# CCXXIV.—*The Catalytic Decomposition of Nitric Oxide at the Surface of Platinum.*

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ON the surface of a heated platinum wire at temperatures from 1000° to 1500° nitric oxide decomposes into nitrogen and oxygen according to the equation $2NO = N_2 + O_2$. This decomposition itself involves no change of volume. If, however, the products are allowed to cool before the reaction is complete, the oxygen combines with the unchanged nitric oxide. This leads to a contraction, $2NO + O_2 = 2NO_2 \rightleftharpoons N_2O_4$.

Thus if the reaction is made to take place on an electrically heated wire and the pressure is measured from time to time with the wire cold, then, as the reaction proceeds, the pressure first decreases until the oxygen formed is just sufficient to combine on cooling with all the residual nitric oxide. After this, it gradually increases again to its original value. Moreover, as long as the residual nitric oxide remains in excess the contraction is proportional to the oxygen produced in the decomposition and is thus a direct measure of the rate of reaction. The actual percentage of nitric oxide which has been decomposed can be calculated from the contraction if the constant, $K$, of the $NO_2/N_2O_4$ equilibrium is known. The maximum contraction is known to occur where there is just enough oxygen to combine with all the nitric oxide, that is, when half the original nitric oxide is decomposed. When the initial pressure of nitric oxide was 200 mm. Hg, the maximum contraction, measured at 0°, was 83 mm. If none of the $NO_2$ had polymerised to $N_2O_4$, the calculated contraction would be 50 mm., if polymerisation were complete, the contraction would be 100 mm. The total pressure in the reaction vessel is $200 - 83 = 117$ mm., of which 50 mm. are due to nitrogen. Thus $p_{NO_2} + p_{N_2O_4} = 67$. If all the $N_2O_4$ became $NO_2$, its pressure would double and $p_{NO_2}$ would become 100. Thus $p_{NO_2} + 2p_{N_2O_4} = 100$. Whence we find that $p_{NO_2} = 34$ and $p_{N_2O_4} = 33$. Therefore $p^2_{NO_2}/p_{N_2O_4} = K_p = 35$.

According to the results of Bodenstein (*Z. physikal. Chem.*, 1922,

**100**, 75), this value of $K_p$ corresponds to a temperature of 11° instead of 0°. The difference is not very serious for the present purpose and is probably due to a number of minor errors. Using this value of $K_p$, it is possible to plot a curve showing the contraction corresponding to any given percentage of the nitric oxide which is decomposed. From this can be read off the percentages corresponding to the experimentally observed contractions.

The following figures show a typical instance :

| Time (mins.) | 1·0 | 2·0 | 3·0 | 5·0 | 8·0 | 12·0 | 18·0 |
|---|---|---|---|---|---|---|---|
| Contraction | 19 | 28 | 35 | 45·5 | 55 | 65 | 76 |
| % NO decomp. | 13 | 18·5 | 23 | 29 | 34 | 40 | 46 |

| Time (mins.) | 24·0 | 30 | 43 | 50 | 75 | 90 |
|---|---|---|---|---|---|---|
| Contraction | 80 | 82 | 79 | 77 | 69 | 65 |
| % NO decomp. | 48 | 49·5 | 53 | 54 | 58 | 60 |

The initial pressure of nitric oxide was 200 mm.

The actual method of experiment was similar to that described in previous papers on gaseous reactions at the surface of heated wires (J., 1925, **127**, 327). The reaction vessel was about 15 cm. long and 3·5 cm. in diameter, and was immersed in melting ice. The platinum wire was stretched axially in the usual way. Its temperature could be controlled to within a few degrees. The temperature–resistance curve was separately determined by comparing the readings of a small resistance thermometer with those of a standardised thermo-couple from 273° Abs. to 1600° Abs. The platinum used gave the following results :

| $T$ (abs.) | 273° | 499° | 686° | 788° | 879° | 947° | 984° |
|---|---|---|---|---|---|---|---|
| $R_T/R_{273}$ | 1·00 | 1·841 | 2·446 | 2·787 | 3·102 | 3·218 | 3·419 |

| $T$ (abs.) | 1123° | 1204° | 1300° | 1387° | 1497° | 1581° |
|---|---|---|---|---|---|---|
| $R_T/R_{273}$ | 3·719 | 3·940 | 4·270 | 4·447 | 4·688 | 4·874 |

The nitric oxide was prepared from mercury and nitric acid in the presence of an excess of concentrated sulphuric acid (" nitrometer " reaction).

Some nitrogen was always admitted first to the reaction vessel to act as a buffer in the manometer and protect the mercury from corrosion. It was without influence on the reaction.

*The Order of Reaction with Respect to Nitric Oxide.*—In a large number of experiments, the influence of the pressure of nitric oxide was determined by measurement of the initial rate of reaction, the decomposition being followed to about 20%. Quite regular curves were obtained by plotting decrease of pressure against time, and very little drift in the activity of the wire was observed. Over a wide range of temperature and on two different wires the reaction was found to be unimolecular with respect to nitric oxide :

Wire I at 1676° Abs.

| Initial pressure of NO (mm.) ............ | 100 | 200 | 300 | 400 | 500 |
|---|---|---|---|---|---|
| Time (secs.) for 13·5% of NO to react | 86 | 86 | 88 | 86 | 87 |

Wire II at 1723° Abs.

| Initial pressure of NO (mm.) ......... | 100 | 150 | 200 | 300 | 400 | 500 |
|---|---|---|---|---|---|---|
| Time (secs.) for 13·5% of NO to react | 60 | 62 | 60 | 58 | 57 | 61 |

Wire I at 1530° Abs.

| Initial pressure of NO (mm.) ......... | 100 | 200 | 300 | 400 |
|---|---|---|---|---|
| Time (secs.) for 9% of NO to react ... | 82 | 82 | 82 | 84 |

Wire II at 1155° Abs.

| Initial pressure of NO (mm.) ......... | 200 | 300 | 400 |
|---|---|---|---|
| Time (secs.) for 6·3% of NO to react | 480 | 484 | 480 |

From these results it is evident that the time required for a given fraction of the total change is independent of the pressure—the criterion of a unimolecular change.

*The Influence of Nitrogen and of Oxygen.*—Nitrogen was found to have no influence whatever on the rate of reaction.

| | Decrease of pressure in (secs.) | | | |
|---|---|---|---|---|
| Temp., 1676° Abs. | 60. | 120. | 240. | 360. |
| 200 mm. NO + 100 mm. $N_2$ ... | 15 | 22 | 32 | 39 |
| 200 ,, + 200 ,, ... | 14·5 | 22 | 31·5 | 39 |
| 200 ,, + 300 ,, ... | 14·5 | 22 | 31·5 | 39 |

The influence of oxygen could not be investigated in the same way, since it would have combined with the nitric oxide, and thus its initial pressure would not have been known. During the experiments, however, while the wire was heated, oxygen must have been present at its surface in increasing amount as the reaction proceeded. Qualitatively, it was found to have a considerable retarding influence, which is best exhibited by calculating the unimolecular velocity coefficient at different stages of the reaction. Although variation of the initial pressure shows the rate of reaction to be accurately proportional to the concentration of nitric oxide, the equation for a unimolecular reaction is not applicable over the whole course of the decomposition. The velocity coefficient falls in a marked manner thus :

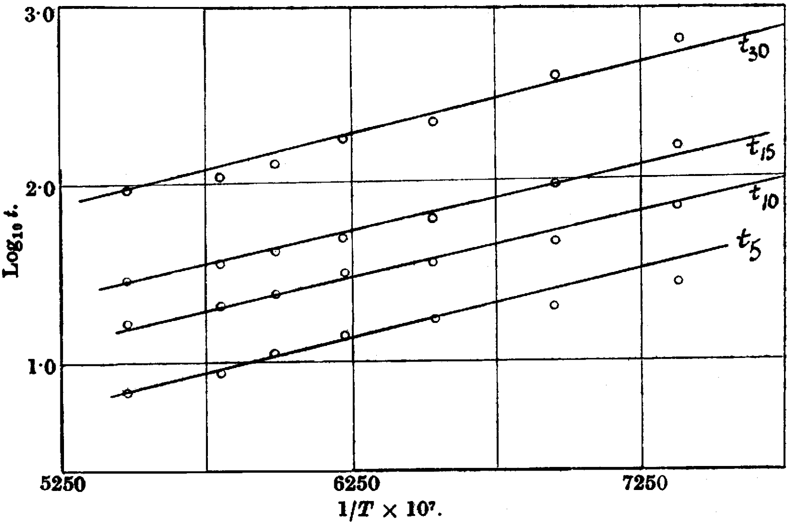
| Time (secs.) ........... | 60 | 120 | 180 | 300 | 720 |
|---|---|---|---|---|---|
| % Decomp. ........... | 13 | 18·5 | 23 | 29 | 40 |
| $k \times 10^3$ (unimol.) ...... | 2·3 | 1·7 | 1·5 | 1·1 | 0·7 |

Since nitrogen has no influence, the retardation must be due to oxygen.

*Influence of Temperature.*—A series of experiments was made at different temperatures with a standard pressure of 200 mm. of nitric oxide. The initial velocity only was measured in each case in order that the influence of oxygen might be a minimum. The logarithms of the times ($t_5$, $t_{10}$, $t_{15}$, and $t_{30}$) required for a decrease of pressure of 5, 10, 15, and 30 mm., respectively, were plotted against the reciprocals of the absolute temperature, and the constant, $E$, of the equation $d(\log k)/dT = E/RT^2$ was calculated. $E$ is the "apparent heat of activation." The values are as follows: from $t_5$, 14,300 cals. per g.-mol.; from $t_{10}$, 15,400 cals.; from $t_{15}$, 16,300 cals.; and from $t_{30}$, 18,400 cals. Thus for the true initial velocity the value is probably in the neighbourhood of 14,000 cals.

In a reaction such as this, which is retarded by one of its products and is of the first order with respect to the reacting gas, the relation of the "true heat of activation" to this "apparent heat of activation" is a complicated one (J., 1925, **127**, 1116, 1552). We have not the data for finding the true value in this instance.

FIG. 1.



## *General Remarks.*

Jellinek (*Z. anorg. Chem.*, 1906, **49**, 229) investigated the thermal decomposition of nitric oxide by a streaming method. The reaction taking place under the conditions of his experiments appears to be partly homogeneous and partly heterogeneous. Thus the results do not lend themselves to theoretical discussion; but it is probably justifiable to conclude from them that the homogeneous reaction is bimolecular. This would be expected on theoretical grounds. The decomposition on platinum thus provides a further example of a reaction which is bimolecular in the gas phase becoming unimolecular at the surface of a catalyst (compare J., 1925, **127**, 327, 1105, 1552, 2896; *Proc. Roy. Soc.*, 1925, *A*, **108**, 211). Presumably the ability of platinum to adsorb nitrogen and oxygen in atomic form is at the basis of this mechanism in the present example. The reaction $NO = N + O$ is thereby rendered possible without the communication of energy in prohibitive amounts.

## *Summary.*

The rate of the reaction $2NO = N_2 + O_2$ at the surface of a heated platinum wire has been measured over a wide range of temperature.

The reaction is unimolecular with respect to nitric oxide, uninfluenced by nitrogen, and retarded by oxygen.

It provides another example of a reaction which is bimolecular in the gas phase becoming unimolecular at the surface of a metallic catalyst.

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