2. *The Reaction between Oxygen and Nitric Oxide.*

By E. M. STODDART.

Baker's observations on the non-interaction between intensively dried oxygen and nitric oxide can be repeated, if care is taken to ensure that mixing takes place entirely in the oxygen-containing bulb. Admission of water to the non-reactive gases has no effect, and therefore inhibition of reaction is wholly due to surface conditions of the containing vessels, "drying" in itself having no effect. It is suggested that the drying removes the adsorbed water film from the glass vessels, thus allowing the surfaces to adsorb a complete gas film in its place. When this gas film is oxygen, no reaction occurs in the mixed gases, but when the gas film is nitric oxide, reaction is possible.

There is evidence for assuming a temporary association of nitric oxide molecules in the form of a complex, the life of which diminishes with rise of temperature. This complex is best formed when the nitric oxide molecules are held close together by adsorption on glass surfaces, and it is this complex molecule which reacts with oxygen to form nitrogen dioxide. When conditions are such that this complex is not formed (*i.e.*, when nitric oxide is passed into oxygen, contained in a vessel with oxygen strongly adsorbed on its walls), reaction does not occur.

HINSHELWOOD ("The Kinetics of Chemical Change in Gaseous Systems," Oxford, 3rd edtn.) points out that intensive drying should not, theoretically, influence the rate of a true homogeneous reaction, although it may influence the rate of heterogeneous reactions, since the adherence of water to a surface alters the nature of the surface and therefore its influence on the reaction. These conclusions are well borne out by observations on the effect of moisture on the rate of union of hydrogen atoms in glass vessels at low pressures (Wartenburg and Schultz, *Z. physikal. Chem.*, 1930, *B*, **6**, 261) and also on the rate of union of oxygen atoms under similar conditions (Copeland, *Physical Rev.*, 1930, **36**, 1221). If an apparently homogeneous reaction is influenced to a small extent by changes in the nature of the surfaces present, it is not entirely a homogeneous change, and intensive drying may be expected to affect its rate.

The reaction between oxygen and nitric oxide is said to be termolecular and homogeneous (Bodenstein, *Z. physikal. Chem.*, 1922, **100**, 68), and consequently it should not be influenced by conditions of the containing walls, *i.e.*, by intensive drying. Although Armstrong (*Proc. Roy. Soc.*, 1884, **40**, 288) predicted that the dried gases would not react, Emich (*Monatsh.*, 1892, **13**, 86) found that the gases reacted just as usual after drying over alkali, followed by phosphoric oxide. Baker (J., 1894, **65**, 611) found that nitric oxide prepared by the action of nitric acid on copper reacted with oxygen just as readily when dry as when moist. He then prepared pure nitric oxide, and when this gas and oxygen were separately dried for ten days over phosphoric oxide no reaction occurred on mixing, but reaction occurred when water was introduced into the gases. Briner (*J. Chim. physique*, 1926, **23**, 848) repeated the experiment and found that drying did not prevent reaction. He prepared the nitric oxide by acidification of nitrite, and purified it by low-temperature distillation. The oxygen and nitric oxide were enclosed in bulbs and dried over phosphoric oxide for periods from 3 months to a year, but on mixing, they always reacted. Briner also showed that the velocity of the reaction is greatest at low temperatures (— 183° to — 193°), at which water has a negligible vapour pressure, and therefore concluded that water is not necessary for the reaction to proceed but may nevertheless conceivably influence it. Hasche (*J. Amer. Chem. Soc.*, 1926, **48**, 2253) dried the gases for two months over phosphoric oxide and investigated the variation of velocity constant of the reaction under various surface conditions. He showed that when the walls of the vessel were coated with paraffin, the rate of reaction was reduced 20% below the normal, and concluded that water could influence the rate of reaction when it was adsorbed by the walls. Smith (J., 1928, 1886) studied the dissociation of nitrogen dioxide, heating the gas in contact with phosphoric oxide, and found : (i) that nitrogen dioxide formed an addition compound with phosphoric oxide, (ii) that nitrogen dioxide dissociated into oxygen and nitric oxide to a greater extent than the " moist " gas ordinarily does, and that these products did not recombine on cooling except when moisture was admitted, and (iii) that the nitric oxide was dissociated into oxygen and nitrogen at a greater rate than usual.

The foregoing account is one of many differences of observation. Baker, using pure nitric oxide, could totally inhibit reaction with oxygen after only 10 days' drying; Smith, using the products of dissociation of nitrogen dioxide, verified this observation; and Hasche showed that the rate of reaction could be affected by the nature of the surfaces, yet Emich did not observe the result, nor did Briner, using extremely pure nitric oxide and a year's drying, nor did Hasche nor Baker with impure nitric oxide. Although such observations cannot be reconciled with one another, many interesting deductions can be made from them. Hasche has found that the velocity constant of the reaction varies according to the surface of the reacting vessel, *i.e.*, the reaction must be heterogeneous, in which case, the reaction is in all probability affected by drying. On the other hand, Bodenstein has found that the reaction is a homogeneous one of the third order, in which case, drying should have no effect on the reaction, a conclusion supported by Briner's observations.

Bodenstein showed that the reaction has a negative temperature coefficient, since the ratio k_{t+10}/k_t is less than unity, gradually changing from 0·912 to 0·997 with rising temperature. In an attempt to explain this, he postulated that two nitric oxide molecules on collision form a temporary complex, the life of which diminishes with temperature rise so that fewer ternary collisions result.

The author has shown (J., 1938, 1459) that Smith's work provides no evidence that drying can affect reaction between oxygen and nitric oxide, because nitrogen dioxide reacts with phosphoric oxide thus: $N_2O_4 + P_2O_5 = P_2O_5,2NO + O_2$, and not, as stated by Smith, to give a compound P_2O_5,xNO_2. When water is added to the first compound, reaction occurs: $P_2O_5,2NO + H_2O = 2HPO_3 + 2NO$, and Smith observed the brown fumes formed by reaction of the liberated nitric oxide with the oxygen present. Unfortunately, he interpreted his observations by assuming that the gas present was a non-reactive mixture of nitric oxide and oxygen which became reactive by admission of moisture. From this new work, it is clear that the evidence for the possibility of affecting this reaction by drying is considerably weakened.

The present communication records a comprehensive investigation into the effect of drying on this reaction, and a theory is put forward which appears to account for all the known facts regarding it.

EXPERIMENTAL.

A. *Experiments employing Phosphoric Oxide as Dehydrating Agent.*

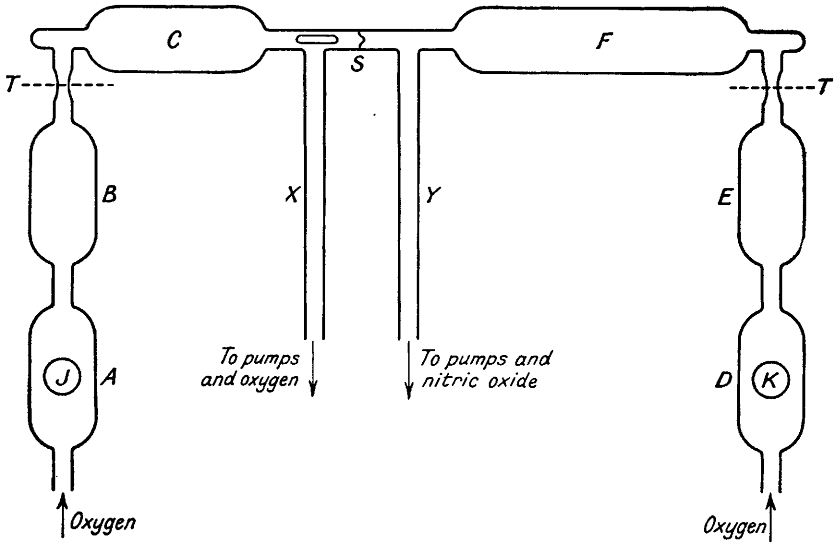
Preparation of Materials.—Nitric oxide was prepared by adding sulphuric acid to a mixture of potassium nitrate and ferrous sulphate, and was washed with water, followed by concentrated sulphuric acid, which removed traces of nitrogen dioxide. Any remaining traces of this impurity were removed by passing the gas through a large glass coil cooled to — 78° with solid carbon dioxide–ether. The nitric oxide was dried by passage through two tubes each containing a 50-cm. length of phosphoric oxide.

Oxygen was prepared by electrolysis of baryta in the apparatus already described (Stoddart, *Proc. Roy. Soc.*, 1935, **152**, 273), and dried over potash pellets, followed by two tubes of phosphoric oxide as above.

The phosphoric oxide was sublimed in a current of oxygen in order to remove any lower oxide, and was stored in large, glass-stoppered bottles until required.

Apparatus and Experimental Method.—The apparatus, Fig. 1, was entirely constructed in soda-glass; since this glass is easily softened in a blowpipe flame, any capillaries in the walls of the apparatus which may occlude moisture are thus removed. No taps were used to separate the gases to be dried; a septum (*S*) was employed instead, thus obviating the use of tap grease which may influence the experiment. The apparatus was cleaned with dichromate–sulphuric acid mixture, washed, and dried. The bulb (*C*) containing the oxygen had approximately half the volume of that (*F*) containing the nitric oxide (500 and 1000 c.c. respectively).

FIG. 1.



Sherwood (*J. Amer. Chem. Soc.*, 1918, **40**, 1645; *Physical Rev.*, 1918, **12**, 448) has shown that glass contains much adsorbed water vapour, carbon dioxide, and nitrogen which are removable by heating it under vacuum. It was clear that such treatment of the apparatus would greatly facilitate intensive drying. Therefore the whole apparatus was connected to a high-vacuum pumping system consisting of a mercury-vapour pump backed by a Hyvac pump, mercury vapour being kept out of the system by a liquid-air trap, and the pressure in the system being measured by a sensitive McLeod gauge. The apparatus was evacuated so that the pressure could not be measured by the gauge and no Tesla discharge was obtainable in the evacuated vessels; *i.e.*, the pressure was evidently less than 10^{-6} mm. This vacuum was maintained for 3 days, and the apparatus was constantly " flamed " with a soft blowpipe flame until, in parts, the glass slightly collapsed. This treatment had the effect of removing all occluded moisture on the glass surfaces and at the same time removing most, if not all, of the capillaries from the glass. The apparatus, at this stage, would maintain a vacuum of less than 10^{-6} mm. indefinitely, and it was now entirely filled with dry electrolytic oxygen.

Pure phosphoric oxide was now introduced into the bulbs *A* and *D* *via* the side tubes *J* and *K*, the apparatus being kept free from atmospheric moisture by a countercurrent of dry oxygen admitted *via* the tubes *X* and *Y*. After the tubes *J* and *K* had been sealed, the phosphoric oxide was sublimed in a current of dry oxygen into the bulbs *B* and *E*, and finally into the bulbs *C* and *F*. After the apparatus had been sealed off at *T* and *T*, the bulbs *C* and *F* were again evacuated to 10^{-6} mm. and gently heated, the phosphoric oxide being thus caused to wander about the glass surfaces of these bulbs, producing a very efficient drying medium.

The bulb *C* was filled with electrolytic oxygen previously dried by storage over phosphoric oxide; the bulb *F* was similarly filled with nitric oxide, and the bulbs were closed by sealing at *X* and *Y*. Drying was allowed to proceed for 30 days.

Now these bulbs were filled at atmospheric pressure, but it was shown, by an independent experiment, that phosphoric oxide slowly absorbs nitric oxide at atmospheric temperature and pressure, presumably to form the compound previously described. Hence, at the end of the drying period, when the septum S was broken, the oxygen was expected to rush into the nitric oxide. When the septum was broken, immediate reaction occurred, but whereas the nitric oxide bulb was full of red vapour after ½ hour, the oxygen bulb was colourless. After an hour, the contents of these bulbs were respectively of a very deep red and a straw colour.

Since the oxygen rushed into the nitric oxide bulb, it was not surprising that the latter should be the darker in colour, but it had been expected that reaction would have occurred in the oxygen bulb as well as the nitric oxide bulb when the original levelling up of pressure had been achieved. A possible explanation of this phenomenon was that when the oxygen rushed into the nitric oxide, reaction occurred, $2NO + O_2 = N_2O_4$, 3 vols. of gas disappearing for the appearance of 1 vol. of dinitrogen tetroxide, and therefore the gas drifted in bulk towards the nitric oxide bulb, giving the observed result; but the following considerations showed that this is not the case. Let us assume (i) that the nitrogen dioxide is completely associated, (ii) that oxygen and nitric oxide have the same rate of diffusion, and (iii) that the bulbs were both filled at atmospheric pressure. All these assumptions are approximately true. Suppose the nitric oxide and the oxygen bulb contain respectively $2N$ and N molecules. After a certain time, suppose n molecules of each kind have diffused into each other. Then in the nitric oxide bulb, $2n$ molecules of nitric oxide will have reacted with these n molecules of oxygen to give n molecules of dinitrogen tetroxide, *i.e.*, the final gas pressure in this bulb will be $(2N - 2n)/2N = (1 - n/N)$ of an atmosphere. Again in the oxygen bulb, $\frac{1}{2}n$ molecules of oxygen will have reacted with the n molecules of nitric oxide, giving $\frac{1}{2}n$ molecules of dinitrogen tetroxide, *i.e.*, the final gas pressure in this bulb will be $(N - n)/N = (1 - n/N)$ of an atmosphere. Hence, in this ideal case, no gas drift will occur. In actual fact, of course, the above three assumptions are not quite correct, and therefore a slight drift is possible. The point was tested experimentally by using untreated vessels; when the gases were allowed to mix, no distinction could be made in the colour of the bulbs, and so the above assumptions are sufficiently valid in these experiments.

A very different state of affairs would be present if the nitric oxide and oxygen bulbs were of equal volume. In this case, it is a simple matter to show that a drift towards the nitric oxide bulb would occur.

In view of these considerations, it appears that the dry gases had reacted in the nitric oxide bulb but not in the oxygen bulb. Nevertheless drying does not prevent reaction.

The above experiment was now repeated with different gas pressures. The results may be summarised :

	Initial pressure of		
Expt. No.	NO.	O_2.	Result.
1	1 atm.	1 atm.	Reaction occurred in the NO bulb.
2	350 mm.	1 atm.	
3	1 atm.	300 mm.	No reaction occurred.
4	400 mm.	300 mm.	

In Expt. 3 no darkening occurred when the gases mixed, and the bulbs were quickly separated by using the blowpipe. The tip of the oxygen bulb was opened under mercury, and a drop of water introduced into the gases. No reaction occurred, and therefore it is clear that water vapour plays no part in this reaction. The gases were now displaced into another vessel, whereupon reaction occurred.

In Expt. 4, mixing occurred in the oxygen bulb, but no reaction occurred until after ½ hour, whereupon it started in the nitric oxide bulb, presumably owing to diffusion from the oxygen bulb.

These experiments show that the intensively dried gases react when the mixing occurs in the nitric oxide-containing bulb, but no reaction is possible when mixing occurs in the oxygen bulb, drying in itself having no effect. It seems that the surface conditions of the glass bulbs were the deciding factor. It is suggested that the heat treatment of the bulbs under vacuum freed the glass from the bulk of its adsorbed water and the phosphoric oxide completed this process. When the gases were admitted to their bulbs, the surfaces adsorbed these gases in a complete film. When the film was oxygen, no reaction occurred in the mixed gases, but when the film was nitric oxide, reaction was possible.

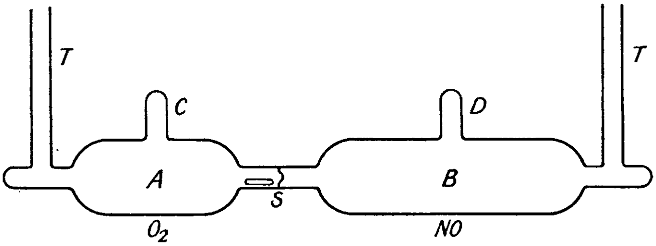
B. *Experiments employing Anhydrous Magnesium Perchlorate as Dehydrating Agent.*

Phosphoric oxide being a volatile dehydrating agent, the glass surfaces may tend to adsorb it to some extent. Therefore the previous experiments deal with phenomena characteristic of glass surfaces with adsorbed phosphoric oxide. Phosphoric oxide also combines directly with nitric oxide at ordinary temperatures and pressures, thereby lowering the pressure of the gas as well as drying it.

Anhydrous magnesium perchlorate ("anhydrone") is non-volatile and is non-reactive towards nitric oxide. It is just as efficient as phosphoric oxide for drying purposes, and so it was decided to repeat the experiments in order to discover if the phenomena were due to the glass surfaces adsorbing phosphoric oxide.

The apparatus, Fig. 2, was chemically cleaned, washed, and dried. After evacuation to 10^{-6} mm., the vessels were flamed for several hours. The apparatus was then filled with dry electrolytic oxygen, and the tubes *C* and *D* were opened. About 10 g. of anhydrone were then introduced into each bulb, against a countercurrent of dry oxygen, and the tubes *C* and *D* were again sealed. Once more the apparatus was evacuated and flamed.

FIG. 2.



Dry oxygen was introduced into bulb *A* (500 c.c.) and dry nitric oxide into bulb *B* (1000 c.c.), both at atmospheric pressure. After sealing at *T* and *T*, the gases were allowed to dry for 35 days, and then the septum was broken. Reaction occurred slowly in the nitric oxide bulb, but no reaction had occurred in the oxygen bulb after ½ hour.

On comparing this experiment with the previous ones, it seemed that the reaction occurred rather more slowly than when phosphoric oxide was employed, although the same general phenomena were noted. The bulbs were now separated by using a small blowpipe flame. The contents of bulb *B* were of a light brown colour, but those of bulb *A* were colourless. Bulb *A* was dipped into boiling water, and the gases reacted; after 5 minutes its contents had become deep brown. The probable explanation of this phenomenon is that gentle heating liberates the adsorbed oxygen from the glass, thereby leaving a surface capable of bringing about reaction between the gases. (It is to be noted that when the bulbs were separated no reaction occurred, probably owing to the fact that only a very small surface of the glass was heated with the blowpipe. When the entire bulb was heated in this manner, reaction occurred.)

The drying experiment was repeated with nitric oxide at atmospheric pressure and oxygen at 500 mm.; reaction did not occur on mixing, but after 15 minutes, reaction occurred in the nitric oxide bulb. These observations are in agreement with the previous experiments.

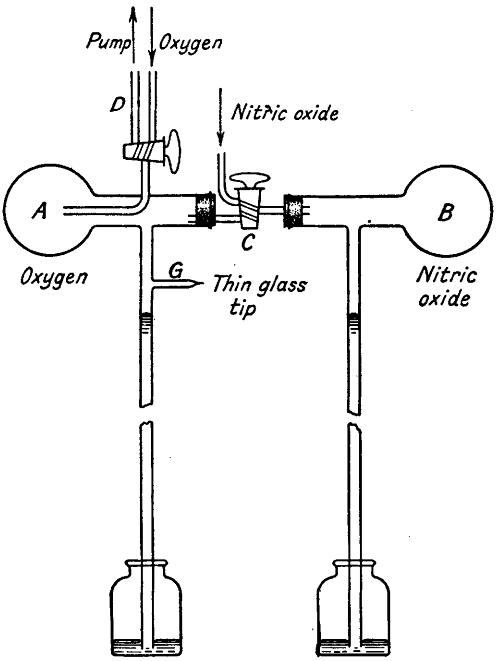
C. *Changes of Pressure after mixing Dried Oxygen and Nitric Oxide.*

The previous experiments were designed to investigate the effect of careful intensive drying on this reaction, the apparatus being constructed with this end in view—taps, tap grease, and manometric fluids being excluded. No such precautions seem to have been taken by Baker, so it was decided to repeat the experiments by using vessels fitted with manometers in order to verify the results quantitatively.

Two 100-c.c. Monax distillation flasks were fitted up as shown in Fig. 3, each having a simple mercury manometer. The mercury was dried by heating, followed by vacuum distillation; the rubber stoppers used were given a coat of shellac varnish in order to seal up any capillaries in them and also to give vacuum-tight joints, and the tap was lubricated with vapourless grease. Each flask contained about 5 g. of freshly sublimed phosphoric oxide. The apparatus was evacuated by a Hyvac pump *via D*, and the phosphoric oxide made to wander over the glass by heating. The flask *A* was filled with electrolytic oxygen and *B* with nitric oxide, both prepared as before, and both gases being at 759 mm. The gases were allowed to dry for 12 days (the period allowed by Baker). The pressure of oxygen after drying was still 759 mm., but that of nitric oxide had dropped continually until on the twelfth day it was 719 mm. This disappearance of nitric oxide is probably due to formation of $P_2O_5,2NO$.

After tap *C* was opened, the oxygen rushed into the flask *B*, and the average pressure was found to be 740 mm. (calculated pressure = 739 mm. if no reaction occurred); reaction occurred in this bulb, and after one hour the pressure was 540 mm. Simple calculation shows that considerable reaction had occurred but had not gone to completion; complete reaction would presumably be attained if the gases had been allowed to mix completely, the reaction being effected in the present work by slow diffusion through the connecting tube.

FIG. 3.



In another experiment, the oxygen pressure was 402 mm., the initial nitric oxide pressure 763 mm., and the final nitric oxide pressure 716 mm. after 17 days' drying. Tap *C* was opened but mixing occurred in bulb *A* this time, and as judged by absence of colour, no reaction occurred. (Tap *C* was closed after 30 seconds.) If no reaction had occurred, the final pressure should have been $(716 + 402)/2 = 559$ mm. The actual pressure first recorded was 556 mm., but this gradually decreased, quickly at first and then more slowly :

Time, mins.	0	3	6	10	20	60
Press., mm.	556	551	548	547	546	546

The pressure was constant at 546 mm. for over 4 hours, and reaction did not seem to occur, the gases being colourless. Admission of ½ c.c. of water to the gases *via* the mercury column did not cause reaction, even after ½ hour.

Oxygen was then admitted to the bulb *A* until atmospheric pressure was attained, and a small flask was attached to the side arm *G* by means of pressure tubing. The tip of *G* was crushed in the tubing, and the gases in *A* displaced into the flask by oxygen. Reaction instantly occurred in the new flask.

These results were in complete agreement with the previous work, and the only new phenomenon noticed was that the pressure quickly decreased when the nitric oxide entered the oxygen, yet reaction did not occur, since the gases remained without colour. In order to elucidate this effect, the experiment was repeated with pure nitrogen (prepared by heating ammonium dichromate) in place of oxygen. When the dry nitric oxide rushed into the dry nitrogen, a similar decrease in pressure was noted (about 10 mm. in 10 mins.). In this case, reaction of the gases was impossible. It was therefore concluded that this pressure change was due to the phosphoric oxide in the oxygen (or nitrogen) bulb adsorbing nitric oxide; it was generally observed in this work that such adsorption does take place.

DISCUSSION.

The only previous workers to have observed non-reactive mixtures of nitric oxide and oxygen are Baker and Smith, but (see p. 6) Smith's conclusions are no longer of value in this respect. Baker's work, however, merits closer examination. His experimental technique in this early work is crude when compared with his own later work, and his conditions of drying have been superseded by later investigators, none of whom has reproduced his results. The present work shows that non-reactive mixtures of nitric oxide and oxygen are possible if the mixing occurs in the oxygen-containing vessel. The question to be considered is whether Baker had conditions where mixing only occurred in his oxygen bulb. His paper lacks the detail necessary for any conclusion in this matter. Nevertheless, Baker noticed that admission of water caused reaction, whereas in the present work it was shown many times that introduction of water did not cause such reaction. One further point mentioned by Baker was that impure nitric oxide reacted with oxygen just as readily when " dry " as when " moist." The author repeated the experiment described in Section C, using the impure nitric oxide prepared from copper and nitric acid, the gas being purified as before. No difference in behaviour was noticed. The enigmatic observations of Baker have thus received partial verification, but it seems clear that his work is of little value in ascertaining the effect of drying on this reaction.

The work of Briner, Hasche, and others gives results agreeing with the present observations; drying in itself has no effect on this reaction, but wall conditions are the deciding factor. Hasche showed that the velocity constant of the reaction could be considerably affected by surface conditions; and the present work has shown that reaction is completely inhibited in vessels whose surfaces possess a strongly adsorbed oxygen film. Thus it is concluded that the reaction is a heterogeneous one.

The present observations have been obtained under a variety of conditions. Really intensive drying seems to have no different influence on the reaction from less rigorous drying. The same observations are obtainable by using the non-volatile magnesium perchlorate as desiccating agent. The author also considers the presence of colour a more sensitive method of detecting reaction, in this particular case, than the use of manometers, which also register adsorption of gas by the drying agent.

Now, Bodenstein has concluded that the reaction under discussion is homogeneous and of the third order. Hasche's work together with that now described shows that the reaction is not homogeneous but heterogeneous. Both Hasche and Bodenstein assumed the existence of a complex nitric oxide molecule. Bodenstein assumed its formation to be a homogeneous reaction, whereas Hasche assumed that this complex could only exist adsorbed on surfaces covered with water molecules. Hasche's suggested mechanism is :

$$\mathrm{NO + H_2O \longrightarrow NO,H_2O}$$
$$\mathrm{NO,H_2O + NO \longrightarrow (NO)_2,H_2O}$$
$$\mathrm{(NO)_2,H_2O + O_2 \longrightarrow (N_2O_4 \rightleftharpoons 2NO_2) + H_2O}$$

the water remaining adsorbed on the glass surface. It was Bodenstein who first assumed the existence of the complex molecule $(NO)_2$, whose life period was assumed to decrease with temperature rise in order to account for the negative temperature coefficient of the reaction.

Briner concluded from his experiments that water, if it does catalyse the reaction, is not necessary for the reaction to take place, and in agreement with him, the author shows that the presence or absence of water is not the deciding factor of this reaction. Therefore Hasche's scheme requires modification and the following suggestions are now put forward.

Drying removes adsorbed water films so that, after drying, glass–gas surfaces only are being dealt with. In the nitric oxide bulb, the glass adsorbs nitric oxide and the complex then formed is free to evaporate into the gas phase, the mechanism being

$$\mathrm{glass, 2NO \longrightarrow glass + (NO)_2}$$
$$\mathrm{(NO)_2 \longrightarrow 2NO}$$
$$\mathrm{NO + glass \dashrightarrow glass, NO \longrightarrow glass, 2NO}$$

If this adsorption is small, the formation of the complex is a bimolecular heterogeneous reaction. The complex has a short life period and is assumed to decompose quickly. Reaction with oxygen will only occur with the complex : $\mathrm{(NO)_2 + O_2 \longrightarrow (N_2O_4 \rightleftharpoons 2NO_2)}$. Now, in the oxygen bulb, the glass will adsorb oxygen slowly. After only a short period of drying, there is enough moisture film left to bring about reaction (the author suggests that glass with a water film will allow the association of nitric oxide since it will not adsorb oxygen while water is present), but eventually all the moisture is removed and oxygen is sufficiently adsorbed so as to prevent nitric oxide molecules being in adjacent positions on the surface, thus preventing complex formation, and so reaction does not take place.

Under ordinary conditions, using glass with a water film, the reaction becomes

$$\text{glass }(H_2O),2NO \longrightarrow \text{glass }(H_2O) + (NO)_2$$
$$(NO)_2 \longrightarrow 2NO;\ (NO)_2 + O_2 \longrightarrow (N_2O_4 \rightleftharpoons 2NO_2)$$
$$\text{glass }(H_2O) + 2NO \dashrightarrow \text{glass }(H_2O),\ 2NO$$

and the reaction will be a termolecular one if it is assumed that the rate of formation of the complex and its rate of reaction with oxygen are of the same order.

The most important difference between Hasche's scheme and the foregoing is that Hasche assumes the reaction to be wholly heterogeneous, in which case the reaction should have a normal temperature coefficient. It is now suggested that the $(NO)_2$ complex is formed heterogeneously and reacts homogeneously; the temperature coefficient of the reaction will then depend upon the rate of decomposition of the complex. On the assumption that the life period of the complex decreases with temperature rise more quickly than its rate of formation increases with temperature rise, the negative temperature coefficient can then be accounted for.

In this way all the facts regarding this reaction can be accounted for except Bodenstein's observation that the reaction is homogeneous. Experiments have shown, however, that the reaction is heterogeneous.

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