INTERACTION OF NITROUS OXIDE, NITROGEN AND PHOSPHORUS UNDER SILENT ELECTRIC DISCHARGE

BY G. S. DESHMUKH, M.SC., AND Y. D. KANE, M.SC.
(Asst. Prof. of Chemistry, Benares Hindu University)

Received November 26, 1946
(Communicated by Prof. S. S. Joshi, D.Sc., F.A.Sc.)

The thermochemical behaviour of a number of gases towards phosphorus, particularly its glow, has been studied by various workers. There is, however, but little quantitative information in the literature on the production of these changes under well-defined conditions of electrical discharge. Joshi gave an important lead in this field of research in observing the general utility of data for the time-variation of the discharge current, in the elucidation of the mechanism of the corresponding reaction. This is illustrated by numerous results in these laboratories, especially on the reaction with hydrogen of gaseous nitrous oxide and in frozen films at liquid air temperature. It was of interest therefore, to extend these observations to a study of the reaction between the phosphorus films and nitrous oxide, under silent discharge.

EXPERIMENTAL

The general arrangement of the apparatus and circuit employed are shown in Fig. 1. A Siemens' type ozoniser made with soft glass tubes (fitted co-axially with a rubber greased ground-joint) was surrounded by a tube filled with salt solution, to serve as a low tension electrode. The whole system was immersed in a jacket, in which a stream of water was kept flowing at a constant rate in order to minimise the heat effects under the discharge. The ozoniser was connected through tap 1 to a mercury manometer and through tap 2 to a Töpler. Nitrous oxide obtained from a commercial cylinder was admitted through tap 8 and stored in glass reservoirs R1 and R2 which had been evacuated previously. With taps 8, 10 and 5 closed, on opening tap 7, most of the nitrous oxide was frozen to a solid of negligible vapour pressure in traps cooled by liquid air in Dewar vessels D3 and D4. The uncondensible gases were removed through tap 5 by the Töpler, tap 2 being closed. Dewar vessels D3 and D4 were then carefully removed; the first portion of the frozen gas to vapourise was pumped out; tap 5 closed; and the middle fraction stored in R3 and R4 after toppling off through tap 5 the last part of the condensed gas to vapourise. After the entire assembly
of the apparatus was tested for vacuum for at least 48 hours, taps 3 and 1 were closed. The inner electrode of the ozoniser was then coated uniformly on the outside with a concentrated solution of phosphorus in carbon disulphide, and fitted in the ozoniser system. The solvent was removed first with a hyvac pump from tap 3 and finally on the Töpler. At the commencement of every experiment nitrous oxide from R₁ and R₂ was frozen in traps cooled by liquid air in D₃ and D₄; the middle fraction of the vaporised gas was led over a train of tubes charged with P₂O₅ and KOH, and introduced into the annular space of the ozoniser through tap 3 at the desired pressure.

The A.C. obtained by means of a 1 K.W. Rotary Converter worked off 220 volt, D.C. mains was fed to the primary of a 3 KVA transformer; one of its secondaries was earthed; the other connected serially through a 10,000 ohm stabilising resistance, was dipped in the salt solution forming the inner electrode of the ozoniser. The outer electrode was earthed through an oxide rectifier type A.C. micro-ammeter μA (see Fig. 1). The applied potential expressed in kilo-volts (r.m.s.) and called V, was calculated from a knowledge of the stepping up ratio of the transformer and of the primary
potential, $V_1$; the latter was regulated by means of a variable resistance in its primary.

**Discussion of Results**

Series of experiments started at various gas pressures were made on the nitrous oxide-phosphorus reaction under conditions mentioned above; a fresh film of phosphorus was employed in each series. In agreement with a general finding due to Joshi, on changes under electrical discharges especially in gases, the interaction between nitrous oxide and phosphorus sets in only above a characteristic 'threshold potential' $V_m$, where the material in the annular space breaks down as a dielectric. $V_m$ depends, *inter alia*, on the gas pressure $p$ and frequency of the electrical supply. The course of the reaction was followed by observations at regular intervals of the gas pressure $p$ at constant volume, and also of the corresponding discharge current $i$. These data for one typical series corresponding to a nitrous oxide pressure of 12.2 cm. Hg, and 4 kilo-volts (r.m.s.) for the secondary potential of 50 cycles frequency are shown in Fig. 2. In all cases observed, $p$ decreased progressively during, and was negligibly small at the end of, the reaction. A further continuation of the discharge even at enhanced $V$ the secondary potential had no effect as judged from the constancy of the spectral nature of the glow and of the gas pressure $p$. As shown by the total time for the reaction and especially by the average time-rate of the pressure decrease, the rate of the change increased with $V$ and $1/p$. This follows readily from Joshi's general finding that the 'threshold potential' $V_m$ increases with $p$ and that the rate of a discharge reaction and the corresponding $i$ depend (increase with) on $V-V_m$.

As observed by Joshi in the decomposition of (pure) nitrous oxide under silent discharge, the current $i$ varied sensibly discontinuously during the present reaction at a given $V$, indicative of consecutive changes (see Fig. 2). Thus, for example, during the short initial stage when $p$ diminished, $i$ increased appreciably. In the next stage which was the longest, both these quantities varied comparatively slowly. The last stage is characterised by a remarkably sudden and rapid decrease of $i$ to a constant minimum at which $p$ also becomes negligibly small, suggestive of the completion of the reaction. From results of a number of reactions at various initial $p$ and $V$, of which the curves in Fig. 2 are one typical illustration, it was found that the last stage during which $i$ dropped suddenly, commenced when the residual $p$ of the reaction mixture reached 3 to 6 mm., *i.e.*, about 4 per cent. of the initial $p$. This sudden drop of $i$ at a constant $V$, was also observed when nitrogen was used instead of nitrous oxide (Fig. 3).
The observed decrease in the over-all $p$ (as also the corresponding changes) are explicable, on the following mechanism for the reaction:

\[
\begin{align*}
N_2O &\rightarrow N_2 + O \quad (ia) \quad \text{(The atomic products in (ia), (ib) and (ii) are removed immediately by phosphorus).} \\
N_2O &\rightarrow NO + N \quad (ib) \\
NO &\rightarrow N + O \quad (ii)
\end{align*}
\]

Changes (ia) and (ib) occur simultaneously and represent the initial stages; (ia) is suggested to be the more predominant reaction. This agrees with Joshi's results for the decomposition of (pure) nitrous oxide under
silent discharge;\textsuperscript{2-4} mixed with an excess of hydrogen;\textsuperscript{2} and when frozen over glass and certain metallic receptacles at the liquid air temperature.\textsuperscript{4} Atomic oxygen and nitrogen produced in (ia) and (ib), react with the phosphorus film, the former practically instantaneously. The fact that free oxygen was not detected in the reaction mixture at any stage is in accord with this deduction. So far as the gas phase is concerned, the net change represented by this stage (ia and ib) is \(2N_2O \rightarrow NO + N_2\) since the other (atomic) products, \textit{viz.}, N and O being removed by phosphorus do not contribute to the gas pressure. It follows from this, that the gas pressure during this stage of the reaction should be constant. This anticipation was realised experimentally by working on the following suggestion due to Prof. Joshi:\textsuperscript{3} It is to reduce the over-all velocity to a minimum by maintaining just \(V_m\) on the ozoniser, so that the otherwise rapid and even transient reactions are slowed sufficiently to enable observations of their time-rate and also the nature of the corresponding products, which ordinarily would escape detection. With this restraint a definite though short lived stage during which \(p\) remained sensibly constant was observed initially in a number of \(N_2O \rightarrow P\) reactions under the discharge. It may be emphasized here that the discontinuous time-variation of \(i\) characteristic of the stage-wise progress of this reaction (Figs. 2 and 3) was more conspicuous when \(V\) did not exceed \(V_m\) appreciably as is to be expected from Joshi’s views.\textsuperscript{3} Studies of other types of discharge reactions in progress in these laboratories have shown the wide applicability of this device, \textit{viz.}, excitation at \(V_m\) for elucidating the characteristic course and mechanism of a discharge reaction.\textsuperscript{3}

Since according to Joshi,\textsuperscript{2-5, 4} \(V \cdot V_m\) determines \(i\), its rise in the initial stage (see Fig. 2) may be attributed to a reduction of the corresponding \(V_m\), due firstly, to \(N_2O\) changing to \(NO\) and nitrogen; and secondly, due to phosphorus being replaced by its oxide (and possibly nitride, \textit{vide infra}). This deduction agrees with the observation by various workers that the oxidation of phosphorus produces ionisation in the surrounding air;\textsuperscript{7} and also with our experimental results with phosphorus films reacting with air (dried carefully with the arrangement shown in Fig. 1) subjected to the ozoniser discharge at 27·2, 31·4, 47·9, 53·4, 60·0, 65·7 and 73·2 cm. Hg pressures at \(V\) varied from 1 to 5 kV of 50 cycles frequency, and the time of exposure to discharge being increased up to 3·5 hours. It was always found that \textit{whilst \(p\) decreased, the corresponding \(i\) increased markedly.}

The decomposition of nitric oxide according to (ii) constitutes chiefly the next stage. Its atomic products would be removed from the gas phase, \textit{oxygen especially being affected very much faster due to its much
greater affinity towards phosphorus. The production of nitric oxide was detected in a series of experiments at various initial pressures on nitrous oxide (a fresh film of phosphorus being used in every case) by introducing from tap 3, a small bubble of air in the ozoniser after exposure to discharge for about 3-5 minutes; this reaction mixture when led over a small amount of pure mercury (shown by Hg, in Fig. 1) fouled it immediately due to formation of nitrogen dioxide; this was never observed after longer exposures; and also in absence of air when the mixture was toplered out at any stage of the reaction. Nitric oxide occurs therefore, in the present reaction as an intermediate product during only early stages. This conclusion was confirmed further by analysis of mixtures from reactions at various initial pressures of nitrous oxide in the range 15 to 42 cm. Hg; the discharge was interrupted after different periods of exposure. The mixture was led by opening tap 1 and lowering the manometric mercury in M, through a trap cooled by liquid air in D, in order to separate nitrous oxide; nitric oxide also freezes to a solid with a small sublimation pressure and can therefore, be toplered out completely from tap 2. The mixture thus pumped out consisting of nitric oxide and nitrogen was collected in a gas burette and analysed for nitric oxide by absorption with acidified ferrous sulphate solution. In no case was nitric oxide observed after 10 minutes i.e., after about 1/30th of the total time for the reaction; furthermore, the ratio NO/N₂ in the mixture increased as the time of exposure was reduced. Nitrous oxide does not react with phosphorus thermochemically "even when touched with a piece of red hot iron." At higher temperatures it inflames, "the products being phosphorus pentoxide and pure nitrogen dioxide." This last is also observed when nitric oxide is substituted for nitrous oxide in the thermal change. It is not unlikely that nitric oxide is formed as an intermediate product at very early stages of the high temperature reaction between phosphorus and nitrous oxide by analogy with the present results for the discharge reaction. The latter differs from the purely thermal change, in that nitrogen dioxide is not observed at any stage. Presumably, this applies also to the interaction under discharge, with nitric oxide (vide infra).

A series of experiments was next carried out in order to investigate the removal by phosphorus of nitrogen from the gas phase, produced by the decomposition of N₂O and NO according to (i) and (ii). The ozoniser in Fig. 1 was filled with cylinder nitrogen (after bubbling slowly through traps containing freshly prepared alkaline pyrogallol in order to remove traces of oxygen) at 7·0, 8·0, 9·0, 11·3, 12·7 and 21·5 cm. pressures and subjected to discharge at V varied in range 2-4 kV at 50 cycles frequency for periods up to 12 hours. In every case p diminished and the corresponding
Interaction under Silent Electric Discharge

 Increased. Towards the end of the reaction, $i$ dropped remarkably suddenly; curves in Fig. 3 refer to a typical run with 11.3 cm. of nitrogen at 4 kV. The general resemblance of the progress of this reaction, as shown by the time-variation of $i$ and $p$ with that, when nitrous oxide (initial $p$ and applied $V$ being smaller) was used instead, is also striking. For the nitrous oxide-phosphorus and nitrogen-phosphorus reactions at the same potential viz., 4 kV and similar initial pressures 12.2 cm. $N_2O$ and 11.3 cm. $N_2$ (see Figs. 2 and 3), the total time for the reaction, $i.e.$, when the gas pressure became negligibly small, was 340 and 330 minutes respectively; this similarity is suggestive. As with nitrous oxide, after its final sudden drop to a minimum, on increasing $V$, $i$ first increased (almost) momentarily to a large value; this remained stationary as long as the corresponding $V$ was constant (see Fig. 3).

If after the removal of nitrogen by phosphorus, a further amount of it was introduced, $p$ and $1/p$ continued to decrease, but on the whole more slowly than before. Thus $i.e.$, in one experiment at 4 kV and initial $p$ of 11.4 cm. Hg of nitrogen, 50 per cent. of the pressure change occurred in 160 minutes; the total time required was about 330 minutes. At the end of this period, when $p$ became negligibly small (see Fig. 3) fresh nitrogen was introduced at 4 cm. pressure in the ozoniser. It now took about 290 minutes for the same, $i.e.$, 50 per cent. pressure change, despite a larger reaction rate due to $1/p$ and $V$ (6 kV) being greater than before. With 21.5 cm. pressure due to a further addition of nitrogen, exposures to discharge at 10.7 kV for 39 hours produced only 60 per cent. of the total pressure decrease. Detailed experiments showed that any thermo-chemical change between the phosphorus film and the nitrogen (also air) in the ozoniser was negligibly small compared with that produced under the discharge. It was also noticed incidentally during this stage, that the 'threshold potential' $V_m$ characteristic of the aerial oxidation of phosphorus by an ozoniser discharge is defined more sharply, if the inner electrode supporting the phosphorus film is cooled (to about 3° C.) than at the room temperature viz., 27° C. It was also found that changes in the appearances of the glow from initial violet to yellow; and of the electrode film of phosphorus from white to yellow, brown and finally almost black, were comparatively more distinct.

Results for the nitrogen-phosphorus reaction under discharge due to fields at 500 cycles and also much higher frequencies obtained with a serial spark, were found to be on the whole similar to those observed at 50 cycles frequency (Fig. 3).

Examination under microscope of the products (of a number of reactions) on the inner electrode after long exposures to the discharge showed
small crystals of (unused) yellow phosphorus mixed with a brown substance. The mixture on treatment with water gave ammonia when treated with Nessler's reagent, indicating that a phosphorus nitride was produced under the discharge. Using Geissler type discharges and metallic electrodes, Strutt (now Lord Rayleigh) found that phosphorus absorbed nitrogen, and that the gas was not reliberated on heating, which he attributed to the formation of a chemical compound; this agrees with the results of Newman and Moldenhauer and Dörsom. In the present work (vide supra), the reaction products always revealed a nitride; its formation would appear therefore, to represent by far the main change in the P–N₂ interaction under the silent discharge. Judged by the time-rate of the variation of both \( p \) and corresponding \( i \), this 'clean up' of nitrogen by phosphorus was more rapid as the applied \( V \) and \( 1/p \) were increased; ultimately, whole of the input nitrogen was removed. As observed in the last stage of each of the reactions with nitrous oxide also (see Fig. 2), when the pressure of the residual nitrogen was very small, \( i \) decreased remarkably suddenly. This supports the deduction made that the decomposition under discharge of nitric oxide is completed during early stages; and that the 'clean up' of nitrogen is practically the only change, which constitutes a later and by far the longest stage in the \( N₂O–P \) interaction under discharge. The remarkably sudden drop of the current \( i \) (cf. Figs. 2 and 3) to stationary values at the end of \( P–N₂O \) and \( P–N₂ \) reactions may be attributed to the production of a vacuum condition in the discharge space by the final 'clean up' of nitrogen by the phosphorus film, which is practically the same sole change during the latter part of both the above reactions; incidentally, this illustrates the marked 'getter' action of phosphorus. The current \( i \) is constant as long as \( V \) is constant e.g., at 4 kV in Fig. 3; it, however, increases immediately to a higher constant value (cf. the step-wise, current-time curve, continued from A to A' in Fig. 3) owing to increased ionisation of the residual gas (and phosphorus vapour) under fields due to larger \( V \).

On general considerations, it is shown easily that the discharge current \( i \) in a gas under a constant applied field would increase as \( p \) is reduced, since the energy gained by motion under the field by an ion (chiefly electron) at the end of a given free path increases with its length \( i.e., \) with \( 1/p \); the limitation, due to the circumstance that the total number of electrons leading to ionisation and therefore, contributing to \( i \) also diminishes with \( p \), is not large. At moderate pressures, obtained during the main course of the reaction of \( N₂O \) and nitrogen with phosphorus, \( i \) is maintained as a balance of two factors mentioned above; on the whole, \( i \) tends to increase as the pressure is diminished (see Figs. 2 and 3), except when it becomes negligible.
towards the end of both these reactions. The large though momentary rise of \( i \) on applying 8 kV before the attainment of the final stage (Fig. 3) in this nitrogen-phosphorus interaction requires, however, further investigation.

In conclusion, we welcome this opportunity of expressing our sincere and grateful thanks to Professor S. S. Joshi, D.Sc. (London), F.A.Sc., Head of the Chemistry Department, for suggesting the problem, instructive advice and kind encouragement during this work.

**Summary**

Interaction with phosphorus films of nitrous oxide, nitrogen and oxygen in silent discharge under fields due to potentials \( V \) of 50, 500 cycles and the high frequencies has been studied at various pressures \( p \). In agreement with a general finding due to Prof. Joshi, the change sets in above a minimum \( V_m \) and that both the current \( i \) and the reaction rate at a given \( V \) depend upon \( V - V_m \). \( p \) decreases progressively to zero, when the reaction terminates; this is characterised by a remarkably sudden drop of the corresponding \( i \). Free \( \text{O}_2 \) is not observed; \( \text{NO} \) occurs only at early stages. Two simultaneous changes \((a)\) and \((b)\), the former being the more rapid, followed by \((ii)\) represent the reaction mechanism viz., \( \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O} \) \((a)\) \( \text{N}_2\text{O} \rightarrow \text{N} + \text{NO} \) \((b)\) \( \text{NO} \rightarrow \text{N} + \text{O} \) \((ii)\). The atomic products react with phosphorus immediately. Removal of molecular \( \text{N}_2 \) from \((a)\) and that formed by recombination of \( \text{N} \) from \((b)\) and \((ii)\) by phosphorus, is the longest stage. Phosphorus nitride is the chief product with both \( \text{N}_2\text{O} \) and \( \text{N}_2 \). The time-variation of \( i \) is markedly synchronous with, but more pronounced than that of \( p \); and more helpful in revealing the stages of the reaction, suggested as a general proposition by Joshi. Interaction with oxygen produces a rise of \( i \) in striking contrast with that with nitrogen.

**References**

10. Moldenhauer and Dorsom \ldots. *Ber.*, 1926, B 59, 926.