Decolourization of Crystal Violet induced by Ultrasonic Waves

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With 5 Figures

Summary

High frequency ultrasonic waves of frequency 1 Mc/s. have been employed to study the decolourization of dilute aqueous solution of crystal violet. The process is irreversible and the kinetic study shows it to be unimolecular one. The deaeration of the solution by nitrogen does not affect the rate of the decolourization. The addition of certain substances such as alcohol, acetone, ether, glycerine, dioxan and allylthiourea inhibits the decolourization to a considerable extent. Oxidation and subsequent destruction of the dye molecule has been found to be the cause of the fading of the dye solution.

Introduction

The aqueous solution of various dyes have been found to be decolourized when subjected to the action of light, X and γ-rays. The action of ultrasonic waves on decolourization of dyes has been reported by Olson and Garden[1], Azami and Hinohara[2] and Prakash and Prakash[3-6]. The latter authors have studied the decolourization of some dyes belonging to triphenylmethane, azo, azine and phthalein groups. The study here described provides data on the effect of ultrasonic waves on the fading of the dilute aqueous solution of crystal violet. According to the results that we have obtained the reaction seems to be very complex one. Crystal violet, a triphenyl methane dye, when dissolved in water produces a deep violet coloured solution. Azami and Hinohara[2] qualitatively studied the ultrasonic decolourization of crystal violet. From results of experiments in which

[1] A. R. Olson and N. B. Garden, J. Amer. chem. Soc. 54, 3617 (1932).

[2] T. Azami and T. Hinohara, J. chem. Soc. Japan Pure Chem. Sect. 72, 515 (1951).

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

[4] Idem, Koll. Zeit. 175, 50 (1961).

[5] Idem, Nature (London) 191, 1292 (1961).

[6] Idem, Z. physik. Chem. (Leipzig) 221, 145 (1962).

oxygen was eliminated they concluded that the decolourization is due to the oxidative action of oxygen activated, in particular, at the interface between the solution and the air.

Experimental

0.05 g. crystal violet ($C_{25}H_{30}N_3Cl$-hexamethyl pararosaniline) obtained from BDH was dissolved in double distilled water to get a relatively concentrated stock solution which was diluted as needed to desired concentration for the detailed study. The solution was quite stable towards the atmosphere over long period of times. All other reagents used in these experiments were of AR grade.

The source of ultrasonic power was Mullard's high frequency generator type E-7562 having a barium titanate ceramic crystal acting as the transduce[7]). All work was done at a frequency of 1 Mc/s. Spectra were obtained by plotting optical densities of the solutions measured on a Beckman DU spectrophotometer before and after the irradiation as a function of wavelength. The measuring glass cells were of 1 cm. thickness. The decolourization produced by ultrasonic waves was followed by observing the change in colorimetric readings from Klett Summerson's photoelectric colorimeter using Klett filter No. 55 (transmission $520-600$ mμ). pH measurements were done by Leeds Northrup direct pH meter using glass electrode.

The aliquot (25 ml.) were irradiated in a round bottom ground stoppered Jena flask which was placed vertically above the transducer in reproducible position. The ultrasonic bath and the arrangements have been described elsewhere. The waves entered the vessel vertically through its bottom and the distance between the vessel and the transducer was so adjusted as to get maximum fountain inside the vessel. This was done because the effect of ultrasonic waves was maximum when maximum fountain was produced in the solution. It was tried, as far as possible, to keep this distance unchanged during the course of the study.

Results

Since crystal violet has been reported to be one of a group of dyes that does not obey BEER's Law, the changes in colorimetric readings with changes in dye concentration were noted. Fig. 1 shows that the BEER's law is obeyed fairly well in the range of the concentrations that have been used (10^{-5} M) in this study. This curve was used to extrapolate the concentrations of the dye at different stages of decolourization.

The absorption spectra of crystal violet solution before and after irradiation with ultrasonic waves are shown in Fig. 2 from which it is seen that the intensity of the main band at 590 mμ decreases with increasing exposure

[7]) W. C. HOLMES, Ind. Engng. Chem. **16**, 35 (1924).

time. It is also evident that the absorption maximum remains unchanged
so long as any colour persists in the solution. This is because the decomposi-
tion of the dye molecules produces colourless products which do not con-
tribute towards the absorption. When the dye solution became colourless
its UV spectra was recorded (Fig. 3). Surprisingly it exhibits no peaks or
shoulders Crystal violet. Itself has a peak at 295 mµ and if carbinol base were
assumed to have been formed it should have a peak at 264 mµ. The absence
of these or any peak shows that the dye molecules have broken down into
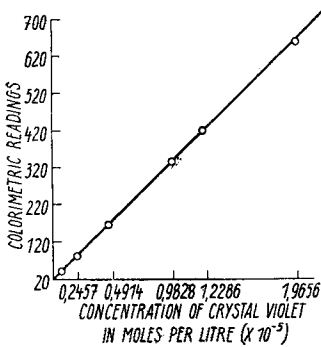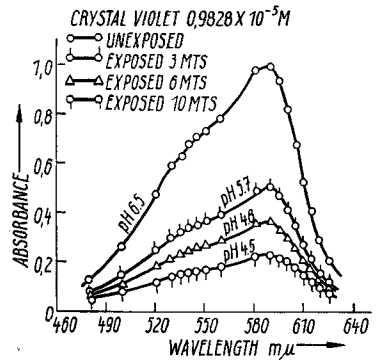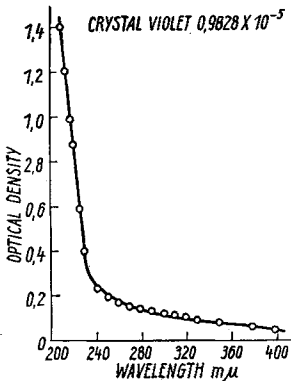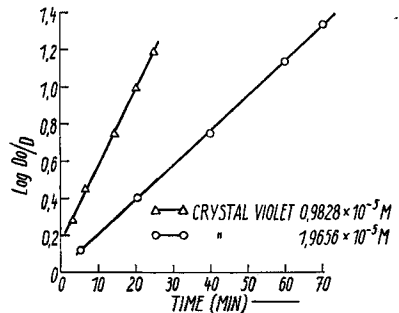very simple ones.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

The kinetic study of the reaction has been followed by plotting $\log \dfrac{D_0}{D}$
against time for which the solutions were exposed (Fig. 4). Here D_0 is the
original dye concentration and D the dye concentration after time t. The
straight line curves have been obtained.

Effect of Hydrogen Peroxide

When water or aqueous solutions are exposed to ultrasound, hydrogen peroxide is one of the products formed[8][9]). Therefore, it was necessary to check whether hydrogen peroxide played any role in the decolourization of the dye solution. This was done by carrying out a blank experiment in which hydrogen peroxide of known strength was added to the unexposed dye solution and the colorimetric readings noted with time. Two concentrations of hydrogen peroxide were tried (Fig. 5). It may be concluded that
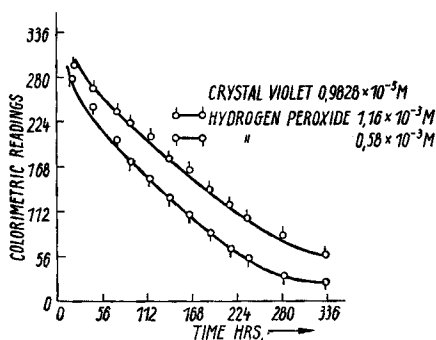
Fig. 5

there is some effect of hydrogen peroxide on the decolourization but the process is very slow. Whereas $0.9828 \cdot 10^{-5}$ M dye solution gets completely decolourized in about 25 mts. when exposed to ultrasonic waves, it takes two weeks when hydrogen peroxide was added and the solution was kept to decolourize by itself. Since hydrogen peroxide produced in water exposed to ultrasonic waves is very small, it is unlikely that there will be any indirect effect resulting from the formation of hydrogen peroxide. It is very likely that the decolourization takes place with a more active reagent prior to the formation of hydrogen peroxide.

Effect of Organic Substances

In Table 1 have been recorded the colorimetric readings after adding 0.5 ml. methyl alcohol, ethyl alcohol, ether, dioxan, glycerine, acetone and allylthiourea solution (10^{-3} M) separately to a mixture of 20 ml. of the dye solution ($0.9828 \cdot 10^{-5}$ M) and 4.5 ml. water and exposing each time for 6 mts. The observations show that the decolourization of the dye solution is con-

8) H. BEUTHE, Z. physik. Chem. A **163**, 161 (1933).
9) R. O. PRUDHOMME, Bull. Soc. Chim. biol. **39**, 425 (1957).

Table 1

Substances added	Colorimetric readings
Dye solution not exposed	335
Dye solution exposed alone	115
Exposed with methyl alcohol	267
ethyl alcohol	305
acetone	287
ether	307
dioxan	319
glycerine	241
allylthiourea (10⁻³ M)	281

siderably inhibited when these substances are present even in very small amount. This inhibition is firstly due to competitive reaction and secondly to the change in vapour pressure, surface tension and internal pressure values. The substances having high vapour pressure, low surface tension and low internal pressure have been found [10-12] to suppress the breakdown of the cavitation bubbles and hence sufficient energy is not available for the reactions to occur. Water has about four times the value of surface tension and internal pressure of the organic liquids. That is why in aqueous medium only most of the reactions induced by ultrasonic waves have been found to occur and no reactions take place in non aqueous media.

In an attempt to relate the bleaching of various dyes to their reversible reduction potential SEITZ [13] observed that in air free aqueous solution of indigo carmine the bleaching could be reversed by the admission of air, this implied that the dye was under these conditions reduced to the leuco form. Whereas in our case when air was removed by replacing it with nitrogen the rate of the decolourization was not changed and also the restoration of the colour was not observed by admitting air.

Discussion

The study of the effect of ultrasonic waves on aqueous solutions has been largely restricted to that of dilute solutions where the cavitation ultimately provides energy necessary for promoting chemical transformations. It is assumed that the cavitational energy (i.e. the energy released upon the

[10] B. H. JENNINGS and S. N. TOWNSEND, J. physic. Chem. 65, 1574 (1961).

[11] O. LINDSTROM and O. LAMM, J. phys. and Colloid Chem. 55, 1139 (1951).

[12] M. HAISSINSKY and A. MANGEOT, Nuovo Cimento 4, 1086 (1956).

[13] W. SEITZ, Strahlentherapie 61, 140 (1938).

rupture of the bubbles formed in the liquid) is largely absorbed by the solvent water. Under these conditions the chemical changes of the solute have been attributed in general to an attack by the H atoms and OH radicals produced by the action of the ultrasonic waves on water according to the net process

$$H_2O \rightarrow H + OH \qquad \Delta E = 120 \text{ kcal.}$$

In addition, the sonolysis of water also leads to smaller extent the molecular products hydrogen and hydrogen peroxide

$$2 H_2O \rightarrow H_2 + H_2O_2.$$
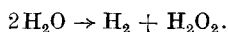
The results of numerous investigations concerning the action of ultrasonic waves and ionizing radiations on water and aqueous solutions are consistent with the view that the primary process of the absorption of such radiations in water results in the formation of H atoms, OH radicals, hydrogen and hydrogen peroxide

$$H_2O \rightarrow H, OH, H_2, H_2O_2.$$
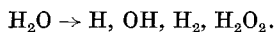
In presence of dissolved oxygen, the H atoms are believed to react with oxygen to give the perhydroxyl radical HO_2

$$H + O_2 \rightarrow HO_2.$$
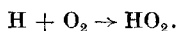
The decolourization of crystal violet may be proceeding by the addition of H or OH to the central carbon atom to destroy the quinonoid structure. H is generally associated with the reversible reductive decolourization and OH and HO_2 are considered to be the cause of irreversible oxidative decolourization. However, this does not seem to be the final stage in the present case and the molecule is subject to further rupture yielding simple molecules as is seen from Fig. 3.

The mechanism of the ultrasonic decolourization of aqueous solutions of dyes is different from that of the photofading in the sense that the primary act in the ultrasonic decolourization is not the activation of the dye molecules. This is further supported by the fact that in photofading of crystal violet the formation of michler's ketone has been reported by IWAMOTO [14]. In our case when the dye solution after exposure to ultrasonic waves was treated with 2:4 dinitrophenylhydrazine to see if keto group was present no indication for its presence was obtained.

As dyes belong to many defferent chemical types it is clear that no single or simple mechanism can be put forward to explain the decolouriza-

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[14] N. IWAMOTO, Bull. chem. Soc. Japan 10, 420 (1935).

tion of dyes. Taking into account that it has not yet been possible to make a complete analysis of the products obtained on irradiation to ultrasonic waves, any attempt to give a detailed mechanism would be premature. According to GEBHARD[15]) the change in colour may result from (1) a molecular change in the structure (2) a change in the dissociation relation (3) oxidation and (4) decomposition products. The ultrasonic fading resulting in permanent destruction of the dye molecules may be due to oxidation, reduction or decomposition process.

[15]) K. GEBHARD, Z. angew. Ch. **22**, 1890 (1909).

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