7562 having a barium titanate ceramic crystal acting as the transducer was used as the source of ultrasonic power. The work reported here was done at a frequency of 1 Mc/sec. The circuit diagram of generator and ultrasonic bath has been reported earlier.[7]

A stock solution of EBT was prepared by dissolving 0.2306 g of the EBT (BDH) in one litre double distilled water. This was diluted to the desired concentration. The solution was found to be quite stable towards the atmosphere during the period of study.

Twenty-five milliliters of dye solution were irradiated in a round bottom ground stoppered jena bottle which was placed vertically above the transducer so that the sound waves entered the vessel vertically upwards. The solution irradiated for different periods and the change in colorimetric readings noted from Klett Summerson Photoelectric colorimeter, employing the filter No. 55 (transmission 520—600 mμ) which was found to be most suitable for the purpose. The absorption maximum of EBT was 560 mμ and this falls well within the range of this filter. For measuring hydrogen ion concentration a Leeds Northrup A.C. pH meter with glass electrodes was used. In order to see the effect of presence of nitrogen gas on the ultrasonic decolourization of EBT solution nitrogen gas, after passing through suitable traps to remove traces of oxygen, was bubbled for 20 min each time before exposure and then the solutions were irradiated for different intervals of time as usual and change in colour noted.

Results and Dicsussion

Figure 1 is a plot of exposure time *vs.* $-\log(a-x)$ where a is the initial dye concentration and $(a-x)$ its concentration after lapse of exposure time t.

---

[1] A. R. Olson and N. B. Garden, *J. Am. Chem. Soc.*, **54**, 3617 (1932).

[2] T. Azami and T. Hinohara, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **72**, 453, 515 (1951).

[3] S. Prakash and S. Prakash, *J. Acoust. Soc. Amer.*, **32**, 138 (1960).

[4] S. Prakash and S. Prakash, *Kolloid. -Z.*, **175**, 50 (1961).

[5] S. Prakash and S. Prakash, *Nature*, **191**, 1292 (1961).

[6] S. Prakash and S. Prakash, *Z. Phys. Chem.*, (*Leipzig.*) **221**, 145 (1962).

[7] S. Prakash, O. Prakash and S. Prakash, This Bulletin, **38**, 1426 (1965).

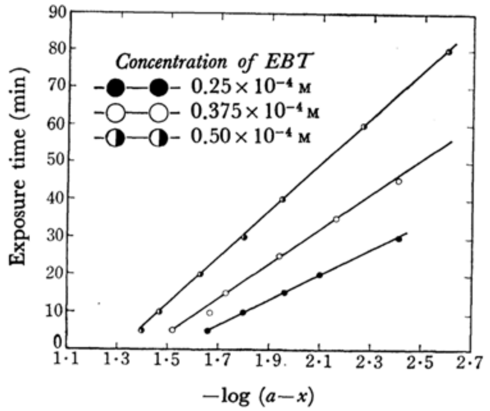

Fig. 1

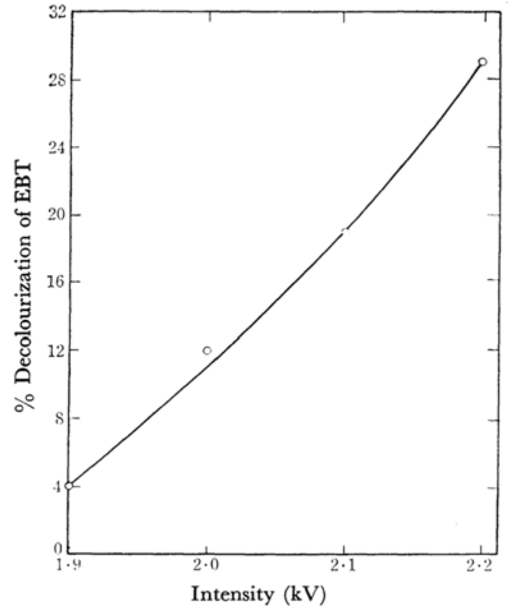

Fig. 2

The decolourisation process has been found to be unimolecular as is evident from the straight line curves obtained. It belongs to the category where the number of molecules of EBT undergoing change per second is proportional to the unreacted molecules present at that instant. This fading varies with change in intensity of the ultrasonic waves (Fig. 2).

The Spectrophotometric studies show that the absorption maximum of the EBT does not change with time of exposure (Fig. 3). Since the molecule breaks up into colourless products which do not exhibit any absorption maximum, the same value is obtained after different intervals of time because of the presence of unbroken EBT molecules.

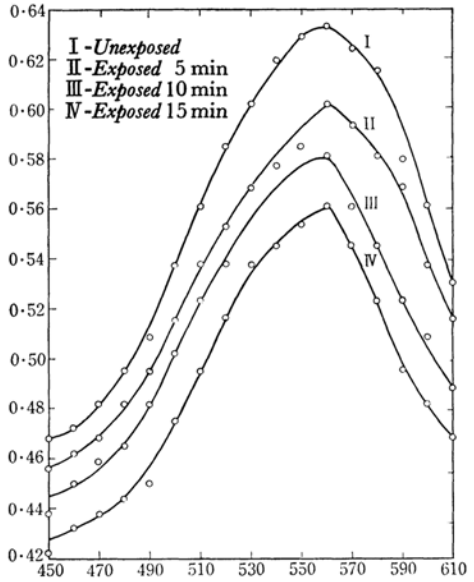

Fig. 3

When an aqueous solution is exposed to ultrasound, hydrogen peroxide is produced along with the formation[8] of H, OH, H_2 and HO_2.

$$H_2O \longrightarrow H,\ OH,\ HO_2,\ H_2O_2$$

A blank experiment was carried out to see whether hydrogen peroxide was responsible for the fading by adding hydrogen peroxide of different concentrations (1.62, 3.25, and 6.5×10^{-2}) to the EBT solution (0.5×10^{-4} M) and keeping it for some time. Even after 24 hr the change was about 6% only. This means that hydrogen peroxide may to some extent be helpful in fading,

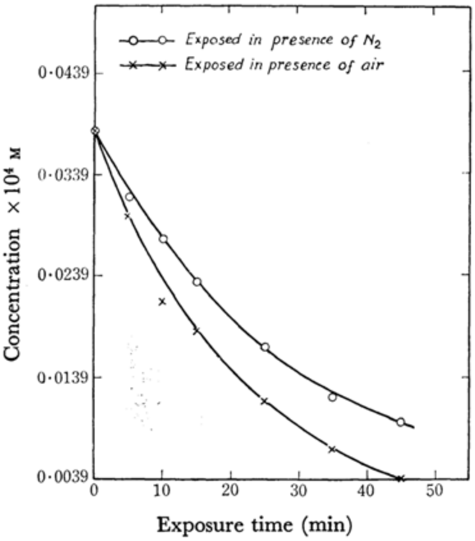

Fig. 4

---

[8] O. Lindstrom and O. Lamm, *J. Phys. Colloid. Chem.*, **55**, 1439 (1951).

but is not wholly responsible for it. It is very likely that the fading takes place with a more active reagent prior to the formation of hydrogen peroxide.

When air of the solution was replaced by nitrogen by bubbling the gas before exposure, even then the decolourization occurred, though the rate was reduced considerably (Fig. 4). This is in confirmity with the observations that the ultrasound is able to bring about chemical change even in absence of air or oxygen.

Organic compounds like acetone, dioxane, methyl alcohol, allylthiourea, ether and acrylamide act as inhibitors when they are present in minute quantity (4% by volume). The inhibiting action can be interpreted as due to high vapour pressure, surface tension and internal pressure changes. Most of the sonochemical reactions have been explained on the basis of cavitation, *i. e.*, formation and collapse of the cavity in the solution. The bursting of these cavities generates what is known as cavitational energy and this energy ruptures the bonds of the molecules undergoing change. In presence of substances having high vapour pressure, low surface tension and internal pressure this cavitation is suppressed to a great extent and hence the required energy is not available either to break the molecules of water to produce reactive species H, OH and HO_2 or the reacting molecules themselves.

Unlike photofading of dyes where the primary action is the activation of the molecules, the sonofading is the result of secondary reaction due to the free radicals produced from water by the ultrasonic waves. Also, once the molecule has been decolourized the colour is not restored back, suggesting that the permanent rupture of the molecule takes place. It is oxidation, sometimes reduction or dealkylation which causes the decolourization. However, it is a complex phenomenon and it is difficult to say what is the exact course of the reaction.