ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 5, pp. 831–833. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © I.N. Zyuzin, D.B. Lempert, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 5, pp. 738–740.

Reactivity of Alkoxy-*NNO*-azoxy Compounds toward Hydrazine Hydrate and Inorganic Reducing Agents

I. N. Zyuzin and D. B. Lempert

Institute of Chemical Physics Problems, Russian Academy of Sciences,
pr. Akademika Semenova 1, Chernogolovka, Moscow oblast, 142432 Russia
e-mail: zyuzin@icp.ac.ru

Received October 7, 2013

Abstract—The chemical stability of alkoxy-*NNO*-azoxy compounds to reduction with hydrazine hydrate has been studied. Methoxy-*NNO*-azoxymethane and bis(methyl-*ONN*-azoxy) formaldehyde acetal are more stable by orders of magnitude than bis(methoxy-*NNO*-azoxy)methane and 2,2-bis(methoxy-*NNO*-azoxy)propane. Methoxy-*NNO*-azoxymethane is also resistant to reduction with titanium(III) under acidic conditions and with iron(II) under basic conditions. Probable reaction mechanisms have been proposed on the basis of the substrate reactivity toward nucleophiles, acids, and alkalies.

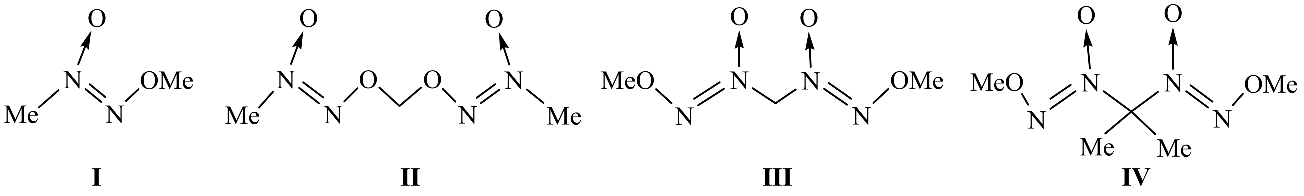
Keywords: alkoxy-*NNO*-azoxy compounds, methoxy-*NNO*-azoxymethane, hydrazine, kinetics, reduction

DOI: 10.1134/S1070363214050077

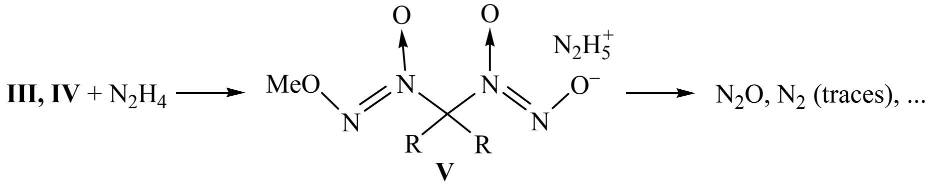
In continuation of our quantitative studies on the chemical reactivity of alkoxy-*NNO*-azoxy compounds (2-alkoxy-1-alkyldiazene oxides) under different conditions (alkaline, acidic, hydrogenation, oxidation with potassium permanganate) [1–5], in the present work we measured the rate constants for the reactions of compounds **I**–**IV** with hydrazine hydrate, taking into account that the latter is widely used for functionnalization of organic compounds. In addition, the ability of methoxy-*NNO*-azoxymethane (**I**) to undergo reduction with Ti(III) ions in acidic medium and with iron(II) ion in alkaline medium was quantitatively estimated (Scheme 1).

Compounds **II**–**IV** are sparingly soluble in hydrazine hydrate; therefore, the kinetic data should be regarded as semiquantitative. However, this fact did not prevent us from drawing some definite conclusions since the rate constants of the hydrazinolysis of compounds **III** and **IV** at 50°C are higher by an order

Scheme 1.



Scheme 2.



R = H, Me.

Effective rate constants of the hydrazinolysis of compounds **I**–**IV** and yields of the products

Compound no.	Temperature, °C	k_{eff}, s^{-1}	Yield[a]	
			N_2	N_2O
I	80	1.0×10^{-7}	0.8	0.2
II	80	$1.5 \times 10^{-6\,b}$	–	–
III	50	$1.6 \times 10^{-4\,b}$	0.03	1.64
IV	50	$1.4 \times 10^{-5\,b}$	0.02	1.94

[a] Moles per mole of the reacted substrate. [b] The value should be regarded as a rough estimate, for the substrate was sparingly soluble in hydrazine hydrate.

of magnitude than those found for compounds diazene oxides **I** and **II** at 80°C (see table).

The formation of the same products (N_2O with traces of N_2) gives us grounds to presume similar reaction mechanisms for the reduction of compounds **III** and **IV**. The rate-determining step is likely to be attack by hydrazine molecule on the methoxy carbon atom (S_N2 reaction), which is followed by decomposition of intermediate **V** (Scheme 2).

Similarity of the rates of hydrazinolysis of compounds **III** and **IV** allowed us to rule out the mechanism involving deprotonation of the central carbon atom in molecule **III** [1]. The formation of trace amounts of nitrogen contradicts alternative mechanisms where hydrazine would act as reducing agent in the rate-determining step. The proposed mechanism is also supported by the formation of *N*-nitroso-*N*-phenylhydroxylamine hydrazinium salt in the reaction of methoxy-*NNO*-azoxybenzene with 2 equiv hydrazine hydrate on heating at the boiling point over a period of 17 h [6].

Unlike azoxy compounds **III** and **IV**, the reactions of **I** and **II** with hydrazine hydrate follow a ionic mechanism, as follows from their higher stability and different composition of the products (mainly N_2). This is likely to be related to strong effect of the leaving group on the S_N2 reaction rate. The anion $MeN(O)=NO^-$ is inferior to anion **V** as leaving group, since the former is stabilized by the electron-acceptor N(O)=NOMe substituent. Probably, the azoxy group is derectly reduced with hydrazine with subsequent decomposition of unstable intermediates [4].

To estimate the reactivity of methoxy-*NNO*-azoxymethane (**I**) toward reducing agents, as the latter we selected Ti(III) ions in acidic medium and iron(II) ions in alkaline medium, taking into account that these reagents are used in quantitative analyses for NO_2, NO, N(O)=N, and other groups [7]. After heating in boiling 20% aqueous HCl over a period of 20 min, 0.071 mol of Ti(III) per mole of **I** was consumed (under these conditions, nitro and nitroso compounds RNO_2 and RNO are quantitatively reduced to the corresponding amines). By special experiment we showed that in the absence of Ti(III) ions, other conditions being equal, 3.8% of initial compounds **I** undergoes hydrolysis [2]. These findings suggest that Ti(III) is consumed for the reduction of the hydrolysis products (~2 equiv) and that direct reduction of **I** almost does not occur. Compound **I** turned out to be resistant to Fe(II) ions in 5 M KOH. After heating for 15 min with excess Fe(II), only 0.12 equiv of the latter was consumed. The reduction of 1 mol of $MeNO_2$ under analogous conditions requires 5.4 equiv of Fe(II). Presumably, the rate-determining step is alkaline hydrolysis of **I** [1] rather then its direct reduction.

Thus, the rates of hydrazinolysis of compounds **III** and **IV** at 50°C are higher by orders of magnitude than the rates of hydrazinolysis of compounds **I** and **II** at 80°C. High stability of compound **I** to the reduction with Ti(III) and Fe(II) ions makes their use for quantitative determination of alkoxy-*NNO*-azoxy group impossible. The relative stability of alkoy-*NNO*-azoxy compounds to hydrazine and inorganic reducing agents opens prospects in the development of new synthetic approaches to compounds of this series; however, the possibility for hydrazinolysis and decomposition should be taken into account while choosing conditions for the reaction of geminal bis(alkoxy-*NNO*)-azoxy compounds with hydrazine.

EXPERIMENTAL

Compounds **I**–**IV** were synthesized according to the procedures described in [8–11]. The kinetics of the hydrazinolysis were studied by the pressure gage technique using a Bourdon tube (100–200 mg of substrate and 2 mL of hydrazine hydrate). The temperature was maintained with an accuracy of ±0.1°C with the aid of a water thermostat. Gaseous products were analyzed on an LKhM-8MD chromatograph equipped with a thermal conductivity detector and copper columns, 6 m × 5 mm, packed with Polisorb-1 (0.2–0.3 mm); carrier gas helium (flow rate 100 mL/min), oven temperature 35°C.

The stability of compound I to reducing agents was estimated according to the procedure described in [7]. *a*. A weighed sample of **I** was added to a solution of 0.5 g of ammonium fluoride in 5 mL of concentrated aqueous HCl. The mixture was purged with argon, 10–40 mL of a 0.08 N solution of titanium(III) chloride in 20% aqueous HCl was added, and the mixture was heated for 20 min under reflux in a stream of argon. The mixture was then cooled, 2 mL of 10% ammonium thiocyanate was added, and the mixture was titrated with a 0.15 N solution of iron(III) chloride.

b. Mohr's salt, 1 g, was added under argon to 30 mL of a 1.5 M solution of potassium hydroxide, a weighed sample of **I** was added, and the mixture was heated for 15 min under reflux. The mixture was cooled, 20 mL of concentrated aqueous HCl and 2 mL of a 10% solution of ammonium thiocyanate were added, and the mixture was titrated with a standard Ti(III) solution.

REFERENCES

1. Zyuzin, I.N. and Lempert, D.B., *Russ. J. Gen. Chem*., 2010, vol. 80, no. 9, p. 1792. DOI: 10.1134/S1070363210090124.
2. Zyuzin, I.N. and Lempert, D.B., *Kinet. Catal*., 2011, vol. 52, no. 1, p. 17. DOI: 10.1134/S0023158411010228.
3. Zyuzin, I.N. and Lempert, D.B., *Russ. J. Gen. Chem*., 2012, vol. 82, no. 6, p. 1105. DOI: 10.1134/S1070363212060114.
4. Zyuzin, I.N. and Lempert, D.B., *Russ. J. Gen. Chem*., 2012, vol. 82, no. 11, p. 1891. DOI: 10.1134/S107036321211031.
5. Zyuzin, I.N. and Lempert, D.B., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 1, p. 162. DOI: 10.1134/S1070363214010253.
6. George, M.V., Kierstead, R.W., and Wright, G.F., *Can. J. Chem*., 1959, vol. 37, no. 4, p. 679.
7. Siggia, S. and Hanna, J.G., *Quantitative Organic Analysis via Functional Groups*, New York: Wiley, 1979, 4th ed.
8. Zyuzin, I.N. and Lempert, D.B., *Bull. Acad. Sci. USSR, Div. Chem. Sci*., 1985, vol. 34, no. 4, p. 753. DOI: 10.1007/BF00948052.
9. Zyuzin, I.N., Nechiporenko, G.N., Golovina, N.I., Trofimova, R.F., and Loginova, M.V., *Russ. Chem. Bull*., 1997, vol. 46, no. 8, p. 1421. DOI: 10.1007/BF02505678.
10. Yandovskii, V.N., Dobrodumova, E.Yu., and Tselinskii, I.V., *J. Org. Chem. USSR*, 1980, vol. 16, no. 5, p. 813.
11. Zyuzin, I.N., *Russ. J. Org. Chem*., 2013, vol. 49, no. 4, p. 536. DOI: 10.1134/S1070428013040076.