PHOTOCHEMICAL AFTER-EFFECT IN H_2O_2-$K_4Fe(CN)_6$ REACTION

By B. B. LAL, F.A.Sc.

(*Chemical Laboratories, Department of Archæology, Dehra Dun*)

INTRODUCTION

IN a previous communication[1] (1939) the results of preliminary investigation on the decomposition of hydrogen peroxide by potassium ferrocyanide and the photochemical after-effect in this reaction were reported, and it was suggested that the after-effect of illumination in this reaction is due to the photo-formation of potassium aquopentacyanoferrite from potassium ferrocyanide.

The above reaction has been studied by a large number of workers. Kistiakowsky[2] (1900) discovered this photochemical after-effect, and studied in detail the kinetics of hydrogen peroxide decomposition and attributed the after-effect to the formation of a catalyser (possibly of a colloidal nature) from ferrocyanide under the influence of light. The decomposition of hydrogen peroxide in the presence of ferrocyanide was found to be unimolecular both before and after irradiation. Weigert[3] (1907) however, came to the conclusion that the insolation of ferrocyanide produces reaction nuclei which catalyse the decomposition of hydrogen peroxide in the dark. Amann[4] (1911) attributed the enhanced reactivity in this reaction after insolation to the production of a photo-phase, but did not describe kinetic measurements of the photochemical after-effect. Winther[5] (1920) explained this after-effect by assuming a gradual formation of an extremely stable substance from ferrocyanide and the acceleration of the decomposition of hydrogen peroxide in the dark due to its catalytic action. In view of these conflicting views regarding the origin and nature of this photochemical after-effect, a detailed kinetic investigation was carried out. As a result of this investigation, it has been possible to substantiate the suggestion originally put forward by the author that the photo-formation of potassium aquopentacyanoferrite from potassium ferrocyanide during insolation is responsible for this marked photochemical after-effect.

MATERIALS AND TECHNIQUE

A summary of the important conclusions of this investigation has already been published[6] (1947). The technique adopted in this investigation has been discussed in detail in an earlier paper by the author[1] (1939). The

244

experiments described here were conducted at 40° C. in the dark. The decomposition of hydrogen peroxide was followed by titration with standard potassium permanganate. The total volume of the reaction mixture was 50 c.c. in all cases. The respective concentrations of potassium ferrocyanide and hydrogen peroxide were M/320 and N/6. A standard solution of potassium permanganate (N/24·6) was used for determining the change in peroxide concentration. The amount of permanganate used up by potassium ferrocyanide has been subtracted from the total volume used in each case. It may be remarked that the gasometric method has also been used by some workers for the study of the decomposition of hydrogen peroxide[7] (Rao and Srikantan, 1933), but this method of following the decomposition of the peroxide is not reliable[8] (Bailey), and hence the titrimetric method described above was adopted in the present investigation.

The peroxide used in most experiments was prepared in the laboratory from Merck's sodium peroxide and sulphuric acid. Experiments were also performed with Merck's 12 volume peroxide. It was observed that from a phenomenal standpoint, the behaviour of the two preparations of peroxide was very similar, but relatively high values of the velocity constants were obtained with pure hydrogen peroxide prepared in the laboratory. Merck's peroxide was distinctly acidic and this fact may account for the lower rate of decomposition in this case[a] (Bailey). In other respects the inhibitors in the peroxide, acidic or otherwise, seem to exert no detectable influence on the photochemical after-effect. It is well known that hydrogen peroxide undergoes spontaneous decomposition due to the surface of the reaction vessel. Rice and Kilpatrick[9] (1927) have shown that this spontaneous decomposition is brought about by dust and motes derived from the surface of the reaction vessel, and even freshly fused glass surface gives out motes and causes heterogeneous decomposition of hydrogen peroxide. The effect of hydrogen and hydroxyl ions on the stability of hydrogen peroxide has long been recognised[11, 10, 12, 13, 14] but the exact mechanism of decomposition of hydrogen peroxide is not yet clearly understood. It was found by experiment that pyrex glass bulbs, duly cleaned and steamed before use, gave fairly reproducible results, and blank tests showed that the spontaneous decomposition of the peroxide due to the surface of the reaction vessel was inappreciable within the time limits of the experiments. The rate of this decomposition was negligible compared with the rates of the dark reaction between hydrogen peroxide and potassium ferrocyanide, and the photochemical after-effect.

Kahlbaum's analytical potassium ferrocyanide was employed in these experiments. The crystals of ferrocyanide were pale yellow and free from

brown and amber colour. Tests for potassium aquopentacyanoferrite in M/320 solution in the dark with nitrosobenzene[15] and *para*-nitrosodimethylaniline[16] were found to be negative. In connection with some experiments under nitrogen (in which oxygen was rigorously excluded) Kahlbaum's analytical potassium ferrocyanide was recrystallised from water at room temperature (18° C.), and reprecipitated with alcohol from its aqueous solution, dried and stored in the dark. The purified ferrocyanide was employed to study the action of light under nitrogen in the absence of air. This sample was found to possess the same photo-sensitivity, and the same pale yellow colour as the original Kahlbaum reagent, and its dilute solutions in the dark gave negative tests both with nitrosobenzene and *para*-nitrosodimethylaniline, thereby demonstrating the absence of detectable amounts of complex aquosalt.

Conductivity water was used for the preparation of all solutions. Freshly prepared solutions were used in these experiments unless otherwise stated. The pyrex glass bulbs used as reaction vessels were cleaned with hot solution of chromic acid, thoroughly washed and well steamed and dried before use.

Dark Reaction between Hydrogen Peroxide and Potassium Ferrocyanide

Freshly prepared hydrogen peroxide and ferrocyanide solutions were mixed in the dark in measured quantities, and the rate of decomposition was followed by taking out 5 c.c. of the reaction mixture at suitable intervals and determining the change in peroxide concentration by titration with standard permanganate. Kistiakowsky[2] (1900) has found this decomposition to be unimolecular, and the following figures also show that the decomposition of hydrogen peroxide by potassium ferrocyanide follows the unimolecular law. The unimolecular velocity constants calculated by the usual equation, $K = 1/t \log a/a - x$, are fairly constant. In this formula, ' t ' represents time in minutes, ' a ' the initial concentration of peroxide in terms of the volume (c.c.) of permanganate, and ' x ' the change in peroxide concentration in time ' t '.

While studying the dark reaction, it was accidentally found that aged solutions of potassium ferrocyanide under otherwise identical conditions are slightly less reactive than fresh solutions in the initial stage of the reaction. This point was followed up by studying the dark reaction, using ferrocyanide solution which had stood in the dark for about a week. The results obtained are shown in Table II. The dark reaction was next studied by using a solution of ferrocyanide which had been heated to about 90° C. for ten

TABLE I

*With freshly prepared
solution*

t	$a - x$	$K . 10^6$
0	20·50	. .
55	19·70	315
121	18·60	350
227	17·05	353
368	14·80	385

TABLE II

*With one week old
ferrocyanide solution*

t	$a - x$	$K . 10^6$
0	20·10	. .
60	19·45	238
125	18·45	298
188	17·25	354
239	16·45	364
303	15·35	387

minutes and used after cooling. These results are recorded in Table III. The dark reaction was also studied by using ferrocyanide solution which had been kept in the dark for fifteen minutes after one hour's insolation by bright sunlight. These results are shown in Table IV.

TABLE III

*With pre-heated
ferrocyanide solution*

t	$a - x$	$K . 10^6$
0	20·40	. .
60	19·80	215
120	18·70	315
180	17·10	426
240	15·90	451

TABLE IV

*With pre-insolated
solution*

t	$a - x$	$K . 10^6$
0	20·30	. .
66	20·05	82
136	19·15	187
196	18·20	242
309	16·20	317

In all the experiments described above, the unimolecular velocity constants show a tendency to rise with the progress of the reaction. A freshly prepared solution of potassium ferrocyanide is distinctly a little more reactive than the one kept in the dark for a few days. A pre-heated solution also gives a distinctly lower dark reaction rate in the initial stage of the reaction. A much more pronounced diminution in the dark rate is brought about by using potassium ferrocyanide which had been kept in the dark for a few minutes after one hour's insolation. Thus in all these cases the velocity constants in the initial stages of the reaction are distinctly lower than those obtained with fresh ferrocyanide solutions.

The end products of this dark reaction are ferricyanide, alkali and part of the original ferrocyanide. It is well known that hydroxyl ions

A2

accelerate the decomposition of hydrogen peroxide. In the presence of alkaline ferrocyanide the decomposition of hydrogen peroxide is considerably accelerated (Kassner, 1896),[17] (Quincke, 1897),[18] (Rupp., 1902),[19] (Sperber., 1913).[20] In fact, the reduction of ferricyanide by hydrogen peroxide in the presence of alkali has been used as a method for the estimation of ferrocyanide (Kassner, 1894),[21] (Quincke, 1891).[22]

The tendency of the unimolecular velocity constants to increase with the progress of the reaction is, therefore, to be attributed to the products of the reaction.

Although the decomposition of hydrogen peroxide is affected by the hydrogen-ion concentration, it is not practicable to keep it constant in the reaction under discussion, without affecting the rates of the dark decomposition and the photochemical after-reaction. The photochemical after-effect is dependent on the photo-formation of potassium aquopentacyanoferrite. The formation of the latter is accompanied by the appearance of alkali. In case the hydrogen-ion concentration is kept constant, this photo-equilibrium will be disturbed with the result that no photochemical after-effect may be detectable under certain conditions. Experiments to be reported later have shown that the rates of photochemical after-effect are much higher than the dark reaction rate in solutions containing a known amount of alkali (N/10 KOH) under otherwise identical conditions. Moreover, this reaction is highly susceptible to inhibitors, sensitizers and extraneous substances in general. Apart from disturbing the photochemical after-effect itself, the use of buffer solutions for keeping the hydrogen-ion concentration constant throughout the course of the reaction, is bound to introduce additional complications, thus rendering the investigation of the photochemical after-effect extremely difficult.

BEHAVIOUR OF FERROCYANIDE SOLUTIONS IN THE DARK

Before the dark reaction between hydrogen peroxide and potassium ferrocyanide and the photochemical after-effect can be properly understood, it is necessary to study the properties of aqueous solution of ferrocyanide both in the dark and in light. The decomposition of aqueous ferrocyanide by light and air has been the subject of many investigations but the exact mechanism of the decomposition has not yet been elucidated.[23-31]   Briggs[32] (1910) reported the existence of two stereoisomeric forms, α- and β-ferrocyanide and remarked that solutions of the α-salt upon prolonged standing are converted into the β-variety. Piutti[33] (1912), Hauser[34] (1912) and Wells[35] (1913), however, failed to establish any difference between the alleged varieties, and Bennett[36] (1917) concluded that the two forms are identical

crystallographically. The work of Kohltoff[30] (1920) showed no difference in the physical properties of solutions of α- and β-ferrocyanide except their colour. It was later suggested by Briggs[37] (1920) that the supposed isomeride or β-variety consists of mixed crystals of potassium ferrocyanide and potassium aquopentacyanoferrite, the amount of latter being too small to detect by qualitative analysis. The amber colour of the crystals of ferrocyanide has been attributed to the presence of the aquo-salt (II), which is a strongly coloured substance. It has been suggested that the two compounds are in aqueous solution in a state of equilibrium.

$$K_4Fe(CN)_6 + H_2O \rightleftharpoons K_3Fe(CN)_5H_2O + KCN \quad (I)$$
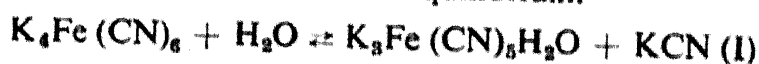
Acids increase the velocity of the reaction towards the right, alkalies to the left.

Iimori[38] has concluded on spectroscopic evidence that aqueous solutions of potassium ferrocyanide are gradually converted by heat, or hydrogen ions into potassium aquopentacyanoferrite in the dark. This evidence of the thermal formation of the aquo-salt from ferrocyanide supports the hypothesis of Briggs that in aqueous solution in the dark, potassium ferrocyanide is in equilibrium with the aquo-salt, the latter being present in quantities too small to be detected by qualitative analysis. · The dependence of the stability of aqueous ferrocyanide on the hydrogen-ion concentration has also been established by Kohltoff and Pearson[39] (1931).

ACTION OF LIGHT ON AQUEOUS FERROCYANIDE

The effect of light on aqueous ferrocyanide has been investigated by a large number of workers, with different results. According to Matuschek[40] (1901) solutions of ferrocyanide are gradually decomposed by light, with the formation of cyanide ions and precipitation of ferric hydroxide. Haber[41] (1905) and Foster[42] (1906) have concluded that under the influence of light ferrocyanide ion dissociates as follows:—

$$Fe(CN)_6'''' \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftharpoons}} Fe^{++} + 6\,CN'$$
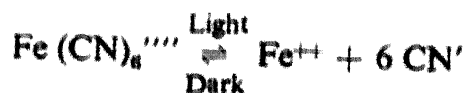
The reaction is reversible, proceeding from right to left in the dark. Kassner[17] (1896) says that an alkaline solution of ferrocyanide hardly undergoes any decomposition when heated, and shows no change at all when exposed to light, except when air is included in the system. It has already been remarked that according to Weigert,[3] aqueous ferrocyanide produces reaction nuclei under the influence of light, while Winther[5] has remarked that the illumination of ferrocyanide results in the formation of an extremely stable substance. None of these workers could, however,

identify the product of insolation. Baudisch[43] (1921) observed that by illumination of freshly prepared aqueous solutions of ferrocyanide, an intense yellow colouration appears momentarily, but it gradually becomes deeper. This colouration does not appear in solutions which are dilute enough to be themselves colourless, and is much weaker, when oxygen-free ferrocyanide solution is illuminated *in vacuo*. The yellow colour was attributed to the formation of potassium pentacyanoperoxoferrite, $K_3Fe(CN)_5O_2$.

In a subsequent paper by Baudisch and Bass[44] (1922) this view was given up and it was stated that the citron yellow colour in air-free solution of ferrocyanide after illumination is not due to the peroxocompound. It was further concluded that the decomposition of ferrocyanide by light can take place in the absence of oxygen, which plays no part in the change of colour from light yellow to citron yellow. It was reported that a pale yellow alkaline solution of potassium ferrocyanide in water speedily becomes lemon yellow in colour when exposed to direct sunlight, but reverts to its original tint when placed in the dark. Only after some months, some ferrous hydroxide was precipitated. This view was again modified by Baudisch[45] (1929), and it was reported that ferrous ions, as well as pentacyanoaquo-ferrite ions are produced when solutions of potassium ferrocyanide, neutral or feebly acid, with carbonic acid, are exposed to the carbon arc or to direct sunlight in the absence of air. In the presence of air and light, the yellow ferrite ions are immediately oxidised to the dark violet pentacyanoaquo-ferrate ions which react with the first named ions to form complex compounds that have a pale yellow colour. This conclusion of Baudisch has, however, been found to be erroneous by the present author.

Rossi[46] and Bocchi (1925) observed that equilibrium conditions for a 0·25% solution of potassium ferrocyanide in water are reached after an exposure of thirty minutes to an arc. Complete reversibility of the reaction was shown after the first exposure to light and darkness, but with successive equal exposures the amount of decomposition increased and the reversibility of the reaction decreased. The decomposition was studied by measuring the alkalinity of the solution of the salt after exposure to sunlight. The reversibility of the reaction was investigated by alternately exposing to light and keeping in the dark a solution of the salt. According to Baur[47] (1925) solutions of potassium ferrocyanide darken in colour on illumination. If oxygen is led through the solution, the phenomenon is accentuated although darkening occurs also with carefully deaerated freshly prepared solutions. If the ferrocyanide solution is passed through a column of granulated aluminium, the original yellow colour disappears, and the solution ceases to be photochemically sensitive. These facts were inter-

preted as indicating that the ferrocyanide ion itself is photochemically insensitive, the light reaction being due to the photo-decomposition of the ferricyanide ion always present in small quantities.

Experiments conducted by the author with very dilute aqueous solutions of ferrocyanide both in air and under nitrogen in the total absence of oxygen have confirmed the observation that potassium aquopentacyanoferrite is produced photochemically and reversibly in the presence of light. Oxygen is not necessary for this photo-reaction. This was confirmed by tests with *para*-nitrosodimethylaniline[15] and nitrosobenzene.[16] Isobutyl alcohol is also a good reagent for demonstrating the influence of light on potassium ferrocyanide.[4a] Exposed solutions of ferrocyanide ion gave unmistakable evidence for the presence of nitroprusside[49] (Hofmann) on the addition of small quantities of nitrite. The presence of aquopentacyano ferrite in aqueous ferrocyanide after momentary exposure to sunlight is, therefore, quite conclusive, and is in line with the spectroscopic evidence of Iimori.[3a] The formation of aquopentacyanoferrite from ferrocyanide under the influence of light and hydrogen ions has been further established by Williams.[50]

The experiments described in this paper and the results reported on the properties of aqueous ferrocyanide solutions, show that the dark reaction between hydrogen peroxide and a pure aqueous freshly prepared solution of potassium ferrocyanide is really due to the action of the former on potassium aquopentacyanoferrite which exists as a substitution product (equation I) in quantities too small to be detected by qualitative analysis. The reaction between hydrogen peroxide and potassium cyanide is inappreciable, under the conditions of the experiments. The concentration of potassium aquopentacyanoferrite gradually diminishes on ageing, and the same effect is hastened by heat or prolonged insolation due to the decomposition of the former. It may be stated here that the suggestion of Baudisch[45] (1929) that in the presence of air, the pentacyanoaquoferrite formed on insolation of neutral ferrocyanide is oxidised to the dark violet pentacyanoaquoferrate, which reacts with the ferrocyanide to give more complex pale yellow compounds has been found to be untenable. Experiments conducted by the present author lead to the conclusion that the diminution in the concentration of potassium aquopentacyanoferrite on prolonged insolation of potassium ferrocyanide in experiments to be described later is really due to the decomposition of the former in the presence of air, light and alkali, and not due to its oxidation. In the presence of excess ferrocyanide, the violet aquo-salt is immediately reduced to the yellow aquo-salt, aquopentacyanoferrite. The same results have been arrived at by Williams[50] (1943),

Photochemical After-Effect in Pre-Insolated H_2O_2-$K_4Fe(CN)_6$ Mixture

The photochemical after-effect has been studied by exposing to sunlight (filtered through water) the reaction mixture for a definite period and studying the decomposition in the dark. It is well known that hydrogen peroxide is not sensitive to visible light[51] (Ellis and Wells, 1941) and the only reactant that is photosensitive to the visible part of the spectrum is potassium ferrocyanide. The photo-decomposition of hydrogen peroxide under the conditions of these experiments is, therefore, out of the question. Moreover the after-effect has been studied by measuring the decomposition of hydrogen peroxide in the dark after initial irradiation of the system. The photo-decomposition of hydrogen peroxide sensitised by ferrocyanide, if any, is, therefore, non-existent as soon as the system is brought in the dark.

In order to study the effect of wide variations in the period of pre-illumination of hydrogen peroxide-ferrocyanide mixtures, it was found necessary to use very low concentrations of potassium ferrocyanide so as to measure the rate of reaction conveniently. The low concentration of ferrocyanide has the added advantage in that the light effect is more marked than when stronger solutions are employed. With $M/64 \cdot 20$ potassium ferrocyanide used in previous experiments by the author[1] (1939) and with long periods of pre-illumination by sunlight, the reaction was very violent and did not lend itself to accurate measurement. In the experiments mentioned here, therefore, $M/320$ potassium ferrocyanide and $N/6$ hydrogen peroxide were used with different periods of pre-illumination. In the following tables, 'T' stands for the time of pre-illumination of hydrogen peroxide-ferrocyanide mixture.

Table V
$T = \frac{1}{2}$ mt.

t	$a-x$	K. 10^5
0	20·10	..
18	16·30	506
42	12·10	525
55	10·35	524
75	8·20	520
100	6·00	526

Table VI
$T = 1$ mt.

t	$a-x$	K. 10^5
0	17·80	..
6	16·50	548
13	15·10	549
26	12·70	564
36	11·20	559
47	9·85	547
58	8·00	599
68	6·95	601

Table VII
$T = 3$ mts.

t	$a-x$	K. 10^5
0	16·20	..
5	14·90	726
11	13·40	749
19	11·80	724
27	10·40	713
37	8·90	703
50	6·90	741
65	5·15	766

TABLE VIII

T = 5 mts.

t	a − x	K. 10^5
0	14·30	..
5	12·90	894
10	11·70	871
15	10·70	839
25	8·65	873
38	6·70	866
50	5·20	879
62	4·00	892

TABLE IX

T = 8 mts.

t	a − x	K. 10^5
0	11·75	..
5·5	10·20	1120
14·5	8·25	1060
28	5·95	1060
43·5	4·05	1060
78	1·40	1190

TABLE X

T = 10 mts.

t	a − x	K. 10^5
0	11·00	..
4·5	9·70	1214
11·5	8·05	1180
19·5	6·40	1207
32	4·50	1213
55	2·40	1202

TABLE XI

T = 15 mts.

t	a − x	K. 10^5
0	7·70	..
5	6·50	1468
12	5·10	1490
25·25	3·35	1432
54	1·30	1430

In these experiments the magnitude of the photochemical after-effect has been determined by subtracting from the total rate, the rate of the dark reaction (Table I, K × 10^5 = 35, average value).

Though the velocity constants obtained here leave something to be desired, they are as good as those reported in the literature [Kistiakowsky,[2] Bredig[52] (1899), (1901), Brossa[53] (1909), Tartar and Schaffer[54] (1928)].

This effect of pre-illumination of the reaction mixture on the magnitude of the photochemical after-effect as measured by the velocity constants has been illustrated in the figure. The effect of the dark reaction has been elimi-nated, as already stated, by subtracting from the observed rate, the rate of the dark reaction, thus determining the magnitude of the photochemical after-effect.

Experiments performed by using light from a 500-watt gas-filled filament lamp operated on 220 volts are recorded in Tables XII to XV.
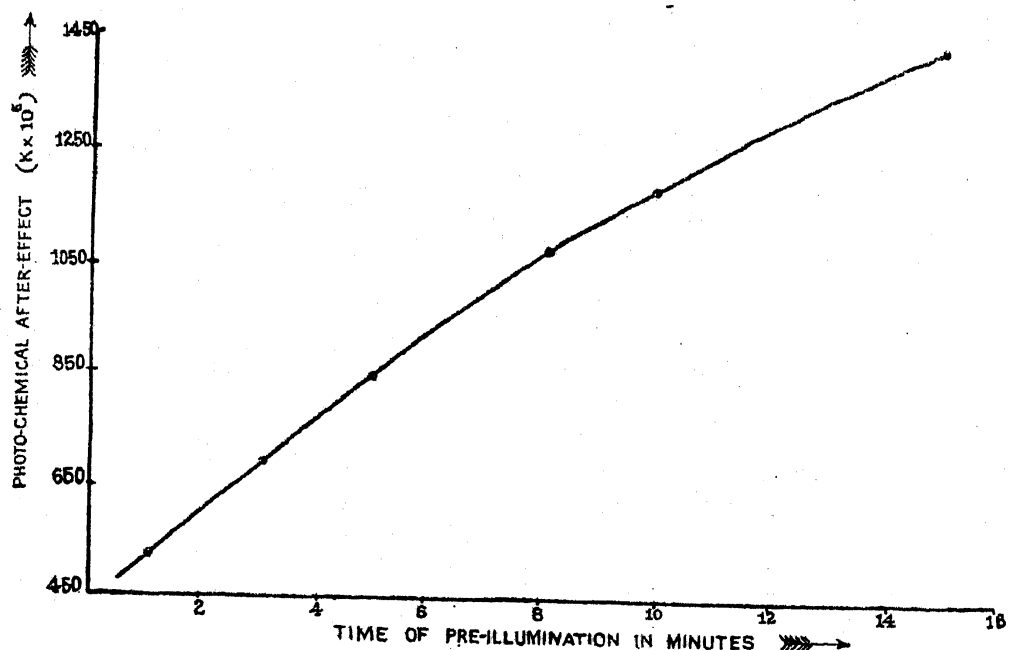
FIG. 1

The velocity constants above the line in Tables XII–XV represent the values for the light reaction.

It is seen from these results that the photochemical after-effect is more marked, the greater the period of pre-illumination of the mixture. The dark equilibrium in aqueous ferrocyanide with the formation of a trace of aquopentacyanoferrite is shifted further to the right on illumination with increased concentration of aquo-ferrite. The latter causes the enhanced rate of decomposition of hydrogen peroxide on subsequent darkening, resulting in the marked photochemical after-effect. In the presence of

	TABLE XII				TABLE XIII	
	$T = 5$ mts.				$T = 15$ mts.	
t	$a - x$	K. 10^5		t	$a - x$	K. 10^5
0	20·05	..		0	20·45	..
5	19·90	64		15	19·40	15
15	19·50	..		25	18·60	..
49	18·00	70		69	15·75	164
122	16·30	73		129	12·85	154
180	14·90	71		192	10·35	153
278	12·00	80		310	7·40	141
400	9·90	77		434	5·40	131

TABLE XIV

T = 30 mts.

t	$a - x$	K. 10^5
0	20·35	..
30	17·55	211
40	16·80	..
80	13·75	217
120	10·90	235
180	7·80	238
261	5·20	231
360	3·10	229

TABLE XV

T = 42 mts.

t	$a - x$	K. 10^5
0	20·60	..
42	15·80	310
52	15·40	..
91	11·65	310
123	9·20	315
157	7·00	326
219	4·45	323
287	2·60	329

hydrogen peroxide the photo-equilibrium continues to shift to the right with the formation of increasing amounts of aquopentacyanoferrite. This explains why on the cessation of illumination, the velocity constants are higher, the longer the exposure.

SUMMARY

The dark reaction between hydrogen peroxide and a pure dilute aqueous solution of potassium ferrocyanide has been critically examined. The experiments described in the paper lead to the conclusion that potassium aquo-pentacyanoferrite produced as a substitution product in very minute concentration in aqueous ferrocyanide in the dark reacts with hydrogen peroxide resulting in the measured dark reaction. Aged solutions of ferrocyanide, as well as pre-heated and pre-illuminated solutions used sometime after treatment show a distinctly lower rate of peroxide decomposition. This diminished reactivity towards hydrogen peroxide appears to be due to the partial decomposition of the aquo-complex salt by heat, prolonged exposure to light and ageing.

The marked photochemical after-effect observed in the pre-insolated mixture of hydrogen peroxide and potassium ferrocyanide has been studied in detail with varying periods of pre-illumination of the reaction mixture. It is found that the greater the period of pre-illumination of the mixture, the greater is the photochemical after-effect within the concentration limits of reactants used in the experiments.

REFERENCES

1. Lal, B. B.   .. *Jour. Ind. Chem. Soc.*, 1939, **16**, No. 7, 321.
2. Kistiakowsky, W. A.   .. *Z. Physikal. Chem.*, 1900, **35**, 431.
3. Weigert, F.   .. *Ann. Phys.*, 1907, **4**, **24**, 243–66.
4. Amann, J.   .. *Z. Chem. Ind. Kolloide*, 1911, **8**, 14.
5. Winther, Chr.   .. *Danske. Viden. Medd.*, 1920, **2**, No. 1, 1.
6. Lal, B. B.   .. *Curr. Sci.*, 1947, **16**, 118–19, 219–21, 281–83.
7. Rao, A. R. and
    Srikantan, B. S.   .. *J. Ind. Chem. Soc.*, 1933, **10**, 29.
8. Bailey, K. C.   .. *Retardation of Chemical Reactions*, 1937, p. 279.
9. Rice and Kilpatrick   .. *J. Phys. Chem.*, 1927, **31**, 1507.
10. Thenard, L. J.   .. *Ann. Chem. Phys.*, 1818, (2) **9**, 441; 1819, (2) **10**, 114, 335, (2) **11**, 85.
11. Bottger, R.   .. *Dingler's Journal*, 1873, **209**, 157.
12. Berthelot, M.   .. *Compt. Rend.*, 1880, **90**, 897.
13. Sabatier, P.   .. *Bull. Soc. Chim.*, 1885, **44**, 169.
14. Lemoine, G.   .. *Compt. Rend.*, 1915, **161**, 47.
15. Baudisch, O. and Bass, L. W.   *Ber.*, 1922, **55 B**, 2701.
16. Gallenkamp, W.   .. *Chem. Zeit.*, 1916, **40**, 235.
17. Kassner   .. *Arch. Pharm.*, 1896, **234**, 330–48.
18. Quincke   .. *Zeit. Physikal. Chem.*, 1897, **22**, 122.
19. Rupp   .. *Ber.*, 1902, **35**, 2434.
20. Sperber   .. *Chem. Zentr.*, 1913, **1**, 502.
21. Kassner   .. *Arch. Pharm.*, 1894, **232**, 226.
22. Quincke, J.   .. *Zeit. Anal. Chem.*, 1891, **31**, 1–43.
23. Schonbein   .. *Fortschritt. Physik.*, 1846, **228**.
24. Donath and Hottenhauser .. *Chem. Zeit.*, 1890, **14**, 323.
25. Modenhauer   .. *Chem. Ztg.*, 1891, **15**, 223.
26. Luckow   .. *Ibid.*, 1891, **15**, 1491.
27. Koninck, de., and Prost   .. *Z. Angew. Chem.*, 1896, **15**, 460, 564.
28. Walker   .. *Jour. Amer. Chem. Soc.*, 1901, **23**, 468.
29. Schaum and Van der Linde .. *Z. Elektrochem*, 1903, **9**, 406.
30. Kohltoff   .. *Z. Anorg. Allgem. Chem.*, 1920, **110**, 47.
31. Kohltoff and Verzyl   .. *Rec. Trav. Chim.*, 1924, **43**, 380.
32. Briggs, S. H. C.   .. *Zeit. Anorg. Chem.*, 1910, **67**, 322.
33. Piutti   .. *Ber.*, 1912, **45**, 1830.
34. Hauser and Biesalski   .. *Ibid.*, 1912, **45**, 3516.
35. Wells   .. *Jour. Amer. Chem. Soc.*, 1913, **49**, 205.
36. Bennett   .. *Jour. Chem. Soc.*, 1917, **111**, 490.
37. Briggs, S. H. C.   .. *Ibid.*, 1920, **117**, 1026.
38. Iimori, S.   .. *Z. Anorg. Chem.* 1927, **167**, 145–72.
39. Kohltoff and Pearson   .. *Ind. Eng. Chem. Analytical Ed.*, 1931, **3**, 381–82.
40. Matuschek, J.   .. *Chem. Zeit.*, 1901, **25**, 565–66.

41. Haber, F.   .. *Zeit. Electro. Chem.*, 1905, **11**, 847.
42. Foster, G. W. A.   .. *Jour. Chem. Soc.*, 1906, **89**, 916.
43. Baudisch, O.   .. *Ber.*, 1921, **54 B**, 414.
44. Baudisch, O. and Bass, L. W.   *Ibid.*, 1922, **55 B**, 2701.
45. Baudisch, O.   .. *Ibid.*, 1929, **62 B**, 2706.
46. Rossi, G. and Bocchi, C.   .. *Gazz. Chim. Ital.*, 1925, **55**, 876.
47. Baur, E.   .. *Helv. Chim. Acta.*, 1925, **8**, 403.
48. Kutzlnigg, A.   .. *Z. Anal. Chem.*, 1929, **77**, 349.
49. Hofmann, K. A.   .. *Annalen*, 1900, **312**, 1–33.
50. Williams, H. E.   .. *Jour. Chem. Soc.*, 1943, 223.
51. Ellis, C. and Wells, A. A.   .. *The Chemical Action of Ultra-Violet Rays*, 1941, p. 339.
52. Bredig   .. *Z. Physikal Chem.*, 1899, **31**, 258; 1901, **37**, **3**, 23.
53. Brossa   .. *Ibid.*, 1909, **66**, 161.
54. Tartar and Schaffer   .. *J. Amer. Chem. Soc.*, 1928, **30**, 2604.