CCCLXIII.—*The Action of Nitric Oxide on Alkaline Hydroxides.*

By EDWARD BARNES.

THAT nitric oxide reacts with caustic potash was first observed by Gay-Lussac (*Ann. Chim.*, 1861, **1**, 397), who found that after 3 months' contact with the solution it gave rise to one-quarter of its volume of nitrous oxide, potassium nitrite being produced simultaneously. The subject was studied more fully by Russell and Lapraik (J., 1877, **32**, 35), who showed that nitrogen is also formed, and by Emich (*Monatsh.*, 1892, **13**, 90), who investigated the interaction of the gas with the solid, and represented the results thus :

$$4NO + 2KOH = N_2O + 2KNO_2 + H_2O$$
$$3NO + 2KOH = N + 2KNO_2 + H_2O$$

The author (*J. Soc. Chem. Ind.*, 1926, **45**, 259) found that the rate of the reaction depends on the area of surface of the potash and may, with powdered material, become rapid, and that solid sodium hydroxide also reacts with nitric oxide, but very much more slowly than potassium hydroxide.

Although the above facts have long been known, a number of workers with nitric oxide appear either to have overlooked them or to have regarded the reaction with caustic potash as taking place so slowly that it could be ignored. For example, Gray (J., 1905, **87**, 160), in his determination of the atomic weight of nitrogen, after fractionating his nitric oxide to remove nitrous oxide, subsequently passed it over solid potash, thus again introducing nitrous oxide. It was thought, therefore, that a fuller investigation of the action of nitric oxide on alkalis might prove useful, and the hydroxides of each of the alkali metals and of the alkaline earths were included, observations being made over wider temperature ranges than heretofore in the case of sodium and potassium hydroxides.

EXPERIMENTAL.

Preparation of Nitric Oxide.—Numerous papers have been published on the preparation of pure nitric oxide, and several reactions have been stated to give the pure gas directly. It is improbable, however, that any reaction will yield perfectly pure gas, for nitric oxide reacts with water, aqueous solutions, many reducing agents, and concentrated sulphuric acid. The best procedure appears to be to prepare the gas by one of the common methods and purify it by fractionation : that used in these experiments was prepared by the action of sodium nitrite solution on ferrous sulphate in hydrochloric acid as described by Thiele. The higher oxides of nitrogen and acid impurities were removed by passage through aqueous sodium hydroxide, and drying was effected by concentrated sulphuric acid. Nitrogen was then removed by solidifying the product in liquid air and pumping out all uncondensed gas. The most difficult impurity to remove is nitrous oxide, the best method apparently being to bubble the gas through liquid nitric oxide, as suggested by Gray. The chief obstacle in the way of carrying out this last step in the purification is the difficulty of collecting and storing a sufficient quantity of the gas, for storage over water or aqueous solutions is not permissible. In view of Lunge's nitrometer method of estimating nitrates and nitrites, it was at first thought then nitric oxide might be stored over concentrated sulphuric acid.* To test this, some clean pumice was boiled with concentrated acid and then sealed in a tube attached to a manometer. After evacuation, the tube was filled with nitric oxide (about 27 c.c.); after a day, the pressure in the tube had fallen by 15 cm., and after 15 days by nearly 50 cm. The residual gas contained sulphur dioxide, nitrogen (1·05 c.c.), and nitrous oxide (1·15 c.c.) besides unchanged nitric oxide. The matter was not further investigated but it is evident that this method of storage is excluded.

Mercury is the best liquid over which to store nitric oxide. The gas-holder should be of the closed type and made entirely of glass, and should have an air-trap; but since such a vessel will be made of blown glass, the great density of mercury will limit its size to an effective capacity of about ½ litre. The use of evacuated glass globes is inconvenient for most kinds of work. In this work the nitric oxide was liquefied, and the middle fraction collected in a mercury gas-holder; it still contained a little nitrous oxide but no appreciable amount of any other impurity.

Analysis of Gaseous Product.—When nitric oxide reacts with alkalis it gives rise to nitrous oxide and nitrogen. It is therefore necessary to analyse gaseous mixtures containing these three gases. No very satisfactory method of doing this has been described. The author (*loc. cit.*) partly worked out a method of analysing mixtures of the oxides of nitrogen, but it was not very convenient for mixtures containing large percentages of nitric oxide. Some further experiments have been done with this object. What is required is a substance that will completely absorb nitric but not nitrous oxide. Liquid reagents will dissolve the latter, and their vapour pressure makes them unsuitable for use in connexion with a Toepler pump. Tests were made with a number of solids such as sodium peroxide, potassium tetroxide, mixtures of potassium hydroxide with potassium bromite, sulphite, permanganate, or plumbate, but the only substance found to be at all suitable was lead peroxide

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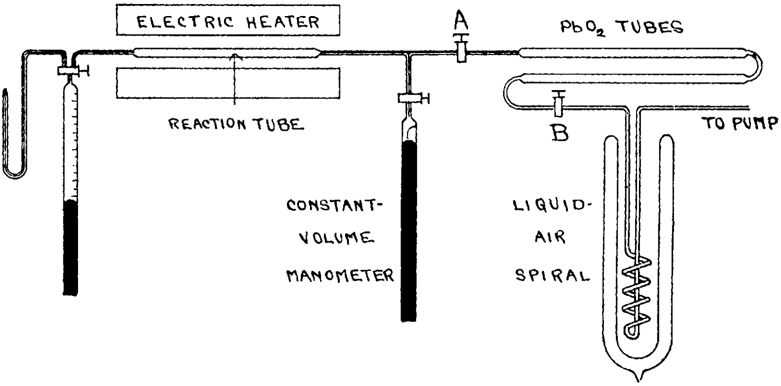
* Very few references are to be found in the literature respecting the action of nitric oxide on sulphuric acid. Gay-Lussac (*Ann. Chim. Phys.*, 1816, **1**, 408), in discussing the formation of chamber crystals, states that the concentrated acid does not sensibly absorb the gas. Rose (*Pogg. Ann.*, 1839, **47**, 605) appears to have used the fuming acid. Bodenstein (*Z. Elektrochem.*, 1918, **24**, 183) found that, after a week's contact, sulphur dioxide was produced, and the acid then attacked mercury. A number of reference books give absorption coefficients for nitric oxide in various concentrations of sulphuric acid, ignoring the possibility of chemical action; most of these figures have been obtained by experiments in which the gas was brought into contact with the acid and mercury, the latter having the effect of partially reversing the reaction by re-forming nitric oxide from the nitrogen compound produced in the acid.

prepared by passing chlorine into alkaline plumbite; the product was washed and boiled with dilute nitric acid, made into a paste with water, and mixed with finely granular pumice which had been separated from dust and coarse particles by sifting. Two tubes were filled with columns of this mixture, about 25 cm. long, between plugs of glass-wool. After being dried in an air-oven, these tubes were sealed together and also sealed to the pump. It was found that under certain conditions they would completely absorb nitric but not nitrous oxide. According to Müller and Barck (*Z. anorg. Chem.*, 1923, **129**, 314), lead peroxide combines with nitric oxide to form lead nitrite, but the tubes described ceased to absorb actively long before all the peroxide had been acted upon, so that their absorbing capacity was rather limited. The method was found suitable for mixtures containing small concentrations of nitric oxide but not for large quantities; and as the gaseous products in the present work usually contained only small percentages of unchanged nitric oxide, the method was generally applicable.

Fig. 1.



The apparatus used is shown in Fig. 1. At the end of an experiment tap *B* was closed and tap *A* was opened. After the gas had been left in contact with the peroxide for a few minutes for the absorption of unchanged nitric oxide, the spiral was cooled in liquid air, tap *B* opened, and the nitrogen formed in the experiment was pumped out and measured. Tap *B* was then closed, the liquid air removed, and the nitrous oxide pumped out and measured. The Toepler pump used was specially made with a large barrel (about 400 c.c.). It was found that when the spiral was immersed in liquid air and nitric oxide was introduced after evacuation, about 0·5 c.c. could be pumped out at each stroke. It was not, therefore, difficult to pump out the nitrogen and nitric oxide from their mixture with nitrous oxide. This method was used in some cases. There is no difficulty in analysing mixtures of the first two gases by liquid reagents.

Procedure.—The powdered alkali was placed in a tube about 1 cm. in diameter between plugs of glass-wool (a silver boat being used if necessitated by the temperature employed). The reaction tube was heated in an electric furnace whose temperature was controlled by rheostats, and read by a thermocouple. In most experiments the volume of nitric oxide, after measurement in the gas-burette, was introduced into the evacuated tube containing the alkali, tap *A* being closed. Pressure changes were observed by means of the constant-volume manometer. At the end of the experiment the manometer tap was closed after the mercury had been raised above the level of the tap, and the resulting gas was analysed. In introducing a volume of gas from a mercury gas-burette into a vacuum, it is almost impossible to avoid small globules of mercury being carried into the reaction chamber; in experiments in which the alkali was contained in a silver boat, the gas-holder was therefore connected directly with the reaction chamber in place of the gas-burette. For all experiments the apparatus was made entirely of glass, all connexions being made by fusing. Most connecting tubes were of capillary tubing, and the taps had obliquely bored keys. The apparatus was tested for leaks before each experiment, and the taps of the burette and manometer were sealed by raising the mercury into the tubes above them during the experiment. Nevertheless, in many cases leaks started during the course of the reaction and the results had to be rejected.

Potassium Hydroxide.—In order to carry out experiments at higher temperatures, and because it is desirable to use a chemical individual rather than a mixture, it was necessary to obtain potash as anhydrous as possible. Several of the best available samples of stick were tested and found to contain 14—16% of water. The potash used was dehydrated as far as possible by heating to 450—500° in a silver boat in a stream of electrolytic hydrogen, which had been purified by passage through a column of red-hot copper gauze, then through syrupy phosphoric acid, and finally over solid potash and phosphoric oxide. The heating and passage of the gas were continued till no more water was given off. When subjected to this treatment, caustic potash (purified by alcohol) yielded a beautiful white crystalline mass having a pearly lustre. It hissed on the addition of a little water, and it dissolved in water much more rapidly than ordinary potash.

Emich studied the action of nitric oxide on potassium hydroxide up to 175°, but the use of anhydrous hydroxide in a silver vessel enabled observations to be extended up to 500°, the temperature at which the thermal decomposition of nitrous oxide becomes appreciable. The hydroxide in a silver boat was sealed in a hard-glass tube, which was sealed to the apparatus by means of graded glass junctions. The tube was evacuated, heated to 500°, and a known volume of nitric oxide introduced. The rate of reaction was too rapid for measurement. After ½ hour the gas was pumped out and analysed : 45·9 c.c. of nitric oxide gave 8·1 c.c. of nitrogen and 0·1 c.c. of nitrous oxide. An experiment at 420° gave a similar result. It was subsequently found, however, that these results do not give much information about the primary reaction, for nitrous oxide, an initial product, is itself decomposed under the experimental conditions, as shown by the following tests.

A bulb-tube with two arms was sealed to the end of the reaction tube in place of the gas-holder or gas-burette. Nitrous oxide from a cylinder was dried and passed through the apparatus after the key of tap *A* had been removed. When the air had been displaced, the key was replaced, and the end of the bulb-tube sealed off. The bulb-tube was cooled in liquid air, and any uncondensed gas was then completely removed by pumping. The liquid air was removed so that the nitrous oxide vaporised, and then replaced, and the apparatus again pumped out. After the reaction tube had attained the desired temperature, the nitrous oxide was allowed to gasify again and come into contact with the alkali. At the end of the experiment the bulb-tube was again cooled in liquid air and the uncondensed decomposition products were pumped out and collected; after 28·8 c.c. of nitrous oxide had been exposed for ½ hour to the action of potassium hydroxide in a silver boat at 420°, only 3·2 c.c. remained undecomposed. Although references in the literature suggest that silver has no action on the gas, yet it was found that the silver boat alone decomposed it at 420°, but less rapidly than the alkali. Further experiments showed that at 350° the silver boat had no appreciable action, but ½ hour's contact with fused hydroxide in the boat at this temperature effected extensive decomposition. At 250° also after exposure for 2—3 days to the action of caustic potash, nitrous oxide was largely decomposed. These experiments show that, owing to the secondary reaction between the nitrous oxide formed and the alkali, it is not to be expected that there will be a constant ratio between the nitrogen and nitrous oxide in the product of the primary reaction : the ratio will depend on the duration of the experiment, the percentage of nitrogen increasing with time. That this is so, is shown by the following results of the action of nitric oxide on caustic potash at 250°.

Duration of experiment.	Composition of resulting gas, %.
15 minutes	N_2O, 54; N, 46
75 ,,	N_2O, 34; N, 68

Even at 100°, after 48 hours' contact, about 2% of the nitrous oxide was decomposed. In the above experiments on the decomposition of nitrous oxide by potash, the gas uncondensed by liquid air was found to contain 11—17% of oxygen in the nitrogen, and the alkali contained a little nitrite after the experiment. If the alkali was fused (m. p. 316°), the silver vessel was attacked and the alkali darkened in colour, since the latter formed a peroxide with the oxygen and this reacted with the silver. According to Briner, Miener, and Rothen (*J. Chim. physique*, 1926, **23**, 609), nitrous oxide is decomposed thermally at and above 700° according to the equations $N_2O \longrightarrow N_2 + \frac{1}{2}O_2$ and $N_2O \longrightarrow NO + \frac{1}{2}N_2$. Apparently in the presence of caustic potash these reactions take place at lower temperatures. The nitrite is formed by the nitric oxide from one reaction and part of the oxygen from the other reacting with the alkali. Although the alkali was the purest available, it is possible that the decomposition of the nitrous oxide was due to the presence of a trace of impurity in it. As some experiments at 250° were carried out without a silver vessel, it appears that this metal was not necessarily concerned in the change

The above experiments show that some of the nitrogen formed in the reaction between nitric oxide and potassium hydroxide at higher temperatures is a secondary product of the decomposition of nitrous oxide, but there appears little doubt that two primary reactions occur, one of which gives rise to nitrous oxide and the other to nitrogen : with rise of temperature the ratio N_2/N_2O increases, but owing to the secondary decomposition it is not possible to determine this ratio at higher temperatures.

Emich (*loc. cit.*) states that when nitric oxide reacts with potassium hydroxide, nitrite but no nitrate is formed; as his experiments were qualitative, however, and as it is difficult to test for nitrate in the presence of nitrite, it was thought desirable to examine this point quantitatively. Nitric oxide was passed over potassium hydroxide at 100°, and the volumes of nitrous oxide and nitrogen formed were measured. The solid was dissolved, and the amount of nitrite in the solution determined by titration with acidified permanganate. The following figures were obtained :

Volumes of gases collected (c.c. at N.T.P.): N_2O, 28·3; N_2, 3·7.
Vol. of $N/10$-$KMnO_4$ required : 62·3 c.c.
,, ,, ,, calc. from vols. of gases : 63·7 c.c.

They show that the amount of nitrite formed is approximately equivalent to the amounts of gases formed according to Emich's equations.

Sodium Hydroxide.—The stick alkali usually contains comparatively small quantities of water. The samples used were (i) A.R. and (ii) " from sodium." They were heated in a silver boat in a stream of pure dry hydrogen at 400—450° till no more water was given off.

At room temperature this alkali, even when powdered, reacts very slowly with nitric oxide. A tube about half full of coarsely powdered hydroxide, fused to a manometer at one end, was evacuated and filled with the gas at atmospheric pressure. The following figures give some idea of the rate of reaction :

Duration of experiment (days)	14	22	39	63	85
Decrease of pressure (cm. of Hg)	12	19	28·5	37	45

It is seen that about 80% of the gas had reacted in 85 days. In another experiment a tube was about one-third filled with finely powdered hydroxide. After 27 days the gaseous contents were : N_2O, 49·4 ; N_2, 1·2 ; NO, 49·4%.

As with potassium hydroxide, heat greatly accelerates the rate of reaction. A series of experiments was carried out with fused sodium hydroxide in a silver boat at 350° (m. p. 318·4° ; von Hevesy). The results of these experiments varied widely as regards the percentages of nitrogen and nitrous oxide in the product. It was subsequently found that, as in the case of caustic potash, this variation was due to a secondary reaction in which nitrous oxide is decomposed, but the decomposition was less rapid than with potash under similar conditions : 28·7 c.c. of the gas, free from nitrogen, after 40 minutes' contact with fused alkali in a silver boat at 360° gave 4·3 c.c. of gas uncondensed by liquid air. In spite of this secondary reaction, an experiment in which contact between nitric oxide and the alkali lasted for 20 minutes gave, after absorption of unchanged nitric oxide, a gas containing 42% of nitrous oxide, and no doubt with shorter time of contact a higher percentage could have been obtained.

Before testing the action of nitric oxide at lower temperatures, the action of nitrous oxide was first examined. The powdered alkali (from sodium) in the absence of silver gave no appreciable amount of gas uncondensed by liquid air after 44 hours' contact at 250°. A series of experiments with this alkali and nitric oxide, in which the duration of contact was varied, gave the following results at 250° :

$$10\text{ mins.}\left\{\begin{array}{l}16\%\ \text{N},\ 84\%\ N_2O.\\ 17\%\ \text{N},\ 83\%\ N_2O.\end{array}\right. \qquad 30\text{ mins.}\left\{\begin{array}{l}13\%\ \text{N},\ 87\%\ N_2O.\\ 16\%\ \text{N},\ 84\%\ N_2O.\end{array}\right.$$

60 mins. 15% N, 85% N_2O.
14 hrs. 18% N, 82% N_2O.

As the volume of nitrogen obtained was only about 1 c.c. (one-thirtieth of nitric oxide used), the accuracy with which this volume of gas could be pumped out and measured probably did not exceed about 3%. It appears, therefore, that at 250° there are produced approximately 85% of nitrous oxide and 15% of nitrogen, and that the secondary reaction either does not take place or is very slow.

Rubidium Hydroxide.—A small quantity of the chloride was converted into the sulphate, and this, in turn, into the hydroxide by double decomposition with recrystallised baryta. After filtration, the solution was concentrated in a platinum dish in a vacuum over solid caustic potash, and then transferred to a silver boat and heated slowly to 300° in a current of dry hydrogen. In this way the hydroxide was obtained as a white crystalline mass. This was roughly powdered and sealed in a tube. After evacuation, a known quantity of nitric oxide was admitted, and changes of pressure at 17° were observed: it fell from about 62·5 cm. to 14·0 cm. in 6 hours and then remained almost constant. The gaseous residue contained approximately 96% of nitrous oxide and 4% of nitrogen.

A tube of the same size and shape was loaded with a quantity of potassium hydroxide (dried in hydrogen), which had been reduced as nearly as possible to the same state of division as the rubidium hydroxide, and was slightly greater in amount. The same volume of nitric oxide was introduced and the tube was maintained at the same temperature as in the previous experiment. After 6 hours, the pressure had fallen only to 48·5 cm., and after 24 hours it had not attained complete constancy.

Hence it appears that rubidium hydroxide is more reactive than potassium hydroxide towards nitric oxide. Owing to the small quantity available, however, no experiments were carried out at higher temperatures.

Cæsium Hydroxide.—A quantity of crude sulphate was available owing to the kindness of Dr. H. F. Harwood; this was converted into the chloride by double decomposition with barium chloride. The chloride was purified from other alkaline chlorides by precipitation as the double antimony compound $CsSbCl_4$, and then converted into the hydroxide, which was rendered anhydrous as in the foregoing case.

Some powdered cæsium hydroxide was treated with nitric oxide under conditions as nearly identical as possible with those described in the previous section. Decrease of pressure was almost complete in $2\frac{1}{2}$ hours; the half period was about 33 minutes. The gaseous product consisted of nitrous oxide with only a trace of nitrogen. Apparently this hydroxide reacts more rapidly than any of its congeners.

Several experiments were carried out with cæsium hydroxide in a silver boat at *ca.* 260°, with the following results :

Period of contact.	Composition of resulting gas, %.
1 minute	N_2O, 29; N, 71
10 minutes	N_2O, 27; N, 73
30 ,,	N_2O, 21; N, 79

In an experiment in which nitric oxide was left in contact with the hydroxide at 290° for about 40 seconds, the product contained 33% of nitrous oxide and 67% of nitrogen. It appears that, as in the case of potassium hydroxide, there is a secondary reaction in which nitrous oxide is decomposed by alkali, but this was not tested by direct experiment. In spite of this secondary reaction, it seems fairly certain that when reaction takes place at 260° a considerably larger percentage of nitrogen is formed by primary reaction than in the case of potassium hydroxide under similar conditions.

Lithium Hydroxide.—Although lithium shows affinities with magnesium rather than with the alkali metals, it was decided to include this hydroxide in the comparative study. It was prepared by double decomposition between the sulphate and baryta. The clear solution was evaporated in a vacuum; it showed a strong tendency to become supersaturated, and crystals were only obtained after several weeks. The large needle-like crystals of the monohydrate were dehydrated by heating in a current of air (hydrogen was used in later experiments). According to de Forcrand (*Compt. rend.*, 1908, **146**, 802), a very stable hydrate, $8LiOH,H_2O$, is formed above 140°, which is very difficult to dehydrate, and therefore the temperature was raised slowly so that the water should be driven out below this temperature.

It was found that even finely powdered lithia reacted extremely slowly with nitric oxide. In an experiment in which the conditions were generally similar to those employed with the alkali hydroxides at ordinary temperatures, except that the lithia was in the form of a fine powder, the pressure fell by about 5 cm. in a month, and by only 10 cm. in 4 months. It would apparently take years for the reaction to become complete. In an experiment at 280°, the reaction appeared to be practically complete in 90 hours, but the fall of pressure was much less than under similar conditions with the other alkalis. The residual gas consisted of 72% of nitrous oxide and 28% of nitrogen. The amounts of these gases were, however, considerably greater than Emich's equations (p. 2606) require for the volume of nitric oxide used. According to Oswald (*Ann. Chim.*, 1914, **1**, 97), lithium nitrite begins to decompose at 185°, and it would therefore appear that the primary reaction at higher temperatures is more complicated than at lower, and that nitrate is formed as well as nitrite (or a basic nitrite). An experiment at 265° gave a somewhat similar result (25% of nitrogen).

Calcium Hydroxide.—This was prepared by slaking lime (from marble), and heating the product to 120° in an oven to drive off excess of water. It consisted of a granular powder, not the impalpable powder given by quicklime from limestone.

A tube was almost completely filled with this substance and sealed to the apparatus. It was thought that, as the hydroxide was porous, some oxygen might be adsorbed on its surface and not completely removed by mere evacuation. Therefore, after evacuation a little nitric oxide was introduced, and after some time the tube was again evacuated, and more gas added. In spite of the large surface of the hydroxide, the reaction was very slow, as is shown by the following figures :

Duration of experiment (days)	7	23	37	73
Decrease of pressure (cm.)	6·8	13·6	16·7	22·5

After 73 days, 17·4 c.c. out of 30 c.c. of the gas remained unchanged, and after absorption of nitric oxide, the residual gas consisted of nitrous oxide with about 5% of nitrogen.

An experiment was also carried out at 115—120°, and the pressure fell by 45 cm. in 24 hours. On repetition with the same alkali, reaction was much slower, and after 67 hours the pressure had decreased by only 41 cm. The composition of the resulting gas was 77% of nitrous oxide and 13% of nitrogen in the first case, and 95% and 5% respectively in the second. Some doubt is felt as to whether this difference is real and not due to error, but there is little doubt that the proportion of nitrogen does not exceed 13%. Experiments at higher temperatures cannot be carried out owing to the instability of the hydroxide in a vacuum.

Strontium Hydroxide.—Some strontium hydroxide was prepared by mixing concentrated solutions of sodium hydroxide and strontium chloride, filtering off the crystals, washing them, and recrystallising them from hot water. The octahydrate was then dehydrated by heating in a silver boat at 100° in a stream of hydrogen till no more water was given off (according to de Forcrand, this hydrate loses all its water at 100°). A tube was filled with this substance in the finely granular condition, and after evacuation nitric oxide was introduced. The following figures give an idea of the rate of reaction at room temperature (16—23°) :

Duration of experiment (days)	18	51	73
Decrease of pressure (cm.)	6·6	14	20

No analysis was made of the products of the reaction.

Barium Hydroxide.—The baryta used was obtained by recrystallising the best available commercial material and removing the water of crystallisation by heating in a silver boat in a current of hydrogen slowly to 100° and then to a higher temperature, care being taken not to reach the m. p., *viz.*, 325°. The porous product was powdered before use. At room temperature nitric oxide reacted very slowly with this material. In one experiment after six days the pressure had decreased by 20 cm.; in another case after 26 days 40% of the gas had reacted. After absorption of unchanged gas, the residue consisted of nitrous oxide with about 3% of nitrogen. At 108—110°, reaction was complete in 5—6 hours. Two experiments gave 7·5 and 7% of nitrogen and 92·5 and 93% of nitrous oxide as the composition of the residual gas.

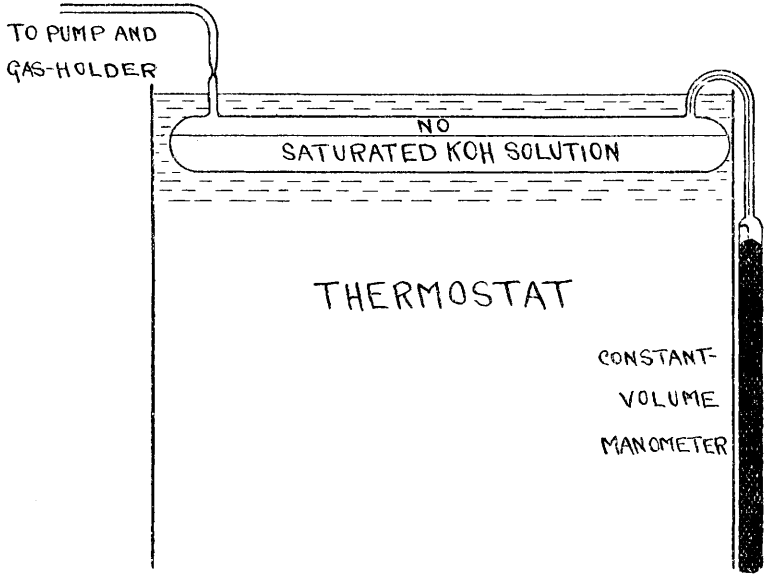
At 250° the reaction required about 1½ hours; three experiments in which the gases were analysed after 2 hours, 1 hour, and 15 minutes gave the following proportions of nitrogen: 7, 5, 5%. The temperature at which barium nitrite begins to decompose is given by Oswald (*loc. cit.*) as 235°, and it is probable that in these experiments the reaction did not follow the normal course. The reaction was then examined at a temperature well above 235°. A tube was made of such a length that the whole of the baryta that it contained was in the middle portion of the electric furnace and at 290° or slightly higher. In two experiments in which nitric oxide was left in contact for 18 hours and for 3 hours, the gaseous product, after absorption of unchanged gas, consisted of nitrous oxide with 20% and 9% of nitrogen respectively. In the first case, the pressure became constant when it had fallen by only 39 cm.; the volumes of the gaseous products were also greater than could have been derived from the volume of nitric oxide if the reaction had been according to Emich's equations. In the second case reaction was incomplete; an attempt was made to estimate the amount of nitrite formed by titration with acidified permanganate. Owing to the impossibility of getting a clear solution of the product without acidification, however, the method could not be applied with any accuracy; it appeared that nitrite had been formed, but in considerably less amount than would correspond with the gases obtained. As with lithium, the reaction appears to become more complex at higher temperatures, and nitrate is apparently formed as well as nitrite.

Sodium Carbonate.—The anhydrous substance was sealed in a tube and heated to 290°. After evacuation, 25 c.c. of nitric oxide were introduced. After 7 hours no change in pressure was observed, and the uncondensed gas pumped out contained only a trace of nitrogen; 0·77 c.c. of gas was condensed in the liquid-air spiral, and on treatment with baryta solution it yielded a white precipitate and about half of it was absorbed. These small quantities of gas may have been due to a little air not having been removed from the surface of the powdered carbonate, or they may indicate a slight reaction.

Order of Reaction.—Barr (J., 1924, **125**, 961) measured roughly the rate of decrease in volume of nitric oxide placed in contact with 50% potassium hydroxide solution at 10—22°. His results suggested that the reaction was probably of a higher order than bimolecular.

Experiments were carried out with the object of determining the order of reaction as accurately as possible. Powdered caustic potash could not be used for this purpose, for the area of active surface decreased during the reaction and so vitiated the results. By shaking a measured volume of nitrous oxide with a known volume of saturated potassium hydroxide solution in a gas-burette, it was found that this gas is practically insoluble, and so the use of the saturated solution appeared to be permissible. In order to reduce the time of reaction to a few weeks so that a thermostat may be used, it is necessary to make the area of the surface of the solution large compared with the volume of gas employed. The arrangement shown in Fig. 2 was devised with this object. A tube about $2\frac{1}{2}$ cm. in diameter and 28 cm. long was about two-thirds filled with caustic potash solution saturated at the temperature

FIG. 2.



of the thermostat (29·7°). One end of the tube was connected by as short a capillary as possible to a constant-volume manometer, and the other end to the pump and gas-holder by means of a narrow tube constricted about 1 cm. above the junction. The tube was evacuated and left over-night. It was then filled with nitric oxide and the narrow tube was sealed off at the constriction. Changes of pressure were read at intervals for three weeks. The following are some of the readings, k being the value of $1/t . \log a/(a-x)$:

t (hours).	Press. change (mm.).	$a-x$ (mm.).	$k \times 10^4$.	t (hours).	Press. change (mm.).	$a-x$ (mm.).	$k \times 10^4$.
0	0	763·3	—	119·5	321·3	334·9	29·9
4·5	18·7	738·4	32·0	168·5	389·7	243·7	29·4
10·5	43·1	705·8	32·4	222·0	442·3	173·6	29·0
30·5	113·8	611·6	31·6	335·5	507·5	86·6	28·2
54·5	185·2	516·4	31·2	432·5	537·3	50·2	27·3
80·5	247·7	433·0	30·6	504·5	553·3	46·9	24·0

The velocity coefficient corresponds more nearly to a unimolecular reaction than to one of a higher order. It therefore indicates a surface reaction or solution effect but gives no other information about the mechanism of the change.

The production of nitrous from nitric oxide by reaction with alkalis suggests the formation of a hyponitrite as a possible intermediate stage. This hypothesis has been put forward by Moser (*Z. anal. Chem.*, 1911, **50**, 401) and by Zimmermann (*Monatsh.*, 1905, **26**, 1293) to explain the reaction of nitric oxide with water, Moser giving the equation $4NO + 2H_2O = 2HNO_2 + H_2N_2O_2$. There appears, however, to be no experimental evidence in support of this theory. A number of samples of the product of the reaction of nitric oxide on alkalis were carefully tested but no indication of the presence of hyponitrite was found. (The test was carried out by adding silver nitrate solution to the alkali solution, acidifying with dilute nitric acid, and then carefully adding sodium carbonate solution : a bright yellow curdy precipitate should be formed.) According to Divers and Haga, the hyponitrites of the alkalis are moderately stable in the dry condition. Even in solution in the presence of excess of alkali they are fairly stable. It was found by the author that sodium hyponitrite solution, made strongly alkaline with sodium hydroxide, still gave the test very clearly after several months' standing, so that if a hyponitrite were formed in the reaction it is highly improbable that it would rapidly decompose either in the dry state or in strongly alkaline solution.

A more probable explanation of the reaction is suggested by the work of Briner and Wroczynski (*Compt. rend.*, 1909, **141**, 1372) and Briner and Boubnoff (*Compt. rend.*, 1913, **156**, 228), who found that, when subjected to pressure, nitric oxide yielded nitrous oxide, nitrogen trioxide, and nitrogen. They concluded that the two primary reactions, $NO = \frac{1}{2}N_2 + \frac{1}{2}O_2$ and $2NO = N_2O + \frac{1}{2}O_2$, take place simultaneously, the second predominating. By measuring the length of the column of blue liquid formed in the capillary in which the gas was compressed, they deduced that at 700 atm. the reaction was half complete in 40 minutes, whilst under 50 atm. more than a year was required before the column of blue liquid appeared. From a large number of experiments, they concluded that these reactions take place even at ordinary pressures but with extreme slowness, and that the effect of pressure in accelerating the reaction is due simply to the increase in absolute concentration of the molecules. In a subsequent paper, Briner, Biedermann, and Rothen (*J. Chim. physique*, 1926, **23**, 157) stated that even in liquid nitric oxide at atmospheric pressure these reactions occur, the blue colour of the liquid deepening in the course of a few days owing to the accumulation of trioxide.

These results have an obvious bearing on the action of nitric oxide on alkalis. That the rate of decrease of pressure corresponds to a unimolecular reaction suggests that the reaction is preceded by adsorption of the gas on the surface of the alkali. In this surface layer the concentration of nitric oxide molecules will be increased, and the rate of the reactions discovered by Briner may become appreciable. The oxygen liberated by these reactions would rapidly react with nitric oxide to give trioxide, which would at once give nitrite with the alkali.

Conclusions.

(1) The hydroxides of all the alkalis and alkaline earths react with nitric oxide at ordinary temperatures with the formation of nitrous oxide mixed with a few units % of nitrogen. The equations $4NO + 2MOH = N_2O + 2MNO_2 + H_2O$ and $6NO + 4MOH = N_2 + 4MNO_2 + 2H_2O$ ($M = $ Li, Na, K, Rb, Cs, $\frac{1}{2}$Ca, $\frac{1}{2}$Sr, $\frac{1}{2}$Ba), suggested by Emich for $M = K$, appear correctly to represent the reactions occurring.

(2) The rate of reaction of nitric oxide with the hydroxides of the alkali metals increases with the atomic weight of the element. It depends on the area of the surface of the alkali; as this area varies greatly with the state of division of the substance, it is possible to make only a very approximate comparison, but the following statement gives a rough idea of the duration of the reaction with the powdered substances at ordinary temperatures:—LiOH, several years; NaOH, several months; KOH, several days; RbOH and CsOH, several hours.

(3) Elevation of temperature increases the rate of the reaction in all the cases examined, and also increases the percentage of nitrogen in the gas produced.

(4) At about 250° the proportion of nitrogen in the gas obtained increases with the atomic weight of the element in the cases of the three alkali metals examined.

(5) Potassium hydroxide, or some impurity present even in the best samples, decomposes nitrous oxide appreciably at 250°. Cæsium hydroxide appears to behave similarly, and sodium hydroxide also at somewhat higher temperatures.

(6) Baryta and lithia react with nitric oxide at temperatures above those at which the nitrites of these elements begin to decompose. Nitrous oxide is formed, but the reactions appear to be more complex than at lower temperatures.

(7) The reactions discovered by Briner in the decomposition of nitric oxide under pressure appear to account for the action of the gas on alkalis. The following equations represent these primary reactions: $NO = \frac{1}{2}N_2 + \frac{1}{2}O_2$ and $2NO = N_2O + \frac{1}{2}O_2$. The rate of conversion of nitric into nitrous oxide corresponds approximately to a unimolecular reaction, and so these reactions appear to take place on the surface of the alkali and not in the body of the gas.

This work was carried out during a limited period of leave from India, and so had to be brought to a close before all was done that might be desired. It was regarded as a preliminary survey of the subject, and no very great quantitative accuracy is claimed.

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