GENERATION OF NO_2 BY LEAD NITRATE PYROLYSIS: NEVER DO MODIFICATIONS *A PRIMA VISTA*

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Abstract. Generation of nitrogen dioxide is a well-known demonstration/experiment, usually performed by pyrolysis of $Pb(NO_3)_2$. In order to prevent obstructing the glass tubes or the test-tube where NO_2 is generated, one may safely use a homogenized mixture of lead(II) nitrate and dry sand. Aesthetically it is not quite appealing, so during the same lesson a colleague experimenter decided to change the standard approach and to use table salt (sodium chloride) instead of sand. However, the result of the experiment turned to be a flaw! This appears to be one more proof for the correctness of the general experimenter's philosophy: never improvise if you do not know the outcome.

Keywords: nitrogen dioxide; pyrolysis; lead(II) nitrate; sodium chloride; metathesis reaction

Introduction

There are several methods for generation of NO_2 (N_2O_4) in laboratory: a) Pyrolysis of lead(II) nitrate (nitrates of other heavy metals may also be used) (G. Fowles 1959), b) Elimination of water from HNO_3 [1)] and c) reaction of concentrated nitric acid and copper [2)]. However, the first method gives NO_2 practically clean of other nitrogen oxides but mixed with oxygen. It may be separated from the oxygen gas in the following way (see Fig. 1, (Petruševski & Najdoski 2000)).

How it goes routinely

The test-tube in Fig. 1 (2) is filled with homogenized mixture of powered lead(II) nitrate and sand (1 : 1) see 2 a. Upon moderate heating (≈ 300 °C) the pyrolysis is fast enough. Dark brown "fumes" escape from the test-tube through tube 5 and enter the micro-wash-bottle (7) placed in a Dewar flask (6) filled with ice and salt mixture (used as a coolant). The NO_2 readily condenses as light yellow liquid (N_2O_4 with traces of NO_2), while the oxygen passes to the pneumatic trough (9). Any NO_2 impurities are dissolved in water and pure oxygen is collected in the cylinder (8). The chemical reactions equations are as follows:

$$Pb(NO_3)_2(s) \rightarrow PbO(s) + 2NO_2(g) + O_2(g) \quad (1)$$
$$2NO_2(\text{g, redishbrown}) \rightleftharpoons N_2O_4(\text{l, yellowish}) \quad (2)$$
$$PbO(\text{s, yellow}) + SiO_2(\text{s, grey}) \rightarrow PbSiO_3(\text{l, greyorange}) \quad (3)$$

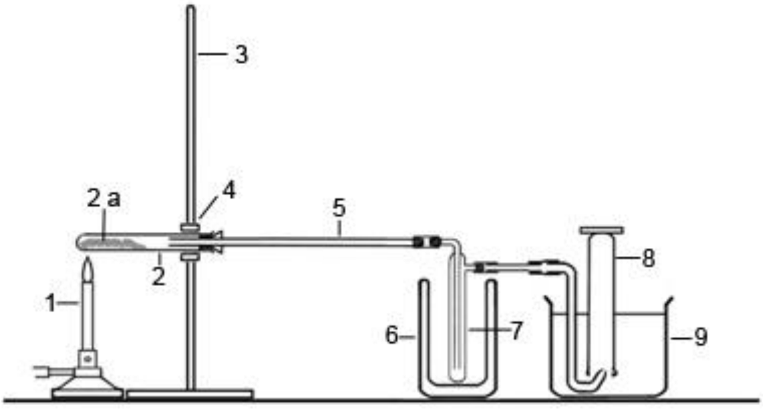

Figure 1. Generation of NO_2 by pyrolysis: 1 – Bunsen burner; 2 – test-tube; 2a – mixture of $Pb(NO_3)_2$ and sand; 3 – metal stand; 4 – clamp; 5 – glass tube; 6 – Dewar flask (coolant is not shown); 7 – micro-wash-bottle; 8 – graduated cylinder; 9 – pneumatic trough filled with water

Everything works perfectly, except for the colour in the test-tube which, at the end of the experiment, is grayishorange, due to the product of the chemical reaction between PbO and the sand, giving molten (at first) and then solid Pb-glass.

The modification

As the colour of the product in the test-tube is not quite appealing in the end (it looks like some dirt is present), my younger colleague and assistant decided that we should improvise (as we never tried it earlier) and substitute the sand with table salt ('clean and white'). I was worried and objected that it is against the basic laboratory rule:

– Never try anything during the lesson, unless you checked it before! Remember that? – I tried to calm down his enthusiastic excitement.
– Why? What could possibly go wrong? – I was immediately opposed by his retort.

I could not give a chemically sound reason why not to implement a novelty (in this case *a prima vista*) so I agreed, albeit unwillingly. The mixture of lead(II) nitrate and salt (1 : 1) was homogenized and put in the test-tube. Long time heating brought no result. No brown "fumes". The instant I saw a colourless liquid forms in the heated test-tube I got it what is wrong. After a while, practically all of the substance in the test-tube was in liquid form. I asked that we stop the experiment and repeat it according to our usual routine.

What went wrong?

In a finely powdered mixture of lead(II) nitrate and table salt, upon heating – it became obvious – a solid-state chemical reaction started:

$$Pb(NO_3)_2(s) + 2NaCl(s) = PbCl_2(s) + 2NaNO_3(s) \quad (4)$$

One of the products (sodium nitrate) has a low-melting temperature (308 °C, [3)]) so it melts first. At still higher temperature (380 °C, [3)]) a pyrolysis of $NaNO_3$ is possible:

$$2NaNO_3(l) \rightarrow 2NaNO_2(s) + O_2(g) \quad (5)$$

In the course of the nitrate decomposition, the product (sodium nitrite) might decompose too, probably at the instant it is formed, as 320 °C is mentioned as its decomposition temperature [4)]:

$$2NaNO_2(l) = Na_2O(s) + 2NO(g) + ½O_2 \quad (6)$$

After a while (at 501 °C [5)]) the $PbCl_2$ melts too.

Other reactions are possible too, but due to mutual disagreement of various authors will not be discussed here.

The bottom of line

On another occasion (Najdoski & Petruševski 2002) we wrote: “We tried to offer a large number of original (i.e. modified/adapted) experiments. We insisted on modifications always when it deemed possible – even in such anthological experiments as is reduction of copper(II) oxide with hydrogen gas. We do believe it is good to have, all the time, a possibility to show the experimenters that nothing has to be done exactly as given in the literature (including this book). Of course, every modification/alteration must be carefully checked/completed prior to its demonstration before a class of pupils/students, as mentioned in the first book…”. We wrote the previous on the basis of our rich experience, as well as the experience of others.

Obviously, we were wrong in our belief that nothing bad can happen with this improvisation, although (if we were clever enough) we could stick to *credo quia impossibile est*, because it indeed appeared to be possible! Good school for both young and experienced ones…

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NOTES

1. https://en.wikipedia.org/wiki/Nitrogen_dioxide, checked April 25, 2021.
2. https://www.angelo.edu/faculty/kboudrea/demos/copper_HNO3/Cu_HNO3.htm,checked June 1, 2021.
3. https://pubchem.ncbi.nlm.nih.gov/compound/Sodium-nitrate, checked June 1, 2021.
4. https://pubchem.ncbi.nlm.nih.gov/compound/Sodium-nitrite#section=Melting-Point, checked June 1, 2021.
5. https://pubchem.ncbi.nlm.nih.gov/compound/Lead-chloride, checked June 1, 2021.

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