

PHOTOCHEMICAL REACTIONS WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION. PART III. ON THE EFFECT OF p_H ON THE PHOTOREDUCTION OF TUNGSTIC ACID SOL IN UNPOLARISED LIGHT.

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The present section deals with the effect of p_H on the velocity of photoreduction of tungstic acid sol. For purposes of comparison, the effect of p_H on the velocity of reaction with three types of reductants viz., electrolytes, non-electrolytes, and ampholytes has been studied.

EXPERIMENTAL.

Preparation of Sol.—The sol was prepared exactly in the same way as before and for variation of p_H of the reaction mixture, solutions of hydrochloric acid or caustic soda (Merck's reagent) were subsequently added as the case may be. This procedure is necessary to ensure the complete formation of the sol. The p_H of the reaction mixture was brought by trial to the required value.

The p_H values were measured by the quinhydrone electrode.

Experimental results.—The effect of the change in the concentration of sodium chloride, formed during neutralisation of acid by NaOH for regulating the p_H , on the velocity of reaction was first studied and found to be nil.

Effect of p_H on the Velocity of Photoreduction.

TABLE I.

d (thickness of the cell) = 0.5 cm., γ = Quantum efficiency. I_{abs} = Intensity of absorbed radiation in ergs/cm²/sec.

(a) Tungstate = 0.05M. Formaldehyde = 0.8425M. I_{abs} (366 μ) = 1166. Temp. = 29.5°.

p_H	...	1.48	1.60	2.12	4.08
$K_9 \times 10^{10}$...	6.50	6.42	3.64	2.27
γ	...	0.91	0.76	0.51	0.32

TABLE I (contd.).

(b) Tungstate = 0.025M. Glucose = 10%. $I_{abs} = 2440$. Temp. = 31°.								
ρ_n	...	1.25	1.50	1.73	1.82	2.12	2.61	4.01
$K_0 \times 10^{10}$...	17.17	15.17	10.42	9.92	8.42	5.60	1.53
γ	...	1.13	0.99	0.68	0.65	0.55	0.37	0.10
(c) Tungstate = 0.025M. Laevulose = 5%. $I_{abs} = 1331$. Temp. = 30°.								
ρ_n	...	1.35	1.48	1.94		2.12		
$K_0 \times 10^{10}$...	8.68	6.30	4.50		3.98		
γ	...	1.07	0.78	0.55		0.49		
(d) Tungstate = 0.025M. Lactic acid = 1.01M. $I_{abs} = 1331$. Temp. = 30°.								
ρ_n	...	0.76	0.85	1.06	1.18	1.61	2.12	2.52
$K_0 \times 10^{10}$...	9.83	12.03	12.78	12.77	8.70	5.53	3.98
γ	...	1.21	1.48	1.57	1.57	1.07	0.68	0.49
(e) Tungstate = 0.025M. Mandelic acid = M/4. $I_{abs} = 1331$. Temp. = 29.5°.								
ρ_n	...	1.13	1.32	1.62		2.12		2.3
$K_0 \times 10^{10}$...	4.57	4.83	3.70		2.76		2.35
γ	...	0.56	0.59	0.46		0.34		0.29
(f) Tungstate = 0.05M. Leucine = 0.666%. $I_{abs} = 2722$. Temp. = 29.5°.								
ρ_n	...	1.31	1.65	1.86		2.33		2.98
$K_0 \times 10^{10}$...	5.67	4.60	3.33		1.58		0.87
γ	...	0.332	0.27	0.196		0.093		0.051
(g) Tungstate = 0.05M. Citraunic acid = 1%. $I_{abs} = 2632$. Temp. = 29.5°.								
ρ_n	...	1.40	1.52	1.74		2.05		2.51
$K_0 \times 10^{10}$...	2.20	1.97	1.28		0.67		0.42
γ	...	0.134	0.120	0.078		0.040		0.025
(h) Tungstate = 0.05M. Hypophosphite = 0.083M. $I_{abs} = 1748$. Temp. = 31°.								
ρ_n	...	1.75	2.21	2.58		3.50		4.10
$K_0 \times 10^{10}$...	12.83	9.75	7.35		3.35		1.67
γ	...	1.17	0.89	0.67		0.31		0.15

DISCUSSION.

From Figs. 1 and 2, it is evident that in all cases at about p_H 4.8, the velocity of reaction is practically nil. Then with the decrease of p_H , the velocity of reaction increases steadily. After the p_H reaches 1.3, the system becomes unstable and the colloid coagulates shortly after its preparation.

FIG. 1.

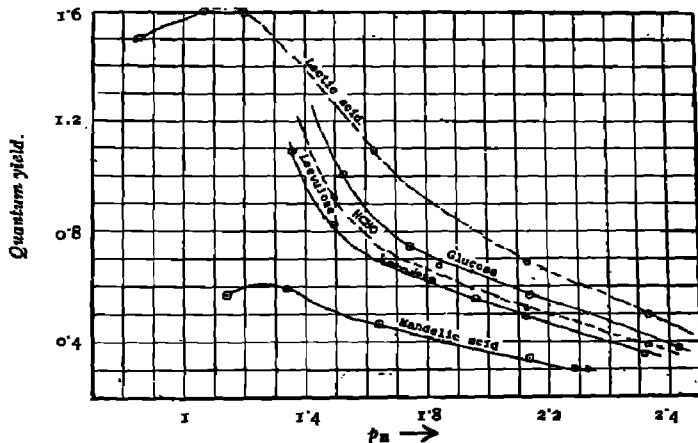


FIG. 2.

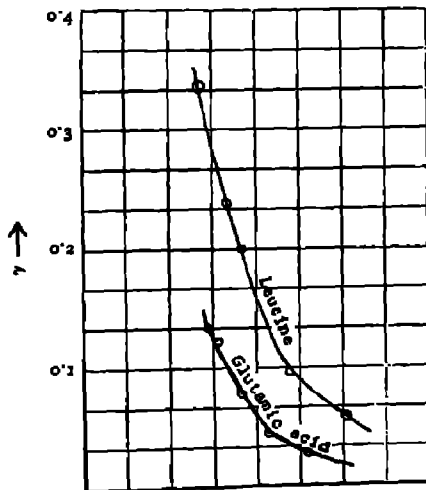
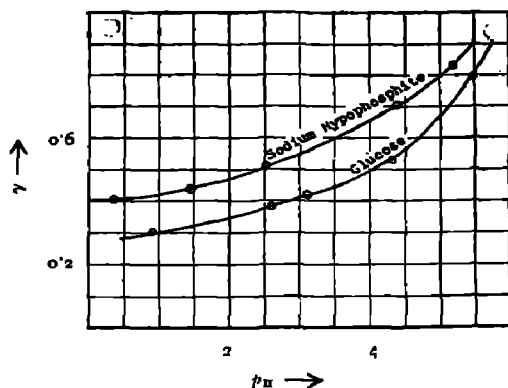


FIG. 3.



Our results can be best explained on the basis of the observations made by Rabinowitsch and Kargin (*Z. physikal. Chem.*, 1931, 152, 26) and G. Jander and others (*Z. anorg. Chem.*, 1929, 180, 138).

Rabinowitsch (*loc. cit.*) from the measurement of specific conductivity of tungstic acid sol at different dilutions came to the conclusion that above p_H 4.8, tungstic acid sol was in state of molecular dispersion. In other words tungstic acid sol formed a true solution. Below p_H 4.8, colloidal micelles are formed. As the p_H is still decreased, the portion of tungstic acid existing as micelles increases.

That the increase in the velocity of reaction is due to the increase in concentration of micelles can be clearly seen from the data recorded in Table II.

TABLE II.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
p_H	γ_{glucose}	γ_{HCHO}	$\gamma_{\text{Laevulose}}$	$\gamma_{\text{Lactic acid}}$	$\gamma_{\text{Mandelic acid}}$	R/A.	F/A.	G/A.	H/A
	(A)	(B)	(E)	(G)	(H)				
2.5	0.40	0.375	0.35	0.50	0.25	0.90	0.84	1.21	0.60
2.25	0.485	0.455	0.43	0.615	0.30	0.90	0.85	1.22	0.59
2.0	0.585	0.555	0.525	0.74	0.355	0.95	0.89	1.26	0.61
1.75	0.70	0.655	0.62	0.92	0.42	0.91	0.87	1.29	0.59
1.5	0.995	0.895	0.80	1.24	0.53	0.90	0.80	1.24	0.53

If we compare the relative rate of increase in quantum yield with laevulose, glucose, etc. in Table II, we find that the ratio between quantum yield at different p_H is practically constant (*vide* columns 7, 8, 9 and 10, Table II).

It may be pointed out that lactic acid and mandelic acid between p_H 1.5 and 2.5 exist practically in the undissociated state.

Lactic acid and mandelic acid stabilise tungstic acid sol below p_H 1.5 but at the same time, the effective specific surface of the sol is much diminished due to increase in the size of the colloidal micelles. So we get a diminution in the velocity in those cases where it is possible to keep the reaction mixture stable below 1.5.

TABLE III.
 γ = Quantum efficiency.

p_H	4.0	3.75	3.5	3.25	3.0	2.75	2.5	2.25	2.0	1.75
$\gamma_{\text{Hypophosphite}}$	0.175	0.235	0.30	0.37	0.465	0.58	0.70	0.845	0.985	1.15
γ_{Glucose}	0.105	0.135	0.18	0.22	0.275	0.335	0.40	0.485	0.58	0.70
$\frac{\gamma_H}{\gamma_0}$	1.67	1.74	1.67	1.68	1.70	1.73	1.75	1.74	1.70	1.65

We know that hypophosphite dissociates more and more as p_H increases. The constancy of the ratio γ_H/γ_0 in Table III indicates that the undissociated or the dissociated hypophosphite has the same effect on the velocity of photoreduction of tungstic acid sol.

TABLE IV.

(1) p_H .	(2) γ_{Glucose} (A)	(3) γ_{Leucine} (C)	(4) $\gamma_{\text{Glutamic acid}}$ (D)	(5) C/A.	(6) D/A.
4.0	0.105	0.02	...	0.19	...
3.75	0.135	0.028	0.008	0.21	0.06
3.5	0.180	0.037	0.012	0.20	0.065
3.25	0.220	0.045	0.015	0.202	0.067
3.0	0.275	0.054	0.018	0.20	0.067
2.75	0.335	0.065	0.022	0.18	0.067
2.5	0.40	0.078	0.027	0.20	0.067
2.0	0.58	0.142	0.045	0.24	0.080
1.75	0.70	0.237	0.070	0.33	0.100
1.5	0.995	0.31	0.12	0.31	0.12

* γ_H & γ_0 denote respectively γ due to hypophosphite and glucose.

In the case of amino-acids (Table IV), the rate of reaction (hence quantum yield) is influenced by a second factor, in addition to the effect of H^+ ions on the tungstic acid sol. We observe from Table IV, columns (5) and (6), that in the case of leucine and glutamic acid, the relative increase in reaction velocity with decrease in p_H is different from that obtained with glucose as reductant.

The abnormal increase in reaction rate as p_H is lowered can be explained in the following manner.

The velocity of the photoreduction with amino-acids as reducing agent can be expressed by the equation

$$\frac{dx}{dt} = K_1 (\text{surface conc. of } NH_3^+R'COOH) + K_2 (\text{surface conc. of } ^+NH_3^+R'COOH)$$

It is the positively charged $^+NH_3^+R'COOH$ and the neutral molecule or the zwitter ion $[^+NH_3^+R'COO^-]$ which alone can get adsorbed on the negatively charged micelle surface.

The concentration of the ions $^+NH_3^+R'COOH$ in a solution of amino-acids, increases rapidly (*vide* Table V) as the p_H is decreased below p_H about 3.0 (Harris, *Proc. Roy. Soc.*, 1924, **B96**, 441).

Assuming that the adsorbability of the "zwitter ion" and the form ^+XH on the surface of the sol micelles is of the same order and remembering that at the same p_H for leucine, the velocity constant is independent of the concentration of leucine, we may express the velocity constant of the reaction by an equation of the type

$$\frac{dx}{dt} = K_1 \frac{C [^+X^-]}{C_{total}} + K_2 \frac{C [^+XH]}{C_{total}}.$$

K_1 is a function of p_H which determines the reactive capacity of colloidal micelles. At p_H 4.0, leucine exists practically in the form $^+X^-$ and K_1 has the value 0.02. It is to be expected that the variation of K_1 with p_H should be the same as that observed in the case of glucose. Similarly K_2 is another function of p_H , being equal to 0.31 at p_H 1.5 where leucine exists practically in the ^+XH form and decreases with p_H at the rate at which the velocity of oxidation of glucose by tungstic acid sol decreases with p_H .

$C_{[+X^-]}$, $C_{[+XH]}$ and C_{total} denote the concentrations of $[+X^-]$, $[+XH]$ and total concentration of amino-acid used in the experiment.

Similar equation was applied in the case of glutamic acid. The agreement between the observed and calculated values indicates that our assumptions are justified.

TABLE V.

	K_B		$K_a = \frac{K_w}{K_b} = \frac{[+X^-][H^+]}{[XH]}$
Leucine	$= 2.3 \times 10^{-12}$		4.348×10^{-3}
Glutamic acid	$= 1.5 \times 10^{-12}$		

6.667×10^{-3}
(L. J. Harris, *loc. cit.*)

$\mu\pi$	Leucine.		Glutamic acid.	
	$C_{[+X^-]}$	$C_{[+XH]}$	$C_{[+X^-]}$	$C_{[+XH]}$
1.5	0.081	0.589	0.174	0.826
1.75	0.132	0.538	0.273	0.727
2.0	0.203	0.467	0.400	0.600
2.25	0.292	0.378	0.543	0.457
2.50	0.388	0.282	0.698	0.302
2.75	0.476	0.184	0.789	0.211
3.0	0.545	0.125	0.870	0.130
3.25	0.593	0.077	0.922	0.078
3.50	0.625	0.045	0.955	0.045
3.75	0.644	0.026	0.974	0.026
4.0	0.655	0.015	0.985	0.015

The results are plotted graphically in Figs. 4 and 5.

FIG. 4.
Glutamic acid.

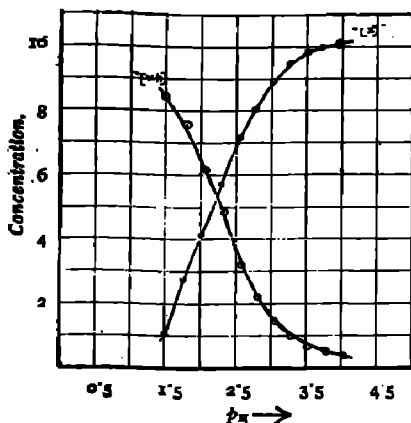


FIG. 5.

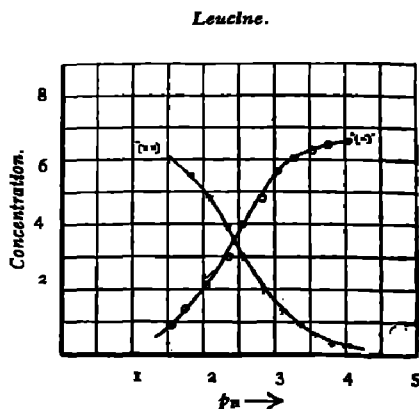


TABLE VI.

p_H	Leucine.		$\frac{dx}{dt}$		K_1	K_2	$\frac{dx}{dt}$	
	K_1	K_2	calc.	(obs.).			calc.	(obs.).
4.00	0.02	0.0326	0.0203	0.02				
3.75	0.0257	0.0419	0.0263	0.028	0.008	0.0163	0.0082	0.008
3.50	0.0343	0.0559	0.0351	0.037	0.108	0.0217	0.0112	0.012
3.25	0.0419	0.0684	0.0449	0.045	0.013	0.0265	0.0141	0.015
3.00	0.0524	0.0855	0.0586	0.054	0.0163	0.0332	0.0185	0.018
2.75	0.0638	0.0942	0.0712	0.065	0.0199	0.0404	0.0242	0.022
2.50	0.0769	0.124	0.0967	0.078	0.0237	0.0482	0.0311	0.027
2.00	0.011	0.180	0.159	0.142	0.0344	0.0700	0.0557	0.045
1.75	0.123	0.218	0.199	0.237	0.0415	0.0844	0.0727	0.071
1.50	0.190	0.310	0.300	0.310	0.059	0.1200	0.110	0.11

On decreasing the p_H we have observed that beyond p_H 1.3, the system becomes unstable, the sol being coagulated. This corroborates the observation of Jander (*loc. cit.*) who found that tungstic acid micelle is coagulated at p_H $1.5 \pm .2$.