

THE ALUMINUM AND BROMINE REACTION REVISITED: ON THE HAZARD DURING WASTE DISPOSAL*

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Abstract

A brief explanation for the absence of reaction between metallic sodium and liquid bromine is offered. A safer variant is proposed for performing the well-known demonstration of aluminum and bromine. An explanation for the increasing induction period for the reaction is given. A serious hazard exists during the disposal of the waste (AlBr_3 dissolved in excess bromine), unless the instructor is familiar with the properties of the products. Attention is paid to this hazard and a possible way for minimizing the risk in waste disposal is pointed out. [AJCE, 1(2), July 2011]

* This work is dedicated to Gligor Jovanovski, member of the Macedonian Academy of Sciences and Arts and a leader of the structural chemistry in Macedonia, on the occasion of his 65th birthday.

INTRODUCTION

The reaction of metallic aluminum and liquid bromine is known for many decades (1-8). It is one of those spectacular chemical reactions that always attract students' attention. Another spectacular reaction of a similar type (albeit much more dangerous) is the reaction of potassium metal and liquid bromine (9, 10). The analogous reaction with sodium and bromine usually fails (11), unless the bromine contains some water dissolved. So, at the very beginning, a question (that, to the best of our knowledge, has not been answered elsewhere) seems to urge an answer:

Why does the reaction of aluminum and bromine occur at room temperature, but the analogous reaction of the much more reactive sodium does not?

In the light that the reaction with potassium (9) proceeds explosively, and the commonly invoked mechanism is usually called 'harpoon mechanism' (11), it really seems important to explain the 'inertness' of sodium to bromine vis-à-vis both potassium and aluminum. In our opinion, one should keep in mind several important facts:

- 1) The bromides of the alkali metals are ionic compounds.
- 2) AlBr_3 is a covalent compound (by the way, Al_2Br_6 is a much more informative formula).
- 3) Potassium is a much more reactive metal than sodium.

Taking the above into consideration, one could say that the reaction of potassium is possible due to the fact that it is extremely vigorous (usually, during performing this demonstration, part of the metal is propelled from the reaction system to the surroundings). The reaction of the much less active aluminum is possible by the

fact that AlBr_3 (being a covalent and, due to its symmetry, non-polar compound) is soluble in bromine. So, once the oxide covering aluminum (which is so to say an obstacle to instantaneous reaction of aluminum and bromine) is gone, aluminum vigorously reacts with bromine, the product being continuously dissolved in the excess bromine. This appears to be impossible with sodium. The reaction is not vigorous enough. It indeed is instantaneous, but here the NaBr crust that forms on the surface of sodium isolates the sodium interior from the action of bromine, so the reaction ceases momentarily.

We start the present contribution by performing this well-known demonstration of the reaction between Al and Br_2 . Then we proceed to the waste disposal, that is actually the truly novel and important part of this work.

EXPERIMENTAL

In order to diminish the hazard (for both the instructor and the audience) during performing this demonstration, we used the experimental setup presented in Fig. 1. This demonstration is to be performed only in a hood.

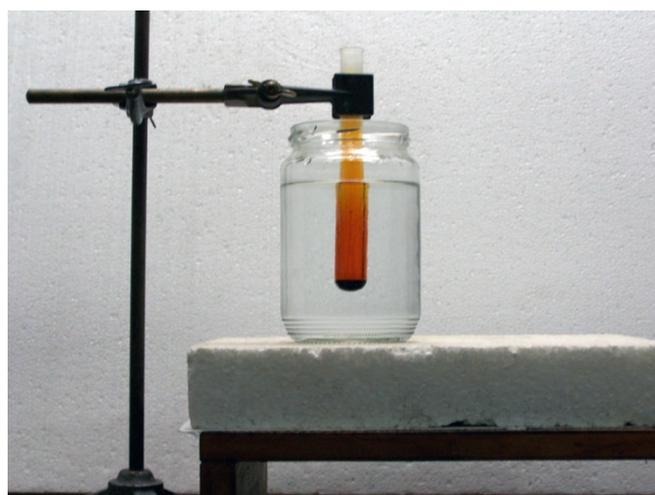


Figure 1: Experimental setup for the reaction of aluminum and bromine

A test tube (size $16 \text{ mm} \times 160 \text{ mm}$) is clamped and the clamp is fastened on a stand. For safety reasons, the test tube is placed in a large jar, filled with water (for

best results use deionized water; tap water should be avoided to prevent formation of bubbles on the test tube). About 1 mL of liquid bromine (**Caution: wear face shield and appropriate gloves**) is placed in the test tube, using a glass pipette. The purpose of the jar is to prevent spilling of the toxic and highly corrosive bromine, if the test tube cracks by accident (there is always a risk that the case might happen). Furthermore, the jar used filled with water enhances the visibility, acting as a cylindrical lens.

Prepare (immediately before the demonstration) few pieces of aluminum wire ($\approx 1.5\text{--}2$ mm thick ≈ 1 cm long). Using a scalpel or a sharp razor, quickly scrap the surface of the aluminum wire, to free the surface of the oxide that is always present. By means of forceps add the pieces (one at a time, **never** more than 3 in a row) to the test tube containing bromine.

After this part of the demonstration is over, the setup presented in Figure 2 was used to add some water to the product (AlBr_3 dissolved in the excess of bromine), before 'neutralizing' the bromine with $\text{Na}_2\text{S}_2\text{O}_3$ solution (have some 50 mL of this solution with a weight ratio of ≈ 10 %w/w). Actually, the inversely mounted micro-wash-bottle to the right of the picture together with the stand and the rubber pump is the safety dropper, the construction of which could be found elsewhere (12).

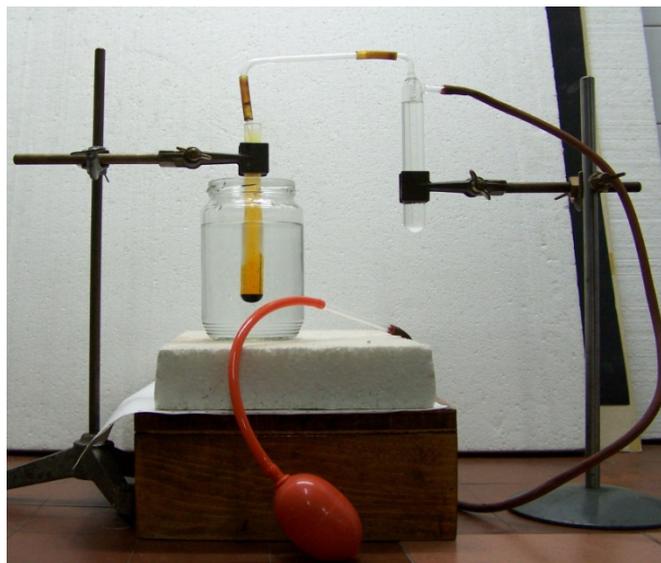


Figure 2: Adding water to the reaction product using the safety dropper.

RESULTS

The results of the first part of the experiment are well-known. Few seconds after adding the piece of aluminum to the bromine (this is the induction period), a hissing sound is emitted from the test tube and soon the glowing **molten** aluminum appears floating and moving over the surface of the bromine (the density of Al is lower than that of Br₂). Some sparkling often occurs, so it is necessary that, once the hissing sound is heard, the **door of the hood be lowered and the ventilation is put on**. The brilliance glow of the aluminum usually lasts some 30 seconds (depending on the size of the piece). If a second piece is added, it may take **more than a minute** for the reaction to occur again. Up to 10 minutes may be necessary for the third piece to start reacting (this extension of the induction period is the reason for restricting the number of pieces to no more than three). A video clip of this part is available upon request from the authors or from the Editor-in Chief of the African Journal of Chemical Education.

When this part of the demonstration is over, put the aspirator off, open the sliding door of the hood and only add the safety dropper to the existing setup from the

right hand side. Slide back the door of the hood, keeping in mind to take the rubber pump out of the hood. In this way, the pump may be safely manipulated.

By pressing the pump, few milliliters of water are added to the product.

Attention: an extremely vigorous reaction (almost an explosion) occurs. Lots of bromine vapor is emitted from the test tube. Immediately put the aspirator on and continue to add water to the test tube, till it is filled to about one half. A video clip of this part of the demonstration is also available upon request.

Add the content of the test tube to a beaker containing about 30 mL of sodium thiosulfate and fill the emptied test tube with the remaining about 20 mL. After some 5 minutes all elemental bromine is converted to bromide and the content of the vessels may be safely disposed under the drain.

DISCUSSION

We shall begin the discussion with the explanation about the longer and longer induction period (on going from the first, to the second and possibly the third piece of aluminum). The induction period is, we believe, needed for (a) complete removal of the oxide covering of the pieces and (b) for the reaction to reach the point where the aluminum piece starts glowing. For the latter, it seems obvious that a feedback is important. The reaction starts relatively slowly, some heat is being released; this increases the rate which in turn releases more heat and so on. In the beginning there are practically pure reactants (aluminum and bromine) and only traces of Al^{3+} and Br^- are present (this notation might be used for simplicity; however, keeping in mind that AlBr_3 is a molecular substance, it would be better to speak about aluminum with oxidation number +3 and bromine with oxidation number -1). That is, the redox potentials of bromine and aluminum are proportional to

$$E_{\text{ox}}(\text{Br}) \propto \ln \frac{[\text{Br}_2]}{[\text{Br}^-]} \qquad E_{\text{red}}(\text{Al}) \propto \ln \frac{[\text{Al}^{3+}]}{[\text{Al}]}$$

meaning that, at the very beginning, the first one is large and positive, and the second is large and negative. Naturally, the reaction proceeds at the highest possible rate. The addition of the second piece requires longer induction period, because the quantities of bromine (-1) and aluminum (+3) are now much larger than they were (only traces could be present in the beginning), and the corresponding absolute values for the redox potentials are much smaller. The same reasoning holds for the third piece, as the quantities of Al(+3) and Br(-1) are even larger. This explanation is missing in the literature where this demonstration is described.

On the other hand, Shakhshiri (1) mentions that "...fumes of bromine, hydrogen bromide, and aluminium bromide are produced by this reaction...". It is not clear what might the source of HBr be, unless the bromine that they used was actually a sample containing water.

The extremely vigorous reaction of the product (containing excess bromine) and water must definitely be explained. As mentioned in the introduction, the product (AlBr_3 or Al_2Br_6) is dissolved in excess of bromine. AlBr_3 is known as a very strong Lewis acid. Water, on the other hand, is a Lewis base. Adding water to the mixture of AlBr_3 and Br_2 is equivalent to neutralization. During this neutralization the temperature of the mixture in the test tube can sharply increase to almost 100 °C. The latter temperature is well above the temperature of boiling (57 °C) of liquid bromine. Under these conditions the excess bromine starts to boil abruptly, this is the cause of the extremely vigorous reaction taking place in the test tube. **This, however, is not mentioned in the above references (1-3), where the instructor is advised to add either water to the product or a solution of sodium thiosulfate.** Thus, the existing

literature about this demonstration includes high hazard and it is almost a miracle that no accidents have been reported so far during performing it.

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