XIV.—*The Decomposition of Nitric Acid by Light.*

By William Colebrook Reynolds and William Henry Taylor.

Although the decomposition of nitric acid by light has been familiar to chemists for a very long time, the nature and conditions of the reaction do not appear to have been closely examined until 1898, when Berthelot (*Compt. rend.*, 1898, **127**, 143) investigated this among several other photochemical reactions. Berthelot showed that the products of the decomposition of the acid under the influence of light are oxygen, nitrogen peroxide, and water, and that the same products are obtained when the anhydrous acid is heated in exhausted tubes to 100° in the dark for some hours. The decomposition might, therefore, be represented by the equation:

$$4HNO_3 = 2H_2O + 2N_2O_4 + O_2,$$

and Berthelot stated that the reaction was not reversible.

Berthelot dealt with the action of light on nitric acid without differentiating between its influence on the vapour and liquid respectively, and was thus probably unaware of the interesting observation which Veley and Manley (*Phil. Trans.*, 1898, **191**, 365) had made a few months earlier, that light appeared to act only on the vapour of the acid, and not on the liquid.

In the course of attempts to prepare specially pure nitric acid by distillation in a vacuum over various materials, the present authors were led to suspect that appreciable decomposition of the distillate occurred through the action of weak diffused daylight.

Examination of this point resulted in several other phenomena connected with the action of light on nitric acid being investigated, and the results obtained may be briefly summarised at the outset as follows:

(1) Veley and Manley's observation that light acts only on the vapour of nitric acid, and not on the liquid, is fairly conclusively confirmed, and a number of further conditions affecting the

decomposition of nitric acid of different strengths have been investigated.

(2) The reaction is reversible, the products of the decomposition of nitric acid by light re-combining in the dark.

(3) Anhydrous nitric acid (100 per cent.) decomposes spontaneously in the dark.

Conditions Affecting the Decomposition of Nitric Acid by Light.

When a glass tube partly filled with nitric acid is exhausted, sealed, and exposed to light, the decomposition may be followed qualitatively by the colour, intensified if necessary by the subsequent addition of various reagents, and quantitatively by the pressure of the oxygen or titration of the nitrogen peroxide by permanganate solution. When long exhausted tubes partly filled with nitric acid of concentrations up to 100 per cent., having the vapour space carefully screened from light by several folds of black silk bandages, were exposed to direct sunlight for several days, the liquid remained colourless, showing that little or no formation of nitrogen peroxide had occurred; subsequent exposure of the vapour to direct sunlight for one minute caused an appreciable amount of decomposition, as was evident from the colour of the vapour. These results, therefore, confirm Veley and Manley's observation that light acts only on the vapour. If a little carbamide is previously dissolved in the acid, the decomposition proceeds in the vapour as before, and oxygen accumulates in the vapour space, but the peroxide is absorbed and decomposed, and the liquid remains colourless.

The bright yellow colour of the solution of nitrogen peroxide in nitric acid renders the decomposition very evident when the strength of the acid is more than 65 per cent. At greater dilutions it becomes less noticeable and smaller in amount. Berthelot states that decomposition does not occur with 60 per cent. acid. Careful comparisons have shown, however, that the colour can be observed with 50 per cent. acid in strong sunlight, and if either *m*-phenylenediamine or potassium iodide is subsequently added to the exposed sample, evidence of decomposition can still be observed, even with acid of 10 per cent. strength.

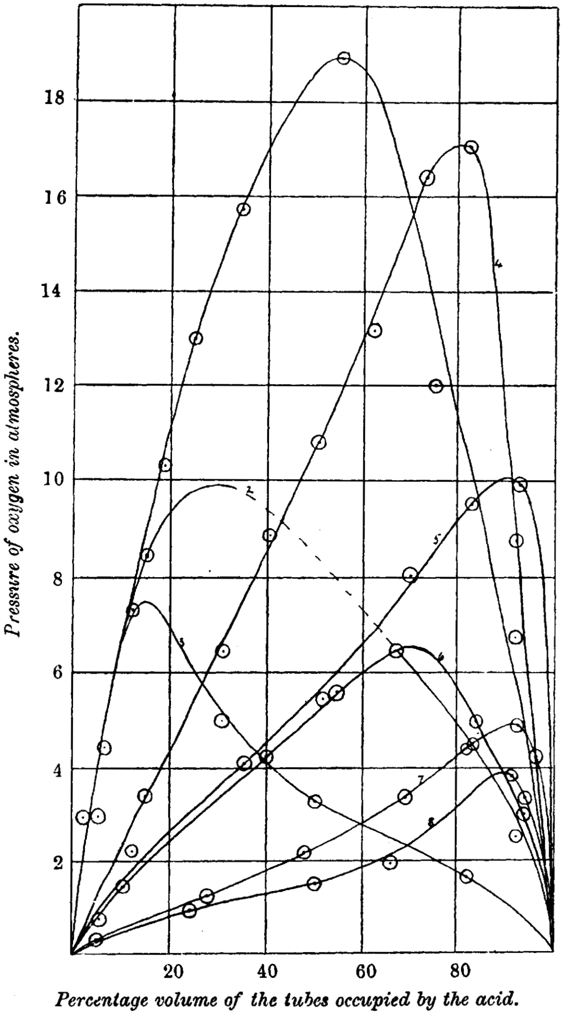
If a number of glass tubes are filled to different extents with nitric acid, and then exhausted, sealed, and exposed side by side to direct sunlight, the pressures in the tubes are very different. Under suitable conditions considerable pressures have been obtained, and it is possible to reach pressures of over eighteen atmospheres, as will be seen in Fig. 1, even in sunlight in the neighbourhood of London. These results form a striking contrast to those obtained by Berthelot, for in only one instance did he observe a pressure greater than one atmosphere. For any given strength of acid and intensity of the light, the maximum pressure is produced when the liquid occupies a certain proportion of the volume of the tube. In the accompanying diagram (Fig. 1) this has been shown graphically. The ordinates indicate the pressure of the oxygen in atmospheres at 18° over acids of 70, 80, 90, and 100 per cent. strengths, and the abscissæ the percentage volume of the tube occupied by the liquid. As the pressure observed depends on the intensity of the light, in comparative experiments for plotting a curve the exposures were made side by side for the same length of time. With weaker light the curve is similar in shape, but falls within that for light of greater intensity, but although in the case of the anhydrous acid the maximum pressure is reached when a much smaller proportion of the tube is occupied than is the case when 70 per cent. acid is present, it will be noticed that the positions of the maxima in Fig. 1 vary with the month in which the exposures were made. This is due partly to the greater intensity of the light during the summer months as compared with the spring months, and partly to the fact that in the summer, the days being longer than in the spring, the light acts for a longer time, inducing decomposition, whilst the nights being shorter recombination (which is referred to later) has less opportunity to take place. If it were possible to get brilliant sunshine continuously all the twenty-four hours, the proportion of the acid corresponding with the maxima might conceivably be nearly the same for different dilutions, namely, when the tube is rather more than nine-tenths filled.

Nitric acid sealed in vessels of very different shape and size and exposed side by side to light gives the same pressures if the acid occupies the same relative volume. The duration of the exposures before the decomposition ceases varies considerably. A tube of 70 per cent. acid one-sixth occupied takes about three to four hours in bright sunlight, but if five-sixths full will require ten to fourteen days. With stronger acid the time is much greater, 100 per cent. acid requiring twice as long an exposure.

Ordinary glass tubes were used in the experiments, but a comparison of glass and clear quartz tubes under similar conditions showed that the pressure was greater in the latter in the ratio of 7 : 10. Blue and colourless glass tubes gave identical results, but only slight decomposition occurred in an amber-coloured tube.

FIG. 1.

Decomposition of nitric acid.



1. 100 per cent. acid exposed 30 days in August and September, 1910.
2. 100 ,, ,, 25 ,, May, 1910.
3. 100 ,, ,, 20 ,, March, 1910.
4. 90 ,, ,, 30 ,, August and September, 1910.
5. 80 ,, ,, 28 ,, May, 1910.
6. 80 ,, ,, 15 ,, March, 1910.
7. 70 ,, ,, 25 ,, May, 1910.
8. 70 ,, ,, 21 ,, February, 1910.

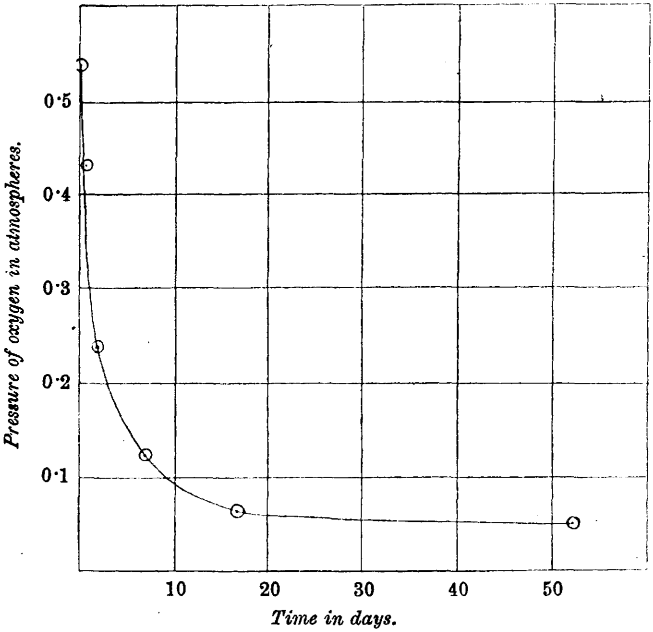
Recombination of the Decomposition Products in the Absence of Light.

Berthelot states that the decomposition is not reversible. Further investigations have shown that he was mistaken, having been misled by the slowness of the change in the reverse direction with concentrated acid, and the fact that he was not aware of the influence of the space relationships referred to above.

When a number of similar tubes of 70 per cent. acid filled to the same extent are fully exposed and then kept in a dark place, the pressure is found to have become halved in thirty-six hours, and after several weeks the acid is only slightly coloured and nearly all the oxygen absorbed.

FIG. 2.

Recombination of 70 *per cent. acid in the dark.*



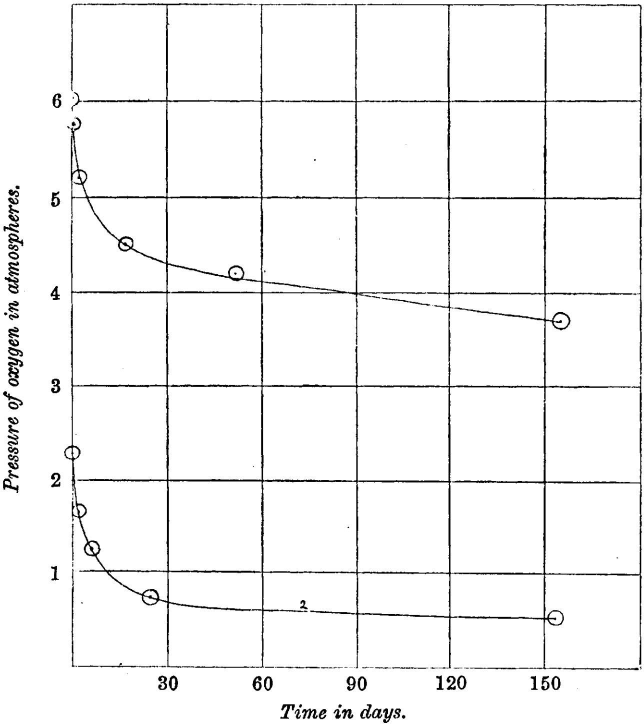
In the case of 85 per cent. acid a similar effect was observed, but the rate of recombination, like that of decomposition, is slower.

When 85 per cent. acid was decomposed in a sealed tube at 240°, the cooled product recombined at a similar rate during several weeks.

When, however, 100 per cent. acid was examined, a somewhat different behaviour was noticed; recombination slowly occurred, but even after many weeks the pressure was still more than half of the original, and no further appreciable diminution was observed. The rate of recombination is shown in the accompanying curves, Figs. 2 and 3. In the last case it will be seen that about half the possible recombination is indicated as probable.

FIG. 3.

Recombination of: 1. 100 *per cent.;* 2. 85 *per cent. acid in the dark.*



Spontaneous Decomposition of 100 *per cent. Nitric Acid in the Dark.*

Samples of 70 and 90 per cent. acids stored in sealed and exhausted tubes in the dark remained colourless after many weeks. Acid of 100 per cent. remained colourless for a few weeks, but after the lapse of twelve months was found to be bright yellow and under a pressure of 9·7 atmospheres (the acid occupied 78 per cent. of the tube).

On repeating the observation with a fresh sample, it again remained colourless for a month, but shortly afterwards commenced to decompose.

A third and fourth series confirmed the results. The pure acid at the ordinary temperature appears to undergo an "induction period" of about a month, during which no noticeable change occurs in the dark; decomposition subsequently occurs, and slowly proceeds, presumably, after many months, reaching the equilibrium, obtained in the reverse of the decomposition by light, when the same proportion of the space is occupied by the acid.

The great difference in behaviour between the anhydrous acid and concentrated aqueous solutions may be due to the presence of a trace of nitrogen pentoxide in equilibrium with the former. Saposchnikoff (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 518; compare Veley and Manley, *Proc. Roy. Soc.*, 1901, **69**, 86; *Phil. Mag.*, 1902, [vi], **3**, 118; and Trans., 1903, **83**, 1015) has shown that a measurable amount of the latter is present in the vapour over mixtures of nitric and sulphuric acids, when the sulphuric acid exceeds a certain proportion. On the other hand, mixtures of equal volumes of pure nitric and sulphuric acids have been kept for nine months in the dark. They remained quite colourless, and no oxygen was liberated.

The high pressure resulting on storing the anhydrous acid in air-tight containers for lengthy periods deserves consideration from those engaged in handling it; it may conceivably have been the cause of accidents.

Discussion of the Results.

The simplest expression in one equation for the changes produced by the action of light on nitric acid is:

$$4HNO_3 \rightleftarrows 2H_2O + 2N_2O_4 + O_2,$$

but the decomposition may possibly take place in stages, the first product being nitrous acid and oxygen, the former and the excess of nitric acid then producing water and nitrogen peroxide.

As a problem in heterogenous equilibrium, the decomposition of nitric acid by light may perhaps be compared to cases of dissociation by heat, but is complicated by several causes. Assuming that both decomposition and recombination take place in the vapour space, according to the above equation the pressure of the oxygen should vary inversely as the square of the concentration of both the water and the peroxide present in the vapour. For a given strength of acid the concentration of the water and the acid in the vapour space may be regarded as constant when more than a small proportion of acid is present. A rapid rise in the pressure of the oxygen, with increasing concentration of the acid, was therefore to be expected. Most of the peroxide dissolves in the acid. If the proportion of this latter is small, it forms a deep yellowish-brown solution; when large it is comparatively pale, and the concentration of the peroxide in the vapour space will vary accordingly. Hence, the pressure of the oxygen should increase when a large proportion of the tube is occupied by the liquid. As this only holds good to a certain point (when the maximum on the curve is reached), it would appear probable that one of the above assumptions is incorrect. The equilibrium may be one between decomposition of certain molecules only present in the vapour, and recombination with formation of ordinary nitric acid proceeding in the liquid, or both liquid and vapour. Hence, when a large proportion of acid is present, the reversal becomes relatively greater than the decomposition; hence the diminution in the pressure of oxygen. The problem is also complicated by the fact that some of the peroxide will be present in the form of the simpler molecules of NO_2, and by the irregular exposure to light during day and night, which cannot be strictly compared to a constant temperature in dissociation.

Probably experiments in which known quantities of the peroxide were added to the acid before exposure would clear up some of the uncertainties, but it is not the intention of the authors to proceed further in this direction.

EXPERIMENTAL.

Preparation of the Acid.

Commercial pure acid (D 1·42) was freed from nitrogen peroxide by treatment with carbamide, chromic acid, or potassium permanganate, and was distilled in a vacuum in artificial light, or it was mixed with its own volume of concentrated sulphuric acid just before the distillation, when the anhydrous acid was desired. The three reagents named appear to be equally effective in purifying the acid, and no difference could be detected in the product.

The glass distilling flask, condenser, and receiver were fused together. The inlet to the flask, consisting of a thistle funnel with 1 mm. cross-bore tap in the stem, was fused through the top of the flask. The outlet from the receiver consisted of a long-drawn-out capillary, the tip of which was broken and re-sealed each time a fraction was removed. Although the flask contained scrap platinum, distillation usually proceeded without ebullition when the flask was immersed in warm water.

It was found impossible to remove nitrogen peroxide from nitric acid by fractionation; its removal must therefore be effected as above. Its presence is conveniently detected by diluting the sample to 10 per cent. and adding a few drops of potassium iodide or *m*-phenylenediamine, which should scarcely colour the sample. Exposure of concentrated colourless acid to diffused daylight or near a Nernst lamp for one hour induces a noticeable decomposition.

Examination of the Decomposition Products.

Berthelot measured the decomposition by opening the vessel over water, and determining the volume of oxygen. The present authors find that there is only one way in which this can be done without introducing large errors. If the tube is under diminished pressure and the water rushes up through the acid, causing admixture, rapid recombination of the products occurs, the extent depending on the time and shaking, but three-fourths of the whole will readily and quickly re-unite when a flask is used.

Long, narrow tubes were therefore employed; after exposure they were held vertically, tip upwards, completely immersed in a tank of water, under a large glass funnel leading into a graduated glass cylinder; if the tube is under pressure, when the tip is fractured the excess of gas is expelled and collected, and no water enters; if under less than one atmosphere pressure, the water merely forms a layer on the top of the heavier acid without appreciable admixture, and recombination, therefore, does not take place.

Another method employed with tubes under diminished pressure is to open them over boiled and cooled nitric acid of the same strength; here no recombination occurs, and correct results are obtained. The accuracy of the results was tested by connecting an exposed flask by pressure tubing to a column of mercury at barometric height, noticing the fall on breaking the tip, and then pumping out the gas with a Sprengel pump. Two determinations of the density of the gas thus obtained gave 15·7 and 16·1.

A number of analyses of the gases obtained were made after collecting them over water as above by treating them with alkaline pyrogallate. In the case of 70 per cent. acid, from 97 to 98 per cent. of oxygen was indicated, whilst 100 per cent. acid gave about 99 per cent. Apparently a little nitrogen is formed by some secondary change in the former case, although it is extremely difficult to free the acid from dissolved nitrogen, even after violent shaking with broken glass in a vacuum. The nitrogen peroxide was determined by pouring the nitric acid solution into a large volume of dilute permanganate; after remaining half-an-hour it was titrated, when it always corresponded with the oxygen collected.

Conditions Affecting the Decomposition.

For comparison a series of tubes 12 inches long, closed at one end, and about 10 c.c. capacity were drawn out at the other end, calibrated, and filled to varying extents with the sample. They were exhausted while remaining in ice and water, sealed, and exposed whilst lying side by side on a sloping board on an open roof facing south. When no further change had been observed during several days, the tubes were removed at mid-day on a bright day (that is, before recombination had occurred), and were at once examined. The results are incorporated in the curves in Fig. 1, which are not strictly accurate when a very small proportion of concentrated acid is present owing to appreciable dilution of the acid by the water formed. The true curves should, at the left hand side, be somewhat outside those plotted.

Recombination of the Products in the Dark.

A number of similar tubes were one-tenth filled with the sample of acid, evacuated, sealed, and exposed side by side as before. When no further change occurred, they were withdrawn and placed in the dark; one of them was at once examined, and the others in turn after various periods of seclusion. The rate and extent of recombination in the case of 70, 85, and 100 per cent. acid is shown in the curves in Figs. 2 and 3 (pp. 135, 136).

It was found that many hours' violent agitation by attachment to a shaking arrangement did not affect the rate of recombination.

Spontaneous Decomposition of the Anhydrous Acid.

Three tubes half filled with the acid were kept in the dark for seven days. One was examined and found colourless, and no oxygen was present. After four weeks the two remaining tubes were colourless; after twelve weeks they were light yellow. After eighteen weeks one was examined; it was under a pressure of 0·67 atmosphere of oxygen. The other was examined after thirty-six weeks, and was found to be under a pressure of 2·66 atmospheres of oxygen.

Two similar tubes were one-fourth filled with the same acid simultaneously with the above. One of them after eighteen weeks was under 0·28 atmosphere pressure; the other, after thirty-six weeks, was under 1·05 atmospheres.

It would appear not unlikely that concentrated solutions of the acid would show very slight decomposition if kept for some years in the dark; the curves for the recombination in Fig. 2 seem to indicate that it would never be quite complete with acids of 70 per cent. strength and upwards.

Wellcome Chemical Works,
Dartford, Kent.