

- *Учебни опити и демонстрации* •
- *Teaching Chemical Experiment* •

REACTION OF ALUMINIUM WITH DILUTED NITRIC ACID CONTAINING DISSOLVED SODIUM CHLORIDE: ON THE NATURE OF THE GASEOUS PRODUCTS

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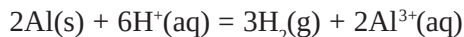
Abstract. Metallic aluminium was found not to react with either concentrated or diluted nitric acid. Providing the diluted acid contains dissolved sodium chloride and traces of copper(II) cations, a vigorous reaction occurs. The product is basically nitrous oxide (possibly containing some elemental hydrogen and nitrogen gases), and was identified by its IR spectrum.

Keywords: nitrous oxide, IR spectrum of, nitric acid, aluminium

Introduction

It is really unusual that some elementary chemistry of such well-known metals as aluminium is either missing from the chemistry textbooks, or is simply wrong. The reactions of aluminium with concentrated and diluted acids may serve as a good example for the above assertion. In many of the standard textbooks of general/inorganic chemistry [1-6] one finds that aluminium does not react with concentrated nitric acid and this is indeed true. However, regarding other strong acids one finds quite a num-

ber of various statements. Some of the above textbooks [1-3] were rather old, and for that reason their reliability was initially considered as being questionable. The information found in the newer ones [4-6] are not consistent. Thus, according to Glinka [4] and Brady [5], aluminium reacts with diluted acids displacing hydrogen, while Greenwood & Earnshaw [6] say that the protective oxide cover prevents any reaction with diluted acids. On the other hand, the experiments show [7] that the only reaction that occurs in real time with diluted acids at room temperature is the reaction with HCl(aq), giving rise to hydrogen gas and aqueous solution of aluminium chloride. Therefore, the simple chemical reaction based on the equation



seems not to be operative for strong acids other than HCl! That being so (and the results of experiments say very clearly it is so, indeed), one is faced with a widely spread preconception about the negligible role of the spectator ions in reactions of hydrogen displacement, at least for reactions including aluminium. This problem will be addressed in more detail elsewhere.¹⁾ At this point it may be interesting to say that, although an old one, Mellor's textbook [1] gives information that seem to be the most accurate and the most relevant ones.

In the course of the reinvestigation of the reactions of aluminium with strong inorganic acids (concentrated and diluted), one fact soon became obvious: aluminium is readily dissolved in practically all strong acids, providing the solution contains chloride anions (obviously acting as a catalyst). Traces of Cu^{2+} ions further catalyze the process. The product thus obtained is practically pure hydrogen, in all cases except when one deals with nitric acid. The product of the reaction with diluted nitric acid is, again, a gas (depending on the quantity of the added Cu^{2+} ions the reaction may be somewhat vigorous). In all instances but one, where a minor puff occurred, the product gas was nonflammable, thus suggesting that hydrogen is far from being the principal component present. One of us (MB), being in the process of completing his B.Sc. thesis in the field of vibrational spectroscopy, proposed to analyze the product using FT-IR spectrometry, thus demonstrating the advantages and elegance of the method used.

Experimental

The spectra were acquired using the Perkin Elmer System 2000 FT-IR interferometer in the $3000\text{-}500\text{ cm}^{-1}$ region. A Perkin Elmer gas cell was used (cell length $\sim 10\text{ cm}$, CsBr cell windows) for the measurements. For measuring the background spectrum, the cell was filled with air. After that, the cell was filled with the product gas (or gaseous mixture) diluted with air and the sample spectrum was recorded. Low resolution spectra (resolution of 4 cm^{-1}) perfectly serve the purpose.

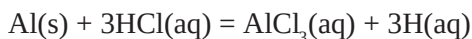
16 scans were accumulated for both the background and the sample spectra. GRAMS 32 program package²⁾ was used for spectra manipulation.

Concentrated nitric acid was diluted to 1 : 2 with distilled water (volume ratios of acid and water). 10 mL of the diluted acid were taken and ~ 1 g of NaCl. After the salt was dissolved a grain of aluminium was added together with a drop of copper(II) chloride solution with $w(\text{CuCl}_2) = 0.05$. After the evolution becomes vigorous enough, the gas was collected in the cell (precautions were taken for preventing microscopic droplets of the liquid to enter the cell). Another sample with several drops of copper(II) chloride was also prepared (this reacts more vigorously with the aluminium). The product was again collected and its spectrum was analyzed.

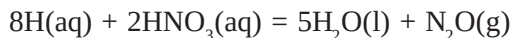
Results and Discussion

The spectrum of the product (presumably a gaseous mixture) is given in Figs. 1 and 2. The wavenumbers of the three strongest bands (ν_3 , 2223; ν_1 , 1285 and ν_2 , 589 cm^{-1}) are in excellent agreement with those reported for nitrous oxide [8]. The band at $\approx 2563 \text{ cm}^{-1}$ can be safely attributed to the $2\nu_1$ mode. Further check and comparison of the spectrum with the spectrum of N_2O taken from a metal cylinder shows beyond any doubt that the polyatomic molecules present belong to N_2O (nitrous oxide). The presence of H_2 or N_2 cannot be precluded in this way (being homonuclear diatomics, they are IR inactive).

The generation of N_2O could be explained by the following reactions. First, due to dissociation of the electrolytes, the solution behaves as a diluted mixture of $\text{HCl}(\text{aq})$ and $\text{HNO}_3(\text{aq})$. Aluminium then reacts with the diluted hydrochloric acid (actually, with the hydrated hydrogen ions) giving atomic hydrogen



A part of the atomic hydrogen inevitably combines into molecular hydrogen, but the rest reduces the diluted nitric acid, according to



The product obtained from the reaction mixture containing several drops of copper(II) chloride (Fig. 2) contains N_2O as the major component, as well as traces of other gases (like NO_2 , evidenced by the band at 1617 cm^{-1} , again in excellent agreement with the literature value [9]).

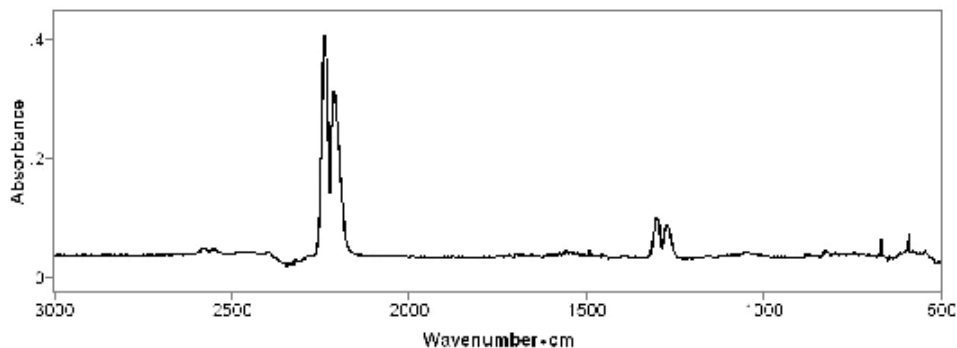


Fig. 1. FT-IR spectrum of the product of the reaction between Al and diluted HNO_3 containing one drop of $\text{CuCl}_2(\text{aq})$. The spectrum matches the spectrum of N_2O (the sharp peak at $\approx 667\text{ cm}^{-1}$ is due to CO_2 uncompensations)

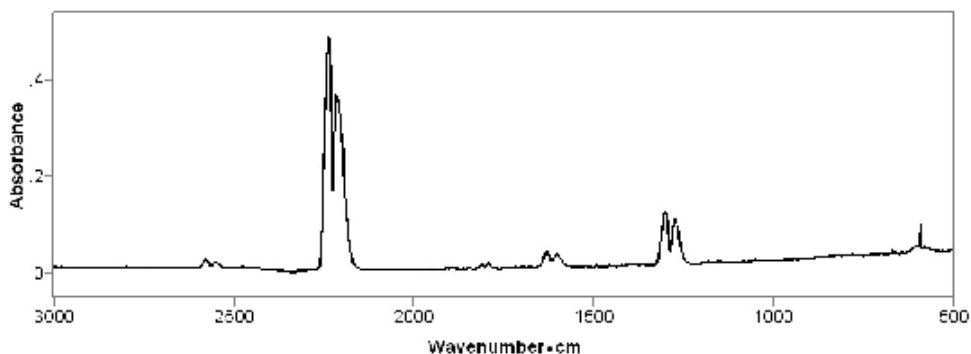
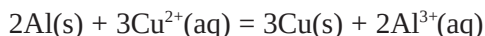
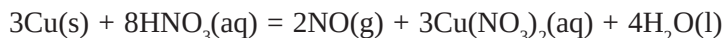


Fig. 2. FT-IR spectrum of the product of the reaction between Al and diluted HNO_3 containing several drops of $\text{CuCl}_2(\text{aq})$. The spectrum matches the spectrum of N_2O (the peak at $\approx 1617\text{ cm}^{-1}$ is due to traces of NO_2 , and the nature of that at $\approx 1800\text{ cm}^{-1}$ is open to discussion)

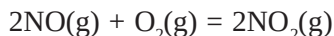
The appearance of the NO_2 impurities, in the presence of higher concentration of Cu^{2+} ions in the solution, might be explained by displacement of copper with aluminium



and subsequent reaction of the elemental copper with the diluted HNO_3



followed by immediate oxidation of the NO gas with atmospheric oxygen



The nature of the very weak vibrational band centered at $\approx 1800\text{ cm}^{-1}$ remains open to discussion.

The principal product of the reaction, N_2O , is also one of the products in the reaction of zinc with diluted nitric acid (together with NO , NO_2 and perhaps N_2). It might be appropriate to recall that both zinc and aluminium are above hydrogen in the electrochemical series of elements.³⁾ However, there is no reaction at all between aluminium and diluted nitric acid (most probably due to the protective covering of aluminium oxide [6]), unless the solution contains chloride anions. One could speculate that in the presence of chlorides, the aluminium oxide film dissolves via formation of aluminium oxide chloride as an intermediate, which is more soluble in acids than Al_2O_3 . Once the film dissolves, the chloride ions (present in the solution) prevent its reformation and aluminium dissolves vigorously. This explanation although logical, is a pure speculation until more direct evidence is offered.

Finally, let us mention that the conclusions about the exact composition of the gaseous mixture would be definitive if the analysis was complemented using a mass spectrometer. Regrettably, we did not have one at our disposal.

Conclusion

For some (not completely clear) reasons, the protective Al_2O_3 covering cannot survive in diluted nitric acid (and in other oxo-acids, as well) containing chloride ions. Aluminium reacts with the hydrogen ions giving atomic hydrogen. The latter partly combines into hydrogen gas, and the rest reacts with the HNO_3 and reduces it to N_2O . If only traces of Cu^{2+} ions (acting as a catalyst) are present, the only oxide of nitrogen that forms is N_2O . This is, to the best of our knowledge, rather unique behavior (in practically all other cases where metals react with nitric acid of medium concentration, a gaseous mixture of various N_xO_y is obtained).

NOTES

1. Petruševski, V.M. & M. Stoianovska, in preparation.
2. GRAMS/32, Spectral Notebase™, Version 4.10 Level 1, 1991-1996, Galactic Industries Corporation.
3. http://en.wikipedia.org/wiki/Table_of_Standard_electrode_potentials

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РЕАКЦИЯ НА АЛУМИНИЙ С РАЗРЕДЕНА АЗОТНА КИСЕЛИНА, СЪДЪРЖАЩА НАТРИЕВ ХЛОРИД

Резюме. Металният алуминий бурно реагира с разредена азотна киселина, когато киселината съдържа разтворен натриев хлорид и следи от медни(II) катиони. Продуктите на реакцията (N_2O , следи от други азотни оксиди и може би газообразни водород и азот), са идентифицирани чрез техните инфрачервени спектри.

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