

Oxidation of Nitrites to Nitrates in Sunlight

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In a communication to *Nature* (1934, 133, 213) it was reported that dilute aqueous solutions of alkali nitrites are oxidised to the nitrate in presence of catalysts like ZnO, TiO₂, Fe₂O₃, etc., when exposed to sunlight. These observations are of great importance in view of the fact that the soil contains nitrates and not nitrites under normal conditions.

We have carried on further experiments on the photo-oxidation of solutions of sodium nitrite of different concentrations in presence of photocatalysts and some of our results are recorded in this communication.

The estimation of the nitrite was carried on colorimetrically using the well known α -naphthylamine-sulphanilic acid test. A Duboscq colorimeter was utilised for this purpose. The total nitric nitrogen was estimated by reducing the solution with alkali and Devarda's alloy and distilling off the ammonia which was absorbed by standard solutions of sulphuric acid. The ammonium salt formed was estimated colorimetrically by Nessler's reagent and this was checked by estimating the excess of sulphuric acid by standard solutions of caustic soda using methyl red as an indicator.

EXPERIMENTAL.

50 C.c. of the nitrite solutions were exposed to sunlight along with 0.5 g. of the photocatalyst in open 400 c.c. Jena glass breakers. The solutions were frequently stirred when exposed to sunlight for five hours every day. Several sets of beakers containing solutions of different concentrations of the nitrite were exposed and in each estimation the total amount contained in a beaker was made up to 100 c.c. 80 C.c. of this diluted solution were employed for the total nitrogen estimation, while 20 c.c. were reserved for nitrite estimation by the colorimetric method. The following results were obtained

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TABLE I.

The original soln. of NaNO_2 contained 0.0348 g. of N per 100 c.c.

Photocatalysts.	Amount of $\text{NO}_2\text{-N}$ in g./100 c.c. after an exposure of			
	30 hours.	60 hours.	90 hours.	120 hours.
Fe_2O_3	0.01137	0.011	0.01	0.0089
ZnO	0.0133	0.01025	0.00471	0.00141
Soil	0.01541	0.01532	0.0136	0.0133
TiO_2	0.0137	0.0115	0.00762	0.0058

The foregoing results show that amongst the photocatalysts examined, namely Fe_2O_3 , ZnO, Soil, TiO_2 , zinc oxide is the best reagent in accelerating the photo-oxidation of nitrite solutions to nitrate. Solutions of nitrite containing no photocatalyst were also exposed but very little oxidation was observed in any of them.

In the following table the results obtained with ZnO as the photocatalyst are summarised. Four different concentrations of sodium nitrite solutions were taken to start with, *viz.*, $N/10.2 = 0.0686$ g.; $N/20.4 = 0.0343$; $N/40.8 = 0.01710$; $N/81.6 = 0.00855$ of $\text{NO}_2\text{-N}$ per 100 c.c.

TABLE II.

Amount of $\text{NO}_2\text{-N}$ and total N expressed in g/100 c.c. and exposed for different periods. The solutions were always tested for ammonia also after the exposure, but in no case was it detected.

Original amount to start with.		20 hours.		40 hours.	
$\text{NO}_2\text{-N}$.	Total N.	$\text{NO}_2\text{-N}$.	Total N.	$\text{NO}_2\text{-N}$.	Total N.
0.0686	0.0686	0.0648	0.0684	0.06034	0.0684
0.0343	0.0343	0.0280	0.03452	0.0234	0.03398
0.0171	0.0171	0.00934	0.016464	0.003226	0.015992
0.00855	0.00855	0.00108	0.00848	Nil	0.00848
Original amount to start with.		60 hours.		80 hours.	
$\text{NO}_2\text{-N}$.	Total N.	$\text{NO}_2\text{-N}$.	Total N.	$\text{NO}_2\text{-N}$.	Total N.
0.0686	0.0686	0.050	0.0684	0.0432	0.0684
0.0343	0.0343	0.01522	0.03396	0.007610	0.03410
0.0171	0.0171	0.000060	0.01598	Nil	0.0162
0.00855	0.00855	Nil	0.00848	Nil	0.00848

The amount of nitrate nitrogen formed by oxidation of nitrite nitrogen can be obtained by deducting the amount of nitrite nitrogen from the corresponding amount of total nitrogen. The results are tabulated below.

TABLE III.

Original amount of NO ₂ -N in g./100 c.c.	Amount of NO ₂ -N in g./100 c.c. after an exposure of 20 hours.	40 hours.	60 hours.	80 hours.
0'0686	0'0036	0'00806	0'0184	0'0252
0'0343	0'00652	0'01058	0'01874	0'02649
0'0171	0'007124	0'012766	0'01592	0'0162
0'00855	0'0074	0'00848	0'00848	0'00848

Some beakers containing 50 c.c. of *N*/81.6-NaNO₂ along with 0.5 g. of ZnO were kept in the dark and analysed after 16 days (the time taken up by these experiments). In none of these beakers any nitrite was converted into nitrate.

The foregoing results show that sodium nitrite of concentration varying from *N*/10.2 to *N*/81.6 are readily oxidised to the nitrate when exposed to light in presence of ZnO. In the more concentrated solutions, the amount of oxidation is less, but in the dilute solutions even after 40 hours' exposure, the oxidation of the sodium nitrite to sodium nitrate is complete. It is clear, therefore, that aqueous solutions of nitrite when exposed to light and air undergo the following reversible change



In dilute solutions the chemical change proceeds from left to right and in strong solutions from right to left, *i. e.*, concentrated solutions of NaNO₃ when exposed to light are decomposed into sodium nitrite with liberation of oxygen, but dilute solutions of sodium nitrite when exposed to air and light are readily oxidised to sodium nitrate.

It may be argued that these solutions exposed to sunlight in open beakers might have been contaminated with the nitrate-formers (Nitro-bacter). In many of our experiments after the necessary exposure we

attempted to detect the presence of nitrate-formers microscopically but in no case the nitrobacter was obtained and hence it is believed that these oxidations of sodium nitrite to nitrate taking place in presence of light are due to light absorption and not to bacteria. At the same time the fact, believed by most of the bacteriologists that strong sunlight is injurious for the growth of nitrate-formers, further eliminates the possibility of the presence of any nitrobacter cells in our nitrite solutions exposed to sunlight. It is well known that solutions of nitrite can absorb ultraviolet light copiously. If this nitrate formation were entirely a bacterial process, as has hitherto been believed, some conversion of the nitrite into the nitrate in the beakers kept in the dark should have taken place, but it has already been stated that in these no nitrate has been formed.

This photo-oxidation of sodium nitrite to nitrate also takes place in presence of soil. Moreover, it is well known that small amounts of ammonium salts are always present in normal soils and these ammonium salts are oxidised to nitrite and finally to nitrate in the soil. Hence the amount of nitrite that can temporarily exist in the soil being small is readily oxidised to the nitrate stage. It is clear, therefore, that the process of nitrification, which has hitherto been considered due to bacteria alone can also be photochemical as our results show that dilute solutions of NaNO_2 are readily oxidised to sodium nitrate in presence of light and nitrite may exist temporarily in the soil only in the highly diluted state possibly adsorbed on the soil surface and undergoes oxidation readily to nitrate on the soil surface.

Hitherto it was universally believed that the conversion of nitrite to nitrate in soil takes place only through the agency of nitrate-formers. In view of our results given above, this universal application of bacterial agency to nitrate oxidation in soil can no longer be taken as a complete truth. In previous communications (*cf.* Dhar. "Influence of Light on some Biochemical Processes, 1935), we have already emphasised the importance of photochemical oxidations in relation to soil processes in tropical countries. The soil temperature in tropical countries in summer months during the day time goes much beyond the maximum temperature necessary for the growth of bacteria in general. In spite of this fact an increment in soil nitrate is always noticed in summer months in every locality of the world. The validity of the bacterial theory of nitrification and the observance of the increment in the nitrate content of the soil in summer months could not be reconciled until very recently. Now with the acceptance of our theory

of photochemical nitrification, it becomes clear why the nitrate content of the soil is largest in the summer.

SUMMARY.

1. Aqueous solutions of sodium nitrite are oxidised to nitrate when exposed to sunlight in presence of photo-catalysts like ZnO, TiO₂, Fe₂O₃; soil etc.

2. The dilute solutions are completely oxidized to nitrate, whilst in stronger solutions, it seems the following equilibrium is attained, —
 $2\text{NaNO}_2 + \text{O}_2 \rightleftharpoons \text{NaNO}_3$.

3. Zinc oxide has been found to be the best photocatalyst in this oxidation.

4. It appears, therefore, that Nitrobacter is not the only agency which can convert a nitrite to nitrate in the soil; light may also perform the same function.

5. In tropical countries in summer months during the day time, the temperatures of the soil are generally much higher than the maximum temperature suitable for the existence of the Nitrobacter. At such times, it seems, the photochemical oxidation of nitrite is the more important process in tropics than the bacterial oxidation.

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