

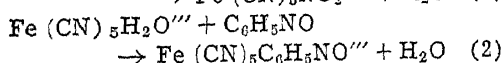
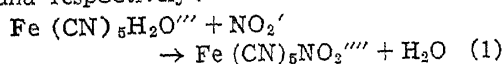
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PHOTOCHEMICAL AFTER-EFFECT IN THE DECOMPOSITION OF HYDROGEN PEROXIDE BY POTASSIUM FERROCYANIDE

It has been shown that the photochemical after-effect in the decomposition of hydrogen peroxide by pre-illuminated ferrocyanide can be reproduced in the dark by adding small quantities of the aquo-salt (II), sodium aquopentacyanoferrite, to the unilluminated H₂O₂-K₄Fe(CN)₆ mixture.¹ Sodium aquopentacyanoferrate, the violet aquo-salt (III), can also be used with similar results. These observations support the view that potassium aquopentacyanoferrite produced photochemically and reversibly in the illuminated solutions of potassium ferrocyanide brings about the photochemical after-effect.

The above view has been tested in another way. It is known² that sodium aquopentacyanoferrite reacts with sodium nitrite and nitrosobenzene forming quaternary nitroprusside and a purple-coloured substitution compound respectively:—



It follows that if the aquo-salt formed from ferrocyanide by insolation causes the photochemical after-effect, the addition of nitrite and nitrosobenzene should considerably reduce or "quench" the after-effect, as the decomposition of hydrogen peroxide by nitrosoprus-

siderate formed in (1) is very slow in the dark,³ and the purple substitution compound formed in (2) is also not very reactive towards hydrogen peroxide.

Potassium ferrocyanide solution (M/64), 10 c.c., was pre-illuminated by direct sunlight for one minute, and added to hydrogen peroxide immediately after darkening, or it was first mixed with aqueous nitrosobenzene or nitrite just after illumination, and then added to hydrogen peroxide in the dark. The concentrations of hydrogen peroxide and ferrocyanide in 50 c.c. of the reaction mixture were N/6 and M/320 respectively. A saturated solution (5 c.c.) of freshly prepared nitrosobenzene in conductivity water was used. Temperature of the reaction was 40° C. The velocity constant has been calculated according to the Unimolecular formula, $K = 1/t \log a/a - x$ where t represents time in minutes, a the initial concentration of H₂O₂, in terms of c.c. of permanganate, and x the change in time t .

TABLE I
Without nitrite or nitrosobenzene

t	$a - x$	$K \cdot 10^4$
0	16.10	..
12.5	13.80	54
26	11.40	58
37	9.80	58
57	7.50	58

TABLE 2
With 5 c.c. aqueous nitrosobenzene

t	$a - x$	$K \cdot 10^4$
0	16.25	..
15	14.60	31
34	12.80	31
65	10.00	32
100	8.00	31

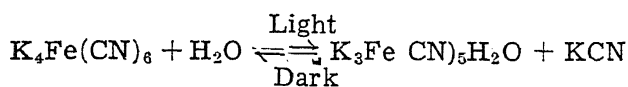
TABLE 3
With 0.0020 gm. sodium nitrite

t	$a - x$	$K \cdot 10^4$
0	13.60	..
15	12.95	14
34	12.40	12
68	12.00	8
120	11.30	7

The slightly higher value of $K \cdot 10^4$ (54-58) in Table 1 (*cf. Curr. Sci.*, April 1947, p. 118) is probably due to a small change in the intensity of sunlight.

It is seen from Table 2 that nitrosobenzene reduces the photochemical after-effect to a considerable extent, while the nitrite is still more effective in suppressing the after-effect.

A mixture of potassium ferrocyanide and potassium cyanide pre-illuminated and then added to hydrogen peroxide in the dark does not show any after-effect. This is to be expected if the photo-formation of the aquo-salt from ferrocyanide is responsible for the after-reaction. In the presence of added cyanide, the equilibrium



is shifted to the left, resulting in practically complete suppression of the concentration of the aquo-salt, so that none exists in such an illuminated solution to produce the after-effect.

It has been further established that the after-effect reproduced in the dark by the addition of minute quantities of the aquo-salt (II) to H_2O_2 - $\text{K}_4\text{Fe}(\text{CN})_6$ mixture is also completely suppressed by CN^- and NO_2^- , while the diminution brought about by nitrosobenzene is of the same order as already reported in the case of the photochemical after-effect. Pre-illuminated ferrocyanide on treatment with suitable quantities of nitrite or cyanide ions does not answer the tests for the aquo-salt (II), and the pure aquo-salt (II) in the presence of these ions is completely converted into nitroprusside and ferrocyanide respectively.

The photochemical after-effect cannot be ascribed either to alkali or to ferricyanide pro-

duced in the course of the reaction, as the experiments with unilluminated ferrocyanide and ferricyanide and alkali failed to show the rapid decomposition characteristic of the illuminated ferrocyanide, which is known to contain minute quantities of the aquo-salt (II). In this connection attention is drawn to an earlier paper by Lal and Singhal⁴ in which the decomposition of hydrogen peroxide by ferricyanide has been discussed.

It has already been reported that aqueous solutions of aquopentacyanoferrite exhibit a slow spontaneous decomposition in the dark at room temperature in the presence of air, and the aquo-salt is completely decomposed into ferric hydroxide, ferri- and ferrocyanide. These changes are greatly accelerated by light and heat, and this appears to be the cause of the photosensitivity of the aquopentacyanoferrite ion.⁵ These observations are in general agreement with those of Imori.⁶ It is significant to note that the sodium aquo-salt after being heated to about 90° C. for a few minutes or exposed to direct sunlight for about an hour does not give the characteristic colour reactions with *p*-nitrosodimethylaniline or nitrosobenzene.⁷ An aqueous solution of the sodium aquo-salt kept in the dark for a few days shows the same behaviour.

Recently, Williams⁸ has studied the causes of discolouration of ferro- and ferri-cyanide crystals and has come to the conclusion that the decomposition of the aquo-salt (II) takes place spontaneously in the dark in the presence of air with the formation of ferric hydroxide and ferricyanide. In view of these results, the suggestion of Baudisch⁹ that prolonged insolation of ferrocyanide in the presence of air results in the formation of an oxygen-rich product which gives a blue colouration with tincture of guaiacum appears to be untenable. Rather, one should expect this guaiacum colour reaction as indicative of the decomposition of the photochemically produced aquo-salt (II) into ferricyanide, which is known to produce a blue colouration with tincture of guaiacum.

Attention may also be drawn to the author's observation that contrary to the findings of Baudisch (*loc. cit.*) there is reason to believe that free aquo-salt (II) exists in illuminated ferrocyanide solutions in the presence of air in the initial stage of insolation. Further Baudisch has remarked that in the presence of air and light the yellow aquo-salt (II) formed from ferrocyanide is oxidised momentarily to deep violet-coloured aquo-salt (III), which then reacts with the aquo-salt (II) to form higher complexes of pale yellow colour. The ready reducibility of the violet aquo-salt (III) to yellow aquo-salt (II) in the presence of excess ferrocyanide as noted by Williams and others and the existence of free aquo-salt in presence of ferrocyanide, however, go against the suggestion of complex formation between the two aquo-salts in aqueous ferrocyanide solutions. Experiments already in progress are expected to elucidate the mechanisms involved in the action of light on ferrocyanide.