

Reaction of Copper with Fuming Nitric Acid: A Novel Lecture Experiment in Passivation

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Received December 15, 2004. Accepted May 12, 2005.

Abstract: Copper is known to react slowly with diluted nitric acid, giving NO, and very vigorously with concentrated ($\approx 70\%$) nitric acid, the product being NO₂. Surprisingly, when copper is brought into contact with pure nitric acid, there is no reaction at all! On dilution of the acid with water, a vigorous reaction occurs producing a great deal of NO₂. We present here a lecture experiment on passivation, which provides an opportunity to discuss the nature of the protective covering that forms and the reasons it is destroyed under dilution.

Introduction

Nitric acid is highly oxidizing and, as such, it sometimes appears to be a very peculiar acid. It is one of only a few acids that, irrespectively of their concentration, do not liberate hydrogen when acting on most metals. Some other (a bit less familiar) acids having the same property are nitrous acid, HNO₂, and hydrogen azide, HN₃. All of these acids contain nitrogen. Magnesium is one exception in that it does react with very dilute HNO₃ to give hydrogen [1].

HNO₃ reacts with metals that are both above and below hydrogen in the electrochemical series of elements. Thus, copper, silver, and mercury all react with nitric acid, the composition of the product depending mainly on the acid concentration. If sufficiently diluted nitric acid is used, the reaction is relatively slow and the product is mainly NO (as well as water and the nitrate salt of the metal used). With commercially available concentrated acid ($\approx 70\%$), the reaction (at least the reaction with copper) is a vigorous one, and NO₂ is liberated in large quantity. Nitric acid of intermediate concentration yields a mixture of NO and NO₂ at a moderate reaction rate.

Given the above, what is expected to happen if fuming nitric acid reacts with copper metal? Knowing that the reaction rate increases with acid concentration, we might be concerned that a furious reaction, perhaps involving the spraying of nitric acid out of the reaction vessel, or something even more dangerous, might occur. We decided to give it a try, taking all proper precautions.

Experimental

Preparation of Pure Nitric Acid. Prior to performing this demonstration, it was necessary to synthesize nitric acid of high purity. The procedure described by Fowles [2] was slightly modified. Concentrated sulfuric acid and dry KNO₃ were put in a retort, so that the retort neck dispensed into a test tube cooled in a beaker with ice. Upon gentle heating, the retort filled with brown fumes (NO₂), and a pale-yellow liquid (i.e., pure nitric acid, the color comes from dissolved NO₂) was collected in the test tube (see Figure 1). If not used immediately, the liquid should be stored in a glass-stoppered bottle.

The Demonstration. Because the effect of the action of pure nitric acid on copper was unknown to the students, we used a safety spoon that we designed some time ago [3]. This device enables the safe addition of solid reagents (in this case, a copper grain) to a liquid when a vigorous reaction is likely to occur. To further ensure safe conditions, the reaction was performed in a hood. A few milliliters of pure, pale-yellow HNO₃ was placed in a test tube. Then, we carefully added a small copper grain to the acid. Surprisingly, absolutely nothing happened (see Figure 2)!

The students were surprised, but convinced that no reaction occurred. We then carefully added a few milliliters of distilled water to the test tube using a small wash bottle or safety dropper [4]. A vigorous reaction occurred instantaneously (Figure 3) and large quantities of NO₂ were generated. After a minute or so, the reaction ceased (Figure 4).

Safety Precautions. Nitric acid and sulfuric acid are very corrosive! Nitric acid is a very strong oxidizer. A face shield and gloves should be worn at all times during the synthesis and performance of the demonstration. The demonstration must be performed in a hood or suitable, safe modification for its presentation on a benchtop.

Discussion

If students are familiar with the basic fact concerning reaction rate as a function of HNO₃ concentration, the results of the demonstration surprise them. The instructor should remind them that concentrated acids, like HNO₃, in particular, are known to show the effect of passivation on certain metals [5]. Passivation usually results from the formation of a thin oxide film on the metal surface, which protects the metal from further action of the acid.

There are two different possibilities for the nature of the protective covering: it may be (as in most cases) a thin oxide film (i.e., CuO) or it may be Cu(NO₃)₂, which is only slightly soluble in fuming nitric acid.

To determine the nature of the covering, we performed four additional experiments. The first was a chemical reaction of copper with nitric acid of high concentration (weight ratio $\approx 85\text{--}90\%$, which is substantially higher than in the commercially concentrated acid, albeit still diluted). The reaction started rather slowly and soon ceased! This seemed to agree with the assumption that copper(II) nitrate is not very



Figure 1. Synthesis of pure nitric acid.

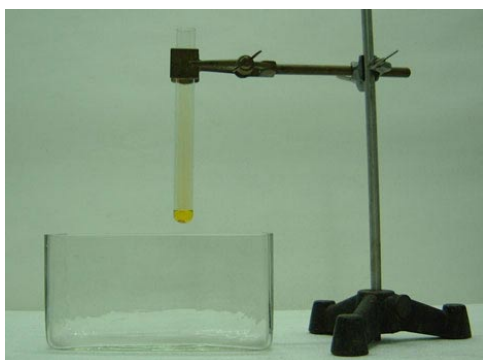


Figure 2. Test tube with pure nitric acid and a copper grain added—no reaction.

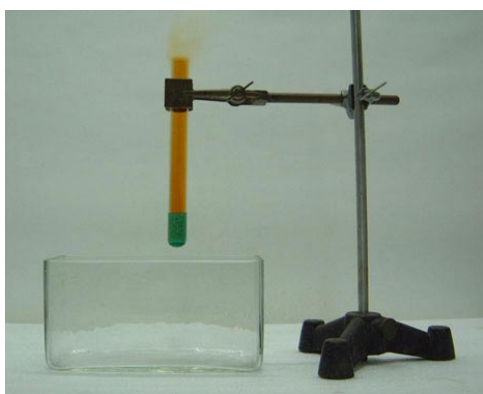


Figure 3. Copper in fuming nitric acid—upon dilution, a vigorous reaction occurs.

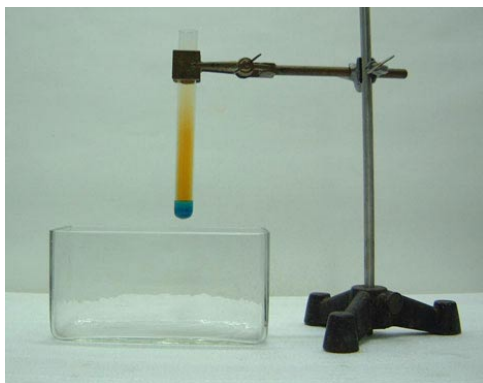


Figure 4. After about 1 min, the reaction ceases.

soluble in highly concentrated nitric acid; once the solution becomes saturated the reaction ceases.

The second experiment was the reactions of finely powdered copper(II) oxide with fuming, commercially concentrated, and diluted (1:1) nitric acid. The same quantity of CuO (0.200 g) was used in all three cases, the volume of the acids also being the same (2 mL). The test tubes were shaken and put in a test-tube rack to stand. In less than a minute, the CuO powder in the fuming HNO₃ behaves as if sintered. This could be explained as a result of the formation of copper(II) nitrate on the surface of each microscopic CuO grain, and this nitrate (sparingly soluble in fuming HNO₃) seems to “glue” the grains together. The same happens with CuO in concentrated HNO₃. After about 1 hour, the “glue” in this case being, most probably, Cu(NO₃)₂•3H₂O. The test tubes were then sealed [6] and photographed to obtain Figure 5a.

Practically all the CuO was dissolved in the diluted HNO₃, a sizeable part of it was dissolved in the concentrated acid (judged from the color intensity of the solution), but only a small part was dissolved in the fuming HNO₃ [7]. After several days, white microcrystals were detected in the test tube with fuming nitric acid, both on the top of the black CuO and on the glass walls (Figure 5b). It is logical to assume that the white substance is Cu(NO₃)₂. In this respect, it resembles copper(II) sulfate (blue when hydrated and white when dehydrated).

To confirm the above observations, a third experiment was performed. This experiment was an attempt to dissolve Cu(NO₃)₂•3H₂O in fuming, concentrated, and diluted HNO₃. As occurred in the previous experiments, the same quantity (mass) of Cu(NO₃)₂•3H₂O was placed in a test tube with equal volumes of fuming, concentrated, and diluted nitric acid. The test tubes were sealed, shaken, and left to stand. The results are shown in Figure 6a. It could be concluded that Cu(NO₃)₂•3H₂O is practically insoluble in pure nitric acid, the latest experiment giving direct evidence for this conclusion.

Again, after several days of standing, the situation changes. White spots develop on the blue Cu(NO₃)₂•3H₂O crystals placed in fuming nitric acid. These spots could easily be identified as Cu(NO₃)₂, obtained by the dehydration of Cu(NO₃)₂•3H₂O in the presence of fuming HNO₃ [8]. A subsequent step, mixing fuming nitric acid and water, showed that, indeed, the mixture become very hot, again resembling the action of concentrated sulfuric acid and water.

In our final experiment, a copper grain was added to fuming nitric acid containing traces of water (to hasten the process) and was left in a specially prepared test tube [9] for several days. During this period, the grain became covered with a white crust. After careful shaking, the test-tube was photographed (Figure 7).

Many white microcrystals appear, both on the surface of the grain and on the bottom of the test tube. Also, the surface of the metal grain appears dark, possibly due to CuO. The white substance, we believe, is copper(II) nitrate. Part of the white microcrystals were separated from the liquor and were dissolved in distilled water. They dissolved instantaneously but, as the amount of substance was very small, the solution remained colorless. Upon treating with aqueous ammonia, however, the blue color that developed indicated that they crystals were indeed a salt of copper.

Water was added to this test tube in the same way as in the first demonstration (see Figures 2–4). After a few seconds, large quantities of NO₂ gas were generated.

Taking all the experimental results into consideration and assuming that the dark color on the surface of the metal grain in Figure 7 is indeed due to CuO, the following explanation for

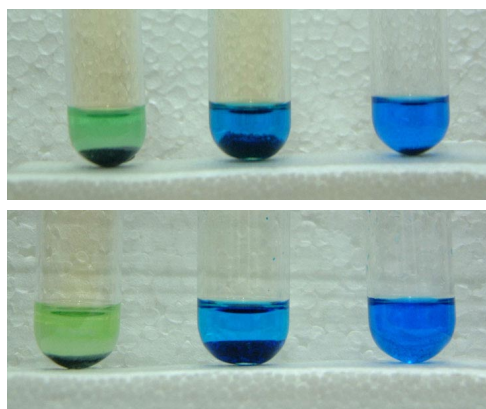


Figure 5. Reaction of CuO with nitric acid, left to right: fuming, concentrated, and diluted HNO₃ (top) 1 hour and (bottom) several days after mixing the reagents.

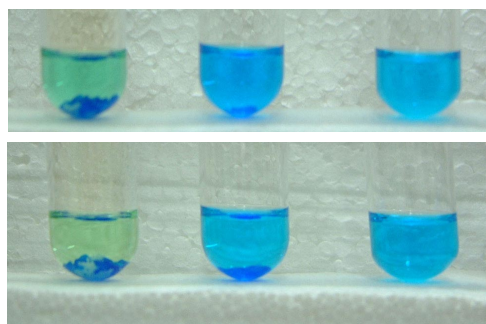


Figure 6. Dissolving Cu(NO₃)₂·3H₂O in nitric acid, left to right: fuming, concentrated, and diluted HNO₃ (top) 1 hour and (bottom) several days after mixing the reagents. White spots are due to formation of Cu(NO₃)₂.



Figure 7. Copper grain in fuming nitric acid containing traces of water (photographed after several days). The white powder is Cu(NO₃)₂ and the dark covering on the grain is possibly CuO.

the observations is given: Upon addition of copper to fuming nitric acid, a thin CuO film is formed (as a result of the very strong oxidizing agent, pure HNO₃). This film dissolves very slowly in the acid because of the formation of sparingly soluble Cu(NO₃)₂. (Traces of water seem to speed up the process significantly.) Consequently, it takes a long time to obtain visible quantities of Cu(NO₃)₂. Upon dilution with water, the copper(II) nitrate is instantaneously dissolved and the reaction proceeds at a high rate. Heating the reaction mixture further accelerates the process and also increases the solubility of the salt in the reaction mixture.

An alternative explanation based on the small number of free protons, due to suppressed dissociation, in the pure acid could be offered. The number of free protons is much larger in the commercially concentrated and the diluted acids; therefore, their reaction rate with the passivation covering (corrosion) would be expected to be much faster. Although this explanation is acceptable from a chemical point of view, we feel that, in the light of all the experimental results presented above, the demonstrated low solubility of Cu(NO₃)₂ in pure nitric acid is the primary reason for the passivation that occurs here.

Conclusion

This is an interesting demonstration with an unexpected result. It may be used to demonstrate the processes of passivation, but it also complements existing demonstrations of the chemistry of nitric acid and nitrogen dioxide.

References and Notes

1. Fowles, G. *Lecture Experiments in Chemistry*, 5th ed.; G. Bell & Sons Ltd.: London, 1959; pp 159.
2. Fowles, G. *Lecture Experiments in Chemistry*, 5th ed.; G. Bell & Sons Ltd.: London, 1959; pp. 156–157.
3. Petruševski, V. M., Najdoski, M. Ž. *Chem. Educator* **2002**, *7*, 81–83; DOI 10.1333/s00897020546a.
4. Petruševski, V. M., Najdoski, M. Ž. *Chem. Educator* **2002**, *7*, 220–222; DOI 10.1333/s00897020583a.
5. Wiberg, E. *Anorganska kemija*; Školska knjiga: Zagreb, 1967; p 273.
6. Sealing is important to prevent mass change of the reaction mixtures due to loss of water (in the test tube with diluted HNO₃) or loss of nitrogen oxides (in the test tube with fuming HNO₃).
7. The color is greenish, probably as a result of a combination of the pale-blue color of the traces of dissolved salt and the paleyellow color of the acid. Another reason for the color difference might be the absence of water in the system; hence, no aqua complexes are formed.
8. The effect with fuming HNO₃ seems to be less pronounced than with concentrated H₂SO₄. A large crystal of CuSO₄·5H₂O, if put in H₂SO₄, loses its color within an hour or so and turns into white CuSO₄ powder. The equivalent process with Cu(NO₃)₂·3H₂O and fuming HNO₃ takes much more time.
9. The test tube has a ground mouth and a glass stopper that match. There is a tiny pinhole in the stopper, which prevents the increase of pressure in the tube (e.g., during gas evolution).