THE DECOMPOSITION OF NITROGEN PENTOXIDE IN THE PRESENCE OF OZONE

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In the course of some work on the oxidation of nitrogen tetroxide by ozone[1] an important phenomenon was noticed. At the end of any particular titration there was always present in the pentoxide formed, the slight amount of free ozone which was not used in the oxidation of the last traces of tetroxide. This excess of ozone was, of course, very small as compared to the quantity of pentoxide. Naturally, therefore, a quick returning of the brown fumes was expected, since the thermal rate of decomposition of pentoxide at $25°$ is known from the work of Daniels and Johnston,[2] to be fairly rapid and brown fumes should have made their appearance as soon as the excess of ozone had been destroyed through oxidizing the tetroxide formed by the decomposing pentoxide.

Actually, a surprisingly long time was found to elapse before brown fumes did reappear. Thus there seemed to be a retarding effect upon the decomposition of the pentoxide resulting from some unknown cause, and a number of special experiments were carried out to investigate this point. These tests all showed that the rate of decomposition in the presence of excess ozone was much slower than that found by Daniels and Johnston in the absence of ozone. The data for one of these experiments are discussed below.

Assuming that nitrogen pentoxide decomposes at the rate found by Daniels and Johnston and is continuously reoxidized by ozone, the expected time required for the decomposition of the excess ozone should evidently be given by the formula,

$$t = \frac{C_{O_3}}{k C_{N_2O_5}} \tag{1}$$

where k is the specific decomposition rate of nitrogen pentoxide at the temperature in question, C_{O_3} the molal concentration of ozone, and $C_{N_2O_5}$ the molal concentration of nitrogen pentoxide.

In the experiment in question, the original partial pressure of the mixture nitrogen dioxide and tetroxide introduced into the reaction vessel was 14 mm. From the constant for the equilibrium between these substances the original partial pressures were calculated to be 12.6 mm. for the dioxide and 1.4 mm. for the tetroxide. This mixture, converted to the pentoxide, would give a pressure of 7.7 mm. of pentoxide, this being the pressure at the end of the oxidation.

This pentoxide was held under the temperature conditions during the

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[1] THIS JOURNAL, preceding article.

[2] Daniels and Johnston, THIS JOURNAL, 43, 53 (1921).

4 hours directly following the completion of the oxidation, as shown in the following table.

Time		Temperature	Observation
Min.		° C.	
0}	heated	0	colorless
35}	constant	80	colorless
110}	cooled	80	colorless
195}	cooled	45	colorless
250		35	distinctly brown

Now the fact that the pentoxide was at 80° for almost $1^1/_2$ hours makes it very clear that there was some retarding effect exerted upon its decomposition for at this temperature the rate of decomposition is extremely rapid; but in order to show without question that such a retardation does exist, let us calculate the time necessary for the reappearance of brown fumes at 25°, assuming that ozone has no retarding effect.

The concentration of the nitrogen pentoxide at the end of the experiment was 0.000408 mole per liter, corresponding to the partial pressure of 7.7 mm. The concentration of ozone due to the introduction of the last "drop" could be calculated from the volume of the ozone bulb and the pressure decrease, and was found to be 0.0000127 mole per liter. The specific reaction rate for the decomposition of pentoxide at 25° is given by Daniels and Johnston as 0.00203 min.$^{-1}$. Hence in accordance with Equation 1, the time necessary for the decomposition of the excess of ozone in the presence of the nitrogen pentoxide, neglecting the specific decomposition of the ozone itself, should have been

$$t = \frac{0.0000127}{0.00203 \times 0.000408} = 15.3 \text{ min.}$$

In accordance with this calculation, even at 25° brown fumes should have reappeared in 15.3 minutes if ozone had exerted no inhibiting effect on the decomposition of nitrogen pentoxide. In the actual experiment as carried out, the gas showed no brown fumes for over 195 minutes; during 75 minutes of this time the gas was at 80°, and during most of the 195 minutes it was warmer than 25°. A similar calculation shows that at 80° the brown fumes would have reappeared in about 0.002 seconds.

The most probable explanation for these facts is to assume a catalytic action on the part of nitrogen dioxide in the decomposition of the pentoxide. Daniels and Johnston,[3] as a matter of fact, found that such a catalytic action was present in the case of the *photochemical* decomposition of the pentoxide, and Lueck[4] has recently reported a similar catalytic action in the case of the *thermal* decomposition of the pentoxide dissolved in carbon tetrachloride.

³ Ref. 2, p. 72.
⁴ Lueck, THIS JOURNAL, 44, 757 (1922).

As to the amount of nitrogen dioxide necessary for the catalysis, it seems probable that a very minute amount is all that is necessary, since Daniels and Johnston in their experiments on thermal decomposition found no evidence that the rate of decomposition increased as the concentration of nitrogen dioxide increased. It should be noted in this connection that the method of removing nitrogen dioxide by the introduction of ozone represents a far more complete removal than the method used by Daniels and Johnston of pumping off the decomposition products from the solid nitrogen pentoxide used in their experiments.

Summary

Pure nitrogen pentoxide in the presence of excess ozone appears to have a much slower rate of thermal decomposition than nitrogen pentoxide which is already partly decomposed. The decomposition is thus apparently autocatalytic.

Small traces of the decomposition products, however, seem to be all that is necessary to secure a constant specific rate of decomposition.

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THE CRYSTAL STRUCTURES OF POTASSIUM CHLOROPLATINITE AND OF POTASSIUM AND AMMONIUM CHLOROPALLADITES

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Introduction

An X-ray examination of the tetragonal crystals of potassium chloroplatinite, K_2PtCl_4, potassium chloropalladite, K_2PdCl_4, and ammonium chloropalladite, $(NH_4)_2PdCl_4$, has been carried out with the object of comparing the structure of these crystals with those of the cubic crystals of the corresponding salts with 6 halogen atoms. The structure of ammonium chloroplatinate has been found by Wyckoff and Posnjak[2] to be such that it may be regarded as containing chloroplatinate groups in which each platinum atom is surrounded by 6 equidistant and equivalent chlorine atoms at the vertices of an octahedron. It would probably be anticipated that in the chloroplatinites, 4 chlorine atoms would be grouped about each platinum atom; but the form and dimensions of this group as well as its situation in the structure could scarcely be predicted with safety.

[1] National Research Fellow in Chemistry.
[2] Wyckoff and Posnjak, THIS JOURNAL, 43, 2292 (1921).