ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 11, pp. 1891–1893. © Pleiades Publishing, Ltd., 2012.
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LETTERS TO THE EDITOR

Kinetics of Catalytic Hydrogenation of Methoxy-*NNO*-azoxymethane and Bis(methoxy-*NNO*-azoxy)methane

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Received May 31, 2011

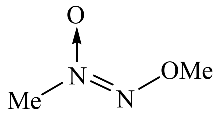
DOI: 10.1134/S107036321211031X

The alkoxy-*NNO*-azoxy compounds are known since the XIX century [1, 2]. The methods of their synthesis along with other azoxy compounds are summarized in [3–5]. Some representatives of this class of compounds are considered as biologically active compounds (the NO donors, anticancer drugs) [5–7], the components of some energy-rich materials [8, 9], and the gas-generating compositions [10]. A surprising chemical resistance of the azoxy compounds has been noticed earlier [2, 11]. The stability of alkoxy-*NNO*-azoxy compounds towards alkali and acids we have studied in detail using the kinetic methods [12–14]. The obtained results allow us to optimize the conditions of the synthesis and functionnalization of the new alkoxy-*NNO*-azoxy compounds in the presence of strong acids and bases.

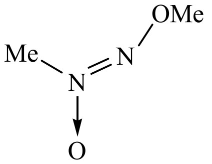
One of the most effective methods of the functionalization of organic compounds is the catalytic hydrogenation. A key step in the synthesis of hexanitrohexaazaisowurtzitane (CL-20), a powerful explosive, is one of the striking examples of the use of this method in the chemistry of energy-rich materials [15, 16].

Only one example of the catalytic hydrogenation of the alkoxy-*NNO*-azoxy compounds was found in the literature. The reaction of methoxy-*NNO*-azoxybenzene with 2 mol of hydrogen on the Adams catalyst (PtO_2) in anhydrous ethanol results in aniline as acetanilide (24%) and the unreacted starting compound (12%) [13].

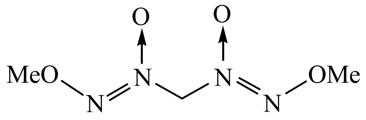
To evaluate the applicability of this method to the catalytic hydrogenation of the alkoxy-*NNO*-azoxy compounds we measured the hydrogenation rate on different catalysts by the example of methoxy-*NNO*-azoxymethane **I** with different content of the minor *E*-isomer and bis(methoxy-*NNO*-azoxy)methane **II**.



Z-**I**



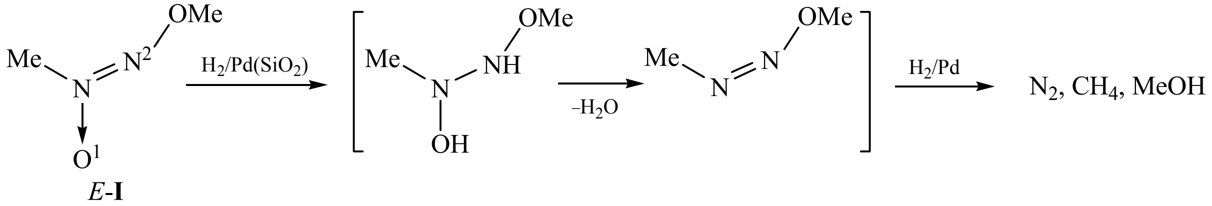
E-**I**



II

At 20°C the hydrogenation of compound **I** in methanol using 5% Pt catalyst on Aerosil does not virtually occur (the initial hydrogenation rate is $w_0 <$ 0.05 normal cm^3 min^{-1} g^{-1}). Both the pure *Z*-isomer of **I** and compound **I** containing 8.7% of the *E*-isomer do not react. When replacing methanol with 10% solution of HCl, the reaction is also not going. For comparison, the initial rate of the nitromethane hydrogenation using this catalyst in the presence of HCl under the same conditions is high enough, the w_0 value is 2.8 normal cm^3 min^{-1} g^{-1}.

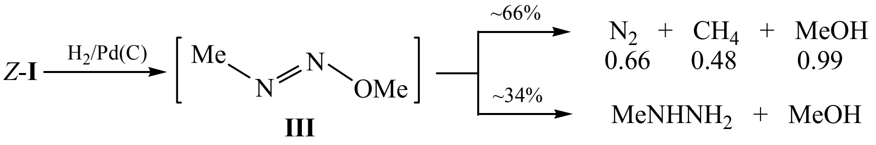
On the palladium catalysts the hydrogenation of **I** proceeds more rapidly. At the hydrogenation of compound **I** containing 6.9% of the *E*-isomer using 5% Pd on Aerosil the initial rate w_0 equals 4.4 normal cm^3 min^{-1} g^{-1}. The *E*-isomer is hydrogenated primarily (after the absorption of 0.14 mol of hydrogen the *E*-isomer content decreases from 6.9 to 0.3%). Under these reaction conditions the pure *Z*-isomer is hydrogenated much slower (w_0 0.5 normal cm^3 min^{-1} g^{-1}). This selectivity can be ascribed to the fact that at the first stage the hydrogen adds to the N^2 and O^1 atoms, which in the *E*-isomer are more available than in the *Z*-isomer.



On the 5% Pd catalyst on activated charcoal the pure *Z*-isomer is hydrogenated with a higher rate (w_0 3.5 normal cm^3 min^{-1} g^{-1}).

The kinetic curves of the hydrogen absorption in the hydrogenation of **I** do not correspond to the common zero order with respect to the substrate but are similar in shape to those of the first order. This can be explained by the formation of nitrogen and methane in the hydrogenation progress. They accumulate in the reactor vessel and reduce the hydrogen partial pressure proportionally to the reacted material, which creates the illusion of the first order reaction. On the other hand, the possibility of poisoning of the catalyst with the nitrogen hydrogenation products should not be excluded.

For a quantitative analysis of the hydrogenation products of the *Z*-isomer of **I** using the 5% Pd/C catalyst, the reaction was performed in a solvent-free conditions in a sealed vessel to control the reaction pressure. Considering the reduction of the pressure in the reaction vessel and the yields of nitrogen, methane and methanol, we calculated the hydrogen consumption as 2.17 mol of hydrogen per 1 mol of compound **I**. The ratio of the hydrogenation products can be explained by two ways of transformation of unstable intermediate **III**.



When trying to perform the hydrogenation of *Z*-**I** using the 5% Pd/C catalyst in 10% solution of HCl, the dissolution of palladium was observed to give a light brown solution.

Probably, the mechanism of the hydrogenation of compound **II** on the 5% Pd/C catalyst is the same as for the *Z*-isomer of compound **I**. This is indicated by a similar composition of the gaseous products. However, the rate of the hydrogenation of **II** is 5 times higher (w_0 18 normal cm^3 min^{-1} g^{-1}). For comparison, a typical rate of the hydrogenation of nitrobenzene on this catalyst is 30–50 normal cm^3 min^{-1} g^{-1}.

$$\mathbf{II} \xrightarrow{H_2/Pd(C)} \underset{2.0}{N_2} + \underset{0.1}{CH_4} + MeOH$$

Thus, the rate of the hydrogenation of the alkoxy-*NNO*-azoxy compounds depends significantly on their structure and on the catalyst type, which made it possible to find the conditions for the selective reduction of the functional groups without affecting the alkoxy-*NNO*-azoxy groups.

Compounds **I** and **II** were synthesized according to the known methods [17, 18]. Compound **I** was distilled twice in a vacuum. Compound **II** was recrystallized twice and thoroughly dried. The kinetics of the hydrogenation was measured volumetrically by a gas buret at atmospheric pressure in a usual hydrogenation vessel for shaking, of 70 ml volume. The temperature 20±0.1°C in a water jacket was maintained by the pumping thermostat. After the catalyst (100–200 mg) in 20 ml of ethanol was saturated with hydrogen, the shaker was stopped. A solution of the reactant (~100 mg) in 10 ml of ethanol was added, and the shaker was started (~120 cycles per min). The initial rates of the hydrogenation w_0 are given relative to 1 g of the catalyst (normal cm^3 min^{-1} g^{-1}).

The isomeric composition of compound **I** was measured by GLC on a LKhM-8MD chromatograph equipped with a flame-ionization detector. The carrier gas was nitrogen (30 ml min^{-1}). The steel column (2 m×3 mm) and 15% Carbowax-20M on Chromosorb W-HMDS (80–100 mesh) were used. The column temperature was 160°C. The retention time of the *Z*-isomer was 11.9 min, of *E*-isomer, 13.7 min.

The gaseous hydrogenation products were analyzed on a LHM-8MD chromatograph equipped with a detector katharometer, carrier gas helium (100 ml min^{-1}). The copper column (l 6 m, d 5 mm) and Polisorb-1 (0.2–0.3 mm) were used. The column temperature was –60 and 35°C. For the analysis of the hydrogenation products, 200 mg of the catalyst (5% Pd/C) and 100 mg of compound **I** were separately placed into a glass vessel with a sickle shaped zero manometer. The vessel was evacuated and filled with hydrogen to 600 mm Hg. The reactants were mixed. The reaction completion was determined from the pressure stabilization. For the analysis of the hydrogenation products of compound **II**, the gas sample was taken from the reactor.

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