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Reactions of Metals in Liquid Ammonium Nitrate

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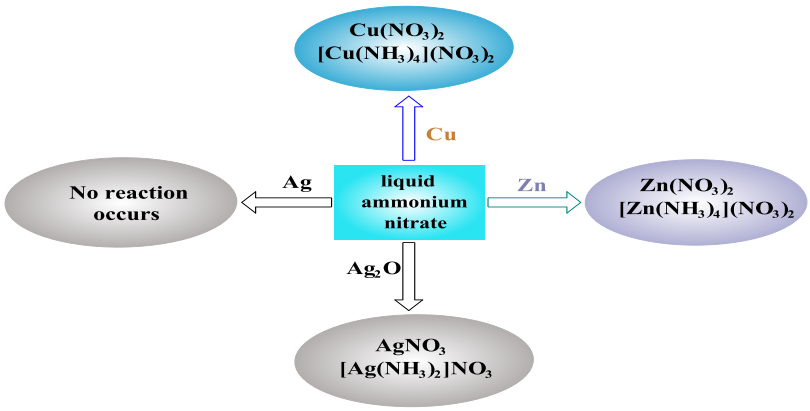
Ammonium nitrate salt has been known for a long time. Many studies have been conducted to determine its properties. Paying attention to the results obtained so far, we conducted research on the reaction of copper, zinc, lead, silver and silver(I) oxide substances in the liquid medium of ammonium nitrate and to study its causes. The conducted research showed that only when metals are oxidized in liquid ammonium nitrate, they can react and form nitrate salts. The fact that silver metal did not react in liquid ammonium nitrate showed that metals cannot react with ammonium nitrate without oxidation. The possibilities of reacting metals with ammonium nitrate were studied using quantum chemical calculations. The results of the calculations helped to prove the correctness of the research conclusions. These reactions can serve to reveal new properties of ammonium nitrate salt.

Graphical abstract



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1. Introduction

Ammonium nitrate is a metal-free nitrogen salt. Ammonium and nitrate ions are located in its crystal lattice. It is known that ammonium nitrate is very soluble in water and is a hygroscopic substance in the solid state. It is mainly used as a nitrogen fertilizer in agriculture [1].

Many countries are phasing out its use because of the potential for misuse. Industrial production of ammonium nitrate is based on the reaction of ammonia with nitric acid [2]. Ammonium nitrate is a crystalline substance with a melting point of 169.6 °C, when heated above this temperature, gradual decomposition begins, and complete decomposition occurs at a temperature of 210°C [3]. Ammonium nitrate is soluble in water, alcohol, acetone and ammonia solution, insoluble in ethers. The pH value of its 0.1 mol/L aqueous solution is 5.43.

Ammonium nitrate can participate in chemical reactions on both cation and anion parts. Solid ammonium nitrate has been observed to decompose on heating, yielding complete dinitrogen oxide and water on decomposition at temperatures below about 300°C:

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

At high temperatures, the following reaction prevails [4].

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$$2NH_4NO_3 \longrightarrow 2N_2+O_2+4H_2O$$

Both decomposition reactions products are gases. Under certain conditions, this reaction can be explosive. Therefore, it is necessary to be very careful when carrying out the decomposition reaction. Many studies provide information on the decomposition mechanism of ammonium nitrate. If we pay attention to the information in the literature, it is shown that ammonia and nitric acid are formed in the gas phase during the initial decomposition of ammonium nitrate [5, 6]. The formation of NO_2 and $^{\cdot}OH$ radical as a result of nitric acid decomposition is expressed. $^{\cdot}OH$ radical reacts with the initially formed ammonia and it is proposed to form amidogen radical ($^{\cdot}NH_2$) and water. As a result of the interaction of these radicals, the formation of dinitrogen oxide is finally shown [7]. Mineral acids destabilize ammonium nitrate. A mixture with concentrated acetic acid burns when heated.

Metals such as Al, Sb, Bi, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Sn, and Zn have been studied to react violently or explosively with liquid ammonium nitrate at temperatures below 200°C [8].

Taking into account the results of the research mentioned above, practical research work was carried out.

2. Results and Discussion

As shown in the literature, ammonium nitrate begins to decompose from the temperature of liquefaction. The formation of ammonia and nitric acid during the initial decomposition is shown in many literatures [5-7]. It is fully proven that dinitrogen oxide gas is formed as a result of the process. It is known that dinitrogen oxide is an oxidizing compound and is reactive [9, 10].

In our research, we observed that some metals undergo a chemical reaction in a liquid ammonium nitrate medium. Copper, zinc, lead, silver and silver(I) oxide were used in the experiments. When copper metal is added to liquid ammonium nitrate at a temperature of 180-200°C, a gradual chemical reaction is observed and the liquid begins to turn dark blue. Gas is also released during the reaction. It was observed that litmus paper soaked in the gas phase formed from the reaction mixture turned blue, and the smell of ammonia was felt in the gas phase (gas evolution is not rapid). Ammonia gas was released during the reaction, and $Cu(NO_3)_2$ was formed during the liquidation. Initially, it was considered that copper is oxidized by exposure to dinitrogen oxide for the reaction to proceed. In general, it can be shown that there were the following reactions:

$$Cu+N_2O \longrightarrow CuO+N_2$$
$$CuO+2NH_4NO_3 \longrightarrow Cu(NO_3)_2+2NH_3+H_2O$$

A certain amount of ammonia gas released in the reaction can be observed to interact with $Cu(NO_3)_2$.

$$Cu(NO_3)_2+4NH_3 \longrightarrow [Cu(NH_3)_4](NO_3)_2$$

Therefore, the product obtained after the reaction contains two types of salts ($Cu(NO_3)_2$ and $[Cu(NH_3)_4](NO_3)_2$). When we put the obtained product in water, it starts to melt, and during melting, an air-color precipitate is formed. When the product dissolves in water, the following reaction occurs:

$$Cu(NO_3)_2+[Cu(NH_3)_4](NO_3)_2+4H_2O \longrightarrow 2Cu(OH)_2+4NH_4NO_3$$

We propose to write the reaction that occurs with copper metal in liquid ammonium nitrate in the following form:

$$2Cu+6NH_4NO_3 \longrightarrow Cu(NO_3)_2+[Cu(NH_3)_4](NO_3)_2+2N_2+6H_2O$$

The reaction between copper (II) oxide and ammonium nitrate can be written in general form as follows:

$$2CuO+4NH_4NO_3 \longrightarrow [Cu(NH_3)_4](NO_3)_2 + Cu(NO_3)_2+2H_2O$$

Similar reactions are observed with zinc metal as with copper.

$$Zn+N_2O \longrightarrow ZnO+N_2$$
$$ZnO + 2NH_4NO_3 \longrightarrow Zn(NO_3)_2 +2NH_3+H_2O$$
$$Zn(NO_3)_2 +4NH_3 \longrightarrow [Zn(NH_3)_4](NO_3)_2$$
$$Zn(NO_3)_2+[Zn(NH_3)_4](NO_3)_2+4H_2O \longrightarrow 2Zn(OH)_2+4NH_4NO_3$$

When lead metal is placed in liquid ammonium nitrate medium, the reaction proceeds rapidly and ammonia gas begins to be released. Because lead(II) salts do not form a complex compound with ammonia.

$$Pb +3NH_4NO_3 \longrightarrow Pb(NO_3)_2 +2NH_3 +N_2 +3H_2O$$

Using this reaction, it is possible to quickly obtain $Pb(NO_3)_2$ crystals. This reaction shows that the mechanisms of the above reactions are correct. So, ammonia gas is formed when metals react with ammonium nitrate. When the obtained product is dissolved in water and Na_2S solution is poured into the solution, a black precipitate is formed. It is known that when Pb^{2+} ions interact with S^{2-} ions, PbS forms a black precipitate.

$$Pb(NO_3)_2 + Na_2S \longrightarrow PbS+2NaNO_3$$

No metal-related reaction effects were observed when silver metal was placed in a liquid ammonium nitrate medium. The heating process was stopped, the crystallized product was dissolved in water and NaCl solution was added to the obtained solution. No reaction characteristic of silver ions was observed in the solution. This proves that there is no reaction between silver and ammonium nitrate. In the next experiment, silver(I) oxide was placed in a liquid ammonium nitrate medium. It is observed that silver(I) oxide dissolves in liquid ammonium nitrate solution.

$$Ag_2O+2NH_4NO_3 \longrightarrow 2AgNO_3+2NH_3+H_2O$$
$$AgNO_3 + 2NH_3 \longrightarrow [Ag(NH_3)_2]NO_3$$

After the reaction, the obtained product was dissolved in water and NaCl solution was poured into the obtained solution. The formation of a white precipitate was observed in the solution. This change proves that $AgNO_3$ was formed [11].

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

There may be a question about the lack of reaction between silver metal and ammonium nitrate. Based on the results of the experiment, it can be said that the reaction does not occur due to the non-oxidization of silver. It is known from the literature that it is difficult to oxidize silver metal in practice [12].

Many literatures have reported that silver-based catalysts decompose nitrogen oxides into nitrogen and oxygen [13-15]. The reason why silver is not oxidized in ammonium nitrate solution is that the high temperature of the solution does not allow the formation of silver oxide. Because silver oxide decomposes at temperatures above 160°C [12].

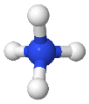
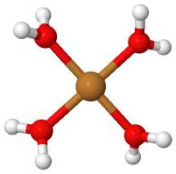
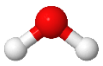
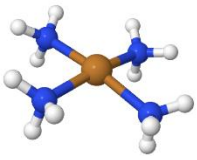
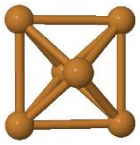
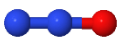
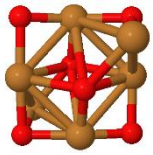
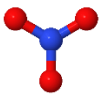
The reactivity of silver oxide is higher than that of silver metal. Therefore, the reaction between silver(I) oxide and ammonium nitrate took place. When the formation of nitric acid in liquid ammonium nitrate was observed in agar, silver metal should have reacted in this medium. However, in the actual experiment, the reaction with silver metal was not observed in liquid ammonium nitrate. This practical result leads to the conclusion that the probability of formation of nitric acid from ammonium nitrate liquefaction is very low.

So, if a metal is oxidized in an ammonium nitrate environment, it can react with ammonium nitrate and form nitrate salts.

To theoretically confirm the above ideas, quantum-chemical calculations were carried out. Calculations were performed using the SPK-DZP basis set, RHF and UHF approximation methods in the GAMESS program [16, 17].

We considered the calculations on the example of exposure of copper to ammonium nitrate. The total energies of molecules and ions were determined through quantum chemical calculations (Table 1).

Table 1. Total energies of molecules and ions that can participate in the reaction between copper and ammonium nitrate.

The formula of molecules and ions	Structures of molecules and ions	Total energy, kJ/mol	The formula of molecules and ions	Structures of molecules and ions	Total energy, kJ/mol
NH_4^+		-148448.887	Cu^{2+}		-4300678.674
NH_3		-147535.297	$[Cu(H_2O)_4]^{2+}$		-5100268.189
H_2O		-199600.205	$[Cu(NH_3)_4]^{2+}$		-4892167.044
N_2		-286054.158	Cu		-25818125.411
N_2O		-482286.157	CuO		-26996274.534
NO_3^-		-731920.122			

We consider the oxidation of copper metal with dinitrogen oxide based on the results obtained by quantum chemical calculations. For this purpose, we chose a structure consisting of 6 copper atoms, which is a part of the crystal lattice of copper, and energetically studied the possibility of interaction with dinitrogen oxide molecules. We also selected a part of its crystal structure for copper(II) oxide, which is expected to be formed in the reaction. There were also 6 copper atoms and 6 oxygen atoms in the fragment of the selected copper(II) oxide crystal lattice.

$$\underset{-25818125.411}{6Cu} + \underset{-2893716,942}{6N_2O} \longrightarrow \underset{-26996274.534}{6CuO} + \underset{-1716324,948}{6N_2}$$

-28711842,353 kJ/mol > **-28712599,482 kJ/mol**

Scheme 1. Energetic parameters of the reaction of copper with dinitrogen oxide

According to the calculation results, the oxidation of copper under the influence of dinitrogen oxide can be considered energetically acceptable (Scheme 1).

The possibility of copper(II) oxide reacting with ammonium ions in liquid ammonium nitrate was studied.

$$\underset{-26996274.534}{6CuO} + \underset{-1781386,644}{12NH_4^+} \longrightarrow \underset{-12902036.022}{3Cu^{2+}} + \underset{- 14676501,132}{3[Cu(NH_3)_4]^{2+}} + \underset{-1197601,23}{6H_2O}$$

-28777661.178 kJ/mol < **-28776138.384 kJ/mol**

Scheme 2. Energetic parameters of the reaction of copper(II) oxide with ammonium ions in liquid ammonium nitrate

The mutual comparison of the total energies of the compounds participating in the chemical reaction and the resulting products showed that it is not energetically preferable for the reaction to proceed by itself (Scheme 2). The supply of energy to the system from the external environment can help the reaction to take place. Therefore, we observe that the reaction takes place at high temperatures. If we take into account the participation of water molecules in the system, then the reaction is written as follows.

$$\underset{-26996274.534}{6CuO} + \underset{-1781386,644}{12NH_4^+} + \underset{-1197601,23}{6H_2O} \longrightarrow \underset{-15300804,567}{3[Cu(H_2O)_4]^{2+}} + \underset{- 14676501,132}{3[Cu(NH_3)_4]^{2+}}$$

-29975262,408 kJ/mol > **-29977305,699 kJ/mol**

Scheme 3. Energetic parameters of the reaction of copper(II) oxide with ammonium ions and water in liquid ammonium nitrate

The participation of water molecules in this reaction causes the reaction to occur energetically by itself (Scheme 3). These conditions can also be observed in practical experience. Initially, copper reacts slowly in an ammonium nitrate medium, which is liquefied under the influence of reaction temperature, and then the reaction increases rapidly. In the first reaction, water molecules formed from the interaction of ammonium ions with copper(II) oxide cause the chemical process to proceed due to its participation in subsequent reactions.

ATR-FTIR spectra of $Cu(NO_3)_2$ and $Cu(NH_3)_4(NO_3)_2$ (additional NH_4NO_3) salts assumed to be formed in the reaction were compared with IR spectra obtained in quantum chemical calculations (Fig.1). UHF and PM3 semi-empirical quantum chemical calculations were used in the theoretical calculations of IR spectra (Fig.2). Quantum chemical calculations were performed for each ion and their IR spectrum results were determined.

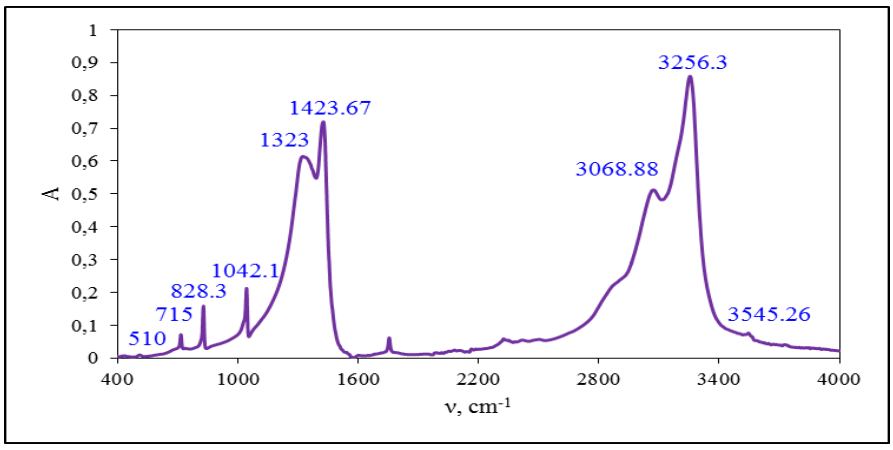


Fig. 1. ATR-FTIR spectra of $Cu(NO_3)_2$ and $Cu(NH_3)_4(NO_3)_2$ (additional NH_4NO_3)

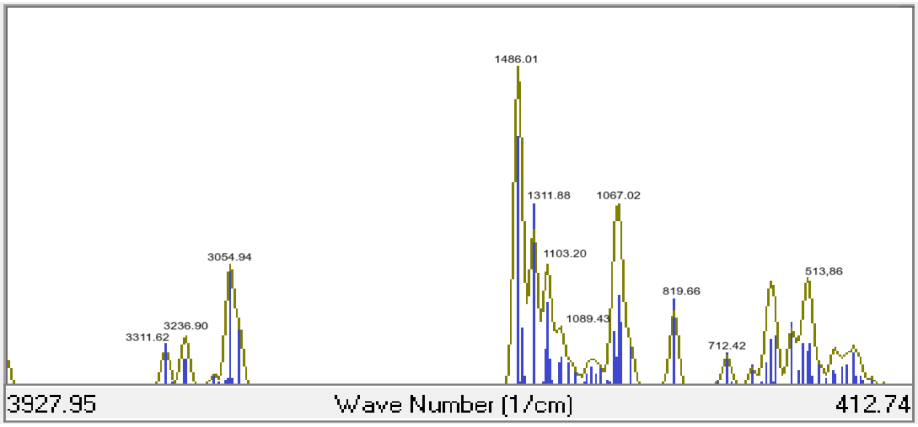


Fig. 2. IR spectra of $Cu(NO_3)_2$ and $Cu(NH_3)_4(NO_3)_2$ (additional NH_4NO_3)

The mutual compatibility of the obtained results confirms that copper salts are formed in the reaction system (Table 2).

Table 2. Theoretical and practical IR spectrum results of a mixture of $Cu(NO_3)_2$, $[Cu(NH_3)_4](NO_3)_2$ and NH_4NO_3

Bonds in the atomic group	IR spectrum values obtained in practice	Calculated IR spectrum values
N^+-H, N-H (stretching)	3545.26 cm^{-1}	3311.62 cm^{-1}
N^+-H, N-H (stretching, hydrogen bonded)	3256.3 cm^{-1}	3236.90 cm^{-1}
N^+-H (deformation)	3068.88 cm^{-1}	3054.94 cm^{-1}
N^+-H (bending)	1423.67 cm^{-1}	1486.01 cm^{-1}
N-O (asymmetric stretching)	1323 cm^{-1}	1311.88 cm^{-1}
N-O (bending)	1042.1 cm^{-1}	1103.20 cm^{-1} 1089.43 cm^{-1} 1067.02 cm^{-1}
N-O (bending)	828.3 cm^{-1}	849.06 cm^{-1} 819.66 cm^{-1}
N-O (bending)	715 cm^{-1}	742.04 cm^{-1} 712.42 cm^{-1}
Cu-O (bending)	510 cm^{-1} 434.4 cm^{-1}	513,86 cm^{-1}
Cu-N (bending)	420 cm^{-1}	396.43 cm^{-1}

3. Material and Methods

Copper (99.999%, Changsha Xinkang, China), lead (99.999%, Changsha Xinkang, China), zinc (99.999%, Changsha Xinkang, China), silver (99.999%, Changsha Xinkang, China), silver(I) oxide and ammonium nitrate (99.99%, Himreagent LTD, Uzbekistan), distilled water, sodium chloride, sodium sulfide (99,99 %, Himreagent LTD, Uzbekistan) were used for experiments. The devices and equipment used are as follows: Electric stove, porcelain cups, glass sticks, litmus paper, porcelain plates, glasses, and pipettes.

Ammonium nitrate crystals and pieces of metal (copper, zinc, lead, silver) were mixed in a 4:1 mole ratio in a porcelain bowl. For the experiments, 0.5 g of each metal was weighed. The mass of ammonium nitrate was measured by comparing the mass of metal to the mole amount. The porcelain bowl containing the mixture is placed in the oven and heated to a temperature of 180-200°C. After the ammonium nitrate crystals are liquefied, the metal begins to react in the liquid medium. The reaction mixture is heated for 5-10 minutes. In the experiment, silver metal did not change in liquid ammonium nitrate. In the above procedure, an experiment was conducted on a mixture of silver(I) oxide and ammonium nitrate in a 1:3 mol ratio. After the experiments, the crystal products obtained were dissolved in water and qualitative analysis reactions characteristic of the metal ions in the obtained solutions were carried out.

4. Conclusions

It became known that metals must first be oxidized for metals to react in liquid ammonium nitrate. This was proved by the non-reactivity of silver metal and the reactivity of silver(I) oxide. It should be noted that when nitric acid was formed in liquid ammonium nitrate, silver metal should have reacted. The fact that the silver metal did not react in the liquid ammonium nitrate indicates that the probability of the formation of nitric acid in the liquid is very low. As a result of the reactions, it became known that simple and metal ammine complex salts are formed. Knowing the properties of this ammonium nitrate can be used in various technological and other scientific fields.

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