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SYNTHESIS OF NITRO-DERIVATIVES OF BIURET AND THEIR SALTS

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Abstract:

The nitration process of biuret and nitrobiuret in nitric and in mixed acids was studied. It was demonstrated that the content of products mixture has an equilibrium nature and depends on the acidity of the nitrating mixture and on the amount of nitric acid in it. The hydrolysis of nitro derivatives of biuret was also studied, and the salts of these compounds were synthesized.

Keywords: *biuret, nitrobiuret, dinitrobiuret, nitration, hydrolysis, salts.*

1. INTRODUCTION

In a quest for new energetic materials special attention is devoted recently to nitroamines and nitroamides, in particular to nitro-derivatives of biuret and their salts. [1,2]. Unlike the nitration reaction of urea, biuret's nitration has not been studied thoroughly yet. In this paper we present the detailed analysis of the biuret's nitration mechanism, hydrolysis of mono- and dinitrobiuret, synthesis of their salts and characterization of their properties.

2. MATERIALS AND METHODS

98 % biuret was used in this research. Nitro and dinitrobiurets were synthesized according to the literature [3]. UV-spectroscopy selecting the probes from the thermostatic reactor ($25 \pm 0,5^\circ \text{C}$) was used to study the nitration and the hydrolysis processes. The probes were diluted to 1.6% of H_2SO_4 . Reaction product contents were calculated using Firordt's method basing on UV spectra. 50 times excess of nitric acid was used, which allowed the calculation of the rate constant as a constant of the first order reaction, while correlation coefficients were 0.99 and better. Salts of mono- and dinitrobiuret were synthesized using the general method as follows. Equimolecular amounts of nitrobiuret and a base (dissolved in methanol) were mixed. Then precipitated salt was filtered and identified using IR spectroscopy and titration. The flash point was determined using standard procedure with the heating speed of 4°C per minute.

3. RESULTS AND DISCUSSION

From the early stages of our experiments it was clear that both mono- and dinitro-derivatives appear in the reaction bulk immediately, and the resulting systems can be considered as three component systems.

Since the reaction rate is very high, it was possible to determine the rate constants only for the solutions in 70% H_2SO_4 . The change in concentration of nitro- and dinitrobiuret is shown on Fig. 1. If the concentration of H_2SO_4 is higher than 85%, the reaction completes in less than 5 min, without any changes in the mixture contents after that. On the figures 2 and 3 some of these results are depicted.

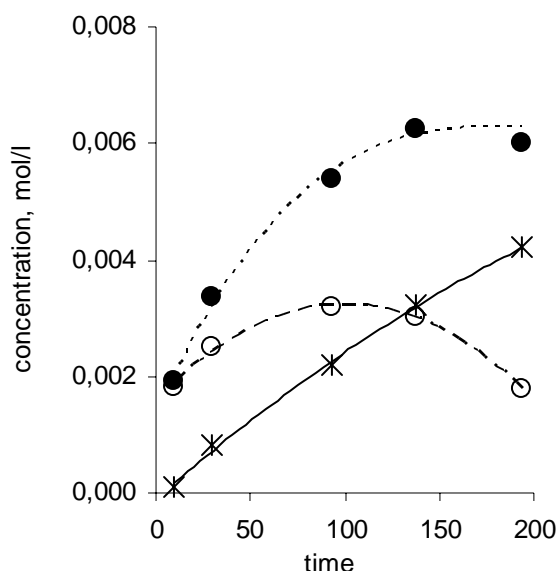


Fig.1: nitrobiuret nitration in 75% sulfuric acid, T25°C, HNO₃ concentration is 2.66 mol/l, biuret concentration is 0.0092 mol/l.

* – dinitrobiuret, ●- total

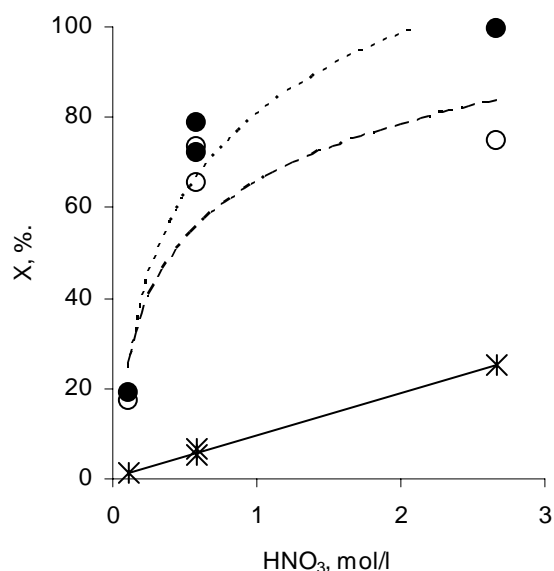
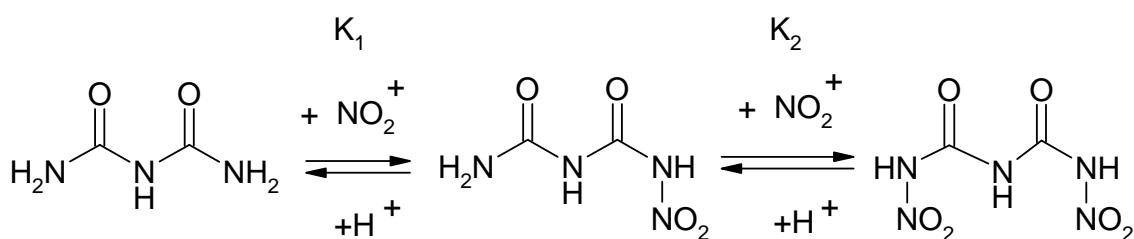


Fig2: dependence of biuret nitration equilibrium products content in 94% of sulfuric acid from the concentration of nitric acid at 25°C.

○ – nitrobiuret, * – dinitrobiuret,
●- total

The experiments we performed demonstrated that in nitration of both biuret and nitrobiuret the content of resulting products is identical, which confirms the suggested model.



$$K_1 = \frac{[\text{NB}][\text{H}^+]}{[\text{B}][\text{NO}_2^+]} \quad ; \quad \log[\text{H}^+] = \text{Ho}$$

$$K_2 = \frac{[\text{DNB}]^*[\text{H}^+]}{[\text{NB}]^*[\text{NO}_2^+]}$$

$$[\text{NO}_2^+] = I_{\text{HNO}_3} \cdot \frac{[\text{HNO}_3]_0}{(I_{\text{HNO}_3} + 1)} \quad ; \quad [\text{HNO}_3]_0 - \text{initial concentration}$$

$$I_{\text{HNO}_3} = \frac{[\text{NO}_2^+]}{[\text{HNO}_3]}$$

[B], [NB] and [DNB] – concentration of biuret, nitrobiuret and dinitrobiuret

$$\ln(I_{\text{HNO}_3}) = -1.27 \cdot H_R - 22,404 \quad [5]$$

H_0 и H_R - acidity function.

To calculate equilibrium constants $\lg K_1$ and $\lg K_2$ we used literature data on sulfuric acid acidity [4] and the conversion level of nitric acid into nitronium ion [5]. The acidity of nitrating mixtures was calculated as additive for H_2SO_4 and HNO_3 at concentrations of mole fractions. The resulting $\lg K_1$ and $\lg K_2$ are 9.5 ± 0.5 and 9.1 ± 0.7 respectively. As it is demonstrated on the Fig.4, the constants do not depend on the sulfuric acid concentration, which confirms that the model we chose is adequate.

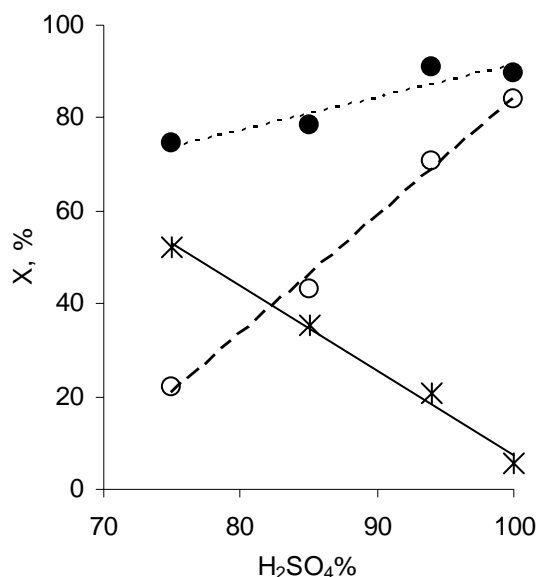


Fig. 3: dependence of biuret nitration equilibrium products content on the concentration of sulfuric acid; nitric acid concentration is 2.66 mol/l, temperature is 25°C.

○ – nitrobiuret, * – dinitrobiuret,

● – total

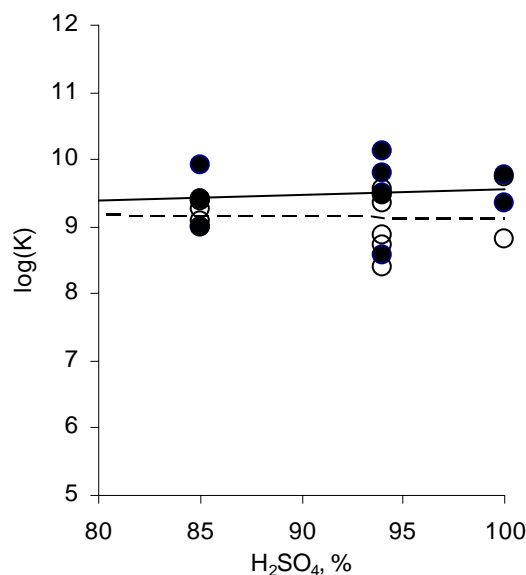


Fig 4: dependence of equilibrium constants on the concentration of sulfuric acid at 25°C.

● – $\lg K_1$, ○ – $\lg K_2$,

This behavior can be observed in the reaction mixtures containing up to 20% (mass) of nitric acid. In the medium containing 99% nitric acid or 49.5% of sulfuric acid and 49.5% nitric acid, fast and practically quantitative conversion of biuret and nitrobiuret into dinitrobiuret takes place. This conversion, however, with a time is followed by reduction of dinitrobiuret concentration, and by creation of the products which do not absorb in UV range. In the 99% HNO_3 medium at 25°C dinitrobiuret is already not present after 30 minutes. One should note that when using dinitrobiuret synthesis method, in which dinitrobiuret is isolated by evaporation of nitric acid under the vacuum [3], the reaction mass is spontaneously heated and decomposed. The reaction mixture is stable only at relatively low temperatures, when the decomposition products are removed from the reaction zone. Therefore, regardless its high yield, this method is dangerous and should not be used for the synthesis of large amounts of dinitrobiuret. Studies of dinitrobiuret hydrolysis in the acidic and base mediums demonstrated that dinitrobiurete is fairly stable in the form of salts, including in up to 50% sulfuric acid solutions. Hydrolysis occurs as the reaction of the first order, and results in biuret in acidic solutions. Dinitrobiuret's stability is low, and even in the 10% sulfuric acid hydrolysis takes place momentarily, producing

nitrobiurete. In the base solutions the hydrolysis results in the undetermined products. The data is summarized in Fig.5.

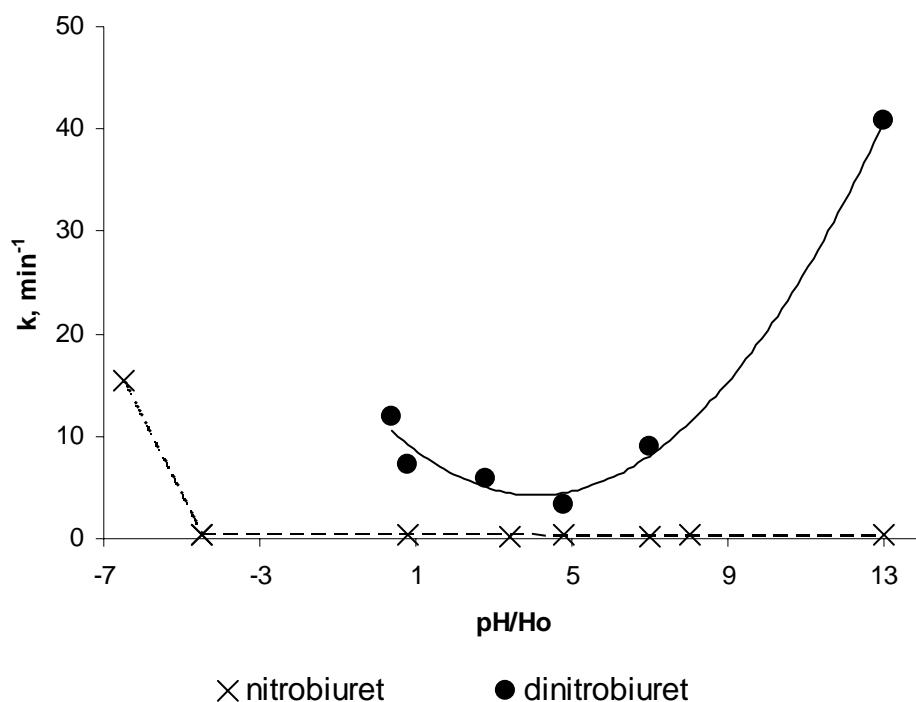


Fig.5: Hydrolysis of nitrobiuret and dinitrobiurete.

Therefore, dinitrobiuret isolation from the reaction bulk is complicated both by its high solubility in the nitrating mixtures and by its low hydrolytic stability.

At the final steps of this research we synthesized hydrazinium, ammonium and potassium salts [2] of nitro- and dinitrobiuret and determined the flash point temperatures of these compounds. The data is presented at Table 2.

Table 2.

Flash point salts of nitro- and dinitrobiuret.

	Flash point, speed of health 4°C/min	Amount, %
Nitrobiuret	132	
Hydrazinium salt of nitrobiuret	132	75
Ammonium salt of nitrobiuret	147	66
Potassium salt of nitrobiuret	177	81
Dinitrobiuret	90	
Hydrazinium salt of dinitrobiuret	95	99
Ammonium salt of dinitrobiuret	120	66
Potassium salt of dinitrobiuret	127	57

As follows from the Table 2, the stability of dinitrobiuret and its salts is very low. Nitrobiurett salts' thermostability is higher, but not to a significant degree.

4. CONCLUSIONS:

This research demonstrates that the results of biuret nitration are determined by the equilibrium conditions, which depend on the acidity of the medium and on the concentration of nitrating reagent. Hydrolytic stabilities of nitro- and dinitrobiuret were analyzed, and proved to be relatively low for dinitrobiuret. The series of nitro- and dinitrobiuret's salts were synthesized and their thermal stability was determined. Thermostability of dinitrobiuret salts is low, which complicates their practical use. Nitrobiuretes' thermostability is higher, which makes their practical use possible.

5. REFERENCES

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