## 203. *The Oxidation of Arsenic in Nitrous Oxide and in Oxygen.*

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OXIDATION by nitrous oxide occurs in general only under conditions such that a preliminary thermal decomposition into nitrogen and oxygen may take place. It is usually assumed, for example, that when an element such as phosphorus is burning in nitrous oxide, the heat of the flame is sufficient to decompose the oxide in the vicinity and furnish the supply of oxygen for combustion. Again, in the case of a homogeneous reaction such as that between nitrous oxide and hydrogen (Melville, *Proc. Roy. Soc.*, 1933, *A*, **142**, 524), the decomposition of an excited nitrous oxide molecule to yield an oxygen atom is one of the essential steps postulated for the initiation of a reaction chain. Sabatier and Senderens's work on the oxidation of metals and their oxides in oxides of nitrogen (*Compt. rend.*, 1895, **120**, 618, 1212; *Bull. Soc. chim.*, 1895, **13**, 870) affords one of the few direct indications yet obtained that any specific oxidising action can be attributed to nitrous oxide itself. These authors found, *e.g.*, that iron will burn in a stream of nitrous oxide at 170°, forming ferric oxide, and nickel is oxidised with incandescence at 300°. These reactions are almost certainly heterogeneous, but their interest lies in the fact that they take place at a temperature well below that at which nitrous oxide will decompose on an inert metal surface, such as that of gold or platinum. The decomposition on platinum is conveniently measurable only between 600° and 1200° (Hinshelwood and Pritchard, J., 1925, **127**, 327). The oxidation of arsenic was chosen for further study in this connexion because its surface resembles that of a metal, but its trioxide, which is the principal oxidation product, is volatile above 300° and will not contaminate the surface; the oxidation therefore affords a satisfactory means both of studying the mechanism of oxidation by nitrous oxide and of comparing it with that in oxygen.

The arsenic–oxygen reaction between 200° and 300° has already been studied (Emeléus, J., 1927, 783), and is found to exhibit chemiluminescence, and to be characterised by an upper critical oxidation pressure, or " glow pressure." The chemiluminescence in a gas stream is inhibited by vapours such as benzene, or by sulphur dioxide, a strong indication that the oxidation is a chain reaction.

## EXPERIMENTAL.

The arsenic was purified as previously described (Eméleus, *loc. cit.*). Oxygen was obtained by heating potassium permanganate contained in an evacuated Pyrex flask, connected directly by a ground joint with the apparatus; it was freed from carbon dioxide and moisture by slow passage through a liquid-oxygen trap, and was stored in glass bulbs before use. Nitrous oxide was taken from a cylinder. It was dried by phosphoric oxide, condensed with liquid oxygen, and freed from permanent gases by pumping with a mercury diffusion pump, vaporising, recondensing, and repumping. The gas was finally distilled in vacuum into a large storage globe.

*Temperature of Incipient Decomposition and Reaction of Nitrous Oxide.*—The thermal decomposition of nitrous oxide between 565° and 852° has been investigated by Hinshelwood and Burke (*Proc. Roy. Soc.*, 1924, A, **106**, 284). Extrapolation of their results shows that a very small decomposition rate is to be anticipated between 350° and 500°, which are the approximate temperature limits for reaction between nitrous oxide and arsenic. Three direct experiments were made to determine the actual rate of decomposition of nitrous oxide under the conditions to be employed subsequently. The nitrous oxide was heated in a 100 c.c. Pyrex flask connected by a ground joint to a constant-volume capillary manometer, with connexions to the pumps and to the nitrous oxide storage bulb. The bulb was heated in a well-lagged electrically heated furnace of 10 cm. internal diameter, 25 cm. long, and uniform in temperature to $\pm 1°$ over the middle 12 cm. of its length. All pressure readings in the results recorded below were made with the reaction bulb in a bath at 20°; time ($t$) is recorded in hours, and pressure ($p$) in mm.

| I. | | | | II. | | | | III. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Furnace temp. = 350°. | | | | Furnace temp. = 460°. | | | | Furnace temp. = 500°. | | | |
| *t.* | *p.* | *t.* | *p.* | *t.* | *p.* | *t.* | *p.* | *t.* | *p.* | *t.* | *p.* |
| 0·0 | 581·1 | 96·7 | 583·2 | 0·0 | 583·2 | 64·0 | 589·5 | 0·0 | 280·7 | 68·0 | 287·1 |
| 22·0 | 582·1 | 117·0 | 583·2 | 18·5 | 584·7 | 81·0 | 593·0 | 25·0 | 282·7 | 87·0 | 289·9 |
| 46·5 | 583·3 | | | 41·5 | 587·1 | 157·0 | 593·1 | 48·0 | 284·4 | | |

There is evidently no appreciable pressure increase, due to decomposition of nitrous oxide, at 350°, and at 460° the reaction is still slight. Values of the velocity constant for the decomposition at 500° and 460° are $24 \times 10^{-6}$ and $5·9 \times 10^{-6}$, compared with $18 \times 10^{-6}$ and $1·4 \times 10^{-6}$ as extrapolated from Hinshelwood and Burke's data (*loc. cit.*). The approximate temperature below which thermal decomposition of nitrous oxide can reasonably be neglected as a factor in its oxidation reactions is therefore taken as 400°.

Measurements were next made to determine the temperature at which arsenic is oxidised by nitrous oxide. The method employed was to heat 1—3 g. of purified arsenic in a cylindrical bulb of 150 c.c. capacity in an atmosphere of nitrous oxide at a definite temperature. All connexions in the apparatus were of fine capillary, and a constant-volume capillary manometer was again employed. As a preliminary, duplicate analyses were made of the oxidation product of purified arsenic heated at 360° and 420° for 72 hours in a 500 c.c. bulb containing nitrous oxide. The arsenious oxide formed was first estimated iodometrically, and the total arsenate in the product was estimated as magnesium ammonium arsenate by the method of Dick (*Z. anal. Chem.*, 1933, **93**, 429). At 360° the product consisted of at least 99% of pure arsenious oxide, and at 420° it contained 5·8% of arsenic oxide. In the latter case the arsenic had apparently burnt in the nitrous oxide. These results agree with those of Bloch on the combustion of arsenic in oxygen, in which up to 5% of arsenic oxide was found in the product (*Compt. rend.*, 1909, **149**, 775).

If formation of arsenious oxide be taken as the main reaction, the amount of nitrogen produced may be taken as a measure of the amount of oxidation. To determine the temperature of the initial reaction between nitrous oxide and arsenic, the latter was therefore heated for 18 hours at each of eight temperatures between 190° and 370°. After each period of heating, the furnace was lowered, and the quantity of residual non-condensable gas was measured by immersing the bulb in liquid oxygen up to a fixed mark on the capillary neck. The results are tabulated below. The initial pressure of the nitrous oxide was 402·2 mm., and all the observations were made in

succession with this one filling of the bulb. This accounts for the decrease in reaction rate at the higher temperatures, when the nitrous oxide was approaching exhaustion.

| Furnace temp. | 190° | 205° | 235° | 265° | 290° | 325° | 355° | 370° |
|---|---|---|---|---|---|---|---|---|
| Press. of $N_2$ at liquid-oxygen temp.(mm.) | 1·1 | 3·0 | 3·3 | 4·3 | 26·2 | 75·1 | 127·3 | 154·0 |
| Increase in press. of $N_2$ (mm.) | 1·1 | 1·9 | 0·3 | 1·0 | 21·9 | 48·9 | 52·2 | 26·7 |

The above results show that there is a very sudden increase in the rate of reaction between arsenic and nitrous oxide between 265° and 290°. As is shown later, this abrupt rise is unaccompanied by any flame phenomena. The exact temperature at which the break occurs will probably depend on the condition of the arsenic surface; indeed, we have observed repeatedly that the presence of moisture will produce a film on the arsenic grains which retards the reaction considerably.

*Surface Reactions of Arsenic with Nitrous Oxide and Oxygen.*—The vapour pressure of arsenic has not been recorded at temperatures below 400°, at which it is 6 mm., but extrapolation of available data (Landolt–Bornstein " Tabellen "), shows that at 250—305° it will be of the order of 0·5—2 mm. This low vapour pressure will favour a surface reaction of arsenic with oxygen or nitrous oxide, but further evidence that such was the case was sought in the relation between the reaction rate and the extent of the arsenic surface. A sample of purified arsenic was sieved between meshes 8—10 to the inch, and various amounts of this graded sample were introduced in turn into a cylindrical bulb (15 cm. long and 2 cm. internal diameter). Heating was carried out in nitrous oxide at an initial pressure of 600 mm. at 377° for 5 hours for each quantity of arsenic, the amount of oxidation in each case being measured by the amount of non-condensable gas formed. The results of such a series of experiments with arsenic and nitrous oxide are tabulated below :

| Weight of arsenic (g.) | 1·0 | 2·5 | 5·0 | 10·0 |
|---|---|---|---|---|
| Press. of $N_2$ at liquid-oxygen temp. (mm.) ... | 8·1 | 23·7 | 45·0 | 90·5 |
| Ratio of nitrogen pressures | 1 | 2·9 | 5·5 | 11·0 |

The figures show a correspondence between the amount of oxidation and the quantity of arsenic up to 10 g. With greater weights of arsenic the amount of oxidation did not increase; this was probably due to the difficulty in obtaining diffusion of nitrous oxide into the lower layers of arsenic.

In the reaction between oxygen and arsenic, direct manometric observations of the reaction rate are possible, and these were made with various quantities of arsenic as in the case of nitrous oxide. The temperature used was 239°, at which there is no chemiluminescence. The results are shown in Fig. 1. The pressure of oxygen decreased linearly with time over the pressure range 15—50 cm., which is consistent with the reaction's taking place at the surface. The slope of the lines representing the rates for 1, 2·5, 5·0, and 10·0 g. are given by tan $\alpha_1 = 0·36$, tan $\alpha_2 = 0·88$, tan $\alpha_3 = 2·00$, and tan $\alpha_4 = 3·60$. The ratios of the rate of oxidation to the weight of arsenic used are as follows : 1 : 1, 2·5 : 2·4, 5·5 : 5, 10 : 10.

*Negative Tests for Chemiluminescence and Upper Critical Oxidation Pressure in the Reaction of Arsenic with Nitrous Oxide.*—Nitrous oxide was freed from any traces of oxygen by slowly passing the gas through two slightly inclined tubes, each 1 m. long, containing a solution of chromous chloride. The gas was then passed over a sample of 5 g. of arsenic, heated in a furnace fitted with an observation window. The arsenic was found to ignite between 410° and 450°, depending on the conditions of heating, but careful observation in the dark failed to reveal any chemiluminescence at temperatures just below the ignition point. The flame appeared quite suddenly in each case. For comparison purposes, the earlier observations on the chemiluminescence of arsenic in oxygen just below the ignition temperature were repeated and confirmed.

A further series of experiments was made to determine if a glow pressure was observable in the reaction between nitrous oxide and arsenic, corresponding with that in the arsenic–oxygen reaction (Emeléus, *loc. cit.*). The first method used was to heat the arsenic for 2 hours in nitrous oxide at each of a series of pressures from 500 mm. to 30 mm. at temperatures from 260° to 380°, measuring the nitrogen formed at each stage. Chemiluminescence, or a " glow pressure," would be accompanied by an abrupt increase in the reaction rate at a certain reduced pressure, shown by an increased formation of nitrogen, and was in no case observed. These runs were confirmed by visual observations carried out in a dark room, the pressure of the nitrous oxide in contact with the arsenic being slowly reduced by pumping whilst the arsenic was heated. Again, no chemiluminescence was detected at pressures down to 1 cm. between 300° and 400°. The

earlier observations on the glow pressure of arsenic in oxygen were confirmed in a series of experiments made for comparison.

*Oxidation of Arsenic in Oxygen at Low Pressures.*—Reference has already been made to the chief characteristics of the reaction between arsenic and oxygen. Hitherto, no observations have been recorded on the occurrence of a lower critical oxidation pressure in this case. It was with the object of obtaining information on this point, and in this way of linking the reactions more closely with the theory of chain reactions, that the experiments described below were carried out. It should be noted that the work of Semenoff and others on the lower critical oxidation pressure of phosphorus (*Z. Physik*, 1926, **39**, 547; 1928, **46**, 109) deals with the reactions of phosphorus vapour, whereas the work on arsenic has so far been carried out in presence of a solid arsenic surface. As is shown below, however, it is possible to differentiate between the



FIG. 1.
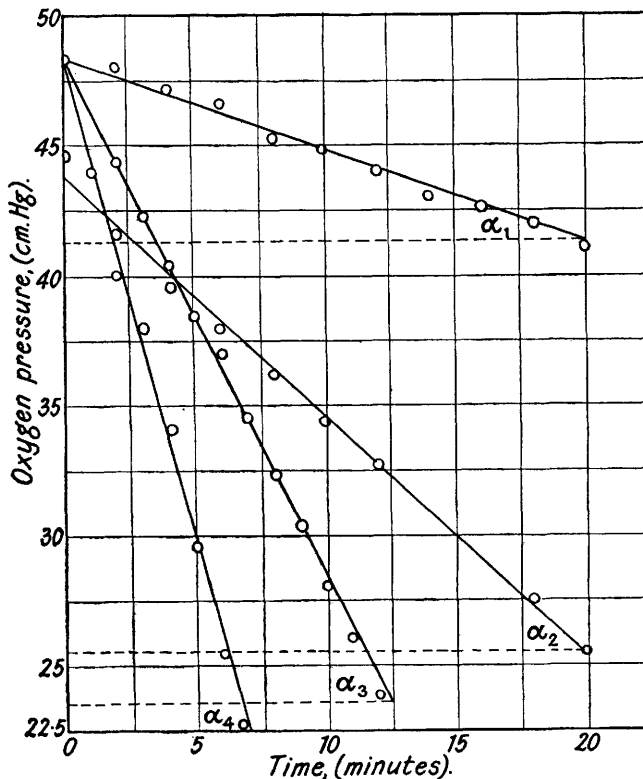
surface and the gas reaction, and in this way to obtain definite evidence for the existence of a lower critical oxidation limit.

The arsenic (2·5 g.) was packed around the bulb of a thermometer in a tube of 2 cm. internal diameter and 35 cm. long, which was connected to a pumping system, a reservoir of oxygen, and to a reduced barometer (U-gauge) and a McLeod gauge. In the first series of experiments the arsenic was heated to a definite temperature between 260° and 310°, and pure oxygen was admitted to a pressure between 2 and 4 cm. The thermometer recorded an immediate rise of 6—8°, a chemiluminescence was observed, and the pressure commenced to fall rapidly as the arsenic was oxidised.

The results of five such experiments are shown in Fig. 2. The four upper curves, obtained at temperatures between 266·5° and 306°, show a break in the curve at a pressure between 10 mm. and 4 mm., the value being lower at the higher temperatures. At the pressure corresponding to this break, the temperature dropped to the value at which the experiment was started, *i.e.*, that recorded in each case on the graph. The lowest curve was obtained at 306°, and the initial oxygen pressure employed was below that at which the break would occur at this temperature for a higher initial oxygen pressure. There was no temperature rise in this case on admitting the

oxygen, and there was no chemiluminescence. The rapid oxidation is accompanied by chemi-luminescence, while the slower rate (that below the break in the curve) represents a non-luminous reaction. The break in the curve is believed to represent a pressure below which the vapour-phase reaction (*i.e.*, the luminous reaction) ceases, and corresponds to the critical oxidation pressure. The values of this critical pressure at 266·5°, 280°, 291°, and 306° were respectively 10, 8, 5, and 4 mm. A further series of experiments was made, a calibrated McLeod gauge being used. Oxygen was admitted through a fine capillary to a pressure of 2—4 mm., and it was found that the slow (surface) reaction only was observed, and continued down to the limit of the McLeod gauge (0·001 mm.). There is no reason why such a surface reaction should show the limit phenomena characteristic of vapour-phase chain reactions. The pressure below which the chemiluminescent oxidation of arsenic ceases is much higher than that for phosphorus (Semenoff, *loc. cit.*), the latter
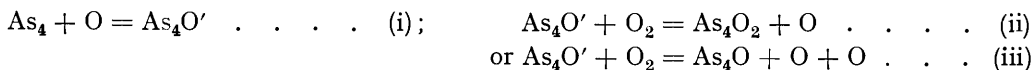
FIG. 2.
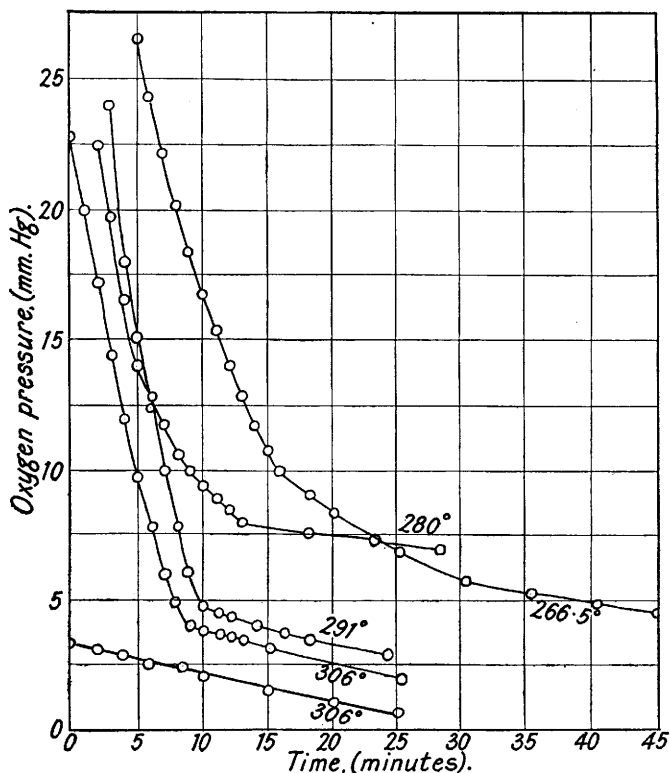


being of the order of a fraction of a mm., and being independent of temperature. The dependence on temperature observed in the experiments described here is due to the fact that the temperature controls the vapour pressure of arsenic, as well as the reaction rate. The decrease in critical oxidation pressure with increasing temperature is therefore probably due to a greater arsenic pressure at the higher temperature. From this point of view the results are in accordance with observations on phosphorus oxidation. Experiments are being made on the oxidation of arsenic vapour in the absence of a solid arsenic surface which will provide an even clearer parallel with the work on phosphorus.

## DISCUSSION.

The mechanism suggested by Hinshelwood for the decomposition of nitrous oxide at the surface of platinum or gold entails the decomposition of the nitrous oxide molecule into a nitrogen molecule and an oxygen atom, followed by recombination of the oxygen atoms at the surface. The fact that the reaction of nitrous oxide on arsenic or on a metal such as iron occurs so much more readily than decomposition on an inert surface indicates either a much greater ease of decomposition on such a surface, followed by reaction in especially

favourable circumstances, or, alternatively, nitrous oxide must be supposed to react specifically with arsenic or iron at the temperatures employed. Nitrous oxide is not, however, decomposed appreciably on an active palladium or platinum catalyst at 400°, and this fact favours the second of the two alternative explanations put forward. The arsenic–nitrous oxide reaction differs therefore from the normal case in which the nitrous oxide is first decomposed and then reacts, owing primarily to the affinity of arsenic for oxygen. As is the case in the oxidation of phosphorus by oxygen, the steps by which the final product, arsenious oxide, is built up are largely hypothetical. The first step is probably a molecule such as $As_4O$, which may be volatile and undergo further oxidation away from the surface, though there is no definite evidence for the stable existence of a sub-oxide of arsenic. It was observed previously (Emeléus, *loc. cit.*) that arsenious oxide appears to inhibit the chemiluminescence of arsenic. A similar effect occurs in the case of phosphorus (Miller, J., 1929, 1823). The significance of this observation is not yet clear, but it suggests that the formation of pentoxide in each case is connected with the inhibition by the trioxide.

The absence of chemiluminescence and the upper critical oxidation pressure in the reaction between arsenic and nitrous oxide is one of the chief points which distinguish it from the reaction of arsenic with oxygen. The chemiluminescence is a vapour-phase reaction (or possibly represents the oxidation of a volatile oxide formed at the surface). If a mechanism be adopted for the oxidation of arsenic by oxygen comparable with that put forward tentatively by Semenoff for the oxidation of phosphorus, one obtains a scheme such as the following :

$$As_4 + O = As_4O' \quad . \quad . \quad . \quad . \quad (i); \qquad As_4O' + O_2 = As_4O_2 + O \quad . \quad . \quad . \quad . \quad (ii)$$
$$\text{or } As_4O' + O_2 = As_4O + O + O \quad . \quad . \quad . \quad (iii)$$

The heat of formation of arsenious oxide is 312 kg.-cals. per g.-mol., or, as a first approximation 52 kg.-cals. per oxygen atom added to the arsenic molecule. If the oxygen atom in stage (i) has 59 kg.-cals. (*i.e.*, half the dissociation energy of the oxygen molecule), the $As_4O'$ molecule will almost certainly have sufficient energy for reactions (ii) and (iii) to take place and branched chains will result. This reaction cannot, however, produce a branched chain in the case where nitrous oxide is the oxidising medium. The reaction $As_4O' + N_2O = As_4O' + N_2 + O$ is possible, but $As_4O' + N_2O = As_4O_2 + N_2$ will not give a branched-chain effect. This is believed to be the reason why chemiluminescence and limit phenomena are not observed in the case of nitrous oxide, but do operate in oxygen. The authors have made observations with ether and carbon disulphide mixed with nitrous oxide, and have failed to observe chemiluminescence. Nickel carbonyl is a further example of a material which is not spontaneously inflammable in nitrous oxide. One would expect also, on the hypothesis put forward, that phosphine and nitrous oxide would not show the upper and lower critical oxidation limits which characterise the reaction of that substance with oxygen.

SUMMARY.

1. The reaction between nitrous oxide and arsenic, forming mainly arsenious oxide, becomes appreciable at 250—270°. Ignition takes place at 400—450°.

2. No chemiluminescence is observed, and there is no upper critical oxidation pressure.

3. The dark reaction of arsenic with nitrous oxide or oxygen is a surface reaction. The chemiluminescent reaction occurs in the vapour phase.

4. At temperatures between 266° and 306°, there is a critical pressure (4—10 mm.), decreasing with increasing temperature, below which the chemiluminescent oxidation of arsenic in oxygen ceases, whilst the surface reaction continues to a pressure of 0·001 mm.

3 T