PHOTOCHEMICAL REACTIONS WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION   PART XV. PHOTOCHEMICAL REDUCTION OF CERIC BORATE SOL WITH GLUCOSE AND LAEVULOSE

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Photochemical reduction of the ceric borate sol with glucose and laevulose has been studied in light. Effect of varying concentrations of the reductants and the sol, intensity of radiations, temperature and the influence of polarised light and also the effect of insolating the sol on the light reaction have been investigated and an equation has been developed which can explain the characteristic features of the observed reaction.

The experimental arrangement has been described in Part I (*J. Indian Chem. Soc.*, 1937, **14**, 500).

Pure ceric ammonium nitrate (B.D.H.) and Merck's pure borax after recrystallisation was used for the preparation of the sol, which was prepared after Prakash and Dhar (*ibid.*, 1930, **7**, 373) dialysis was continued till the dialysate showed no test of ammonia with Nessler's reagent.

Estimation of Ceric Borate Sol:—A definite volume of the sol was run into 10 c.c. of 4% sulphuric acid contained in a stoppered conical flask. It was then shaken for 1 minute and after 5 minutes titrated slowly with standard ferrous ammonium sulphate solution with constant shaking using one or two drops of diphenylamine (25%) as internal indicator.

The reliability of this method of estimation will be evident from the following potentiometric titrations.

TABLE I

A sample of ceric borate sol was taken and titrated potentiometrically with $0.01N$-FeAmSO$_4$. Amount of ceric borate sol taken was 0.376 c.c.

Amount of titre in c.c. (x)	— 0	0 5	0·8	0·85	0·9	0 95	1·0	1·05	1·10	1·20
E.M.F. (E)	0·585	0·554	0·498	0·477	0·430	0·355	0·230	0·236	0·215	0·195
dE/dx	—	6	19	42	91	150	156	88	42	20

The experiment was repeated several times and the maximum value for dE/dx was found when the amount of titre added was 0.95 c.c.

Again 0.376 c.c. of the above ceric borate sol was titrated with FeAmSO$_4$ ($0.01N$) using diphenylamine as the internal indicator. Titre required for complete reduction was 0.95 c.c.

By concentration of the sol we shall always understand the ceric equivalent of the sample of the sol.

Ceric borate sol was not reduced by glucose or by laevulose for a period of 10 hours in the dark. The sol and glucose or laevulose, when insolated, showed a long induction period followed by an irregular reaction and a photo-stationary state. This irregularity of the reaction and the photo-stationary state have been traced to be due to dissolved atmospheric oxygen which oxidises the reduced sol. Hence pure nitrogen was passed through the reaction mixture for a sufficiently long time before it was exposed to light   Pipetting of solution for titration was done in an atmosphere of pure nitrogen.

TABLE II

Study of the light reaction.

d (thickness of the reaction cell)$=0.5$ cm.   Conc. of ceric borate sol$=0.0144M$. Conc. of glucose$=2.5\%$. $p_a=6.9$.   Temp.$=29°$. $\gamma=366\mu\mu$.   Intensity of radiation absorbed$=405$ ergs/cm^2/sec.

Time.		Vol. of 0.002(M) ferrous ammonium sulphate $=$ 18 c.c. of reaction mixture	$k=\dfrac{2}{t(sec)}\left\{\dfrac{1}{\sqrt{a-x}}-\dfrac{1}{a}\right\}.$
(a)	0 min.	1.30 c.c.	
(b)	240	1.05	Induction period
(c)	310	0.86	4.7×10^{-5} (from b & c)
(d)	380	0.72	4.7×10^{-5} (from b & d)

The reaction was attended with a long induction period. The velocity of reaction with excess of reductant is best explained by the equation,

$$dx/dt=k(a-x)^{3/2}$$

which on integration gives

$$k=\frac{2}{t}\left\{\frac{1}{\sqrt{a-x}}-\frac{1}{a}\right\} \qquad \text{... (i)}$$

TABLE III

Effect of varying the concentration of the reductants.

d (thickness of the reaction cell)$=0.5$ cm.   Sol conc.$=0.0144M$.

Temp.	I_{abs} in ergs/cm^2/sec.	Reductant used.	Conc. of reductant.	k (1) mean.	Quantum yield.
29°	405	Glucose	2.5%	4.7×10^{-5}	1.95
29	,,	,,	1.25	3.6	1.65
29	,,	,,	0.625	2.52	1.25
25	1215	Laevulose	2.5	9.4	1.80
25	,,	,,	1.25	5.55	1.05
25	,,	,,	0.625	2.8	0.53

$1/k$ plotted against $1/c$ (reductant) gives a straight line.

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TABLE IV

Effect of varying the concentration of ceric borate sol.

$\lambda = 366\mu\mu.$ $p_\text{H} = 6\cdot9.$ I_abs in ergs/cm^2/sec. $= 571.$

Temp	Sol. conc.	Reductant used.	Reductant conc.	$k(\text{1})$
29°	0·0145M	Glucose	2·5%	5·58 × 10⁻⁴
29	0·0072	,,	,,	5·32
25·5	0·0144	Leavulose	0·625	1·9
25	0·0072	,,	,,	1·8

From the above table it is evident that the velocity constant is independent of the sol concentration, under otherwise identical conditions.

TABLE V

Effect of varying the intensity of radiation.

$\lambda = 366 \mu\mu.$ $p_\text{H} = 6\cdot9.$ Sol. conc. $= 0\cdot0144M.$

Temp.	I_abs in ergs/cm^2/sec.	Reductant used.	Conc. of reductant.	$k(\text{1})$
29°	405	Glucose	2·5%	4·7 × 10⁸
29	650	,,	,,	5·67
25·5	1215	Laevulose	0·625	2·8
25·5	2230	,,		3·65

The above table shows that the velocity constant is proportional to the square root of the intensity of radiant energy absorbed.

Effect of Varying the Temperature.

The temperature coefficient of the photo-reduction is small, being of the order of 1·1 to 1·2.

TABLE VI

Influence of polarised light.

$\lambda = 366 \mu\mu.$ $p_\text{H} = 6\cdot9.$

(a) Sol. conc. $= 0\cdot0144M$; glucose $= 2\cdot5\%$

Temp.	I_abs in ergs/cm²/sec.	Nature of light used.	$k(\text{1})$
29°	405	Unpolarised	4·7 × 10⁻⁴
,,	290	Plane polarised	3·65
30	135	d-Circularly polarised	1·35
,,	135	l-Circularly polarised	2·53

(b) Sol. conc. $= 0\cdot0144M$; laevulose $= 1\cdot25\%$

Temp.	I_abs in ergs/cm²/sec.	Nature of light used.	$k(\text{1})$
25°	1215	Unpolarised (ordinary)	5·55
,,	604	Plane polarised	3·72
,,	251	d-Circularly polarised	1·5
,,	251	l-Circularly polarised	2·35

It is clear from the above table that on the assumption that square root law holds good, $V_\text{u} = V_\text{p} = V_\text{l} > V_\text{d}$, the terms V_u, V_p, V_l, V_d having the same significance as before.

Effect of Pre-insolating the Sol.

From Table II, the reaction seems to possess an induction period of about 3 hours; for weak illumination it is even 6 hours.

The sol was insolated for nearly four hours in a quartz test tube, in an atmosphere of nitrogen gas and then mixed with other constituents of the reaction mixture and exposed to light (366 $\mu\mu$). The reaction is now marked by the absence of any "induction period." That the velocity constant also remains unaffected is shown by the following data.

TABLE VII

Conc. of sol = $0.0144M$. Conc. of glucose = 2.5%. Intensity of radiation absorbed = 405 ergs/cm²/sec.

Time.	Titre.	$k(1) \times 10^5$.	$k_{mean} (1) \times 10^5$.
0 min.	1.22 c.c.		
50	1.04	4.75	
104	0.90	4.65	4.7

When the sol was not preactivated the velocity constant was also 4.7×10^{-5} (Table II). It has been observed that the active sol does not react with glucose or laevulose in the dark. The activation does not take place in an atmosphere of ordinary air. The active sol looses its activity within half an hour in the dark. Pre-insolation of the glucose and laevulose cannot avoid the induction period.

Very dilute ($0.0002M$) ferric chloride, ferrous ammonium sulphate, copper sulphate, and manganous sulphate have practically no influence on the velocity constants of the reactions.

DISCUSSION

Any mechanism proposed for the photo-oxidation of glucose and laevulose by sol of ceric borate should be in a position to explain the following characteristic features :—

(i) That the velocity of reaction is proportional to the 3/2th power of the concentration of the photoactive reagent,

(ii) that the velocity constant varies as the square root of intensity of absorbed radiation under otherwise identical experimental conditions,

(iii) that the inverse of velocity constant plotted against the inverse of concentration of reductant is a straight line,

(iv) that the quantum efficiency is generally greater than unity which indicates the existence of some kind of chain mechanism.

The mechanism of oxidation of sugars by air in presence of cerous hydroxide gels has been studied by Ghosh and Rakshit (*J. Indian Chem. Soc.,* 1935, **12**, 357). There the formation of ceric hydroperoxide in course of oxidation of sugars was experimentally demonstrated. It appears that a ceric compound activated by absorption of radiation is not capable of reacting according to the simple mechanism.

Ceric compound (activated) + AH_2 (substrate) → cerous compound + H^+ + AH.

If that were so, the kinetics of photo-oxidation would have been extremely simple. The fact is that the substrate AH_2 cannot part with its hydrogen atoms singly ; whenever it enters into any reaction both the hydrogen -atoms must be removed simultaneously. A mechanism which takes into consideration this central fact, and also the intermediate existence of ceric hydroperoxide compound, may be developed as follows :—

(i)   A molecule of ceric compound $[Ce^{++++}] + h\nu \longrightarrow$ activated molecule (Ce^{++++}act.)

(ii) Ce^{++++}act. $+ Ce^{+++}$ normal $+ 2H_2O \longrightarrow$ cerous compound + ceric hydroperoxide.

(iii)   Ceric hydroperoxide $+ AH_2 +$ ceric compound $\longrightarrow A +$ cerous compound + active ceric compound.

(iv)   2 Activated ceric compound molecules $+ AH_2 \longrightarrow A + 2$ cerous compound molecules.

It is easily seen that this mechanism will give us the following value of velocity of reaction if reaction (iv) is, as is very probable, small compared with reaction (iii).

$dx/dt = k_1[Ce^{++++}$act.$][Ce^{++++}$normal$].C_s$, where C_s is the surface concentration of the reductant on the colloid micelle.

$$= k_2 \left[\frac{I_{abs} \text{ by } Ce^{++++}}{Nh} \right]^{\frac{1}{2}} [Ce^{++++}]\, C_s.$$

Our experiments on the measurement of the extinction coefficients of radiations 366 $\mu\mu$ by ceric and cerous borate sols, show that these magnitudes are of the same order. Hence we may assume that of the total light (I_{abs}) absorbed by the system, $I_{abs}(a-x)$, is the fraction absorbed by the ceric compound.

Hence $dx/dt = k_2 \sqrt{I_{abs}}\; (a-x)^{3/2}.C_s$

The surface concentration of the reductant glucose is given by the well known Langmuir equation

$$C_s = \frac{k_3 c(\text{bulk})}{k_4 + k_3 c(\text{bulk})}.$$

The equation thus developed explains at once the characteristic features of the reaction which we have observed. In view of the chain mechanism postulated in reactions (ii) and (iii) and the break in the chain due to reaction (iv), the probability of the quantum efficiency being greater than unity is indicated.

The difference in the efficiencies of these photochemical reactions in circularly polarised light can be best explained from our knowledge of the anisotropic factor for ceric borate sol in the region of 366 $\mu\mu$ (Ghosh and Banerjee, *Kolloid Z.*, 1939,**86**, 3).

Conc. of ceric borate sol 0·0032 M	I_{abs} =570 ergs/cm^2/sec.	Anisotropic factor for $\lambda = 366$ $\mu\mu$
	Period of preexcitation =12 hours. *d*-Circularly polarised light. *l*·Circularly polarised light.	$g = \frac{A_l - A_d}{\frac{1}{2}(A_l + A_d)}$ −0·0401 +0·0261

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