

# PHOTOCATALYTIC REDUCTION OF NITRATE AND THE SIMULTANEOUS OXIDATION OF AMMONIA TO NITRITE.

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It is well known that potassium nitrate decomposes to nitrite in aqueous solution when exposed to ultraviolet light. Warburg [1918] studied the energetics of this reaction. His results showed (1) that the photolysis is more rapid in alkaline than in acid solutions and (2) that the quantum yield is much less than unity and falls off rapidly above 2500 Å. Anderson [1924] stated that this is a process in which a photo-stationary state is reached according to the equation



Anderson's work was criticised by Villars [1927] who denies the existence of a photo-stationary state in this reaction.

When a solution of potassium nitrate is exposed in a glass vessel to sunlight there is no decomposition of the nitrate to nitrite, but if it is exposed to sunlight in a glass vessel together with ignited ferric oxide photolysis takes place. There is no reaction in the dark. It has also been observed that sterilised soil can markedly photocatalyse this reaction. Further, if an ammonium salt was present in the solution, ammonia disappears and there is an increase in the amount of nitrite formed. Thus it appears that the photocatalytic decomposition of nitrite brings about the oxidation of ammonia to nitrite. As these reactions are important for the nitrogen problem of the soil they have been studied in detail in the following investigation.

## EXPERIMENTAL.

Ferric oxide was precipitated from ferric sulphate solution, by the addition of the requisite amount of sodium hydroxide solution; the precipitate was washed free from sulphate and alkali; it was dried in a steam oven, powdered and sieved through a sieve of 80 mesh. 100 c.c. of a 0.1 N potassium nitrate solution was exposed with 1 gm. of the ferric oxide in a 500 c.c. pyrex flask. The nitrite nitrogen was estimated from time to time by the Griess-Ilsovy colorimetric method. The following table gives results obtained on the variation of the rate of photolysis with the pH.

TABLE I.

pH	M.gms. of nitrite nitrogen formed		
	20 hrs.	40 hrs.	60 hrs.
7.0	0.21	0.41	
7.58	0.72	1.19	1.5
8.09	0.82	1.36	1.81
8.61	0.97	1.93	2.2
9.08	1.08	2.1	2.56
10.20	1.16	2.30	3.24
10.80	1.86	3.97	4.97

*Influence of variations of concentration of nitrate.*

The following table shows that the rate of photolysis of nitrate decreases with diminishing concentration of nitrate. The experiments were done at pH 10.8.

TABLE II.

No. of hours of exposure	M.gms. of nitrite nitrogen		
	M/10 KNO <sub>3</sub>	M/100 KNO <sub>3</sub>	M/1000 KNO <sub>3</sub>
20	1.42	....	....
45	2.04	0.54	....
75	3.50	0.66	0.12
100	7.14	1.59	0.19
130	9.03	1.95	0.28

*Influence of ammonium chloride.*

The following table gives the amount of nitrite nitrogen formed on exposing 100 c.c. of M/10 potassium nitrate with different concentrations of ammonium chloride in the presence of 1.0 gm. of ferric oxide. The experiments were conducted at pH 7.0.

TABLE III.

No. of hours of exposure	Amount of nitrite nitrogen in m.gms. per litre		
	M/50 NH <sub>4</sub> Cl.	M/100 NH <sub>4</sub> Cl.	M/200 NH <sub>4</sub> Cl.
20	0.52	0.45	0.40
45	1.10	0.95	0.85
75	2.20	1.95	1.50
130	8.4	7.77	6.97

Another set of experiments were done at pH 10.8 but otherwise similar to those described before. The results are tabulated thus :—

TABLE IV.

No. of hours of exposure	Amount of nitrite nitrogen in m.gms. per litre		
	M/50 NH <sub>4</sub> Cl.	M/100 NH <sub>4</sub> Cl.	M/200 NH <sub>4</sub> Cl.
20	1.87	1.49	1.29
45	3.73	3.26	2.63
75	6.82	5.97	3.65
100	11.67	10.22	7.41
130	16.53	14.22	11.03

These results show that in the presence of ammonium chloride there is an increased formation of nitrite.

*Experiments with soil as photocatalyst.*

Waltair red soil was washed with distilled water until free from salts and then sterilised by heating at 160–170°C for 10 hours. It was then powdered and passed through a 40 mesh sieve. This was used as a photocatalyst.

100 c.c. of potassium nitrate solution were exposed to sunlight in a pyrex flask with 5 gms. of red soil. The results at different pH values are recorded below.

TABLE V.

pH	M.gms. of nitrite nitrogen per litre		
	20 hrs.	40 hrs.	60 hrs.
9.6	3.33	4.7	6.31
10.2	3.46	4.93	6.60
10.8	3.54	5.15	7.00

*Influence of ammonium chloride on the photo-decomposition of nitrate.*

The following table shows the amount of nitrite nitrogen formed when 100 c.c. of M/10 potassium nitrate solution was exposed with different concentrations of ammonium chloride in the presence of 5 gms. of soil at pH 7.0.

TABLE VI.

No. of hours of exposure	M.gms. of nitrite nitrogen formed		
	M/50 NH <sub>4</sub> Cl.	M/100 NH <sub>4</sub> Cl.	M/200 NH <sub>4</sub> Cl.
20	1.75	1.42	1.26
45	2.63	1.81	1.67
75	3.59	2.69	2.38
100	7.87	5.97	4.83
130	13.93	10.49	9.91

In one set of experiments the estimation of ammonia nitrogen was made and it was found that this figure decreased progressively. However, there was more loss of ammonia than could be accounted for by the increase in the nitrite content over the blank. Further work is in progress on different aspects of the problem.

*The photo-oxidation of nitrite to nitrate.*

Dhar and co-workers [1934, 1936] have observed that sodium nitrite in aqueous solution is oxidised to sodium nitrate when exposed to sunlight in the presence of zinc oxide, titania, or ferric oxide. Sarkaria and Fazal-uddin [1933] have also found that sodium nitrite is oxidised to nitrate photocatalytically in the presence of animal charcoal or ferric oxide. We have now found that sterilised soil can also act as a photocatalyst. In the following experiments 100 c.c. of 0.001 molar sodium nitrite solution was exposed to sunlight with 5 gms. of sterilised soil at different pH values.

TABLE VII.

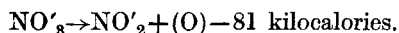
No. of hours of exposure	M.gms. of nitrite nitrogen remaining per litre		
	Exposed at pH 7	Exposed pH 8.61	Exposed at pH 10.8
..	14.0	13.90	14.00
40	12.10	12.60	12.75
75	9.83	10.76	12.13

It appears from these results that the rate of oxidation decreases as the pH is increased. On the other hand the photo-reduction of nitrate to nitrite is faster in alkaline than in neutral or acid media. It must be noted in this connection that the oxidation of nitrite to nitrate occurs in the dark when the medium is definitely acidic; no oxidation, however, takes place at

pH 7 and above. In sunlight, however, there is appreciable oxidation even in alkaline media when catalysed by ferric oxide or sterilised soil.

In previous publications Gopalarao and Dhar [1931] and Gopalarao [1934] have suggested that nitrification in soils is partly a photo-chemical reaction taking place at the surface of the soil under the influence of sunlight. Corbet [1934, 1935] is also of the opinion that nitrification in soils, specially those of the tropics, is a photo-chemical reaction.

As shown above potassium nitrate in aqueous solution can decompose to nitrite in light transmitted by glass provided ferric oxide is used as a photo-catalyst. The decomposition of nitrate is an endothermal reaction occurring with the absorption of energy (81 kilocalories)



This corresponds to radiation of wavelength 3500 Å. The experiments of Warburg [1918] have shown that the quantum yield with radiation of 2070 Å is only 0.25 while with 2820 Å it is much lower, e.g. 0.024. Thus it appears that as the wavelength of the light is increased the quantum yield rapidly decreases. Our observations show that in the presence of a suitable heterogeneous catalytic surface, e.g., ferric oxide or sterilised soil, the energy of activation is considerably lowered thus making it possible for the reaction to occur in visible light. The mechanism of this photocatalytic action raises questions of theoretical interest which are beyond the scope of this paper and will be discussed elsewhere.

The observations that sterilised soil also acts as a photocatalyst, and that if an ammonium salt is present the ammonia is simultaneously oxidised to nitrate, lend further support to the photochemical view of nitrification put forward in earlier publications.

We have also noticed that nitrate can be oxidised to nitrite photochemically in the presence of ferric oxide. It thus appears likely that many reactions hitherto supposed to be due entirely to the action of bacteria can also be brought about by sunlight with soil as photocatalyst.

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