THE PHOTOLYSIS OF POTASSIUM NITRATE SOLUTIONS

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Many investigators[1] have noted that light decomposes potassium nitrate solutions, yielding potassium nitrite and oxygen. However, only one of these, Warburg,[1c] has investigated the reaction in detail, and his report is not as complete as could be desired. Consequently, in view of the importance of this photolysis, it was considered advisable to submit it to further study.

The potassium nitrate employed was of very high grade, neutral to phenolphthalein and litmus, and gave no reactions for nitrite. The solutions used were 0.1, 0.5, 1.0 and 2.0 M.

The apparatus consisted of a transparent quartz tube of 50mm. diameter placed 50 mm. from the light source, a 110-volt d. c. quartz mercury-vapor arc lamp.

The solutions were not maintained at a constant temperature, and unless otherwise stated, were not · stirred. The concentration of the nitrite formed was determined by titration with 0.0106 N potassium permanganate solution according to the method of Fresenius,[2] and a few of the results were checked by titration of iodine liberated from acidified potassium iodide in an atmosphere of hydrogen with 0.0112 N sodium thiosulfate solution, a method somewhat similar to that employed by Warburg.

[1] (a) Berthelot and Gaudechon, *Compt. rend.*, **152**, 522 (1911). (b) Baudisch, *Ber.*, **45**, 1771 (1912); *Ind. Eng. Chem.*, **15**, 451 (1923). (c) Warburg, *Sitzungsb. preuss. Akad. Wiss.*, **52**, 1228 (1918). (d) Moore and Webster, *Proc. Roy. Soc.*, **90B**, 158 (1919).

[2] Fresenius, "Quantitative Chemical Analysis," trans. by Cohn, John Wiley and Sons, Inc., New York, **1**, 433(1903).

The agreement between the two methods was good. A fresh sample of nitrate solution was illuminated for each determination, the time of illumination being noted in each case. The results are recorded in Table I.

TABLE I

THE RATE OF FORMATION OF NITRITE IN 20 CC. OF POTASSIUM NITRATE SOLUTION

Time of illumination Min.	Cc. of 0.0106 N KMnO$_4$ required for			
	0.1 M KNO$_3$	0.5 M KNO$_3$	1.0 M KNO$_3$	2.0 M KNO$_3$
0	0.07	0.05	0.05	0.08
5	.30	.32	.36	.34
10	.50	.54	.56	.52
15	.66	.62	.70	.64
20	.76	.80	.84	.79
30	.90	.92	.96	.93
40	.98	1.00	1.04	1.03
60	1.00	0.98	1.00	1.06
180	0.97	1.04	1.06	1.04
360	1.02	1.03	1.00	0.95
480	1.00	..	0.97	..

It appears from these results that the rate of decomposition of the nitrate rapidly decreased, and that after illumination for about 40 minutes a maximum concentration of nitrite was obtained. This maximum concentration in the 20 cc. of solution employed was only 0.45 mg. of potassium nitrite. The existence of a steady state in this reaction was missed by Warburg because he did not illuminate his nitrate solutions for longer than 20 minutes. Furthermore, he failed to observe a decrease in reaction velocity, for under his conditions of experimentation the amount of nitrite formed in 20 minutes was about the same as that formed in the author's experiments in ten minutes, during which time experimental error masked any differences in the rate of nitrite formation. The good agreement between the results obtained for the four solutions described above may probably be attributed to the fact that nitrates obey Beer's law.[3] A 0.1 M potassium nitrate solution of 50mm. thickness absorbs all the radiant energy of wave length 2570 Å. and shorter, all between 2850 and 3120 Å., and transmits slightly between 2570 and 2850 Å., and between 3120 and 3330 Å. The 0.5, 1.0 and 2.0 M solutions absorb correspondingly in accordance with Beer's law.

The action of light on nitrite solutions was studied employing three solutions, 20 cc. of which contained 0.45 mg., 4.5 mg. and 9.1 mg. of potassium nitrite, respectively. The results are given in Table II.

It appears from these results that nitrites would be quite stable during the course of the preceding nitrate decomposition. Furthermore, the nitrate solutions before and after illumination were neutral to indicators, which could not be the case if nitrite itself were being decomposed. Potassium nitrite solutions are not oxidized by atmospheric oxygen.

[3] Schäfer, Z. wiss. Phot., 8, 212, 257 (1910); 17, 193 (1918).

TABLE II

INFLUENCE OF RADIATION ON DILUTE POTASSIUM NITRATE SOLUTIONS

Time of illumination Min.	Solution 1	Cc. of 0.0106 N KMnO₄ required for Solution 2	Solution 3
0	1.00	10.02	20.10
20	0.97	10.08	20.03
40	1.05	10.05	20.07
60	1.12	10.00	20.05
120	1.02	9.98	20.02
360	1.07	10.03	20.08

It would seem that the nitrite formed by the decomposition of the nitrate was by some secondary reaction inhibiting further nitrate decomposition. If this be so, it should be possible by the addition of nitrite to nitrate solutions to stop the photolysis. With solutions of nitrate of the concentrations employed, a considerable quantity of nitrite must be added to be effective, for whereas in the illuminated nitrate solutions the nitrite formed is bunched towards the light source, in the prepared solutions, it is evenly distributed. By Beer's law, a given concentration of nitrite should be more effective as an inhibitor, the more dilute the nitrate solution. Accordingly, 0.1, 0.5, 1.0 and 2.0 M nitrate solutions were prepared such that 20 cc. of each contained 0.5 mg. of potassium nitrite. The results obtained are incorporated in Table III.

TABLE III

EFFECT OF ADDITION OF NITRITE TO NITRATE SOLUTIONS

Time of illumination Min.	0.1 M KNO₃	Cc. of 0.016 N KMnO₄ required for 0.5 M KNO₃	1.0 M KNO₃	2.0 M KNO₃
0	1.10	1.08	1.08	1.13
20	1.17	1.52	1.78	1.82
40	1.25	1.78	1.97	2.03
60	1.28	1.78	1.95	2.05
120	1.28	1.83	1.95	2.07
180	1.30	1.80	1.98	2.03

Comparison of Tables I and III shows that in the case of the 0.1 M nitrate solution the addition of the nitrite has decreased the decomposition of the nitrate to about 15% of its former value, and of the 0.5 M solution to about 75% of the previous value. The 1.0 M and 2.0 M solutions were only very slightly affected. As indicated above, these results are a necessary consequence of Beer's law.

To test further the action of nitrite on the nitrate decomposition, a 1.0 M solution of nitrate containing 9.1 mg. of potassium nitrite in 20 cc. was prepared. This solution corresponded to 20.22 cc. of 0.0106 N potassium permanganate solution. After illumination for 360 minutes, the solution required on titration 20.70 cc. of the permanganate solution. The difference, 0.48 cc., corresponded to the nitrite formed. This amount is just about half that formed in a nitrate solution free from nitrite and

illuminated under similar conditions. The result given is the average of a number of determinations made with this solution, all of which agreed very closely. Similar solutions substantiated the inhibitory action of nitrite.

The decomposition of potassium nitrate by light has been represented as $KNO_3 \rightleftharpoons KNO_2 + O; O + O \rightleftharpoons O_2$. If it be assumed that the first reaction is reversible, it is possible to explain the nitrate-nitrite equilibrium and the inhibitive action of nitrite.

If the preceding hypothesis be valid, it should be possible to add to the nitrate solution some substance that will combine with some of the newly liberated atomic oxygen, displacing the equilibrium toward the nitrite. It was thought that such a substance might be potassium hydroxide, the reaction being $KOH + O \longrightarrow KOOH$ and the product the potassium salt of hydrogen peroxide, a substance that is quite stable in ultraviolet light. Warburg[1c] has found that the addition of an hydroxide to the nitrate solution increased the rate of nitrite formation, and furthermore that when the alkali content was quite high, such as 0.1 N, a substance was formed that liberated iodine from potassium iodide in alkaline solution, a reaction that nitrite will not give. This oxidizing substance was not formed when an aqueous solution of the hydroxide alone or an alkaline solution of potassium nitrite was illuminated. The presence of the nitrate was required. The writer has been unable to substantiate the formation of such a substance. Alkaline peroxides do not liberate iodine from potassium iodide. A 0.1 M solution of potassium nitrate 0.1 N with potassium hydroxide after illumination for 120 minutes required on titration 1.83 cc. of 0.0106 N permanganate solution instead of the 1.00 cc. required when the potassium hydroxide was absent. Alkalies increase the rate of decomposition of nitrate solutions and shift the "steady state" toward the nitrite.

The addition of an acid to a nitrate solution decreased the rate of photolysis, but did not displace the equilibrium. A 0.1 M potassium nitrate solution on illumination attained equilibrium in 40 minutes. This same solution when made 0.1 N with sulfuric acid required 420 minutes to reach the same equilibrium point. It is difficult to explain this retardation unless the reason be that nitrous acid is more readily oxidizable than the salt.

The nitrate-nitrite equilibrium in an unstirred illuminated potassium nitrate solution that absorbs all active light is independent of the intensity of illumination, as would be expected, but is entirely dependent on the size of the surface exposed to the light source, and on the concentration and thickness of the solution. For these reasons all the preceding results have been obtained under precisely the same conditions, as otherwise they would not be comparable.

Stirring a solution of potassium nitrate during illumination decreased the rate of photolysis and displaced the equilibrium toward the nitrite. In the case of a 0.1 M nitrate solution the displacement was for obvious reasons negligible. However, a 1.0 M solution after 480 minutes of stirring and illumination contained 5.0 mg. of nitrite per 20 cc., or more than ten times that in a similar solution not stirred. Warburg, employing a 0.333 M nitrate solution, concluded that stirring had no effect. Under his experimental conditions this was nearly correct. If he had used a reaction tube of greater diameter, or a more concentrated solution, he would have found a considerable difference between the stirred and unstirred solutions. Since the equilibrium nitrate-nitrite is so far on the nitrate side, it is not possible by stirring to convert a very large percentage of the nitrate into nitrite.

The heat from the lamp was an important factor in controlling the rate of reaction. Stirring the solution or increasing the distance between the tube and the lamp decreased the rate of photolysis. With the reaction tube surrounded by another transparent quartz vessel containing water at a constant temperature of $20°$, the rate of decomposition of the nitrate solution was very considerably decreased. The nature of the reaction made the determination of a temperature coefficient impracticable.

The nitrate solutions are decomposed by ultraviolet light of wave length 3300 Å. and shorter. No decomposition was detectable in a solution that had been exposed to light behind a glass screen that transmitted none of these wave lengths. Employing glass filters similar to those described in Bulletin No. 148 of the United States Bureau of Standards,[4] in Curves 68, 69 and 78, it was established that the shorter wave lengths of the mercury arc were the most effective; however, only the rate of decomposition was affected, the nitrate-nitrite equilibrium being in all cases the same.

Warburg concluded that the Einstein law of photochemical equivalence did not hold for the decomposition of potassium nitrate solutions, four quanta being required per molecule of nitrate decomposed. His measurements were extended over 20 minutes of illumination and his calculations were based on the assumption that the reaction $KNO_3 \longrightarrow KNO_2 + O$ proceeded to completion. Inasmuch as after the first few seconds of illumination the reverse reaction, $KNO_2 + O \longrightarrow KNO_3$, is occurring at an appreciable and increasing rate, it is not possible by the experimental methods employed to determine the total amount of nitrate that has been decomposed in any interval of time. Consequently, it is impossible to derive quantum relationships, and Warburg's calculations are not justified.

Summary

1. Aqueous potassium nitrate solutions are decomposed by ultraviolet radiation of 3330 Å. and shorter, yielding potassium nitrite and

⁴ Gibson, Tyndall and McNicholas, *Bur. Standards, Tech. Paper*, **148** (1920).

oxygen. The reaction is auto-inhibited by the nitrite, a "steady state" being established when only a very small quantity of nitrate has been decomposed.

2. Aqueous potassium nitrite solutions are stable in ultraviolet light.

3. The addition of potassium nitrite to a solution of potassium nitrate inhibits partially or completely the photolysis of the nitrate solution.

4. Hydroxides increase the rate of photolysis, and displace the "steady state" towards the nitrite, possibly due to the formation of a peroxide.

5. Acids decrease the rate of decomposition, but do not displace the "steady state."

6. Potassium nitrate solutions obey Beer's law, as a result of which the nitrate-nitrite equilibria in a stirred and unstirred solution are quite different, the disparity depending on the concentration of the solution.

7. The nitrate-nitrite equilibrium in an unstirred solution is entirely dependent on the size of the surface exposed to the light source, and on the concentration and thickness of the solution.

8. The rate of reaction is accelerated by heat, but complications make the determination of a temperature coefficient impracticable.

9. Warburg's calculations of quanta are shown to be untenable.

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A STUDY OF THE VISCOSITIES OF SOLUTIONS CONTAINING MIXTURES OF MERCURIC, CUPRIC AND COBALTOUS CHLORIDES WITH OTHER CHLORIDES FOR THE PURPOSE OF FINDING THE COMPOSITION OF THE COMPLEX IONS FORMED

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Introduction

It has been known for a very long time that certain properties of the solution undergo a change with the change in constitution of the solute, and some of these properties have been utilized in investigating the formation and composition of the complex compounds so formed in the solution. Sidgwick and Tizard,[1] for example, have investigated the composition of the complex compounds formed in the cases of cobalt and copper salts by studying the colors of their solutions at different concentrations.

[1] Sidgwick and Tizard, *J. Chem. Soc.*, **93**, 187 (1908).