

INVESTIGATION OF PHOTOCHEMICAL AFTER-EFFECT: THE DECOMPOSITION OF HYDROGEN PEROXIDE BY POTASSIUM FERRICYANIDE

In the decomposition of hydrogen peroxide by potassium ferrocyanide or sodium nitroprusside, a pronounced after-effect of illumination has been observed by many workers.^{1,2,3} From a study of the decomposition of hydrogen peroxide by potassium ferricyanide, however, Rao and Srikantan⁴ have come to the conclusion that no after-effect of illumination is detectable in the reaction. On the other hand, the illuminated ferricyanide has been found by them to produce a distinctly lower rate of decomposition than the unisolated solution. In view of the closely related nature of ferrocyanide, nitroprusside and ferricyanide the complete absence of the photochemical after-effect in the latter appeared to us rather surprising. It was, therefore, thought desirable to investigate the decomposition of hydrogen peroxide by potassium ferricyanide in detail.

We have been able to observe a remarkably large photochemical after-effect in the decomposition of hydrogen peroxide by pre-insolated ferricyanide, particularly when some unilluminated ferrocyanide is also present in the reaction mixtures. The irradiated ferricyanide solution shows a much enhanced reactivity towards hydrogen peroxide in the dark. Furthermore, this enhanced reactivity which manifests itself as the photochemical after-effect is retained for a long time, although after irradiation it continues to diminish gradually on standing in the dark.

The dark reaction between N/10 H₂O₂ and M/300 K₃Fe(CN)₆ at 25 ± 1° C. is exceedingly slow and shows an autocatalytic course with the progress of the decomposition. We have been wholly unable to observe a constant unimolecular rate of decomposition at any stage of the reaction. The ferricyanide solution, insolated for 20 minutes, produced a considerably higher rate of decomposition of the peroxide, but the course of this decomposition was likewise autocatalytic as that of the dark reaction. This after-effect is markedly increased by the addition of a suitable amount of unisolated ferrocyanide to the reaction mixture, and what is more important, the unimolecular velocity constants maintain a fairly uniform, though much higher value throughout the course of the decomposition.

Dark reaction between H₂O₂ and K₃Fe(CN)₆

<i>t</i>	<i>a-x</i>	K.10 ⁵
0	22.20	—
2885	21.90	203
3348	21.80	236
4300	21.65	253
6010	21.40	256
7817	20.90	336
8815	20.30	495
12792	18.80	564

Dark reaction between H₂O₂, K₃Fe(CN)₆ and M/300
K₄Fe(CN)₆*

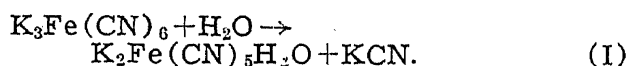
<i>t</i>	<i>a-x</i>	K.10 ⁶
0	20.40	—
81	19.70	186
235	18.80	149
448	16.30	217
775	12.50	274

* With K₄Fe(CN)₆ alone, apparently the same order of K is obtained.

Dark reaction between H₂O₂ and pre-insolated
ferricyanide and M/300 ferrocyanide

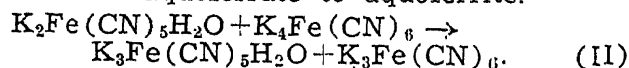
<i>t</i>	<i>a-x</i>	K.10 ⁶
0	22.40	—
965	21.00	29
1493	19.85	35
Added 0.038 gm. K ₄ Fe(CN) ₆		
1631	12.40	—
1687	10.05	1627
1750	8.05	1553
1795	7.00	1515

A study of the irradiated aqueous solution of potassium ferricyanide has led us to the conclusion that an appreciable amount of potassium aquopentacyanoferrate is produced under the influence of radiation.

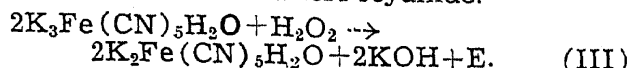


The presence of the aquo complex salt has been proved by a number of qualitative colour reactions. The aquo complex salt causes the measured photochemical after-effect.

The addition of K₄Fe(CN)₆ results in the reduction of aquoferrate to aquoferrite.



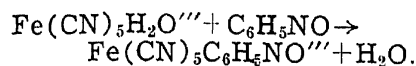
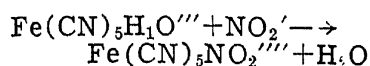
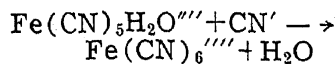
Potassium aquopentacyanoferrite so produced causes a very rapid decomposition of H₂O₂ at a constant unimolecular rate in the presence of a suitable excess of ferrocyanide.



It is suggested that the energy liberated in (III) causes the decomposition of a large number of H₂O₂ molecules. The catalytic system Fe(CN)₅H₂O ≤ Fe(CN)₅H₂O₂ thus causes a uniform decomposition of H₂O₂ as measured by the after-effect.

Experimental evidence in support of the suggested mechanism of the photochemical after-effect has been adduced by studying the after-reaction in presence of CN', NO₂' and C₆H₅NO. The after-effect has been found to be very largely quenched in the presence of these substances. This is to be expected if the photoformation of potassium aquopentacyanoferrate

from ferricyanide is responsible for the after-effect. The quenching is produced because the highly reactive aquopentacyanoferrite ion is converted into much less reactive substances as follows:—



The above conclusions have been experimentally verified and fully substantiated by studying the decomposition by unisolated ferricyanide and a trace of the photo-catalyst, sodium aquopentacyanoferrate. We have been able to reproduce the photochemical after-effect in the dark by adding a trace of aquopentacyanoferrate ions to H_2O_2 - $\text{K}_3\text{Fe}(\text{CN})_6$ mixture. A quenching of this effect is also observed in the presence of CN' , NO_2' and $\text{C}_6\text{H}_5\text{NO}$.

The details of the investigation will be published elsewhere.

Chemical Laboratories,
St. John's College,
Agra,
August 9, 1943.

B. B. LAL.
C. P. SINGHAL.

1. Kistiakowsky, W., *Zeit. Physikal. Chem.*, 1900, **35**, 431.
2. Lal, B. B., *Jour. Ind. Chem. Soc.*, 1939, **16**, 7, 321.
3. Qureshi, M., *Jour. Physical. Chem.*, 1931, **35**, 656.
4. Lal, B. B., *Proc. Ind. Acad. Sci.*, 1941, **14**, 652.
5. Rao and Srikantan, *Jour. Ind. Chem. Soc.*, 1933, **10**, 29.

A NEW VARIETY OF ISOACHLYA ANISOSPORA (deBARY) COKER

In 1888, deBary¹ described a fungus as *Saprolegnia anisospora*. Recently its name has been changed to *Isoachlya anisospora* by Coker and Matthews² on sporangial characters. The present material was isolated from a pond, ten miles from Allahabad, using hempseeds as baits. All observations recorded below were made on cultures growing on hempseeds in distilled water.

Isoachlya anisospora (deBary) Coker, var. *indica*, nov. var.

Mycelium 8.18-16.36 μ thick. Spores of two kinds, smaller 9 μ in diameter while bigger ones upto 12 μ . Sporangia 14.5-24.5 μ thick and 99-163.63 μ long. Oogonia are spherical; terminal and also rarely intercalary; wall smooth; 37.14-92.85 μ mostly 60-66 μ in diameter; thickness of the wall 1.4 μ .

Antheridia present on all oogonia; long; androgynous and declinuous; applied by sides. Eggs 1-10 in number, never more than ten; 21.81-55.71 μ in diameter, mostly 24.54-35.45 μ ; thickness of the wall 3 μ ; not completely filling the oogonium; centric or subcentric.

I. anisospora var. *indica* differs from the main species in the structure of the egg which, in the present form, is either centric or subcentric (Figs. 1 and 2). In no case eccentric eggs were

formed as described by Coker and Matthews for the main species. Since the egg structure in this form does not agree with that of the

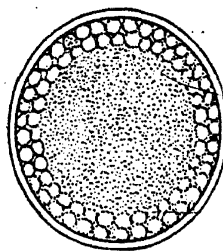


FIG. 1
A centric egg

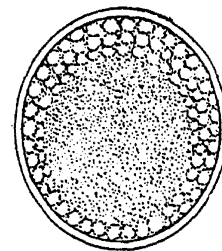


FIG. 2
A subcentric egg

American species, the authors consider it to be a new variety. Prof. W. C. Coker suggests us to call it a form of *I. anisospora*.

We thank Prof. W. C. Coker, University of North Carolina, U.S.A., for his kind advice, and also Prof. S. R. Bose, Carmichael Medical College, Calcutta, and Dr. John Dearness of Canada for communicating our description of the fungus to Prof. Coker.

Botanical Laboratory,
The University,
Allahabad,
February 5, 1944.

R. K. SAKSENA.
K. S. BHARGAVA.

1. deBary, A., *Bot. Zeit.*, 1888, **46**, 619.
2. Coker, W. C., and Matthews, V. D., *North American Flora*, 1937, **2**, 17-58.

PROGRESS OF HOMOZYGOSITY DUE TO BACKCROSSING

ACCORDING to Mendelian segregation in self-fertilized plants or in selfing cross-fertilized plants involving a single pair of genes, the fraction of the heterozygous individuals gets halved at every successive generation and at the end of a few generations a very large percentage of the population becomes homozygous. Where a large number of genes are concerned, the reduction in the percentage of heterozygous individuals is comparatively slow in the first few generations but later, say after ten generations, this percentage forms only a very small fraction of the population. The formula for determining the percentage of homozygous individuals in any generation following a cross is $(1 - \frac{1}{2^n})^m$ where n is the number of segregating generations which have elapsed since the cross was made and m , the number of independently inherited pairs of genes involved.

Let us now consider this principle in the case of practical stock breeding, say, improving milk yield in cows. In herds which lack the genes controlling high yield of milk, they may be introduced through mating them to bulls known to possess these genes. The rate of transfer of the genes will be the speediest when the sires selected for mating are homozygous for all the genes involved and the progenies are back-crossed in each succeeding generation to these same individuals or mated