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Tetraacetyl-dibenzyl-hexaazaisowurtzitane Nitrosation – Studies on Scale-up Synthesis of HNIW

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Abstract

A study made on 2,4,6,8-tetraacetyl-10,12-dibenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (TADBIW) nitrosation in acetic acid to 2,4,6,8-tetraacetyl-10,12-dinitroso-2,4,6,8,10,12-hexaazaisowurtzitane (TADNOIW) allows the reaction time to be considerably shortened. During the study, the reaction yield was found to be affected by variables such as temperature, time and UV radiation. The major factor controlling the reaction rate was found to be the concentration of NO_2 molecules in the reaction mixture. Under optimal conditions the product is obtained in a 90–93% yield after 6 h of the reaction conducted at 70 °C. UV radiation increases the reaction rate, yet the product obtained is of inferior purity on account of the by-product formed.

Keywords: HNIW, Nitrosation, Tetraacetyl-dibenzyl-hexaazaisowurtzitane, Tetraacetyl-dinitroso-hexaazaisowurtzitane, UV Radiation

1 Introduction

One of the most powerful explosives of these days is the material manufactured worldwide on a semi-commercial scale known as CL-20 or HNIW, which is 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane. A wider popularity of this material is restricted by the fact that its manufacturing process is expensive and complex. Currently it is manufactured by a multi-step process, the first step of which is the 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (HBIW) synthesis. This compound cannot be directly nitrated to CL-20 and debenzylation steps are required.

A major step in this synthesis is the formation of an intermediate, 2,4,6,8-tetraacetyl-10,12-dinitroso-2,4,6,8,10,12-hexaazaisowurtzitane (TADNOIW).

The first method for TADNOIW synthesis described in the literature (Figure 1) is the reaction that used Olah's salt (NOBF_4) as a nitrosating agent [1]. The starting compound in

this reaction was 2,4,6,8-tetraacetyl-10,12-dibenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (TADBIW). This reaction affords a product of high purity, which is the highest in comparison with other methods. A disadvantage of this method, however, is its moderate yield that is up to 55% and a high price of the nitrosating agent, nitrosotetrafluoroborate. Use of nitrosotetrafluoroborate is also associated with troubles in handling and costs of fluoroborate-laden waste treatment. For these reasons, the method is unsuitable for a commercial-scale TADNOIW production. The other two methods are described in the literature as the methods that meet these requirements [1, 2]. The starting material in these methods is TADBIW, while dinitrogen tetroxide is used as a nitrosating agent. The difference between these two methods is that in the former method the reaction runs in liquid dinitrogen tetroxide with a minor addition of water, whereas in the latter, an additional solvent was used, viz. glacial acetic acid and the amount of N_2O_4 was significantly reduced. The nitrosation reaction in liquid dinitrogen tetroxide proceeds much faster (16 h) than the analogous reaction in acetic acid (72 h). Likewise, the product yield and purity are reported to be somewhat higher for the method with only dinitrogen tetroxide.

Despite the differences mentioned, the method using glacial acetic acid as solvent appears to be more promising for the commercial-scale CL-20 production. The reason for this is the hazard associated with the reaction conducted in liquid dinitrogen tetroxide. A very high excess of that reagent in relation to the starting material (TADBIW) could cause explosion hazard and might result in the contamination of the natural environment. Dinitrogen tetroxide is a potent oxidant and in combination with the starting material (TADBIW), that could serve here as a fuel, it may form explosive mixtures. Glacial acetic acid used in the reaction allows the amount of dinitrogen tetroxide to be significantly reduced which substantially enhances the safety of this process.

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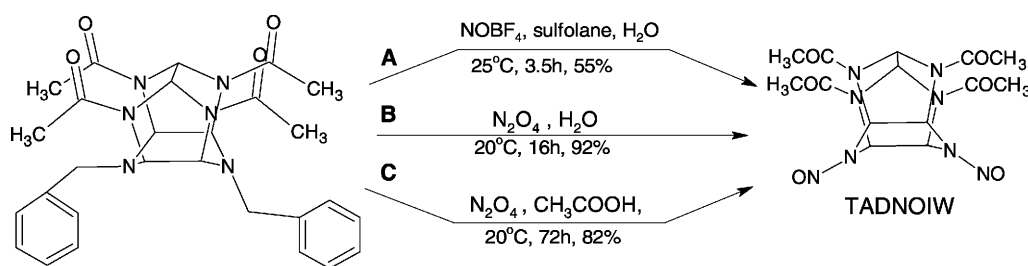


Figure 1. TADBIW nitrosation reactions.

The purpose of this study was to examine the effect of various factors, such as reaction time, temperature and UV radiation, on the yield of the TADBIW nitrosation and the purity of the product (TADNOIW). This study could be useful for the development of CL-20 manufacturing process.

2 Experimental Part

2.1 General

Materials: TADBIW – prepared at Warsaw University of Technology, The Division of High Energetic Materials [3], Glacial Acetic Acid (CH_3COOH) – POCh Gliwice, Dinitrogen Tetroxide (N_2O_4) – obtained by the method [4], Acetic Anhydride – POCh Gliwice, Dimethylformamide – POCh Gliwice.

The product was analysed by HPLC (high performance liquid chromatography) using a C-18 column and an acetonitrile/water mixture, in a ratio of 60:40, as eluent. The flow rate applied equalled 1 mL min^{-1} . The analysis was carried out at 35°C using a UV detector at 230 and 254 nm wavelengths. Samples were taken directly from the reaction mixture and each sample of $10\text{ }\mu\text{L}$ volume was diluted in 1 mL of acetonitrile.

2.2 Example Preparation Process

2.2.1 TADBIW Nitrosation Using N_2O_4 in CH_3COOH

Into a solution of 50 mL of glacial acetic acid (CH_3COOH) and 5 mL dinitrogen tetroxide (N_2O_4) placed in a 100-mL flask, 5 g of TADBIW was added at 20°C . Next, the stirrer was turned on and the system heated to the reaction temperature. The reaction was carried out for 6 h . Samples of the reaction mixture were taken from the flask during the process and analysed by HPLC. After 6 h , the reaction was brought to a stop by removing excess nitrogen oxides by means of a water-jet vacuum pump and by allowing the mixture to cool to room temperature. Subsequently, acetic acid was removed from the reaction mixture by evaporation and ethanol (ca. 50 mL) was added into the residue. The solid residue completely dissolved in ethanol and after some time, the desired product, TADNOIW, separated. The product was filtered off and dried in

air. TADBIW nitrosation using N_2O_4 in CH_3COOH with UV radiation was carried out in the same manner. The reaction temperatures were 40 and 50°C . The system was irradiated with a lamp emitting UV light (power 40 W , wavelengths 254 and 336 nm).

2.2.2 Example of a Commercial-scale Process

Based on the study, the following values for the variables were chosen for a commercial-scale process: The TADBIW: N_2O_4 : CH_3COOH ratio was $800\text{ g}:1200\text{ g}:8\text{ l}$, respectively, reaction temperature: 70°C , reaction time: 6 h .

Into a 10 L capacity reaction vessel equipped with a heating system, a mechanical stirrer, a thermometer and a reflux condenser, TADBIW was poured and acetic acid was added along with N_2O_4 dissolved in part of the acetic acid. The vessel was sealed off, the stirrer was turned on, and subsequently the reaction mixture was heated to the required reaction temperature (70°C). At that temperature the vessel content was stirred for 6 h . After that time of the nitrosation, the reaction mixture was allowed to cool to room temperature and the acetic acid was removed under reduced pressure. Ethanol (5 L) was added to the residue. The precipitated product was filtered off, washed with fresh ethanol and dried at room temperature.

3 Results and Discussion

3.1 Optimization of the Process

At first the effect of the reaction time on the reaction yield was studied. The reaction was conducted at 20°C and the reaction time was extended to 336 h . The results obtained are shown in Figure 2.

The reaction at 20°C proceeds at a relatively slow rate so that a product yield of 97% is obtained only after 336 h . A further extension of the reaction time does not improve the yield. The TADNOIW isolated from the samples taken during the reaction showed melting points in the range of $280\text{--}288^\circ\text{C}$ and a purity of $93\text{--}95\%$ as measured by HPLC. The final product melted at $285\text{--}287^\circ\text{C}$ and its purity was 95% .

The extension of the reaction time for TADNOIW resulted in a higher yield (97%) than the literature value

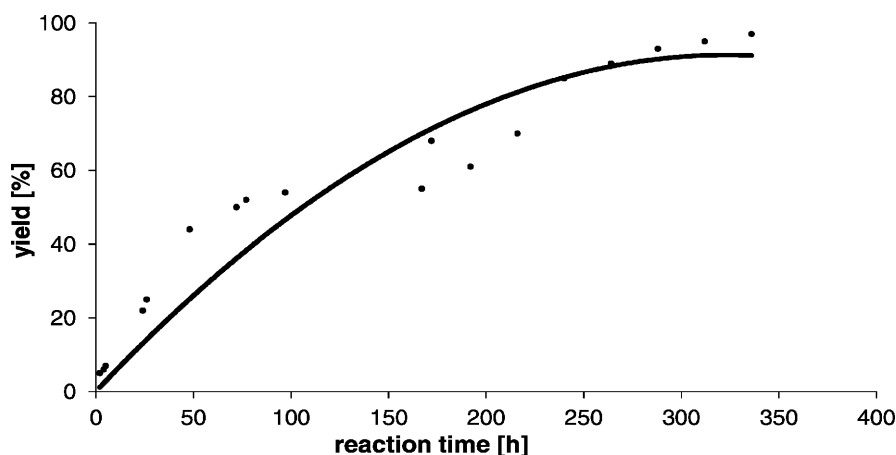


Figure 2. Variation of TADNOIW yield versus time of the reaction conducted at room temperature.

(82%) [2]. After 72 h of the reaction (the time reported in the literature), a crude product was obtained in the form of oil from which TADNOIW could not be isolated. Our study showed that a pure product in 97% yield could be obtained after 336 h. The rising yield with time is indicative for a selective course of the reaction. In other words, the products obtained after a shorter time of the reaction must be contaminated by the starting material or by some intermediates, which makes isolation of TADNOIW unfeasible.

From the commercial process standpoint the running of the process for 14 days seems impracticable. Therefore in a further part of this study our research was focussed on the effect of temperature on this reaction. The results obtained are shown in Figure 3.

The results obtained show that with rising temperature of the TADBIW nitrosation process the product yield increases. The highest yield (92%) was obtained at a process temperature of 70 °C and a reaction time of 5 h. Thus the

higher temperature of the process significantly increases the TADNOIW formation rate and the time of the process can be substantially shortened.

The yield, however, does not increase with additional reaction time. There is an optimal time for each temperature of the process which, if exceeded, results in a decline of TADNOIW yield. This is particularly shown for the reactions conducted at high (80 °C) temperatures. The decrease in TADNOIW yield observed may be due to a TADNOIW conversion to trinitroso-triacetylisowurtzitane derivative. This idea is confirmed by results of HPLC analysis in which a rise in peak area of the trinitroso-derivative at the expense of TADNOIW is seen. The trinitrosoisowurtzitane derivative formation can be also responsible for a melting point depression of the product.

In a further stage of the study, the effect of UV radiation on the reaction course was investigated. The results are visualized in Figure 4.

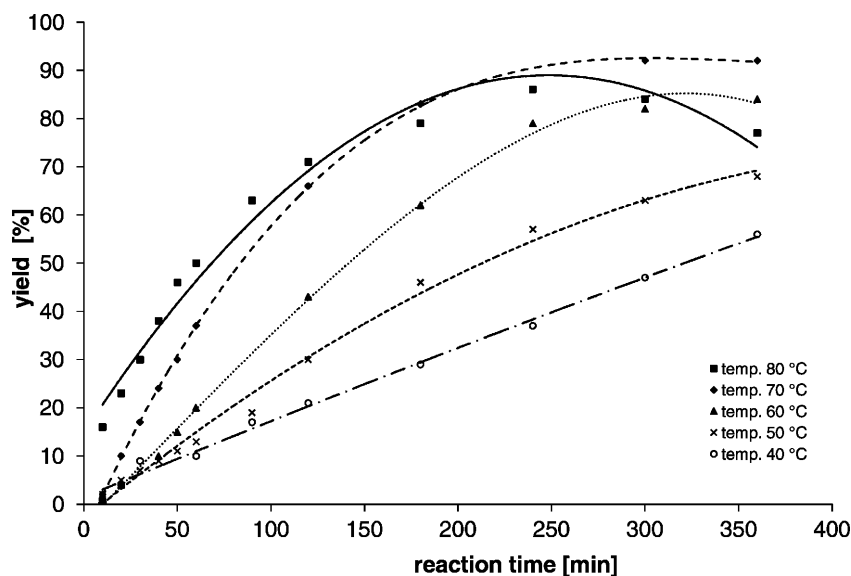


Figure 3. The effect of temperature and time of the TADBIW nitrosation reaction on TADNOIW yield.

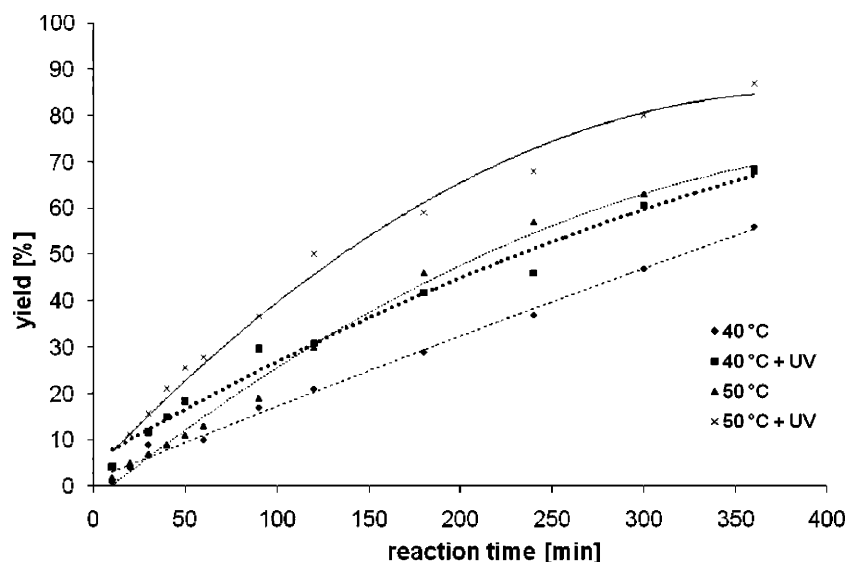


Figure 4. The effect of UV radiation on TADNOIW yield.

One can see that UV irradiation increases the TADNOIW formation rate.

For the reaction conducted at 40 °C, the TADNOIW yield after 6 h was 56%. The use of UV light allowed raising the TADNOIW yield after the same time to 68%. This is also the case for the process conducted at 50 °C where the TADNOIW yield rose from 68 to 87% after 6 h of reaction time. The melting point of the product obtained in the reaction with UV light is slightly lower, as compared with the product formed without UV (285–287 °C) and it was equal to 278 °C. This melting point depression for the product may be due to some side reactions occurring during UV irradiation of the reaction mixture.

The influence of the scale increase on the reaction yield was also investigated. For this an enlarged-scale process was run in a 10 L reaction vessel at 70 °C for 6 h (without UV irradiation) which gave 90–93% yields and 95% purity. Recycling of the recovered acetic acid to a subsequent reaction resulted in a lower TADNOIW yield.

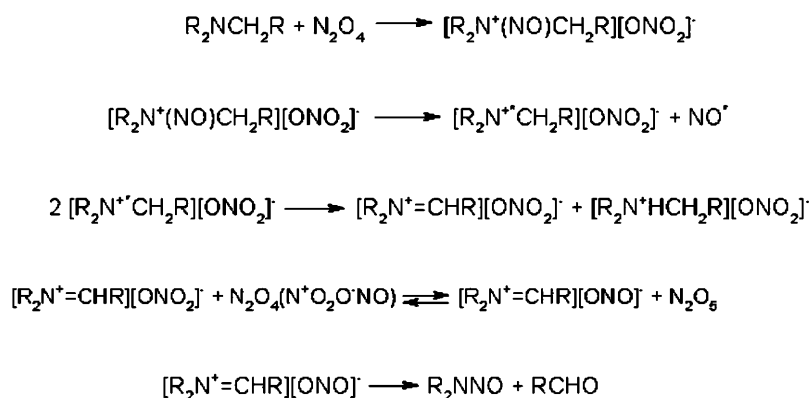
As can be seen, an increased process scale has no effect on the yield of the product. Likewise, product purity remains

unaffected. Despite a considerably increased scale and a higher reaction temperature (70 °C), no rise in the emission of nitrogen oxides could be noted.

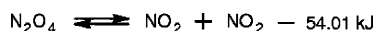
3.2 Mechanism of Nitrosation

The mechanism of tertiary amines nitrosation by N_2O_4 was studied by Boyer [5]. (Scheme 1). According to that mechanism, the key intermediate is the imine cation $R_2N^+=CH_2R$. The imine cation forms as a result of an α -hydrogen transfer between aminium cation-radical. The aminium cation-radical, in turn, forms as a result of a reaction of an α -hydrogen-containing tertiary amine with dinitrogen tetroxide, followed by a homolytic dissociation of the nitrosoammonium cation formed. In a subsequent reaction stage, the imine cation reacts with a nitrite anion to form nitrite ester. In consequence of a dissociation, ester nitrosoamine and a carbonyl compound are formed.

It follows from the mechanism suggested above that the nitrosonium cation (NO^+) is the active entity that initiates



Scheme 1. Tertiary amines nitrosation mechanism using N_2O_4 .



Scheme 2. Homolytic N_2O_4 dissociation.



Scheme 3. Heterolytic N_2O_4 dissociation.

nitrosation reaction. The results of the experiments suggested that the TADBIW nitrosation reaction may alternatively proceed via a mechanism where the major part is played by NO_2 .

One can assume that the major reactant in the TADBIW to TADNOIW nitrosation is dinitrogen tetroxide (N_2O_4). For this reason, it is necessary to learn the properties of the nitrosating agent and the factors affecting its concentration.

Dinitrogen tetroxide may be considered as an associate consisting of two molecules of NO_2 (Scheme 2).

At lower temperatures the equilibrium of this reaction is shifted towards N_2O_4 formation, whereas at higher temperatures the reaction proceeds towards N_2O_4 to NO_2 dissociation. At 50°C under a pressure of 0.1 MPa ca. 50% of the molecules correspond to the N_2O_4 formula. At 150°C , the dissociation is virtually complete. NO_2 and N_2O_4 differ by electron structure of their molecules: the former one has an odd number of electrons, the latter one has only paired electrons. NO_2 shows paramagnetic properties, whereas N_2O_4 is diamagnetic.

Liquid N_2O_4 or dissolved in suitable solvent may undergo dissociation after equations shown in Schemes 2 and 3 [6].

As a result of heterolytic N_2O_4 dissociation (Scheme 3), nitrosonium cation and nitrate anion are formed. However, liquid N_2O_4 hardly dissociates according to this equation. Nitrosonium nitrate $[\text{NO}]^+[\text{NO}_3]^-$ occurs only in negligible amount in the equilibrium of N_2O_4 in liquid state. On the other hand, in solutions with high dielectric constant, e.g. in anhydrous nitric acid, the equilibrium is shifted to the right.

The major reaction for dinitrogen tetroxide in solutions is the homolytic dissociation reaction (Scheme 2). Equilibrium constants K_{DIS} in liquid phases are measured by Nuclear Magnetic Resonance (NMR) or Electron Paramagnetic Resonance (EPR) spectroscopy. The homolytic N_2O_4 dissociation constant varied with the solvent used [7]. K_{DIS} values in π - and n -donor solvents are clearly lower than in a pure liquid N_2O_4 . The lowest values are in n -donor solvents

where dissociation constants decrease with increasing donor number of the solvent. This indicates that the major role here is played by N_2O_4 solvation. In non-donor solvents such as cyclohexane, carbon tetrachloride, or n -hexane, K_{DIS} is somewhat higher than in pure liquid N_2O_4 . This indicates that in these solvents NO_2 solvation prevails. Heterolytic N_2O_4 dissociation (Scheme 3) might also affect the homolytic dissociation constants K_{DIS} but the conductivity values for N_2O_4 solutions indicate that the degree of the heterolytic dissociation is insignificantly low.

Dielectric constant and the homolytic dissociation constant for N_2O_4 in certain solvents in which the nitrosation reaction was carried out, as well as the TADNOIW yields, are compared in Table 1.

It follows from the data presented in Table 1 that the lowest value of dielectric constant occurs in liquid dinitrogen tetroxide and the highest, in dimethylformamide. As presented above, the dielectric constant affects the degree of heterolytic N_2O_4 dissociation constant in solvents; in other words, it has an effect on the nitrosonium ion (NO^+) concentration in solution. If the reactions occur according to the mechanism suggested by Boyer, the highest nitrosation reaction rate should be observed for the reaction in dimethylformamide and the lowest, in liquid N_2O_4 . The yield values show, however, that the case is opposite.

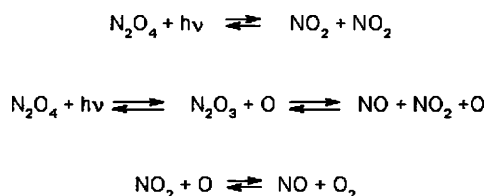
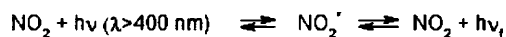
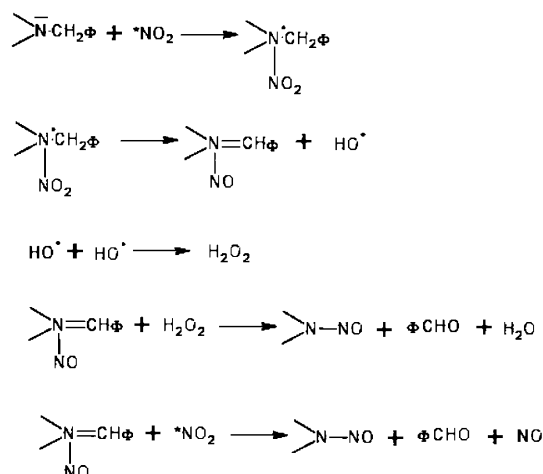
On the other hand, liquid N_2O_4 has the highest value for the homolytic dissociation constant K_{DIS} , which means that in these solutions the highest NO_2 concentration at a given temperature is attained. Nearly six-fold lower is the value of that constant in acetic acid and 30-fold lower in dimethylformamide. A comparison of the N_2O_4 homolytic dissociation constant values with the nitrosation reaction yields shows a positive correlation between these values. The higher NO_2 concentration in the reaction mixture at a specified temperature, the higher are reaction rate and yields achieved. This can be clearly seen from comparison of the TADBIW yields in the reactions conducted in liquid N_2O_4 with the yields for the reactions carried out in acetic acid. To sum up, the most probable nitrosating agent is NO_2 , which is formed in the N_2O_4 homolytic dissociation. Concentration of NO_2 depends on the solvent used and N_2O_4 homolytic dissociation constant.

Another factor affecting NO_2 concentration in the reaction mixture is the temperature. The higher the temperature, the more N_2O_4 dissociation equilibrium is shifted towards NO_2 . As mentioned earlier, at temperatures above

Table 1. Comparison of the TADBIW nitrosation yields for various dielectric constants and homolytic dissociation constants for several solvents.

Solvent	Dielectric Constant	Homolytic N_2O_4 Dissociation Constant $K_{\text{DIS}} \cdot 10^{-5}$	TADBIW Nitrosation Yield after 192 h Reaction at 20°C
Dinitrogen tetroxide	2.42	3.2	89 ^{a)}
Acetic acid	6.19	0.58	68
Acetic anhydride	20.7	–	64
Dimethylformamide	37	0.1	11

a) Yield value after a 16 h reaction.

**Scheme 4.** Radiation-induced N_2O_4 dissociation reactions.**Scheme 5.** N_2O_4 dissociation reactions induced by radiation of $\lambda > 400 \text{ nm}$.**Scheme 6.** Suggested mechanism for the TADBIW nitrosation reaction (Φ – phenyl substituent).

50 °C more than half of the N_2O_4 molecules undergo dissociation to NO_2 . This is reflected in the yields obtained and in the rates of the reaction conducted in acetic acid (Figure 3). The higher the reaction temperature, the higher is the reaction rate, which is also affected by a higher NO_2 concentration in the reaction mixture.

One more factor of potential influence on the NO_2 concentration in the reaction mixture is UV radiation. Dinitrogen tetroxide readily absorbs radiation, as a result of which the following reactions occur (Scheme 4) [8].

The reactions shown occur when the wavelength λ is lower than 400 nm. For $\lambda > 400 \text{ nm}$, the photon energy fails to induce decreasing of NO_2 but merely induces excitation of this molecule to a higher level (Scheme 5):

Increasing the TADNOIW yield observed in the reactions conducted under UV irradiation indicates a free-radical mechanism. It is known that NO_2 and NO molecules occur as free radicals in the reactions studied. An increased concentration of these molecules in the reaction systems will promote a free-radical mechanism. This results in the difference of the product yields in the reactions with or without UV irradiation equal to 12 and 19%, respectively,

for the reactions carried out for 6 h at 40 and 50 °C (Figure 4).

Based on the data presented, the suggested mechanism for the TADBIW nitrosation is shown in Scheme 6.

In the first reaction step, the intermediate nitrammonium free radical is formed, with which NO_2 free radical as a single-electron Lewis acid forms a bond with a free electron pair on the nitrogen. Subsequently, abstraction of the hydroxide free radical ($\cdot\text{OH}$) from nitrammonium radical to give nitrosoimine takes place. Hydroxyl radicals may recombine with each other to produce hydrogen peroxide. In a further reaction step, nitrosoimine undergoes oxidation as a result of a reaction with dinitrogen tetroxide or hydrogen peroxide to yield nitrosoamine and benzaldehyde.

4 Conclusions

The process of TADBIW nitrosation was studied. The TADNOIW synthesis was modified by using N_2O_4 in CH_3COOH . The influence of temperature, reaction time and UV radiation on the reaction yield was examined and a mechanism for TADBIW nitrosation was proposed.

In conclusion, the yield of TADBIW nitrosation using N_2O_4 in CH_3COOH depends on the reaction time, i.e. the yield increases with time. Moreover, it is shown that the reaction at higher temperature (70 °C) allows to obtain a high yield (92%) in shorter reaction time (5 h). The use of UV light increases the reaction rate. It seems likely that the nitrosation proceeds according to a free-radical mechanism.

This method has practical value for industrial interest, because the scale-up gives the same yield and purity of the product (TADNOIW). Crude TADNOIW may be used in the next HNIW synthesis step without purification.

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