PHOTOCHEMICAL STUDIES IN SOLS AND GELS. PART II.

THE REDUCTION OF FERRIC CHLORIDE BY MANDELIC ACID IN LIGHT OF DIFFERENT FREQUENCIES IN MEDIA OF THIXOTROPIC THORIUM PHOSPHATE AND THORIUM MOLYBDATE SOLS AND GELS.

By SIR J. C. GHOSH, *Kt., D.Sc., F.N.I.*, S. K. BHATTACHARYYA, *D.Sc.* *and* R. BANERJEE, *B.Sc., Department of Pure and Applied Chemistry, Indian Institute of Science, Bangalore.*

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In the present investigation we have used thixotropic thorium phosphate and thorium molybdate sols and gels as solvent media as they are transparent and perfectly colourless and have studied a very simple reaction—the photoreduction of ferric chloride by mandelic acid in light of wavelengths 366 and 436$\mu\mu$. The kinetics of this reaction were studied, in details, in the aqueous phase by a number of workers, notably by Eder, Jodin, Lemoine, Ross, Winther and Oxolt-Howe, Kornfeld and Mencke, Ghosh and Purakayastha, Purakayastha, Allmand and Young, Kornfeld, Talpade and Bavdekar.

In aqueous phase and with mandelic acid as a reductant, Ghosh and Purakayastha (*loc. cit.*) have shown that (i) the reaction is zero-molecular with respect to ferric chloride; (ii) the zero-molecular velocity constant increases with increasing concentration of the reductant and in fact, $\frac{1}{\Delta x/\Delta t}$ plotted against $\frac{1}{\text{(Reductant)}}$ gives a straight line; (iii) the velocity constant is directly proportional to the intensity of absorbed radiation; (iv) the velocity constant varies very slightly with increasing concentration of hydrochloric acid; (v) the quantum efficiency was found to be 1·06, 1·18 and 1·36 in wavelengths 488, 448 and 390$\mu\mu$ respectively.

The reaction has been studied in media of (1) thorium phosphate and thorium molybdate sols, (2) thorium phosphate and thorium molybdate gels, and (3) water, and a comparative study of the photoprocess has been made under these conditions.

The reaction may be expressed by the equation,

$$2FeCl_3+C_6H_5CH(OH)COOH = 2FeCl_2+2HCl+CO_2+C_6H_5CHO.$$

Section A—deals with the photoreduction of ferric chloride by mandelic acid in unpolarised light of wavelengths 366 and 436$\mu\mu$.

Section B—deals with the photoreduction of ferric chloride by mandelic acid in polarised light of wavelength 436$\mu\mu$.

Experimental.

The experimental arrangement was the same as was described by the authors in Part I of this series with the following alteration:—

(*a*) The reaction cell was 4 cm.×4 cm.×1 cm. thick and made of plane glass plates fused into one another with a stopper at the top for measurements in unpolarised light.

(*b*) For measurements in polarised light, a circular corex glass cell of 1 cm. thickness and 2·5 c.c. capacity was used.

Reagents:

Kahlbaum's extra-pure ferric chloride, Merck's extra-pure mandelic acid, thorium nitrate, potassium phosphate (KH_2PO_4), potassium iodide, hydrochloric acid and sodium thiosulphate and sodium molybdate supplied by B.D.H. were used. For making solutions bi-distilled water was used.

Preparation of thorium phosphate sol and gel:

Thorium phosphate sol and gel were prepared according to the method of Prakash and Dhar by mixing 0·25 c.c. of a solution of potassium phosphate (22·0%) with 5 c.c. of a solution of thorium nitrate (48·14 g./litre), making the total volume in all cases to 6 c.c. The mixture on shaking for 3 minutes and allowing to stand for 5 minutes gave a transparent, colourless and viscous sol which set to a firm gel after 4 hours.

Preparation of thorium molybdate sol and gel:

Thorium molybdate sol and gel were prepared according to the method of Prakash and Dhar (*loc. cit.*) modified to some extent by Mata Prasad *et al.* 5 c.c. of a solution of thorium nitrate (48·14 g./litre) were taken in one test tube and in another test tube were taken 1·5 c.c. of a solution of sodium molybdate (3%), 1·5 c.c. water and 2 c.c. of HCl (0·1N). The solution contained in one test tube was poured into the other when a white precipitate was formed, which on shaking for 5 minutes, dissolved giving a transparent and colourless sol, which set to a firm gel after about 1 hour.

To study the reaction in the gel phase, the reactants were mixed in the corresponding sol and allowed to stand in the dark until the reaction mixture set to a firm and transparent gel. The set reaction mixture was then exposed to monochromatic light.

To study the reaction in the sol phase, the reactants were mixed in the corresponding sol and exposed just after mixing to monochromatic light. The reaction was stopped within 60 minutes during which the sol did not set to a gel. In order to prevent the hydrolysis of ferric chloride, a certain amount of hydrochloric acid was added to the solution of ferric chloride. When the reaction mixtures were made in thorium molybdate sol or gel, a large number of air bubbles were always found entrapped in the viscous liquid. Since these bubbles did not disappear spontaneously, they were removed before pipetting, by the application of vacuum. A clear reaction mixture was then obtained.

Measurement of the velocity of reaction:

Thorium phosphate as well as thorium molybdate gels, though thixotropic, liquefy to a very viscous liquid on shaking vigorously and so it was found very difficult to pipette out the exposed reaction mixture at definite intervals. For this reason 2 c.c. of the reaction mixture were exposed in the reaction cell each time and the whole amount was taken out in a stoppered conical flask after a definite period and the ferric chloride was estimated iodometrically by titration, in an atmosphere of CO_2, with standard thiosulphate solution by means of a micro-burette. The initial concentration of ferric chloride was determined in the same way.

The *p*H of the reaction mixture was determined potentiometrically by using glass electrode. The *p*H of different mixtures were kept constant by required quantities of HCl or KOH. The *p*H of the reaction mixture was varied by adding HCl.

Measurement of intensity:

The intensity of radiation absorbed by the reaction mixture was measured in the same way as was described in Part I of the series. The intensity of absorbed radiation was measured by noting the deflections when the light passed through (*a*) pure solvent, *i.e.* water or pure sol or pure gel, and (*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 here that thorium phosphate and thorium molybdate sols and gels have got no absorption in 366 or 436$\mu\mu$. There is no difference in the absorption of the sol before and after gelation.

It was found that the intense yellow colour produced by mixing mandelic acid with ferric chloride solution in water became pale yellow in media of thorium phosphate as well as thorium molybdate sols and gels. The extinction coefficients of ferric chloride were measured in different media by means of intensity measurements, keeping the concentration of mandelic acid greater than that of ferric chloride and the ratio $\frac{(\text{Mandelic acid})}{(FeCl_3)}$ constant. The extinction coefficients at different wavelengths and in different media were found in the following way: the deflections in the galvanometer were noted, first of all, with the solvent alone and secondly with ferric chloride and mandelic acid mixtures of known concentrations. The molecular extinction coefficients of ferric chloride were then calculated according to the equation,

$$\epsilon = \frac{1}{c.d.} \log_{10} \frac{I_0}{I_t}$$

where ϵ = molecular extinction coefficient,
c = concentration of ferric chloride in gm. mol. per litre,
d = thickness of the reaction cell in cm.,

and I_0, I_t are the incident and transmitted radiations measured. The extinction coefficients of ferric chloride were also measured in presence of varying quantities of thorium nitrate. The results are tabulated in tables I and II.

TABLE I.

(λ)	*phase*	
366	Aqueous	1629·0
,,	Thorium phosphate sol ..	106·2
,,	Thorium phosphate gel ..	106·2
,,	Thorium molybdate sol ..	217·6
,,	Thorium molybdate gel ..	217·6
436	Aqueous	610·3
,,	Thorium phosphate sol ..	47·6
,,	Thorium phosphate gel ..	46·2
,,	Thorium molybdate sol ..	52·1
,,	Thorium molybdate gel ..	52·1

TABLE II.

$\lambda = 366\mu\mu$

Concentration of ferric chloride $= 1{\cdot}94 \times 10^{-4}$M
,, mandelic acid $= 2{\cdot}24 \times 10^{-4}$M

(Thorium nitrate) 10^4	0	2·3	6·9	13·8	20·3	33·2
ϵ	1629·0	1173·0	739·0	565·7	438·5	366·1

From table II we can see that even a small amount of thorium nitrate lowers the extinction coefficient to a great extent.

The reactions which do not take place in the dark were carried out at 25°C. The experimental data, are recorded in tables III to XV. The reaction was found to be zero-molecular with respect to ferric chloride. In the given tables, in media of thorium phosphate sol and gel, $\frac{\Delta x}{\Delta t}$ = zero-molecular velocity constant = changes in concentration of ferric chloride in 2 c.c. of reaction mixture per minute in terms of c.c. of 0·0029N thiosulphate and in media of thorium molybdate sol and gel, $\frac{\Delta x}{\Delta t}$ = changes in concentration of ferric chloride in 2 c.c. of reaction mixture per minute in terms of c.c. of 0·0017N thiosulphate.

In the tables, θ = temperature; $I_{abs.}$ = number of quanta absorbed per c.c. per sec.; a = Initial concentration of ferric chloride in gm. mol. per litre and b = Initial concentration of mandelic acid in gm. mol. per litre; γ = Quantum efficiency.

SECTION A.

Determination of the order of the reaction.

TABLE III.

Medium = Thorium phosphate gel; $\lambda = 436\mu\mu$; $\theta = 25°$C.; $a = 6{\cdot}23 \times 10^{-3}$M; $b = 7{\cdot}4 \times 10^{-3}$M; $I_{abs.} = 300{\cdot}7 \times 10^{13}$; pH = 1·74

Time	0·0029N—thio for 2 c.c. reaction mixture	$\frac{\Delta x}{\Delta t} . 10^3$
(I) 0	4·30	7·67 from (I) and (II)
(II) 60	3·84	7·50 from (II) and (III)
(III) 120	3·39	
		7·59 (mean)

TABLE IV.

Medium = Thorium molybdate gel; $\lambda = 366\mu\mu$; $\theta = 25°$C.; $a = 6{\cdot}1 \times 10^{-3}$M; $b = 7{\cdot}4 \times 10^{-3}$M; $I_{abs.} = 107{\cdot}0 \times 10^{13}$; pH = 1·42.

Time	0·0017N—thio for 2 c.c. reaction mixture	$\frac{\Delta x}{\Delta t} . 10^{13}$
(I) 0	7·30	9·3 from (I) and (II)
(II) 30	7·02	9·0 from (II) and (III)
(III) 60	6·75	
(IV) 90	6·47	9·3 from (III) and (IV)
		9·2 (mean)

Effect of varying the concentration of ferric chloride.

TABLE V.

Medium = Thorium phosphate gel; $\theta = 25°$C.; pH = 1·74; Thiosulphate = 0·0029N.

λ ($\mu\mu$)	$a.10^3$ (mol.)	$b.10^3$ (mol.)	$I_{abs.}10^{-13}$	$\frac{\Delta x}{\Delta t} . 10^3$	$\frac{\Delta x}{\Delta t} . 10^{18}/I_{abs.}$	γ
366	9·33	7·4	128·5	5·2	4·0	0·06
,,	6·22	,,	120·9	4·7	3·9	0·06
,,	3·11	,,	76·3	3·0	3·9	0·06
436	12·44	7·4	386·8	9·0	2·3	0·03
,,	9·33	,,	355·0	8·4	2·4	0·04
,,	6·22	,,	300·7	7·6	2·5	0·04
,,	3·11	,,	206·2	4·6	2·2	0·03

TABLE VI.

Medium = Thorium molybdate gel; θ = 25°C.; pH = 1·42; Thiosulphate = 0·0017N.

λ ($\mu\mu$)	$a.10^3$ (mol.)	$b.10^3$ (mol.)	$I_{abs}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^3$	$\frac{\Delta x}{\Delta t}.10^{18}/I_{abs}$.	γ
366	6·1	7·4	107·0	9·2	8·6	0·07
,,	3·05	,,	90·2	7·8	8·6	0·07
,,	1·53	,,	54·1	4·6	8·4	0·07
436	6·1	7·4	153·5	11·0	7·2	0·06
,,	3·05	,,	138·1	10·0	7·2	0·06
,,	1·53	,,	97·0	7·0	7·2	0·06

Effect of varying the concentration of mandelic acid.

TABLE VII.

Medium = Thorium phosphate gel; θ = 25°C.; pH = 1·74; Thiosulphate = 0·0029N.

λ ($\mu\mu$)	$a.10^3$ (mol.)	$b.10^3$ (mol.)	$I_{abs}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^3$	$\frac{\Delta x}{\Delta t}.10^{18}/I_{abs}$.	γ
366	6·22	14·8	122·2	5·3	4·4	0·07
,,	,,	7·4	120·9	4·7	3·9	0·06
,,	,,	3·7	110·1	3·7	3·4	0·05
436	6·23	14·8	343·7	9·5	2·8	0·04
,,	,,	11·1	339·3	9·0	2·6	0·04
,,	,,	7·4	300·7	7·6	2·5	0·04
,,	,,	3·7	231·9	4·0	1·7	0·03

TABLE VIII.

Medium = Thorium molybdate gel; θ = 25°C.; pH = 1·42; Thiosulphate = 0·0017N.

λ ($\mu\mu$)	$a.10^3$ (mol.)	$b.10^3$ (mol.)	$I_{abs}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^3$	$\frac{\Delta x}{\Delta t}.10^{18}/I_{abs}$.	γ
366	6·1	7·4	107·0	9·2	8·6	0·07
,,	,,	3·7	,,	8·6	8·0	0·07
,,	,,	1·85	,,	7·3	6·8	0·06
436	3·05	7·4	138·0	10·0	7·2	0·06
,,	,,	3·7	110·0	7·9	7·1	0·06
,,	,,	1·85	49·0	3·5	7·1	0·06
,,	1·53	5·55	77·0	5·5	7·1	0·06
,,	,,	3·7	48·2	3·3	7·0	0·06
,,	,,	1·85	28·0	2·0	7·0	0·06

Effect of varying the intensity of absorbed radiation.

TABLE IX.

Medium = Thorium phosphate gel; θ = 25°C.; pH = 1·74; Thiosulphate = 0·0029N.

λ ($\mu\mu$)	$a.10^3$ (mol.)	$b.10^3$ (mol.)	$I_{abs}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^3$	$\frac{\Delta x}{\Delta t}.10^{18}/I_{abs}$.	γ
366	6·22	7·4	120·9	4·7	3·9	0·06
,,	,,	,,	76·3	3·0	3·9	0·06
436	6·22	7·4	300·7	7·6	2·5	0·04
,,	,,	,,	186·1	5·0	2·7	0·04

TABLE X.

Medium = Thorium molybdate gel; θ = 25°C.; pH = 1·42; Thiosulphate = 0·0017N.

λ ($\mu\mu$)	$a.10^3$ (mol.)	$b.10^3$ (mol.)	$I_{abs}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^3$	$\frac{\Delta x}{\Delta t}.10^{18}/I_{abs}$.	γ
366	6·1	3·7	240·1	19·0	7·9	0·07
,,	,,	,,	100·0	8·0	8·0	0·07
436	1·55	5·55	56·0	4·0	7·1	0·06
,,	,,	,,	36·0	2·6	7·2	0·06
,,	,,	3·7	36·0	2·6	7·2	0·06
,,	,,	,,	18·6	1·33	7·1	0·06

Effect of varying pH.

TABLE XI.

Medium = Thorium phosphate gel; θ = 25°C.; Thiosulphate = 0·0029N.

λ ($\mu\mu$)	$a.10^3$ (mol.)	$b.10^3$ (mol.)	pH	$I_{abs}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^3$	$\frac{\Delta x}{\Delta t}.10^{18}/I_{abs}$.	γ
366	6·22	7·4	1·74	120·9	4·7	3·9	0·06
,,	,,	,,	1·43	,,	4·7	3·9	0·06
436	6·22	7·4	1·74	300·7	7·6	2·5	0·04
,,	,,	,,	1·43	,,	7·5	2·5	0·04

TABLE XII.

Medium = Thorium molybdate gel; θ = 25°C.; Thiosulphate = 0·0017N.

λ ($\mu\mu$)	$a.10^3$ (mol.)	$b.10^3$ (mol.)	pH	$I_{abs}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^3$	$\frac{\Delta x}{\Delta t}.10^{18}/I_{abs}$.	γ
366	6·1	3·7	1·80	118·2	9·7	8·2	0·07
,,	,,	,,	1·48	,,	9·5	8·0	0·07
436	1·55	5·55	1·42	56·0	4·0	7·1	0·06
,,	,,	,,	1·18	56·0	4·0	7·1	0·06

Effect of the nature of medium.

TABLE XIII.

θ = 25°C.; pH = 1·74; $a.10^3$ = 6·22M; $b.10^3$ = 7·4M; Thiosulphate = 0·0029N.

λ ($\mu\mu$)	Medium.	$I_{abs}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^3$	$\frac{\Delta x}{\Delta t}.10^{18}/I_{abs}$.	γ
366	Aqueous	131·0	9·5	7·3	0·11
,,	Thorium phosphate sol ..	120·9	4·7	3·9	0·06
,,	Thorium phosphate gel ..	120·9	4·7	3·9	0·06
436	Aqueous	595·7	25·7	4·3	0·06
,,	Thorium phosphate sol ..	300·7	7·6	2·5	0·04
,,	Thorium phosphate gel ..	300·7	7·6	2·5	0·04

TABLE XIV.

$\theta = 25°C.; pH = 1·42; a.10^3 = 6·1M$; Thiosulphate = 0·0017N.

λ ($\mu\mu$)	$b.10^3$ (mol.)	Medium.	$I_{abs}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^3$	$\frac{\Delta x}{\Delta t}.10^{18}/I_{abs}$.	γ
366	3·7	Aqueous	142·6	15·2	10·7	0·09
,,	,,	Thorium molybdate sol ..	100·0	8·0	8·0	0·07
,,	,,	Thorium molybdate gel ..	100·0	8·0	8·0	0·07
436	7·4	Aqueous	394·6	29·0	7·3	0·09
,,	,,	Thorium molybdate sol ..	335·0	24·0	7·2	0·06
,,	,,	Thorium molybdate gel ..	335·0	24·0	7·2	0·06

SECTION B.

Ghosh and his collaborators have made an extensive study of a large number of chemical reactions on the surface of certain inorganic micro-heterogeneous photocatalysts under the influence of light in various states of polarisation. In their experiments, they have observed in certain cases a differential reaction velocity with *d*- and l- circularly polarised light of equal amplitudes.

It appeared interesting to investigate the effect on the photoreduction of ferric chloride by mandelic acid in thixotropic thorium molybdate gel as a solvent medium.

Experimental.

The apparatus and the experimental procedure were the same as in Section A with the following alterations:—

The polarising apparatus was placed between the ultraviolet filter and the reaction cell. The polarising appaıatus consists of a nicol prism and a glass Rhomb. For plane polarised light, the nicol prism was used and for the circularly polarised light, the nicol prism and the Rhomb were used in conjunction. The description and working principle of the polarising apparatus have been discussed by Ghosh, Banerjee and Mukherjee.

The experimental results are recorded in table XV.

TABLE XV.

$\lambda = 436\mu\mu; \theta = 25°C.; a.10^3 = 6·1M; b.10^3 = 7·4M; pH = 1·42$.

Nature of light.	$I_{abs}.10^{-13}$	$\frac{\Delta x}{\Delta t}.10^3$	$\frac{\Delta x}{\Delta t}.10^{18}/I_{abs}$.
Unpolarised	334·9	24·0	7·2
Plane polarised—			
(*a*) Axis of vibration—vertical ..	27·9	2·0	7·2
(*b*) Axis of vibration—horizontal ..	27·9	2·1	7·5
Circularly polarised—			
(*a*) *d*-circularly	21·0	1·5	7·1
(*b*) l-circularly	21·0	1·5	7·1

DISCUSSION.

The reaction has the following similar characteristics in both thorium phosphate and thorium molybdate gels as solvent media:—

(1) The reaction is zero-molecular with respect to ferric chloride.

(2) The zero-molecular velocity constant increases with increasing concentration of mandelic acid, the intensity of absorbed radiation being also

increased. In fact, $\frac{\Delta x}{\Delta t} \cdot 10^{18}/I_{abs.}$ increases slightly with increasing concentration of mandelic acid.

(3) The velocity constant increases with increasing concentration of ferric chloride. In fact, $\frac{\Delta x}{\Delta t} \cdot 10^{18}/I_{abs.}$ remains always constant.

(4) The velocity constant is directly proportional to the intensity of absorbed radiation. In fact, $\frac{\Delta x}{\Delta t} \cdot 10^{18}/I_{abs.}$ remains always constant for a particular wavelength but increases with increase in the magnitude of the quanta absorbed.

(5) The velocity constant is practically independent of pH.

(6) The rate of reaction remains the same in media of both sol and gel but it is greater in aqueous media. In thorium phosphate sol and gel as media, $\frac{\Delta x}{\Delta t} \cdot 10^{18}/I_{abs.}$ remains the same but in water it is much greater. In thorium molybdate sol and gel as media, $\frac{\Delta x}{\Delta t} \cdot 10^{18}/I_{abs.}$ has got the same value as in aqueous medium.

(7) The velocity constant remains the same in polarised light having axes of vibration vertical as well as horizontal.

(8) The velocity constant remains the same in both *d*- and l- circularly polarised light of equal amplitudes.

(9) The quantum efficiency is much less than unity.

On the observations made by Kistler that the dielectric constants of thixotropic sols remain the same before and after gelation and also on the observations made by Heyman that there is no change in volume of transparent thixotropic sols after gelation so that the average distance between the constituent particles does not alter, we can explain the reason for the same rate of reaction in media of thixotropic sol, before and after gelation, by assuming that the activated ferric ion deactivates to the same extent in media of both sol and gel.

The same rate of reaction in media of thixotropic sol, before and after gelation, means that the reaction can proceed equally fast whether the water of the medium is *free* or *bound*.

The quicker reaction in water may be due to a complex formation between mandelic acid and ferric chloride as is evidenced by the deep yellow colour of the mixture.

REFERENCES.

Allmand and Young (1931). The Photolysis of Potassium ferrioxalate solution, Part III. *J.C.S.*, 3079.

Banerjee (1937). Photochemical reactions with some inorganic colloids as active agents under the influence of light in various states of polarisation, Part XIII. *J. Indian Chem. Soc.*, **14**, 611.

Bavdekar (1943). The photochemical reduction of ferric chloride in aqueous solutions. *J. Bombay Uni.*, **12**, 47.

Eder (1881). Decomposition of ferric chloride and some ferric salts of organic acids by light. *Wien. Akad. Ber.*, **82**, 606.

Ghosh, Banerjee and Mukherjee (1937). Photochemical reactions with some inorganic colloids as active agents under the influence of light in various states of polarisation, Part I. *J. Indian Chem. Soc.*, **14**, 495.

Ghosh and Banerjee (1937). Photochemical reactions with some inorganic colloids as active agents under the influence of light in various states of polarisation, Part XIV. *J. Indian Chem. Soc.*, **14**, 617.

Ghosh and Purakayastha (1929). The photochemical reduction of ferric salts by mandelic, lactic and tartaric acids. *J. Indian Chem. Soc.*, **6**, 827.

Heyman (1936). Studies on Sol-gel transformation, Part II. *Trans. Farad. Soc.*, **82**, 462.
Jodin (1882). Photochemical reaction of ferric oxalate. *Compt. rend.*, **94**, 1315.
Kistler (1931). Dielectric constant and structure of thixotropic sols. *J. Phys. Chem.*, **35**, 815.
Kornfeld (1940). Photochemical reduction of ferric ion by oxalic acid. *J. Phys. Chem.*, **44**, 949.
Kornfeld and Mencke (1928). Photochemical reduction of ferric ion by oxalic acid. *Z. Electrochem.*, **34**, 598.
Lemoine (1884). Chemical action of light: decomposition of oxalic acid by ferric chloride. *Compt. rend.*, **97**, 1208.
Mata Prasad *et al.* (1938). Studies in thixotropic gelation of thorium molybdate gel. *J. Indian Chem. Soc.*, **15**, 365.
Prakash and Dhar (1929). Preparation of jellies of some inorganic substances. *J. Indian Chem. Soc.*, **6**, 587.
Purakayastha (1932). The reduction of ferric chloride by citric acid, malic acid and sugars. *J. Indian Chem. Soc.*, **9**, 237.
Ross (1906). On the chemical action of ultraviolet light. *J. Amer. Chem. Soc.*, **28**, 786.
Talpade (1941). *Proc. Nat. Akad. Sc.*, **2**, 1.
Winther and Oxolt-Howe (1914). The sensitiveness to light of ferric salts. *Z. Wiss. Phot.*, **14**, 196.