

DECOMPOSITION OF HYDROGEN PEROXIDE BY SODIUM NITROPRUSSIDE

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QURESHI (1931) pointed out that the decomposition of hydrogen peroxide by sodium nitroprusside in visible light is followed by a marked photochemical after-effect. The reaction in the unilluminated mixture was found to be exceedingly slow, but the decomposition in the pre-illuminated mixture was observed to follow the unimolecular law. He suggested that the after reaction is due to colloidal Prussian blue formed from nitroprusside during irradiation. Preliminary experiments conducted by the present author showed that although the dark decomposition is very slow, the reaction in the pre-insolated mixture is not unimolecular. An attempt was, therefore, made to investigate this after-effect, and to ascertain the nature and the rôle of the catalyst, which is responsible for the non-cessation of the reaction after cutting off the illumination. The photochemical after-effect in $\text{H}_2\text{O}_2\text{-K}_4\text{Fe}(\text{CN})_6$ reaction has been shown by the author (1939) to be due to the photo-formation of potassium aquopentacyanoferrite. It was of interest to examine whether the after-effect in the above reaction might also be traced to a similar cause.

In view of the meagre experimental work on this reaction, it was thought desirable to take up an exhaustive investigation of the problem and try to elucidate the chemical mechanism of the after-effect. Experiments have been conducted with:—

- (i) pre-insolated H_2O_2 -nitroprusside reaction mixture;
- (ii) pre-insolated sodium nitroprusside added to hydrogen peroxide in the dark;
- (iii) end solutions of pre-insolated H_2O_2 -nitroprusside mixtures added to fresh hydrogen peroxide in the dark.

All the experiments were carried out at 35°C . The volume of the reaction mixture was 50 c.c. in all cases, and the strength of hydrogen peroxide was N/10. The velocity constants have been calculated from the usual unimolecular formula, $K = 1/t \log a/a-x$, where 't' is the time in minutes,

and 'a-x' is the concentration of H₂O₂ in terms of c.c. of KMnO₄ at time 't'.

Photochemical After-effect

The dark reaction is negligibly slow. Sodium nitroprusside (0.0200 gm.) dissolved in conductivity water was added to the calculated amount of hydrogen peroxide and the mixture was made up to 100 c.c. It was insulated and when the evolution of oxygen became marked, it was transferred to the dark room. The reaction in this mixture was found to be autocatalytic. It has been observed in connection with another investigation that the decomposition of hydrogen peroxide by sodium aquopentacyanoferrate follows an autocatalytic course, but fairly uniform unimolecular velocity constants are obtained in presence of a suitable excess of potassium ferrocyanide. It was consequently of interest to see if the addition of potassium ferrocyanide to the insulated mixture could give uniform values of the unimolecular constant.

In order to study the effect of potassium ferrocyanide, 100 c.c. of the reaction mixture was insulated as above. It was then divided into 50 c.c. portions and kept in the thermostat. The reaction in the first portion was followed as usual. The other portion of the insulated mixture was treated with the requisite amount of potassium ferrocyanide. The mixture was allowed to stand in the thermostat until all the ferrocyanide had dissolved, and then the decomposition of hydrogen peroxide was followed volumetrically. The amount of permanganate taken up by ferrocyanide was allowed for (by subtraction) from the total volume used in each titration.

TABLE I

Without K₄Fe (CN)₆

<i>t</i>	<i>a-x</i>	K.10 ⁵
0	13.45	..
23	11.50	296
61	7.70	397

TABLE II

With K₄Fe (CN)₆ = 0.1320 gm.

<i>t</i>	<i>a-x</i>	K.10 ⁴
0	9.20	..
10	6.90	125
15	5.80	134
24	4.50	129
35	3.50	120
54	1.90	127
72	1.10	128.

It is evident that in the absence of ferrocyanide, the reaction shows an autocatalytic course and the velocity constants calculated by the unimolecular formula increase with the progress of the reaction. In the presence of an excess of ferrocyanide, however, constants are obtained for the

unimolecular formula. Their absolute values are also much higher than when no ferrocyanide is used.

After-effect with Pre-insolated Nitroprusside added to H_2O_2 in the Dark

Experiments were performed with pre-insolated nitroprusside added to hydrogen peroxide in the dark. Sodium nitroprusside (0.2500 gm.) was made up to 500 c.c. in conductivity water and insolated in bright sunlight, until a pale brownish yellow colour appeared. This did not take more than 7 to 10 minutes. The solution was removed to the dark before any blue tint could be noticed. The volume of this solution used in the following experiments was 20 c.c. (0.0100 gm.). (See Table III.)

The unimolecular velocity constants are seen to increase with time. The effect of ferrocyanide in varying quantities was next investigated and the following results were obtained. The volume of pre-insolated nitroprusside was 20 c.c. in each case.

TABLE III

t	$a-x$	$K \cdot 10^6$
0	15.00	∞
60	14.80	97
128	14.60	105
230	14.15	110
310	13.70	127
418	13.15	137

TABLE IV

$K_4Fe(CN)_6 = 0.0060 \text{ gm.}$

t	$a-x$	$K \cdot 10^6$
0	14.35	∞
42	13.00	1020
76	12.45	812
108.5	11.95	732
134	11.80	634
210	10.95	559
293	10.05	528
354	9.45	512

TABLE V

$K_4Fe(CN)_6 = 0.0132 \text{ gm.}$

t	$a-x$	$K \cdot 10^5$
0	14.40	∞
43	11.70	210
75	10.20	200
99	9.15	199
209	5.65	194
295	4.55	170
356	3.90	159

TABLE VI

$K_4Fe(CN)_6 = 0.0396 \text{ gm.}$

t	$a-x$	$K \cdot 10^5$
0	13.75	∞
20	10.25	638
60	6.10	588
83.5	4.30	605
101.5	3.10	637

For the sake of brevity, the other tables are not reproduced, but the results have been summarised below and illustrated in Fig. 1, curve 'a'.

The after-effect has been calculated by subtracting the dark rate of unisolated nitroprusside-ferrocyanide-hydrogen peroxide mixture from the rate of pre-insolated nitroprusside-ferrocyanide-hydrogen peroxide mixture.

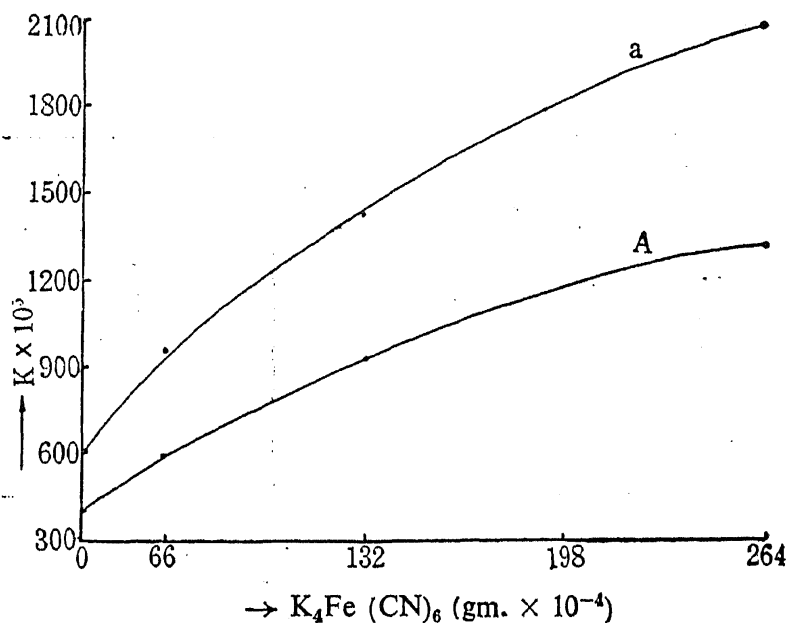


FIG. 1

TABLE VII

$K_4Fe(CN)_6$ used in gm.	After-effect $K \cdot 10^5$
0.0060	Decreasing rate
0.0132	do.
0.0396	609
0.0660	957
0.1320	1415
0.2640	2079

The above results show that in presence of an excess of ferrocyanide, not only are uniform values of unimolecular velocity constants obtained, but their absolute values are very much higher than those obtained in experiments in which no ferrocyanide is added. Moreover, the greater the amount of ferrocyanide added, the higher is the velocity constant. When very small amounts of ferrocyanide (0.0060 gm., 0.0132 gm.) are used, the velocity constants show a falling off with time. This result is strikingly similar to that observed in ferrocyanide-hydrogen peroxide reaction from the view-point of the photochemical after-effect. The pre-insolated nitroprusside solution does not show any colour change with dilute sulphuric acid, *p*-nitrosodimethylaniline, or nitrosobenzene. But when ferrocyanide is added to pre-insolated nitroprusside solution containing any of the above reagents, very characteristic colour changes are produced in the dark. The first two reagents give a green colouration while the third reagent, *i.e.*, nitrosobenzene, gives a violet colouration. These tests are not given by un-insolated nitroprusside to which ferrocyanide has been added in the dark.

Effect of Concentration Change on Pre-insolated Nitroprusside with Constant Concentration of Ferrocyanide

The results obtained by employing varying quantities of pre-insolated nitroprusside solution with a constant amount (0.0660 gm.) of ferrocyanide have been summarised below and illustrated in Fig. 2, curve 'b'. The

details of one experiment, using 1 c.c. of pre-insolated nitroprusside (0.0005 gm.) are given below:

TABLE VIII

Pre-insolated nitroprusside
1 c.c. (0.0005 gm.)

t	$a-x$	$K \cdot 10^5$
0	14.10	∞
22	13.05	153
50	11.80	155
126	9.55	134
154	8.75	135
181	8.10	133
209	7.40	134

TABLE IX

Nitroprusside in gm.	After-effect $K \cdot 10^5$
0.0005	148
0.0015	279
0.0025	432
0.0050	650
0.0100	957
0.0150	1157
0.0200	1337

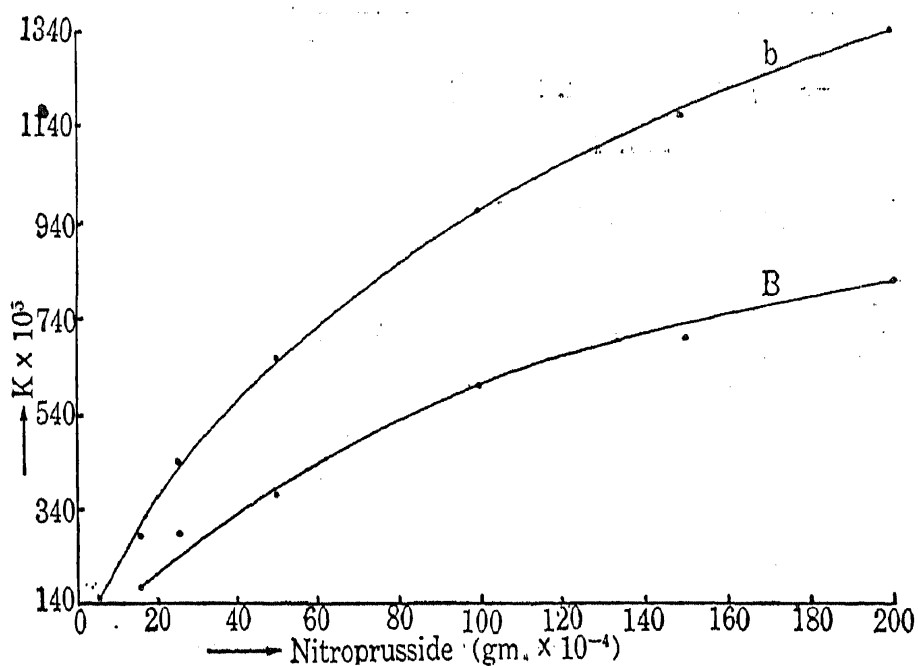


FIG. 2

The concentration of ferrocyanide being kept constant, the velocity constants depend upon the amount of pre-insolated nitroprusside. The greater the concentration of pre-insolated nitroprusside, the higher is the value of the velocity constant. Potassium ferrocyanide has been employed in considerable excess in the above experiments.

The following experiment shows the effect of potassium ferricyanide on the reaction mixture of hydrogen peroxide and pre-insolated nitroprusside. The concentration of ferricyanide was the same as that of ferrocyanide, *i.e.*, $M/320$, and the amount of pre-insolated nitroprusside was 20 c.c., *i.e.*, 0.0100 gm.

TABLE X

t	$a-x$	$K.10^5$
0	14.95	..
16	14.60	64
61	13.40	78
121.5	7.00	271
181	1.80	508
211	0.85	590

The effect of ferrocyanide (in increasing and keeping constant) on the unimolecular velocity constants is quite specific, as ferricyanide does not regulate the reaction. The obvious conclusion is that the catalyst, formed from nitroprusside on insolation, is changed to a more reactive substance by interaction with ferrocyanide and is kept at a constant concentration when the latter is used in excess. Potassium ferricyanide does not show this behaviour.

Diminution in the Reactivity of Pre-insolated Nitroprusside

The catalyst formed by insolation of nitroprusside is fairly stable, as by heating the pre-insolated solution to about 90° C. for a few minutes before mixing with hydrogen peroxide-ferrocyanide mixture, the same rate of decomposition is obtained as with the unheated solution. Moreover, a pre-insolated solution of nitroprusside continues to give the same rate of decomposition even many days after insolation. But a very striking change was observed when a mixture of ferrocyanide and pre-insolated nitroprusside was heated to about 90° C. for a few minutes before adding to hydrogen peroxide. The value of the velocity constant ($K. 10^6$) comes down from 4450 to about 250. It is significant that pre-heated ferrocyanide, when added to pre-insolated nitroprusside, does not show this tremendous diminution in the catalytic activity. It is evident, therefore, that the catalyst obtained by irradiation of nitroprusside is comparatively stable towards heat, but the more reactive substance formed by interaction of pre-insolated nitroprusside and ferrocyanide in the dark is destroyed by heating the mixture to 90° C. This change was also observed when ferrocyanide-pre-insolated nitroprusside mixture was kept in the dark at room temperature (30° C.) for 48 hours before the experiment. The product of interaction between ferrocyanide and the catalyst formed in pre-insolated nitroprusside thus undergoes a slow spontaneous change in the dark with a concomitant diminution in its catalytic activity. The reactivity of pre-insolated nitroprusside in the presence of ferrocyanide is much suppressed by cyanide ions. The after-effect due to the pre-insolated nitroprusside is almost completely 'quenched'

by sodium nitrite also. The strength of potassium cyanide was N/400 and that of sodium nitrite, N/100. Sodium nitrite was added to pre-insolated nitroprusside and ferrocyanide and this mixture was added to hydrogen peroxide. The excess of nitrite had reacted with hydrogen peroxide before the first reading was taken, and consequently no allowance for nitrite in the titrations was necessary. The effect of heat, standing in the dark for 48 hours, cyanide ions and sodium nitrite is recorded in Tables XI, XII, XIII and XIV respectively. The curves A, B and C in Fig. 3 illustrate

TABLE XI

t	$K \cdot 10^6$
0	261
20	208
61	184
108	176
138	

TABLE XII

t	$K \cdot 10^6$
0	244
25	205
60	160
196	

TABLE XIII

t	$K \cdot 10^6$
0	203
30	153
120	148
188	147
205	169
310	

TABLE XIV

t	$a-x$	$K \cdot 10^6$
0	14.60	150
30	14.45	152
60	14.30	130
117	13.60	167
185	13.20	172
255		

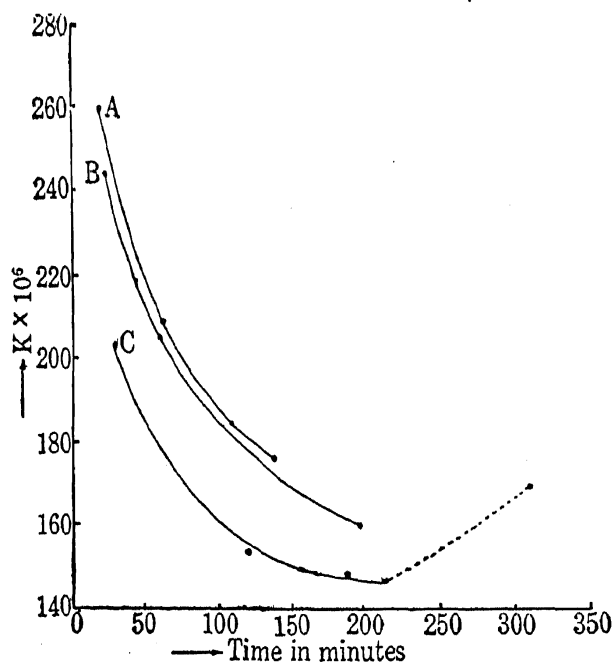


FIG. 3

N.B.—The unisolated nitroprusside-ferrocyanide mixture gives constant values ($K \cdot 10^6 = 126$).

the respective effect of heat, spontaneous change in the dark after 48 hours and lastly of cyanide ions.

The control experiment between unisolated nitroprusside (0.0025 gm. and ferrocyanide (0.0660 gm.) gave constant values of unimolecular velocity constant, $K \cdot 10^6 = 126$. The same value of K is obtained when no nitroprusside is used. When potassium cyanide (N/400) was employed together with the above two reactants in the dark, the course of the reaction became autocatalytic, probably due to the alkali obtained from potassium cyanide by hydrolysis. It is clear that the velocity constants obtained above tend to approach the values obtained in the control.

Secondary After-effect

The effect of adding fresh hydrogen peroxide in the dark to the end solution of pre-insolated nitroprusside-hydrogen peroxide mixture has been called the secondary after-effect (*cf.* MacMahon and Lal, 1940). It has been studied by restoring in the dark the hydrogen peroxide used up in the insolated mixture. A mixture (500 c.c.) of hydrogen peroxide (N/10), and nitroprusside (0.2500 gm.) was prepared and insolated, until the evolution of oxygen became marked. It was then brought back to the dark room, and allowed to stand until all hydrogen peroxide was decomposed. This end solution was taken in measured quantities and the reaction performed by adding fresh hydrogen peroxide to restore the original strength (N/10). (See Table XV.)

The end solution, when added to fresh hydrogen peroxide in the dark, shows an autocatalytic course similar to that observed with pre-insolated nitroprusside. The effect of ferrocyanide in varying amounts was studied on this mixture as well. The amount of the end solution used in each case was 20 c.c. (0.0100 gm.).

TABLE XV

End solution = 20 c.c.

<i>t</i>	<i>a-x</i>	$K \cdot 10^6$
0	14.70	..
55	14.55	80
116	14.10	156
175	13.70	175
236	12.95	233

TABLE XVI

$K_4Fe(CN)_6 = 0.0132$ gm.

<i>t</i>	<i>a-x</i>	$K \cdot 10^5$
0	14.10	..
13	12.95	284
39	11.90	184
72.5	10.85	157
107	9.80	148
140	8.95	141
176.5	8.20	133
243	7.10	123
278	6.60	119

The other results are summarised below (Table XVIII). The after-effect has been calculated by subtracting from the total rate the dark rate with unisolated nitroprusside and ferrocyanide in each case.

TABLE XVII

$$K_4Fe(CN)_6 = 0.0396 \text{ gm.}$$

t	$a-x$	$K.10^5$
0	14.10	..
20	11.55	433
40	9.30	454
73	7.20	400
109	5.25	394
142	3.70	409
178	2.30	443

TABLE XVIII

$K_4Fe(CN)_6$ in gm.	After-effect $K.10^5$
0.0132	Decreasing rate
0.0396	414
0.0660	597
0.1320	925
0.2640	1419

These results have been illustrated in Fig. 1, curve 'A'. They show that except when a very small amount of ferrocyanide is used, the velocity constants are uniform and higher than in the experiments in which no ferrocyanide is used to an extent depending upon its concentration.

Variation of the End Solution with Constant Amount of Ferrocyanide

In the following experiments the amount of potassium ferrocyanide was kept constant (0.0660 gm.) and the amount of the end solution was varied. The results have been graphically shown in Fig. 2, curve 'B', and summarised below:

TABLE XIX

Nitroprusside in end solution in gm.	After-effect $K.10^5$
0.0015	169
0.0025	288
0.0050	366
0.0100	597
0.0150	689
0.0200	815

The results show that for a fixed amount of ferrocyanide the rate of decomposition is higher, the greater the amount of the end solution.

Reproduction of the Photochemical After-effect in the Dark

Previous investigation of the photochemical after-effect in $H_2O_2-K_4Fe(CN)_6$ reaction by the author (*loc. cit.*) has shown that the photoformation of potassium aquopentacyanoferrite from aqueous potassium

ferrocyanide causes the phenomenon. It was only natural to suppose that sodium nitroprusside on insolation produces a similar or identical product, which continues to exert its influence even after darkening. It was, therefore, thought desirable to study the decomposition of hydrogen peroxide in presence of sodium aquopentacyanoferrate and unisolated nitroprusside. Sodium aquopentacyanoferrite was prepared in the laboratory by the method of Hofmann (1900). It was oxidised with hydrogen peroxide, and sodium aquopentacyanoferrate of violet colour was obtained in required amounts.

In the following experiments, 0.0010 gm. of sodium aquopentacyanoferrite was oxidised with hydrogen peroxide. The oxidation was quick, and when all the peroxide had decomposed, the aquopentacyanoferrate so formed was added to unisolated nitroprusside solution (0.0100 gm.) and hydrogen peroxide, both in presence and absence of potassium ferrocyanide.

TABLE XX

Without ferrocyanide

<i>t</i>	<i>a-x</i>	K.10 ⁵
0	14.80	∞
12	14.60	49
26	13.60	142
35.5	12.90	168
51	11.45	219
72	8.90	307
115	6.00	341

TABLE XXI

$K_4Fe(CN)_6 = 0.0660$ gm.

<i>t</i>	<i>a=x</i>	K. 10 ⁵
0	14.00	∞
9	11.80	825
23	8.80	877
34.5	7.25	826
49	5.70	796
66	4.10	808
109	1.50	890

The concentration of sodium aquopentacyanoferrate in the following experiments was 2.5 times the concentration employed above.

With higher concentrations of ferrocyanide, uniform velocity constants were obtained. The following are the results (Table XXIII).

TABLE XXII

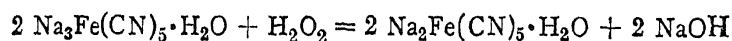
$K_4Fe(CN)_6 = 0.0132$ gm.

<i>t</i>	<i>a-x</i>	K.10 ⁵
0	14.10	∞
10	11.50	885
22.5	9.90	683
35	8.70	599
51.5	7.50	532
78.5	6.00	473
112	4.60	434
149	3.30	423

TABLE XXIII

$K_4Fe(CN)_6$ in gm.	K.10 ⁴
0.0396	114
0.0660	135

In the above experiments, aquopentacyanoferrate obtained by oxidation of aquopentacyanoferrite, according to the reaction



contains alkali. It was feared that these traces of alkali might react with nitroprusside and vitiate the results. It was, therefore, thought necessary to prepare pure sodium aquopentacyanoferrate, from sodium nitroprusside, caustic soda and bromine according to the method of Hofmann (*loc. cit.*). The blue violet powder so obtained was used with unisolated nitroprusside and the following results were obtained. The amounts of sodium aquopentacyanoferrate and sodium nitroprusside in 50 c.c. of the reaction mixture were 0.0010 gm. and 0.0100 gm. respectively.

TABLE XXIV

Without ferrocyanide

<i>t</i>	<i>a - x</i>	K.10 ⁵
0	9.70	..
40	9.40	34
80	8.30	85
93	7.60	114
108	7.05	128
135	6.10	149

TABLE XXV

 $K_4\text{Fe}(\text{CN})_6 = 0.0660 \text{ gm.}$

<i>t</i>	<i>a - x</i>	K.10 ⁴
0	9.05	..
7	8.00	76
16	7.10	66
30	6.00	60
51	4.60	58
85	2.90	58
115	1.80	61

TABLE XXVI

Heated ferrate-nitroprusside-ferrocyanide mixture to 90° C., cooled and added to H₂O₂ K₄Fe(CN)₆ = 0.0660 gm.

<i>t</i>	<i>a - x</i>	K.10 ⁴
0	9.10	..
18	8.95	4
55	8.70	4
97	8.00	6
121	7.70	6

It is clear that the reaction with a mixture of aquoferrate and nitroprusside is autocatalytic as already seen in the above experiments. An excess of ferrocyanide regulates the reaction, and gives considerably higher velocity constants. These results show that unisolated nitroprusside-aquopentacyanoferrate mixture qualitatively reproduces the results obtained with insolated nitroprusside. The effect of heat on the unisolated nitroprusside-aquopentacyanoferrate mixture containing ferrocyanide is shown

in Table XXVI. Here also, by heating the above mixture to about 90° C. for a few minutes before adding to hydrogen peroxide, a tremendous fall in the velocity of decomposition is observed. The mixture to which ferrocyanide is added after heating does not show any fall in its catalytic activity. Again, the effect of cyanide ions on the unisolated nitroprusside-aquopentacyanoferrate mixture has been observed to be the same as in the case of pre-insolated nitroprusside, namely, a considerable diminution in the velocity constants. Sodium nitrite, which has been shown to suppress the after-effect almost completely, shows the same retarding effect in this case also. The details are given in Table XXVII. The strength of nitrite was N/100.

Effect of Alkali on H₂O₂-Nitroprusside Dark Reaction

Although the rate of reaction was not measurable in the dark, it was observed that the addition of alkali to the mixture causes a rapid decomposition of hydrogen peroxide, similar to that obtained in pre-insolated nitroprusside-hydrogen peroxide-ferrocyanide mixture. In the following experiment (Table XXVIII), 0.0100 gm. of sodium nitroprusside was used, and the strengths of alkali and hydrogen peroxide were N/200 and N/10 respectively. No ferrocyanide was added.

TABLE XXVII

*Treated ferrate-nitroprusside mixture with sodium nitrite and added this mixture to H₂O₂
NaNO₂ = N/100*

<i>t</i>	<i>a - x</i>	K.10 ⁴
0	6.50	∞
22	6.40	3
46	6.05	5
88	5.70	6
139	5.15	7
207	4.60	7
242	4.20	8

TABLE XXVIII

<i>t</i>	<i>a - x</i>	K.10 ⁵
0	14.80	∞
28	12.40	275
55	10.65	260
81	9.20	255
125	7.10	255
186	4.60	273
235	3.10	289

It is well known that traces of alkali render hydrogen peroxide extremely unstable. In order to test the effect of alkali, therefore, a control experiment was performed using ferrocyanide and sodium hydroxide (0.0660 gm., and N/200 respectively). The resulting velocity constants were almost of the same order as without alkali, although the reaction was slightly autocatalytic. It is, therefore, clear that the amount of alkali employed above does not account for a rapid decomposition of hydrogen peroxide, observed in the foregoing experiment. The end solution was deep yellow

and gave an emerald green colour with *p*-nitrosodimethylaniline, and a violet colour with nitrosobenzene, indicating the formation of sodium aquopentacyanoferrite. The effect of potassium cyanide on the above mixture was next investigated to see whether a suppression of the decomposition was produced. Mixtures (50 c.c.) of nitroprusside, caustic potash, hydrogen peroxide, and potassium ferrocyanide were prepared, in which the respective strengths were 0.0100 gm., N/200, N/10 and 0.0660 gm. The strength of KCN was N/50.

TABLE XXIX

Without potassium cyanide

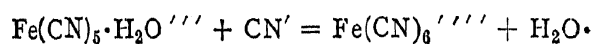
<i>t</i>	<i>a - x</i>	K.10 ⁴
0	14.00	∞
10	10.40	129
25	6.30	139
38.5	3.70	150
50	2.10	163

TABLE XXX

With potassium cyanide

<i>t</i>	<i>a - x</i>	K.10 ⁴
0	13.30	∞
5	12.60	47
15	11.60	40
33	9.85	40
64	8.10	34
101	6.90	28
127	6.40	25
160	5.90	22
190	5.60	20

The reaction in presence of ferrocyanide is slightly autocatalytic. When, however, N/50 potassium cyanide is used, a tremendous decrease in the velocity constant is observed and the values show a falling off with time. The explanation is that sodium aquopentacyanoferrite is produced by interaction of alkaline nitroprusside and hydrogen peroxide (Hofmann, *loc. cit.*). The aquopentacyanoferrite so formed decomposes hydrogen peroxide at a rapid rate. On the addition of potassium cyanide, the following reaction takes place:—



Aquopentacyanoferrite ions disappear producing ferrocyanide with a concomitant decrease in the velocity constant.

These results are similar to those obtained with pre-insolated nitroprusside-ferrocyanide-cyanide-hydrogen peroxide mixtures, and aquopentacyanoferrate-uninsolated nitroprusside-ferrocyanide-cyanide-hydrogen peroxide mixtures. In view of these observations, the suggestion of Qureshi (*loc. cit.*) that colloidal Prussian blue, formed by insolation, causes the after-effect, seems to be untenable. To examine this point, colloidal Prussian blue was prepared in the laboratory by the method of Hofmann, and added to hydrogen peroxide both in presence and absence of ferrocyanide. The

amount of Prussian blue (0.0025 gm.) was the same as that of aquopentacyanoferrate used before.

TABLE XXXI

Without $K_4Fe(CN)_6$

t	$a - x$	K.10 ⁷
0	14.80	∞
66	14.70	455
132	14.60	447
194	14.50	464
248	14.45	419

TABLE XXXII

$K_4Fe(CN)_6 = 0.0660$ gm.

t	$a - x$	K.10 ⁵
0	14.80	∞
65	11.80	151
131	10.90	101
191	10.20	85
247	9.60	76

It is clear that colloidal Prussian blue causes a very slow unimolecular decomposition. In the presence of ferrocyanide, the velocity constants, although higher, show a diminution with time—a behaviour different from that of aquopentacyanoferrate-ferrocyanide-hydrogen peroxide mixture, or pre-insolated nitroprusside-ferrocyanide-hydrogen peroxide mixture. It appears, therefore, that colloidal Prussian blue does not cause the after-effect.

The pre-insolated nitroprusside solutions as well as the end solutions of hydrogen peroxide-nitroprusside insolated mixtures developed a turbidity and showed colloidal particles under the ultramicroscope. An aqueous solution of sodium aquopentacyanoferrate also shows colloidal particles. The effect of colloidal ferric hydroxide was insignificant, indicating that it does not cause the observed after-effect.

Discussion

Qureshi's suggestion (*loc. cit.*) that the photochemical after-effect in the above reaction is due to the formation of colloidal Prussian blue has been experimentally found to be untenable. The latter is produced when aqueous nitroprusside is insolated for a long time, but the results set out above lead to the conclusion that it is not responsible for the after-effect. It is necessary to mention here that preliminary experiments showed that the blue nitroprusside solutions obtained by prolonged insolation gave erratic results, although even in these blue solutions the suggested catalyst, sodium aquopentacyanoferrate, could be chemically detected. Satisfactory results were, however, obtained by employing solutions of nitroprusside which had become pale yellowish brown on insolation and in which no blue tint was noticeable. These observations show that in the initial stage of insolation a new substance is formed which causes the after-effect, and longer exposures lead to the formation of colloidal Prussian blue. The results set out above show

that qualitatively the behaviour of pre-insolated nitroprusside, the pre-insolated mixture of hydrogen peroxide and nitroprusside, and the end solution of pre-insolated mixture of hydrogen peroxide and nitroprusside is identical with that of sodium aquopentacyanoferrate and nitroprusside mixture in the dark.

A reference to the literature on the action of light on nitroprusside shows that the formation of colloidal Prussian blue has been taken to be the result of insolation. According to Overbeck, sodium nitroprusside decomposes slowly in sunlight, yielding NO and $\text{Fe}_7(\text{CN})_{18}$. The latter corresponds to Prussian blue, $\text{Fe}_4^{\text{III}}(\text{Fe}^{\text{II}}\text{CN}_6)_3$. On the other hand, Justin-Mueller (1935) says that when exposed to sunlight in an open vessel, an aqueous solution of sodium nitroprusside is decomposed giving NaNO_2 , HCN and $\text{Na}_2\text{Fe}_2(\text{CN})_6$. The last named, in the presence of caustic soda, is converted into Prussian blue. When nitroprusside is exposed to sunlight in a closed vessel, nitric oxide is evolved. It has, however, been observed by the present author that the initial colour change in a dilute aqueous solution of nitroprusside during insolation, from brownish red to a pale yellowish brown, is accompanied by the formation of sodium aquopentacyanoferrate. The latter can be identified by several tests. This substance is formed within 5 to 10 minutes when direct sunlight is used. A longer exposure produces in addition to sodium aquopentacyanoferrate, colloidal Prussian blue.

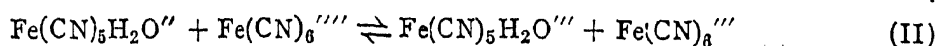
The catalyst which causes the after-effect has been found to be sodium aquopentacyanoferrate. Several tests are available to detect the formation of sodium aquopentacyanoferrate in a pre-insolated solution of nitroprusside. The latter was mixed with a little dilute aqueous solution of *p*-nitrosodimethylaniline, when a yellow solution was obtained. A little ferrocyanide was added to this mixture in the dark, when an emerald green colouration at once developed. This indicates that ferrocyanide converts aquopentacyanoferrate into aquopentacyanoferrite which is known to react with *p*-nitrosodimethylaniline giving a green colour (Baudisch, 1921). A green colour is also developed in the above mixture when *p*-nitrosodimethylaniline is replaced by dilute sulphuric acid. A direct test for aquopentacyanoferrate is furnished by the starch-iodide reaction. Hofmann (*loc. cit.*) has shown that the former liberates iodine from potassium iodide. A pre-insolated nitroprusside solution was mixed with a little iodide and starch, when a blue iodide of starch was formed. This colour was discharged by thio-sulphate. Another reagent which shows that the pre-illuminated pale yellowish brown solution of sodium nitroprusside contains some sodium aquopentacyanoferrate is nitrosobenzene. A little aqueous solution of the sparingly soluble nitrosobenzene was mixed in the dark with pre-insolated

nitroprusside, and then a freshly prepared solution of potassium ferrocyanide was added, when a violet colour was immediately formed. This colour is given by aquopentacyanoferrite, or aquopentacyanoferrate containing some ferrocyanide. This reagent gives a clear indication of the presence of aquopentacyanoferrate in solutions of nitroprusside which have been insolated for 5 to 10 minutes in direct sunlight. It is significant that these tests are not given by mixtures of pre-insolated nitroprusside and ferrocyanide, which have been heated to about 90° C. in the dark for a few minutes before the addition of the enumerated reagents. An alcoholic solution of guaiacum produces a blue colouration with pre-insolated nitroprusside, and the same blue colour is formed with sodium aquopentacyanoferrate. Unilluminated nitroprusside solutions do not give any of these tests, neither does colloidal Prussian blue answer them. It is thus evident that the mechanism of the photochemical after-effect consists in the formation of sodium aquopentacyanoferrate from sodium nitroprusside in light:—



The aquopentacyanoferrate ions cause catalytic decomposition after darkening as revealed by the after-effect. The autocatalytic nature of the decomposition in the after reaction is reproduced in the dark by aquopentacyanoferrate-uninsolated nitroprusside mixture.

The effect of ferrocyanide in regulating the reaction and producing a high velocity of decomposition follows from the following scheme:—

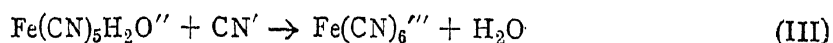


Highly reactive aquopentacyanoferrite is produced by interaction of ferrocyanide and aquopentacyanoferrate contained in pre-insolated nitroprusside. In presence of an excess of ferrocyanide, the amount of aquopentacyanoferrite is kept constant and at a high level, to an extent depending upon the concentration of the former. From this it is clear why a uniformly high velocity is obtained in the presence of an excess of ferrocyanide. When smaller amounts of ferrocyanide are used, the velocity constants show a falling off with the progress of the reaction, as the former ions are gradually oxidised, and the equilibrium reaction shifts to the left with a decrease in the concentration of aquopentacyanoferrite ions. It is clear why ferricyanide is not effective in maintaining a rapid rate of decomposition.

Sodium aquopentacyanoferrate is comparatively stable towards heat, whereas sodium aquopentacyanoferrite undergoes a slow spontaneous change in the dark at room temperature. This change is considerably accelerated by heat. This explains why pre-insolated nitroprusside, heated and added

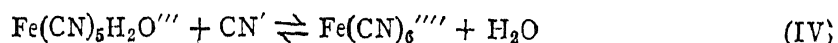
to hydrogen peroxide, does not show lowered reactivity. When a mixture of pre-insolated nitroprusside and ferrocyanide is heated to about 90° C. for a few minutes and then added to hydrogen peroxide, the activity is noticed to diminish considerably, because of the destruction of aquopentacyanoferrite. The same change continues slowly in the dark, and hence a mixture of pre-insolated nitroprusside and ferrocyanide, kept in the dark for some hours before use, shows a lower rate of decomposition than a freshly prepared mixture.

The effect of cyanide ions in suppressing the photochemical after-effect as well as the reaction performed in presence of aquopentacyanoferrate lends support to the mechanism of the photochemical after-effect outlined above. This 'quenching' effect of cyanide ions is due to the conversion of aquopentacyanoferrate to ferricyanide:—

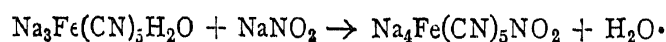


The excess of cyanide ions react with ferricyanide ions to give ferrocyanide ions in the end. The slightly autocatalytic effect noticed in experiments with potassium cyanide is due to the alkali produced by hydrolysis.

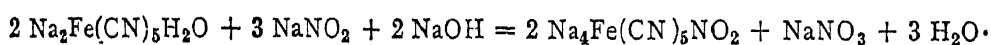
When ferrocyanide is first added to pre-insolated nitroprusside, the formation of aquopentacyanoferrite takes place. This is converted by cyanide ions to ferrocyanide ions:—



The effect of sodium nitrite in suppressing the catalytic activity of the pre-insolated solutions of nitroprusside is to be attributed to the formation of nitroprusside by the interaction of nitrite and aquopentacyanoferrite (Hofmann, *loc. cit.*). The latter is formed when ferrocyanide reacts with aquopentacyanoferrate according to (II). Aquopentacyanoferrite reacts with nitrite as follows:—



When nitrite is added to pre-insolated nitroprusside, which has been shown to contain aquopentacyanoferrate, the following reaction takes place.



The quaternary nitroprusside is produced in each case, and as it does not decompose hydrogen peroxide in the dark with a high rate, the photochemical after-effect is 'quenched' by nitrite. It has been seen that aquopentacyanoferrate or aquopentacyanoferrite reacts with nitrite and the resultant solution gives a purple colour with alkali sulphides showing the conversion of the two substances into nitroprusside. The nitrite-treated pre-insolated nitroprusside, containing ferrocyanide, or aquopentacyanoferrite after

treatment with nitrite does not give the characteristic colour tests mentioned previously, showing the complete conversion of aquopentacyanoferrate and aquopentacyanoferrite into nitroprusside.

Hofmann (*loc. cit.*) has shown that aquopentacyanoferrite is formed when alkaline nitroprusside reacts with hydrogen peroxide. That the addition of alkali to hydrogen peroxide-uninsolated nitroprusside mixture in the presence of ferrocyanide reproduces the photochemical after-effect qualitatively in the dark, and further that the cyanide ions suppress this activity, show that aquopentacyanoferrate causes the after-effect. This furnishes further evidence in support of the mechanism involving the photo-formation of aquopentacyanoferrate from nitroprusside.

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Summary

The photochemical after-effect in the reaction between hydrogen peroxide and sodium nitroprusside is due to the photo-formation of sodium aquopentacyanoferrate. The formation of aquopentacyanoferrate in pre-insolated nitroprusside solution has been proved by qualitative tests. Colloidal Prussian blue does not cause the after-effect.

Pre-insolated nitroprusside continues to react in the dark in the manner indicated by the after-effect. Addition of ferrocyanide causes the reduction of aquopentacyanoferrate to aquopentacyanoferrite, which decomposes hydrogen peroxide with a high velocity. The validity of the suggested mechanism for the after reaction has been tested by the effect of potassium cyanide and sodium nitrite, which have been shown to suppress the after-effect by converting aquopentacyanoferrate to ferrocyanide and nitroprusside respectively. Sodium aquopentacyanoferrate, prepared in the laboratory and added to hydrogen peroxide-uninsolated nitroprusside mixture in the dark in presence and absence of ferrocyanide, has been shown to reproduce the observations obtained by insolation.

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