

PHOTOCHEMICAL STUDIES IN SOLS AND GELS. PART 1.

THE OXIDATION OF GLYCERINE BY METHYLENE BLUE IN LIGHT OF DIFFERENT FREQUENCIES WITH COLLOIDAL ZINC OXIDE AS THE PHOTO-SENSITISER IN MEDIA OF THIXOTROPIC ALUMINIUM HYDROXIDE SOL AND GEL.

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Photochemical reactions in liquid as well as in gaseous phases have been studied in considerable detail but in comparison, very few reactions have been studied in a sol or a gel phase. As examples, we may cite the decomposition of silver halides in gelatine studied by a number of workers, notably by Eggart and Noddack in wavelengths 365, 406 and 436 $\mu\mu$ and the decomposition of AgCl (sensitised by Ag) on printing out paper studied by Weigert in wavelength 436 $\mu\mu$. But no worker has yet made any comparative study of the kinetics of any reactions in both sol and gel phases. It would, therefore, be very interesting if methods could be devised by means of which photochemical reactions could be studied in a sol phase and the results compared with those studied in the gel phase. Chemical processes in nature mostly take place in sol and gel phases. It is hoped that similar laboratory investigations in sol and gel phases may throw light on the mechanism of such chemical processes in nature. With this idea in mind, we started our work using some transparent and colourless thixotropic sols and gels as solvent media. The advantage of using the thixotropic gels is that they liquefy on shaking which set again on standing for some time.

In the present investigation we have studied the oxidation of glycerine by methylene blue with colloidal zinc oxide as the photosensitiser in light of frequencies, 366, 406 and 436 $\mu\mu$ in media of thixotropic aluminium hydroxide sol and gel.

The action of zinc oxide in photosensitising the decomposition of various organic compounds and a large number of inorganic reactions has long been known. Eibner was the first to observe that several inorganic and organic coloured substances (e.g., prussian blue, lead chromate, etc.) are reduced in the light by zinc oxide in the presence of a depolariser such as glycerine or sugar. Winther studied the fluorescence of zinc oxide and some of its photosensitising action. For both processes, the near ultraviolet spectral region was found to be effective. Winther suggested that the zinc oxide remains chemically unchanged during these reactions and supported the view by experiments, which indicate that actually the size and shape of single zinc oxide particles remain unchanged even on prolonged illumination in presence of glycerine and lead carbonate. Tammann observed that, in presence of solid zinc oxide, silver is deposited from a solution of silver nitrate on illumination and zinc goes into solution. Tammann suggested that light accelerates the ionic exchange according to the equation, $ZnO + 2AgNO_3 = Ag_2O + Zn(NO_3)_2$. Kohlshutter and d'Almeida demonstrated that metallic silver and not its oxide is the product of light action. In this connection the investigations carried out by Baur and his collaborators are outstanding. Baur and Perret and Perret studied the photosensitising action of zinc oxide by exposing to sunlight a suspension of zinc oxide or other insoluble inorganic substances in silver nitrate solutions. The result indicates that the photosensitised decomposition of silver nitrate solution is due to a specific action of zinc oxide and not to the presence in general of solid particles in the solution. It

was further observed that on short illumination, not only metallic silver, but also silver oxide and peroxide are deposited on zinc oxide surfaces and that an equivalent amount of this latter goes into solution. The photochemical reaction was also found to be followed by evolution of gas, identified as pure oxygen. Perret suggested that the integral process taking place on illumination is expressed by the following equation:



and demonstrated that, actually, the total amount of oxygen formed (free and bound in silver oxides) is given roughly by the relation

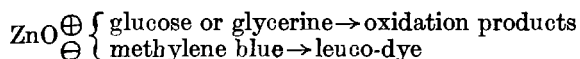
$$1/4 \text{O}_2 = \text{Ag}$$

Baur developed in a series of publications a novel theory of photosensitisation to explain the action of zinc oxide or uranyl salts in promoting various photochemical processes. The sensitiser is thought to become on absorption of light a polarised molecule comparable to the two electrodes of an electrolytic cell. Perret (loc. cit.) observed that solid zinc oxide particles exert a specific photosensitising action also on solutions of mercuric chloride and the reaction proceeds according to the equation

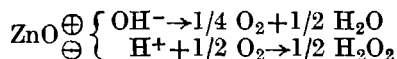


The reaction is greatly accelerated by dextrose and by sucrose, when the reaction is of zero-order. The third reaction of zinc oxide, studied by Perret, was its action in light on methylene blue. Methylene blue has long been known to be light-sensitive. Lasareff studied the kinetics of reduction of methylene blue solutions in solid gelatine. He found that the process was reversible and that, under the influence of free oxygen, the methylene blue leuco base was oxidised in the dark to the dye-stuff again. According to Perret (loc. cit.) the photochemical reaction of methylene blue is noticeably accelerated by the presence of zinc oxide.

In presence of glycerine or glucose, the reaction has been schematically described as follows:



Baur and Neuweiler have shown that by exposing aqueous suspensions of zinc oxide in contact with air to sunlight hydrogen peroxide is formed. They represented the reaction as follows:



References may also be made to the work done by Bohi; Fukhushima; McMorris and Dickinson; Goodeve; Narasimhachari and Qureshi and lastly by Dhar and Bhattacharyya.

None of these workers, however, have studied the *kinetics* of the reactions sensitised by zinc oxide, because such studies present considerable difficulties on account of the heterogeneity of the reacting substances.

After a number of trials we have succeeded in getting a suitable protective colloid,—thixotropic aluminium hydroxide sol,—which keeps zinc oxide in a colloidal state for nearly 10–12 hours during which each experiment recorded in this paper was completed.

Section A—deals with the reaction in aluminium hydroxide sol as medium.

Section B—deals with the reaction in aluminium hydroxide gel as medium.

EXPERIMENTAL.

The source of light was a mercury arc lamp whose strength of current and voltage were maintained constant by means of a regulating resistance. Parallel beams of light were obtained by means of quartz cylindrical lenses of different focal

lengths. Monochromatic radiations at 366 and 406 and 436 $\mu\mu$ were obtained by using as filter a dilute solution of copper sulphate in combination with the corresponding Schött and Gen monochromatic filter. The reaction cell was made of corex glass and was circular with a thickness of 1 cm. and having a capacity of 2.5 c.c. The cell was placed inside a double jacketed metal box with a window in front. The temperature was kept constant by passing, with the aid of a circulating pump, water from a thermostat through the annular space of the box. It is essential for accurate work that no extraneous light should enter the reaction cell and the reaction was carried out in a perfectly dark room, the only light entering the reaction cell being that obtained from the lamp through the window.

Reagents.

Merck's extra pure zinc oxide, bi-distilled glycerine and methylene blue supplied by B.D.H. were used throughout. For making thixotropic aluminium hydroxide sol, extra pure aluminium sulphate, lead acetate and barium acetate supplied by B.D.H. were used. For making solutions bi-distilled water was used.

Preparation of thixotropic aluminium hydroxide sol.

Thixotropic aluminium hydroxide sol was prepared by slow hydrolysis of aluminium diacetate following the method of Crum. This information being not generally accessible, the method is given in detail below. Aluminium acetate was first prepared by mixing together strong solutions of tersulphate of alumina and of acetate of lead. They were poured slowly together into a beaker surrounded with ice cold water. To the filtrate was added H_2S to precipitate lead sulphate which remained in solution and next barium acetate to throw down sulphuric acid.

The filtrate, thus obtained free from lead and H_2SO_4 , speedily became turbid on heating and a heavy deposit of white crystalline powder was formed. This basic diacetate of aluminium was washed several times with distilled water and then dissolved in 200 times its weight of boiling bi-distilled water. The solution was then maintained at about 90°C. for 15 days when complete hydrolysis occurred. The liquid was then boiled in a wide beaker for nearly 12 hours with constant addition of fresh water to retain the same volume so that most of the acetic acid had been volatilised and then the aluminium hydroxide sol was put to dialysis for nearly a week until the sol became neutral. The dialysed sol was concentrated, filtered and used.

Estimation of the Aluminium hydroxide sol.

The concentration of aluminium hydroxide in the sol was estimated by dissolving $Al(OH)_3$ in HNO_3 and precipitating $Al(OH)_3$ by ammonia. The investigated sol contained 11.65×10^{-2} Mols of Al_2O_3 per litre.

Preparation of colloidal zinc oxide.

It is not possible to prepare colloidal zinc oxide in water as a medium. After many trials we have found that thixotropic aluminium hydroxide sol acts as a protective colloid in keeping zinc oxide in a colloidal state for more than 12 hours. The colloidal zinc oxide was prepared daily, before use, by triturating a weighed quantity of zinc oxide with $Al(OH)_3$ sol in a glass mortar for 10 minutes and then diluting it either with bi-distilled water or with further quantity of $Al(OH)_3$ sol.

To study the reaction in sol-phase dilution was made by adding water whereas for studying in the solid gel phase dilution was made by adding $Al(OH)_3$ sol. For solid phase reaction Merck's extra pure K_2SO_4 was used for setting the sol to a jelly.

Measurement of the velocity of reaction.

Spectrophotometric method was adopted for the estimation of methylene blue at any moment. For this purpose 'Spectrophotometer Assembly' supplied by the Gaertner and Co. was used. Spectrophotometer readings (θ) were taken with the Corex cell filled with mixtures of different concentrations of methylene blue and colloidal zinc oxide in the green region ($546 \mu\mu$) where the leuco-dye has got no absorption—the blank corex cell being filled up with $\text{Al}(\text{OH})_3$ sol of the same concentration as in the dye solution. The calibration curve was obtained by plotting $\log \tan \theta$ against the concentration of methylene blue at a particular sol concentration (Fig. 1).

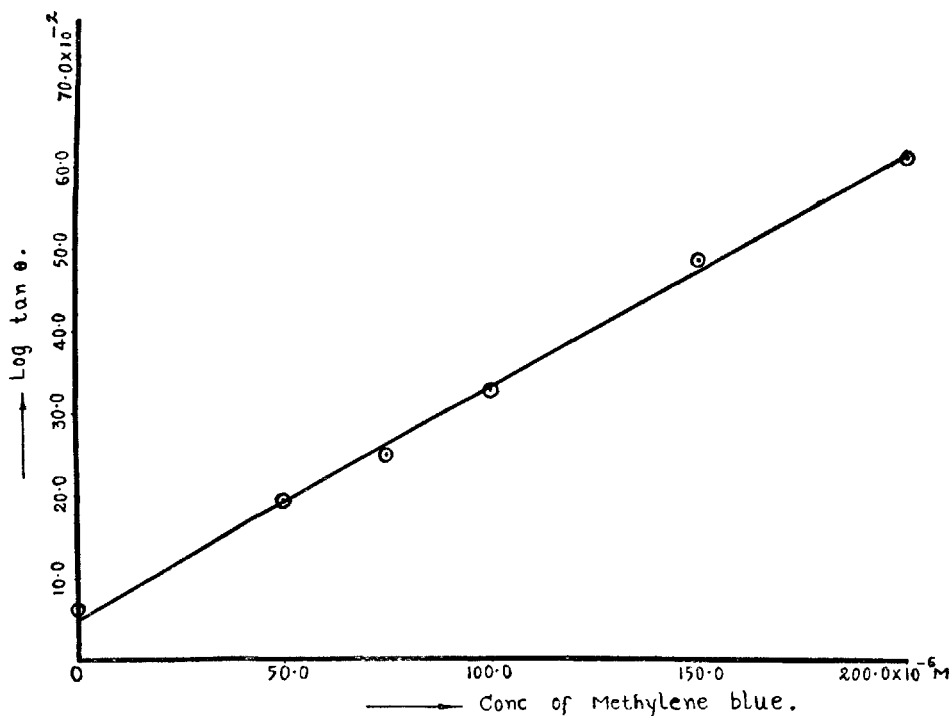


FIG. 1.

As colloidal zinc oxide has got appreciable general absorption in the visible, separate curves for absorption at $546 \mu\mu$ were obtained corresponding to different concentration of colloidal zinc oxide in the mixture.

TABLE I.

Concentration of colloidal zinc oxide.	Concentration of methylene blue.	Spectrophotometer readings.		$\log \tan \theta$
		with mixtures of dye and colloidal zinc oxide (θ).	With water in both the cells (θ').	
$\times 10^4 \text{ M}$	$\times 10^4 \text{ M}$			
6.15	2.0	76.8	45.0	0.6208
"	1.5	72.0	"	0.4882
"	1.0	64.9	"	0.3294
"	0.75	60.6	"	0.2491
"	0.5	57.0	"	0.1875
"	49.0	"	0.0608

The cell containing the reaction mixture was made absolutely airtight by covering the stopper with paraffin wax as the leuco-methylene blue is easily oxidised by air. There is an induction period in this reaction which was eliminated mostly by passing pure and dry N_2 gas through the reaction mixture just after mixing the ingredients and partly by exposing the reaction mixture to the whole light of the mercury-arc for 5 minutes.

It was observed that methylene blue does not get reduced when exposed to light of frequencies 366, 406 and 436 $\mu\mu$ either alone or in presence of glycerine or in presence of aluminium hydroxide sol. No dark reaction was observed when a mixture of colloidal zinc oxide, methylene blue and glycerine was kept in the dark for more than 24 hours.

Determination of pH.

The pH of the reaction mixture was determined potentiometrically by using a glass electrode.

Measurement of Intensity.

The intensity of radiation absorbed by the reaction mixture was measured by means of a 'Weston's Photronic cell' and a sensitive galvanometer. The photronic cell was calibrated by means of a standard lamp (12V; 4.0 W) standardised by means of a Moll thermopile and a Hefner lamp. The intensity of absorbed radiation was measured by noting the deflections when the light passed through (a) thixotropic aluminium hydroxide sol of the same concentration as was used in the reaction mixture, (b) the reaction mixture. The difference in deflections in the two cases gave the intensity of radiation absorbed by the reaction mixture. It is to be pointed out that aluminium hydroxide sol or gel has got no absorption in 366, 406 and 436 $\mu\mu$.

As mentioned before, light absorbed by methylene blue is not effective in the photochemical reduction by glycerine and hence the photo-oxidation of glycerine by methylene blue is due to the light absorbed by colloidal zinc oxide alone.

The amount of light absorbed by colloidal zinc oxide alone can be calculated by the formula for mixtures. I_{abs} for colloidal zinc oxide =

$$I_0 \left(1 - e^{-\epsilon_1 \cdot c_1 \cdot d - \epsilon_2 \cdot c_2 \cdot d} \right) \times \frac{\epsilon_1 \cdot c_1}{\epsilon_1 \cdot c_1 + \epsilon_2 \cdot c_2} \quad \dots \quad \dots \quad \dots \quad (\alpha)$$

where ϵ_1 = molecular extinction coefficient of colloidal zinc oxide.

ϵ_2 = molecular extinction coefficient of methylene blue.

c_1 = conc. of colloidal zinc oxide in gm. mols/litre.

c_2 = conc. of methylene blue in gm. mols/litre.

d = thickness of the reaction cell in cm.

I_0 = intensity of incident radiation.

The relation (α) can be roughly taken as

$$I_{\text{abs.}} = I \frac{\epsilon_1 \cdot c_1}{\epsilon_1 \cdot c_1 + \epsilon_1 \cdot c_2} \quad \dots \quad \dots \quad \dots \quad (\beta)$$

where I = intensity of radiation absorbed by the reaction mixture.

The molecular extinction coefficients ϵ_1 and ϵ_2 of colloidal zinc oxide and methylene blue were determined experimentally by intensity measurements in the following way. The deflections in the galvanometer were noted, first of all, with the solvent alone (e.g., aluminium hydroxide sol in the case of colloidal zinc oxide or water in the case of methylene blue) and secondly with colloidal zinc oxide or

methylene blue of known concentrations. The molecular extinction coefficients ϵ_1 and ϵ_2 were then calculated according to the equation,

$$\epsilon = \frac{1}{c.d} \log_e \frac{I_0}{I_t}$$

where c and d have their usual significance and I_t = intensity of transmitted light.

The values of ϵ_1 and ϵ_2 for different wavelengths (λ) e.g., 366, 406 and 436 $\mu\mu$ are recorded in Table II.

TABLE II.

$\lambda(\mu\mu)$..	366	406	436
ϵ_1 ..	633.4	478.6	220.8
ϵ_2 ..	2500.0	1710.0	1733.0

The extinction coefficients of colloidal zinc oxide as recorded above cannot be taken as perfectly accurate as the necessary corrections for the scattered light have not been made. As the concentrations of colloidal zinc oxide had been taken throughout this investigation so low, that the colloid had a pale white opalescence, the errors due to scattered light might have been very small.

The reaction was studied at 25°C. The experimental data are recorded in Tables III to XII. The reaction was found to be zero-molecular with respect to methylene blue. In the following tables,

$$\frac{\Delta x}{\Delta t} = \text{zero molecular velocity constant.}$$

= No. of gm. mols of methylene blue transformed per litre per minute.

In the tables, T = temperature; $I_{\text{abs.}}$ = No. of quanta absorbed by colloidal zinc oxide per c.c. per sec.;

a , b , A and B are the concentrations of methylene blue, glycerine, colloidal zinc oxide and aluminium hydroxide sol respectively, in gm. mols/litre.

Section A.

Determination of the order of the reaction.

TABLE III.

$\lambda = 436 \mu\mu$. $a = 15.0 \times 10^{-5} \text{M}$. $b = 20.0 \times 10^{-2} \text{M}$.
 $A = 6.15 \times 10^{-4} \text{M}$. $B = 5.96 \times 10^{-3} \text{M}$. $I_{\text{abs.}} = 160 \times 10^{13}$
 Temperature (T) = 25°C. $p\text{H} = 6.92$.

	Time (minutes).	Spectro reading.- (θ)	$\log \tan \theta$	C. 10^5 Methylene blue.	$\frac{\Delta x}{\Delta t} \cdot 10^7$	
(1)	$t+0$	68.4	0.4024	12.57	19.7	from (1) and (2).
(2)	$t+10$	65.6	0.3433	10.6	19.8	from (1) and (3).
(3)	$t+20$	62.8	0.2891	8.6	19.5	from (1) and (4).
(4)	$t+30$	60.0	0.2386	6.8	19.0	from (1) and (5).
(5)	$t+40$	57.2	0.1908	5.0	—	
					19.5	(Mean)

Effect of varying the concentration of methylene blue.

TABLE IV.

λ ($\mu\mu$)	$T = 25^\circ\text{C.}$				$\text{pH} = 6.92$			
	$a.10^5$ (Mol.)	$b.10^2$ (Mol.)	$A.10^4$ (Mol.)	$B.10^3$ (Mol.)	$I_{\text{abs.}}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^7$	$\frac{\Delta x}{\Delta t}.10^{21}/I_{\text{abs.}}$	γ
366	20.0	10.0	6.15	5.96	40	32.0	8.0	0.08
"	15.0	"	"	"	"	29.5	7.4	0.07
"	10.0	"	"	"	"	32.7	8.2	0.08
"	7.5	"	"	"	"	32.0	8.0	0.08
"	5.0	"	"	"	"	31.0	7.8	0.08
406	20.0	10.0	12.3	11.92	20	2.9	1.4	0.014
"	15.0	"	"	"	"	2.6	1.3	0.013
"	10.0	"	"	"	"	2.6	1.3	0.013
"	7.5	"	"	"	"	2.6	1.3	0.013
"	5.0	"	"	"	"	2.6	1.3	0.013
436	20.0	20.0	6.15	5.96	160	19.3	1.2	0.012
"	15.0	"	"	"	"	19.5	1.2	0.012
"	10.0	"	"	"	"	17.8	1.1	0.01
"	7.5	"	"	"	"	17.8	1.1	0.01
"	5.0	"	"	"	"	17.8	1.1	0.01

Effect of varying the concentration of glycerine.

TABLE V.

λ ($\mu\mu$)	$T = 25^\circ\text{C.}$				$\text{pH} = 6.92$			
	$a.10^5$ (Mol.)	$b.10^2$ (Mol.)	$A.10^4$ (Mol.)	$B.10^3$ (Mol.)	$I_{\text{abs.}}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^7$	$\frac{\Delta x}{\Delta t}.10^{21}/I_{\text{abs.}}$	γ
366	10.0	20.0	6.15	5.96	34	26.7	7.8	0.08
"	"	8.0	"	"	"	26.7	7.8	0.08
"	"	4.0	"	"	"	23.6	6.9	0.07
"	"	2.0	"	"	"	18.6	5.5	0.06
"	"	1.0	"	"	"	12.8	3.8	0.04
406	15.0	20.0	12.3	11.92	20	2.6	1.3	0.013
"	"	10.0	"	"	"	2.6	1.3	0.013
"	"	8.0	"	"	"	2.6	1.3	0.013
"	"	4.0	"	"	"	2.3	1.2	0.012
"	"	2.0	"	"	"	2.1	1.1	0.011
"	"	1.0	"	"	"	1.7	0.9	0.009
436	10.0	20.0	6.15	5.96	160	17.8	1.1	0.01
"	"	10.0	"	"	"	18.0	1.1	0.01
"	"	8.0	"	"	"	18.0	1.1	0.01
"	"	5.0	"	"	"	14.5	0.9	0.009
"	"	2.5	"	"	"	9.8	0.6	0.006

Effect of varying the concentration of colloidal zinc oxide.

TABLE VI.

λ ($\mu\mu$)	$T = 25^\circ\text{C.}$				$\text{pH} = 6.92$			
	$a.10^5$ (Mol.)	$b.10^2$ (Mol.)	$A.10^4$ (Mol.)	$B.10^3$ (Mol.)	$I_{\text{abs.}}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^7$	$\frac{\Delta x}{\Delta t}.10^{21}/I_{\text{abs.}}$	γ
366	10.0	10.0	12.3	11.92	50	36.0	7.2	0.07
"	"	"	6.15	5.96	40	32.7	8.0	0.08
"	"	"	3.08	2.98	20	15.7	7.5	0.075
406	15.0	10.0	12.3	11.92	20	2.6	1.3	0.013
"	"	"	6.15	5.96	10	1.4	1.3	0.013
436	20.0	10.0	12.3	11.92	166	20.6	1.2	0.01
"	"	"	6.15	5.96	123	14.0	1.1	0.01
"	"	"	3.08	2.98	69	6.95	1.0	0.01

Effect of varying the intensity of incident and hence of absorbed radiation.

TABLE VII.

λ ($\mu\mu$)	$T = 25^\circ\text{C.}$				$p\text{H} = 6.92$				
	$a.10^5$ (Mol.)	$b.10^2$ (Mol.)	$A.10^4$ (Mol.)	$B.10^3$ (Mol.)	$I_{\text{abs.}}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^7$	$\frac{\Delta x}{\Delta t}.10^{21}/I_{\text{abs.}}$	γ	
366	10.0	10.0	6.15	5.96	68	53.0	7.8	0.08	
"	"	"	"	"	40	32.7	8.0	0.08	
"	"	"	"	"	34	26.7	7.8	0.08	
406	15.0	10.0	12.3	11.92	24	3.2	1.3	0.013	
"	"	"	"	"	12	1.6	1.3	0.013	
436	10.0	10.0	6.15	5.96	160	17.8	1.1	0.01	
"	"	"	"	"	123	14.0	1.1	0.01	
"	"	"	"	"	81	9.0	1.1	0.01	

Effect of varying the concentration of aluminium hydroxide sol.

TABLE VIII.

λ ($\mu\mu$)	$T = 25^\circ\text{C.}$				$p\text{H} = 6.92$				
	$a.10^5$ (Mol.)	$b.10^2$ (Mol.)	$A.10^4$ (Mol.)	$B.10^3$ (Mol.)	$I_{\text{abs.}}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^7$	$\frac{\Delta x}{\Delta t}.10^{21}/I_{\text{abs.}}$	γ	
366	10.0	8.0	6.15	5.96	34	26.7	7.8	0.08	
"	"	"	"	47.6	"	26.7	7.8	0.08	

Section B.

Effect of varying the concentration of K_2SO_4 .

TABLE IX.

λ ($\mu\mu$)	$T = 25^\circ\text{C.}$				$p\text{H} = 6.92$				
	$[\text{K}_2\text{SO}_4].10^4$ (Mol.)	$a.10^5$ (Mol.)	$b.10^2$ (Mol.)	$A.10^4$ (Mol.)	$B.10^3$ (Mol.)	$I_{\text{abs.}}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^7$	γ	
366	..	16.0	8.0	12.3	47.6	40	29.8		
"	2.0	"	"	"	"	"	21.5		
"	3.0	"	"	"	"	"	14.2		

* The reaction mixture set to a firm jelly within 5 minutes when the concentration of added $\text{K}_2\text{SO}_4 = 3.0 \times 10^{-4}\text{M}$.

Effect of varying the concentration of methylene blue.

TABLE X.

λ ($\mu\mu$)	$T = 25^\circ\text{C.}$				$p\text{H} = 6.92$				
	$a.10^5$ (Mol.)	$b.10^2$ (Mol.)	$A.10^4$ (Mol.)	$B.10^3$ (Mol.)	$I_{\text{abs.}}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^7$	$\frac{\Delta x}{\Delta t}.10^{21}/I_{\text{abs.}}$	γ	
366	16.0	8.0	12.3	47.6	40.1	14.2	3.5	0.035	
"	12.0	"	"	"	"	14.2	3.5	0.035	
"	8.0	"	"	"	"	13.7	3.4	0.034	
"	4.0	"	"	"	"	14.0	3.5	0.035	

Effect of varying the concentration of glycerine.

TABLE XI.

λ ($\mu\mu$)	$T = 25^\circ\text{C.}$		$p\text{H} = 6.92$		$\text{K}_2\text{SO}_4 = 3.0 \times 10^{-4}\text{M.}$			
	$a.10^5$ (Mol.)	$b.10^2$ (Mol.)	$A.10^4$ (Mol.)	$B.10^3$ (Mol.)	$I_{\text{abs.}} \cdot 10^{-13}$	$\frac{\Delta x}{\Delta t} \cdot 10^7$	$\frac{\Delta x}{\Delta t} \cdot 10^{21}/I_{\text{abs.}}$	γ
366	16.0	8.0	12.3	47.6	40.1	14.2	3.5	0.035
"	"	4.0	"	"	"	12.1	3.0	0.030
"	"	2.0	"	"	"	7.4	1.8	0.018

Effect of varying the intensity.

TABLE XII.

λ ($\mu\mu$)	$T = 25^\circ\text{C.}$		$p\text{H} = 6.92$		$\text{K}_2\text{SO}_4 = 3.0 \times 10^{-4}\text{M.}$			
	$a.10^5$ (Mol.)	$b.10^2$ (Mol.)	$A.10^4$ (Mol.)	$B.10^3$ (Mol.)	$I_{\text{abs.}} \cdot 10^{-13}$	$\frac{\Delta x}{\Delta t} \cdot 10^7$	$\frac{\Delta x}{\Delta t} \cdot 10^{21}/I_{\text{abs.}}$	γ
366	16.0	8.0	12.3	47.6	40.1	14.2	3.5	0.035
"	"	"	"	"	62.1	21.1	3.4	0.034

DISCUSSION.

The reaction has got the following common characteristics in both the sol and gel states:—

- (1) The reaction is zero-molecular with respect to methylene blue.
- (2) There is a slight induction period in the sol phase whereas in the gel phase it is appreciable.
- (3) The velocity constant is independent of the initial concentration of methylene blue.
- (4) The velocity constant is independent of the initial concentration of glycerine when $[\text{glycerine}] \geq 0.08\text{M}$. Below 0.08M , the velocity constant diminishes with decreasing concentration of glycerine. In fact, $1/\frac{\Delta x}{\Delta t}$ plotted against $\frac{1}{C_{\text{glycerine}}}$ gives a straight line (Fig. 2).
- (5) The velocity constant increases with increase in the concentration of colloidal zinc oxide, but $\frac{\Delta x}{\Delta t}/I_{\text{abs}}$ remains practically the same. With the maximum concentration, the light is, more or less, completely absorbed.
- (6) For the same concentration of glycerine, the velocity constant is directly proportional to the intensity of radiation absorbed by colloidal zinc oxide. In fact, $\frac{\Delta x}{\Delta t}/I_{\text{abs}}$ is constant for a particular wavelength, which increases with increase in the quanta absorbed.
- (7) The quantum efficiency is much less than unity.
- (8) The photo-active range of ZnO and consequently its absorption extends up to the mercury violet, i.e., $436 \mu\mu$.

Winther has studied the light absorption of ZnO in the ultraviolet by its effect in reducing the fluorescence of mercurous chloride with which it is intimately mixed.

He gives a curve for ZnO with a maximum at $360 \mu\mu$ and a minimum at about $300 \mu\mu$. Goodeve from a study of the diffuse reflecting power of the solid ZnO has obtained

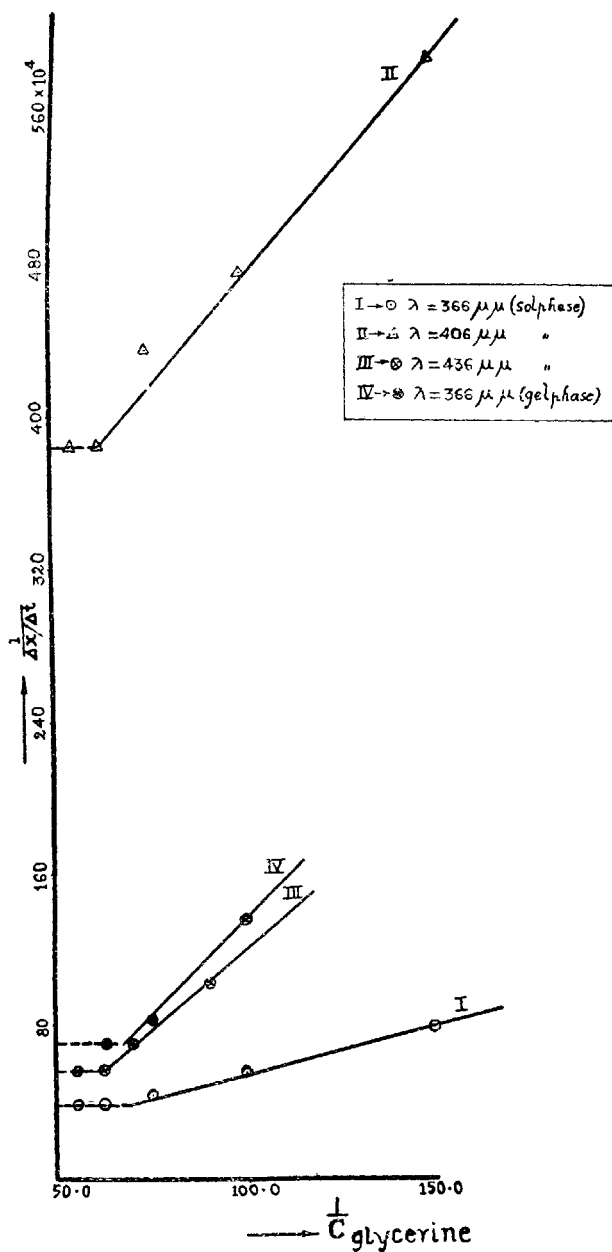


FIG. 2.

the absorption spectra of ZnO. He has observed that there is a sharp fall in the reflecting power of the powder at $385 \mu\mu$ and the curve becomes flat again at a reflecting power of about 2% and remains unchanged as the wavelength is decreased.

The rapid fall in the reflecting power indicates the entry of a strong absorption band with a fairly sharp threshold at the wavelength. The light of wavelength below this threshold, reflected from the powder, undoubtedly comes from the front surface of the particles—this accounting for the flatness of the curve. From these observations Goodeve has concluded that zinc oxide absorbs in the near ultraviolet, which is exactly the region in which the oxide is found to be photoactive.

The results of the present authors show that the photoactive range and consequently its absorption extends even up to the mercury violet, i.e. $436 \mu\mu$. From a recent investigation on the formation of H_2O_2 from water in presence of solid ZnO as a sensitiser, Narasimhachari and Qureshi have drawn similar conclusions.

The following mechanism will explain all these characteristic features:—

The colloidal zinc oxide surface is completely covered with a unimolecular layer of the dye-molecules even at very low concentration of the dye. It is remarkable that the absorption of radiation by the dye-molecules directly does not lead to the photoreduction by reaction with glycerine. But a dye-molecule can be brought into activated state by receiving energy from the elementary spaces of the colloidal zinc oxide surface which is also excited by the absorption of radiation.

The low quantum efficiency may be due to two reasons:—

- (a) Only a small fraction of the radiation absorbed by the colloidal ZnO is available for the activation of the dye-molecules adsorbed on the surface of the colloidal ZnO, or,
- (b) the velocity of reaction between activated molecules and the reductant adsorbed on the surface of ZnO is so slow that most of the former reverts spontaneously to the normal state. It is difficult to decide between these two possibilities.

The velocity is given by

$$\frac{\Delta x}{\Delta t} = K' \frac{I}{N \cdot h \cdot \nu} \cdot C_s^R \quad \dots \dots \dots \quad (i)$$

where C_s^R is the surface concentration of the reductant. According to Langmuir

$$C_s^R = \frac{K_1 C_B^R}{K_3 + K_2 C_B^R} \quad \dots \dots \dots \quad (ii)$$

where C_B^R is the concentration of reductant in solution.

When C_B^R is very large, $K_3 + K_2 C_B^R$ may be taken equal to $K_2 C_B^R$

or

$$\frac{\Delta x}{\Delta t} = K' \frac{I}{N \cdot h \cdot \nu} \cdot \frac{K_1}{K_2} \quad \dots \dots \dots \quad (iii)$$

That is, the velocity constant is independent of reductant concentration when the latter is high as has been experimentally found to be the case.

At a lower concentration of glycerine, K_3 cannot be neglected in comparison to $K_2 C_B^R$.

Hence

$$\begin{aligned} 1/\frac{\Delta x}{\Delta t} &= K_4 \frac{K_3 + K_1 C_B^R}{K_2 C_B^R} \\ &\doteq \frac{K_5}{C_B^R} + K_6 \quad \dots \dots \dots \quad (iv) \end{aligned}$$

That is, at low concentration of reductant, $1/\frac{\Delta x}{\Delta t}$ plotted against $1/C_{\text{glycerine}}$ should give a straight line. This has been found experimentally.

The velocity of reaction has been found to be proportional to the intensity of absorbed radiation as is demanded by equation (i).

The rate of reaction and consequently the quantum efficiency is greater in medium of thixotropic aluminium hydroxide sol than that in aluminium hydroxide gel. This is not in agreement with the observations made by the authors in their work on the photo-reduction of ferric chloride by mandelic acid in media of thorium phosphate and thorium molybdate sols-gels (Part II of the series) where they have found equal rate of reaction in both sol and gel states of thorium phosphate and thorium molybdate as media.

This discrepancy may be explained by the observations made by the authors that the number of colloidal zinc oxide particles diminishes with the addition of coagulating agent, e.g., K_2SO_4 with the consequent diminution in the rate of reaction. The particles of zinc oxide become bigger with additions of coagulating agent with the result that the specific reaction surface becomes reduced. The following table will clearly show that the approximate number of particles observed by means of an ultramicroscope with a very narrow slit opening is much smaller in the gel phase than in the sol phase, the concentration of colloidal zinc oxide being the same.

TABLE XIII.

Concentration of Colloidal Zinc Oxide	= $6.1 \times 10^{-4}M$
Aluminium hydroxide	= $47.6 \times 10^{-3}M$
Glycerine	= $8.0 \times 10^{-2}M$
$[K_2SO_4]$	$3.2 \times 10^{-4}M$
$n-30$	5

where n = approximate no. of particles instantaneously visible in an ultramicroscope with a very small slit opening.

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* The reaction mixture sets to a gel with $3.2 \times 10^{-4}M$ K_2SO_4 within 5 minutes.

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