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Kinetics of Methoxy-NNO-Azoxymethane Hydrolysis in Strong Acids

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Abstract—The kinetics of methoxy-NNO-azoxymethane (**I**) hydrolysis in concentrated solutions of strong acids (HBr, HCl, $HClO_4$, and H_2SO_4) has been investigated by a manometric method. The gas evolution rate is described by the equation corresponding to two consecutive first-order reactions, with the rate constant of the second reaction considerably exceeding the rate constant of the first reaction, i.e., $k_2 \gg k_1$. The temperature dependences of k_1 (s^{-1}) in 47.59% HBr in the temperature range from 60 to 90°C and in 64.16% H_2SO_4 between 80 and 130°C are described by Arrhenius equations with $\log A = 12.7 \pm 1.5$ and 13.6 ± 1.4 and $E_a = 115 \pm 10$ and 137 ± 10 kJ/mol, respectively. The parameters of the Arrhenius equation for the rate constant k_2 for the reaction in 64.16% H_2SO_4 between 80 and 130°C are $\log A = 9.1 \pm 2.5$ and $E_a = 91 \pm 18$ kJ/mol. An analysis of the UV spectra of compound **I** in concentrated H_2SO_4 shows that **I** is a weak base ($pK_{BH^+} \approx -6$). The rate-determining step of the hydrolysis of **I** is the attack of the nucleophile on the carbon atom of the MeO group of the protonated molecule of **I**. The resulting methyldiazene dioxide decomposes via a complicated mechanism to evolve N_2, NO, and N_2O. The pseudo-first-order rate constant k_1 of the reaction at 80°C depends strongly on the acid concentration and on the type of nucleophile (Br^-, Cl^-, or H_2O). The relationship between k_1 and the rate constant k of the bimolecular nucleophilic substitution reaction (S_N2) is given by the linear equation $\log[k_1/(C_H + C_{Nu})] = m^{\neq}m^*X_0 + \log(k/K_{BH^+})$, where C_{H^+} and C_{Nu} are the concentrations of H^+ and nucleophile, respectively; X_0 is the excess acidity; and $m^{\neq}$ and m^* are coefficients. The Swain–Scott equation $\log(k_{Nu}/k_{H_2O}) = ns$, where n is the nucleophilicity factor and s is the substrate constant ($s = 0.72$), is applicable to the rate constants k of the S_N2 reactions of the protonated molecule of **I** with Br^-, Cl^-, and H_2O.

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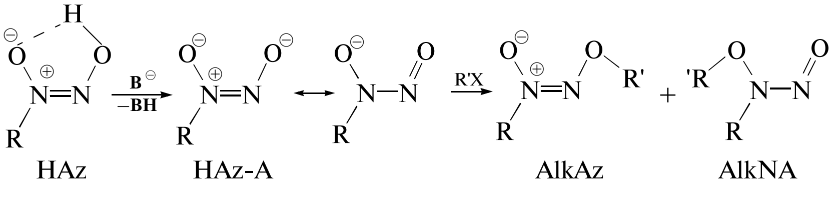
Alkoxy-NNO-azoxy compounds (AlkAz) have been known since the end of the 19th century [1, 2]. Some representatives of this poorly studied class of compounds are now considered as components of gas-generating compositions [3] and biologically active compounds (NO donors, antineoplastic drugs) [4–6].

The AlkAz synthesis methods were systematizes in a number of reviews [4, 7, 8]. Usually, AlkAz compounds are synthesized by reacting hydroxyl-NNO-azoxy compounds (HAz, also called *N*-nitrosohydroxylamines) or their anions (HAz-A) with electrophilic agents [4, 7–10]. The main drawback of this reaction is its insufficient selectivity. Along with target AlkAz, by-products (alkoxynitrosoamines AlkNA) are always formed due to the electrophilic attack of an HAz-A anion on the O(1) atom (Scheme 1).

Usually, it is unnecessary to synthesize AlkNA via Scheme 1 because these compounds can be obtained by the simple and fully predictable alkylalkoxyamine nitrosylation reaction. As a consequence, only a few



Scheme 1.

examples of the isolation of AlkNA along with AlkAz from the reaction according to Scheme 1 are known [1, 2, 11–13]. It is substantially more important to remove the AlkNA traces from the target compound AlkAz and from the reaction mixture and synthesis waste, because the AlkNA compounds are potentially dangerous carcinogens [14, 15]. A number of AlkAz's [2, 11–13] was purified by making use of the high thermal stability of AlkAz [16] as compared to AlkNA [13, 17]. However, this approach requires rather severe conditions in some cases. In particular, allyloxy-NNO-azoxymethane was purified from an *N*-allyloxy-*N*-methylnitrosoamine by heat treatment at 140°C for 1.5 h [11], based on the thermal decomposition constant data for this AlNA (2.8×10^{-6} and 4.9×10^{-3} s^{-1} at 80 and 130°C, respectively [11]). In our opinion, acidic treatment is more appropriate for the removal of AlkNA's, since these compounds are readily hydrolyzable in solutions of strong acids at room temperature [15, 18–21]. For example, after treatment with 40% H_2SO_4 for 3 h at 25°C, ethoxy-NNO-azoxymethane becomes purer than the initial sample [19].

The kinetics and mechanisms of the acidic hydrolysis of selected AlkNA's were studied in [15, 21]. AlkAz was found to have very high chemical resistance toward strong acids [2, 19, 22]. For instance, bis(methoxy-NNO-azoxy)methane was recrystallized from 70% HNO_3, and methoxy-NNO-azoxybenzene was isolated unchanged after heat treatment at 100°C with 85% H_2SO_4 [22]. However, we found no examples of studying the kinetics of AlkAz acidic hydrolysis.

Chemical modification of the substituents in AlkAz obtained via Scheme 1 constitutes an important group of methods for the synthesis of functionalized AlkAz. Many of these reactions, for instance nitration, are carried out in strong acids [22]. Strong acids can also act as reactants [23–25]. To optimize the conditions for the preparation of these and similar reactions, it would be pertinent to estimate the hydrolytic stability of the AlkAz group at different temperatures and for various types and concentrations of acids.

The kinetics of the acidic hydrolysis of methoxy-NNO-azoxymethane (**I**), the simplest AlkAz, was studied in this work to elucidate the mechanism of the reaction.

EXPERIMENTAL

Chemicals

The synthesis and characteristics of compounds **I** [26], 2,2-dimethyl-1-(methoxy-NNO-azoxy)propane (**II**) [26], and hydroxy-NNO-azoxymethane sodium salt (**III**) [27] were studied earlier. Solutions of HCl, $HClO_4$, and H_2SO_4 were obtained by dilution of the corresponding acids (reagent grade) with distilled water. HBr solutions were obtained from the azeotrope (47.59% HBr). The HBr azeotrope was obtained by distillation of the acid (analytical grade). The solution concentrations were determined by titration and were checked by density measurements. The molarity of acids was derived from their density by extrapolating the data available for HCl [28], HBr [28], H_2SO_4 [29], and $HClO_4$ [30] to the experimental temperature. The molarities of the Cl^-, Br^-, and H^+ ions in HCl, HBr, and $HClO_4$ solutions, respectively, were taken to be equal to the molarities of the acids. The molarity of the H^+ ions in H_2SO_4 solutions at 25°C [31] were calculated taking into account the density of the solution at the experimental temperature, assuming that the molarity is proportional to the density.

Kinetic Measurements

The kinetics of acidic hydrolysis was studied in sealed evacuated glass vessels 140–170 ml in volume fitted with a crescent-shaped null manometer. The sample weight was 100–200 mg, and the acid volume was 10 ml. In the hydrolysis of compound **I** in H_2SO_4 and $HClO_4$ at 80 and 90°C, the acid volume was 2 ml and the free volume was 3.3–8.2 ml. The hydrolysis kinetics of hydroxyl-NNO-azoxymethane (**IV**, also called *N*-methyl-*N*-nitrosohydroxylamine) was studied by placing an acid solution in a "finger" sealed to the reaction vessel and pouring this solution to salt **III** after heating the vessel. The temperature was maintained with an accuracy of ±0.1°C with a water thermostat, and an oil thermostat (±0.2°C accuracy) was used above 100°C.

Product Analysis

UV spectra were recorded on a Specord UV VIS spectrophotometer. Gaseous hydrolysis products were analyzed on an LKhM-8MD chromatograph (thermal-conductivity detector, helium as the carrier gas, flow rate of 100 ml/min, copper columns 6 m in length and 5 mm in diameter, Polisorb-1 with a particle size of 0.2–0.3 mm as the stationary phase, column temperatures of –78 and 90°C).

RESULTS AND DISCUSSION

The kinetic curves describing the pressure rise in the system are similar to first-order curves, except for their initial portions (up to a conversion of 0.1), where most of them are S-shaped. A typical curve is shown in Fig. 1. The kinetic data were processed by least squares using the steepest descent method and the kinetic equation for consecutive first-order reactions:

$$P = P_0 + P_\infty\{1 - [k_2\exp(-k_1t) - k_1\exp(-k_2t)]/(k_2 - k_1)\}, \tag{1}$$

where k_1 and k_2 are the apparent pseudo-first-order rate constants ($k_2 > k_1$), t is time, P_0 is the vapor pressure over the acid after heating (2–3 min), $P = (P_0 +$

P_{pr}) is the observed pressure, P_{pr} is the pressure of the gaseous hydrolysis products, and $P_\infty = P_{pr}$ at $t \longrightarrow \infty$. Four parameters were optimized, namely, P_0, P_∞, k_1, and k_2. At $k_2/k_1 > 10^4$, the curves were fitted to a first-order kinetic equation and P_0, P_∞, and k_1 were optimized. Next, we fixed the P_0 and P_∞ values thus found and refined k_1 and the error of its determination by the least squares method. The refined errors are presented for the 95% confidence level. The points obtained below a conversion of 0.8 were taken into account. P_∞ ranged from 300 to 500 Torr. The root-mean-square deviation of the calculated pressure from the experimental pressure, $s(\Delta P)$ (Table 1), is close to the instrumental error of pressure measurement. In the slow hydrolysis reactions of compound **I** in H_2SO_4 and $HClO_4$ at 80, 90, and 108.5°C, the conversion was 0.006–0.30. In these cases, P_∞ was calculated from the yield of the gaseous products ($\alpha_\infty = P_\infty/P$) in 64.16% H_2SO_4 at 119.8°C and from the temperature dependence of a_∞ for the hydrolysis of **I** in 47.59% HBr. Next, having fixed P_∞, we optimized k_1, k_2, and P_0. The results are listed in Table 1.

The temperature dependences of the rate constant k_1 (s^{-1}) for compound **I** hydrolysis in 47.59% HBr at 60–90°C and in 64.16% H_2SO_4 at 80–130°C are satisfactorily described by the Arrhenius equation with $\log A = 12.7 \pm 1.5$ and 13.6 ± 1.4 and $E_a = 115 \pm 10$ and 137 ± 10 kJ/mol, respectively. The constant k_2 obeys the Arrhenius law to a much lesser extent: $\log A = 9.1 \pm 2.5$ and $E_a = 91 \pm 18$ kJ/mol for 64.16% H_2SO_4 in the temperature range from 80 to 120°C.

The strong dependence of the hydrolysis rate of compound **I** on the acid concentration (Table 1) indicates that the first reaction step is the protonation of molecule **I**. To estimate the basicity of compound **I**, we recorded its UV spectra in water and in H_2SO_4 solutions (Table 2). The π–π* transition band of the protonated molecule of **I** is shifted relative to the same band of the free molecule **I** to the short wavelengths (Table 2). In 94.3% H_2SO_4, the protonated and neutral forms of compound **I** are observed in comparable amounts (the band is asymmetric, broadened, and less intense at the maximum point). In 64.16% H_2SO_4 (the most acidic medium used in the study of the hydrolysis kinetics), the proportion of the protonated form is small. Accepting that the concentrations of protonated (C_{BH^+}) and free (C_B) compound **I** in 94.3% H_2SO_4 are the same, one can approximately estimate pK_{BH^+} for compound **I** using the equation [31]

$$pK_{BH^+} = \log(C_{BH^+}/C_B) - \log C_{H^+} - m^*X_0, \qquad (2)$$

where $X_0 = -H_0 - \log C_{H^+}$ is the excess acidity (H_0 is the Hammett acidity function) and m^* is a coefficient. The concept of excess acidity was reviewed in [32, 33]. Knowing the product $m^{\neq}m^*$ derived from kinetic data (see below; Table 3) and assuming that $m^{\neq} = 1$ and that m^* is temperature-independent, we can estimate m^* at 0.58. Using the known values of $\log C_{H^+}$ [31] and H_0 [34], we found that $pK_{BH^+} = -6.26 \approx -6$. For comparison, Et_2O is one order of magnitude stronger base ($pK_{BH^+} = -5.2$ [35]) and $MeNO_2$ is a much weaker base ($pK_{BH^+} = -11.9$ [35]).

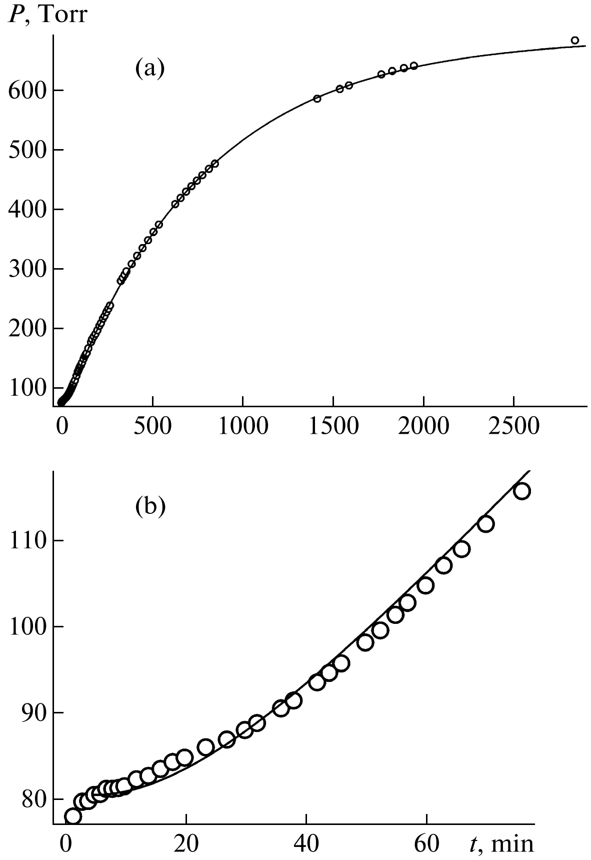


Fig. 1. (a) Typical kinetic curve for the acidic hydrolysis of compound **I** in 47.59% HBr at 70°C and (b) its initial portion. The points represent experimental data, and the curves represent the data calculated using Eq. (1). $P_0 = 80.5$ Torr, $P_\infty = 609.6$ Torr, $k_1 = 2.162 \times 10^{-5}$ s^{-1}, and $k_2 = 6.87 \times 10^{-4}$ s^{-1}.

The π-electron system of molecule **I** can be viewed as a set of mesomeric forms (Scheme 2) [36], and protonation at the N atom (**V**) seems most probable (Scheme 2).

However, protonation at the *N*-oxide O atoms (**VI**) with stabilization by an intramolecular hydrogen bond similar to that in hydroxy-NNO-azoxy compounds (*N*-nitrosohydroxylamines) cannot be excluded [37,

Table 1. Apparent rate constants of the pseudo-first-order hydrolysis reactions of compounds **I**, **II**, and **IV** in solutions of strong acids

Compound	Acid	Acid concentration, %	T, °C	k_1, s^{-1}	k_2, s^{-1}	$s(\Delta P)$, Torr*	α_∞^{**}
I	HBr	24.25	80	4.678×10^{-7}	4.12×10^{-4}	0.5	1.74
		30.03	80	$(1.485 \pm 0.007) \times 10^{-6}$	(***)	2.4	2.00
		34.84	80	3.775×10^{-6}	6.70×10^{-4}	1.0	2.27
		39.30	80	9.49×10^{-6}	1.2×10^{-2}	1.2	2.39
		45.10	80	4.335×10^{-5}	5.40×10^{-4}	2.8	2.15
		47.59	60	6.022×10^{-6}	4.70×10^{-4}	0.9	2.10
		47.59	70	2.162×10^{-5}	6.87×10^{-4}	1.7	2.07
		47.59	80	6.75×10^{-5}	1.60×10^{-3}	2.2	2.14
		47.59	90	1.824×10^{-4}	8.67×10^{-3}	2.2	2.22
	HCl	16.36	80	$(2.487 \pm 0.008) \times 10^{-7}$	(***)	0.7	2.37
		19.34	80	5.517×10^{-7}	3.31×10^{-3}	1.3	2.49
		22.34	80	1.107×10^{-6}	1.08×10^{-3}	0.8	2.63
		25.26	80	2.252×10^{-6}	4.37×10^{-4}	0.6	2.66
		28.25	80	4.407×10^{-6}	3.90×10^{-4}	1.3	2.54
	H_2SO_4	35.30	80	2.28×10^{-8}	1.95×10^{-5}	1.2	1.20
		51.52	80	7.92×10^{-8}	2.33×10^{-5}	2.0	1.20
		64.16	80	2.42×10^{-7}	4.42×10^{-5}	1.4	1.20
		64.16	90	7.08×10^{-7}	1.13×10^{-4}	2.6	1.25
		64.16	90	1.00×10^{-6}	8.44×10^{-5}	0.4	1.25
		64.16	105.8	5.78×10^{-6}	3.90×10^{-4}	0.5	1.33
		64.16	119.8	2.77×10^{-5}	8.87×10^{-4}	1.1	1.39
		64.16	130	$(7.250 \pm 0.008) \times 10^{-5}$	(***)	1.1	1.69
	$HClO_4$	42.93	80	3.08×10^{-8}	7.4×10^{-5}	2.1	1.20
II	HBr	47.01	80	1.153×10^{-4}	1.19×10^{-3}	1.6	1.42
	H_2SO_4	64.16	119.8	$(6.87 \pm 0.04) \times 10^{-5}$	(***)	1.2	1.73
IV	HBr	47.59	50	$(6.41 \pm 0.05) \times 10^{-4}$	(***)	0.8	1.01
		47.59	60	$(1.522 \pm 0.06) \times 10^{-3}$	(***)	0.6	1.01

*Standard deviation $s(\Delta P) = [(n-1)^{-1}\Sigma(P_{exp} - P_{calc})^2]^{0.5}$.

**The yield of gaseous products at $t \longrightarrow \infty$: $\alpha_\infty = (P_\infty - P_0)/P_{1\,mol}$, where $P_{1\,mol}$ is the calculated pressure of an equimolar amount of an ideal gas.

*** $k_2/k_1 > 10^4$.

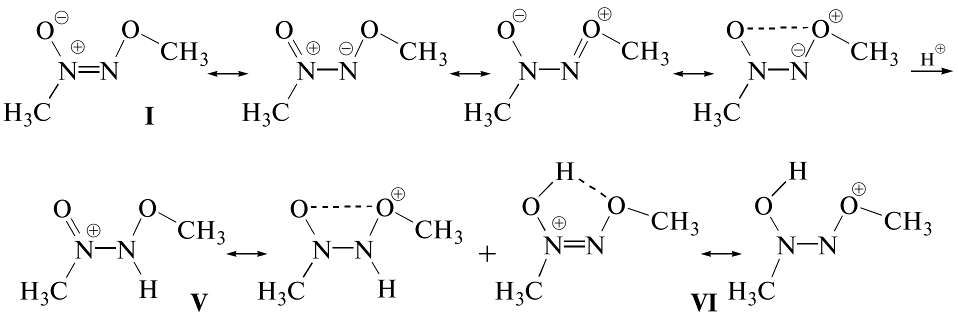
38]. This protonation is suggested by the fact that it is this O atom that serves as the donor for the hydrogen bond [39].

Table 2. UV spectra of compound **I** at different H_2SO_4 concentrations

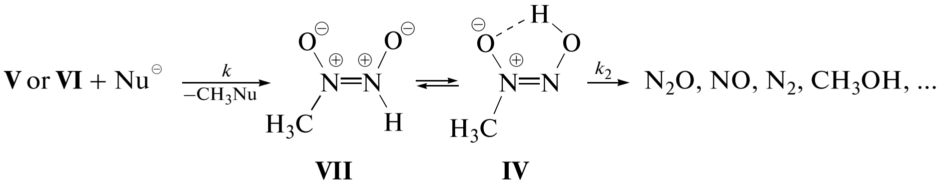
H_2SO_4 concentration, %	λ_{max}, nm	ε	Band width at half-ε, nm
0	233.7	9130	28.9
64.16	230.1	7950	28.2
94.3	224.7	5110	36.2

At a comparable acidity, the hydrolysis rate of compound **I** depends strongly on the nature of the acid: k_1 decreases in the order HBr > HCl > $H_2SO_4 \approx HClO_4$ (Table 1). This order coincides with the nucleophilicity order $Br^- > Cl^- > H_2O$ [40]. This suggests that the rate-determining step of the reaction is the attack of a nucleophile on the C atom of the CH_3O group of the protonated molecule of **I**. The leaving group is *N*-methyldiazene dioxide (**VII**) or hydroxy-NNO-azoxymethane (**IV**), depending on the type of molecule **I** protonation (Scheme 3).

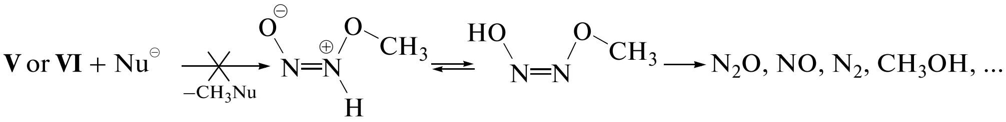
The S-shaped initial portion of the kinetic curves (Fig. 1) explains the accumulation of intermediates **IV** or **VII**, and the constant k_2 (Table 1) characterizes the



Scheme 2.



Scheme 3.

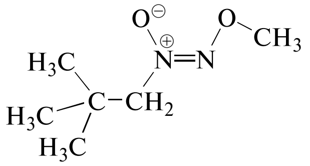


Scheme 4.

stability of intermediates **IV** and **VII** under the hydrolysis conditions.

The possibility of a nucleophilic attack on another C atom of the protonated molecule of **I** cannot be excluded a priori (Scheme 4).

To check this possibility, we used 2,2-dimethyl-1-(methoxy-NNO-azoxy)propane (**II**)



II

instead of compound **I**. Due to steric hindrance, the S_N2 reaction rate for compound **II** at the $\underline{C}H_2$ atom of the neopentyl group might be expected to be lower by several orders of magnitude [40]. In fact, the experimentally measured hydrolysis rate of compound **II** is even higher than the hydrolysis rate of compound **I**: in 47.01% H_2SO_4 at 80°C it is higher by a factor of 1.8, and in 64.16% H_2SO_4 at 119.8°C it is 2.5 times higher (cf. k_1, Table 2). Thus, the mechanism shown in Scheme 4 is ruled out.

The influence of the acid concentration on the hydrolysis rate of compound **I** was studied at 80°C. The relationship between the constant k of the bimolecular nucleophilic substitution reaction (S_N2) and

Table 3. Parameters $m^{\neq}m^*$ and $\log(k/K_{BH^+})$ at 80°C in Eq. (4)

Acid	Nucleophile	$m^{\neq}m^*$	$\log(k/K_{BH^+})$, l^2 mol^{-2} s^{-1}	Estimate of k, l mol^{-1} s^{-1}
HBr	Br^-	0.77 ± 0.06	−7.96 ± 0.11	2×10^{-2}
HCl	Cl^-	0.63 ± 0.04	−8.57 ± 0.07	5×10^{-3}
H_2SO_4 и $HClO_4$	H_2O	0.58 ± 0.05	−10.74 ± 0.13	3×10^{-5}

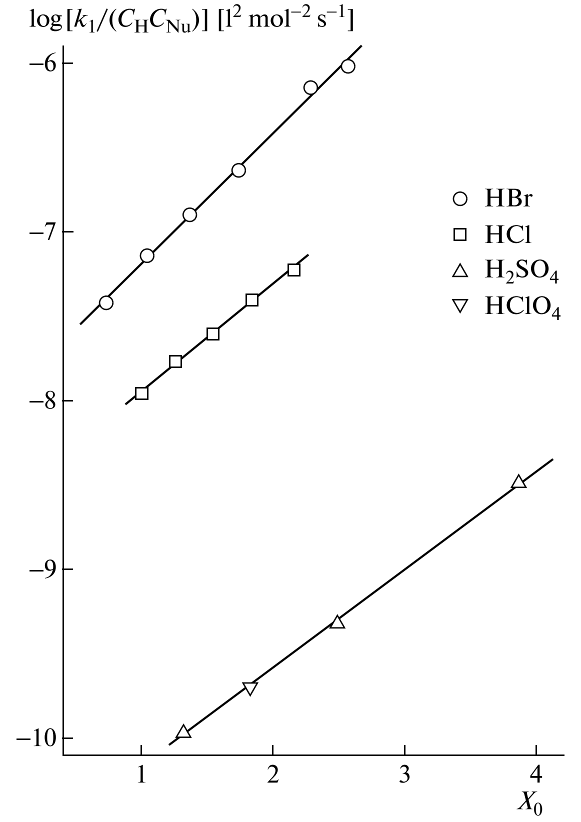


Fig. 2. Applicability of Eq. (4) to the description of the effect of the medium on the acidic hydrolysis rate constant k_1 of compound **I** at 80°C. The X_0 values at 25°C were calculated via a polynomial formula [44] for HBr and $HClO_4$ and via the formula $X_0 = -H_0 - \log C_{H^+}$ for HCl and H_2SO_4. The acidity functions H_0 were taken from the literature (HCl [44], H_2SO_4 [34]).

the experimental pseudo-first-order reaction rate constant k_1 (Table 1) is as follows [41]:

$$\log k_1 - \log[C_B/(C_{BH^+} + C_B)] - \log C_{H^+} = m^{\neq} m^* X_0 + \log C_{Nu} + \log(k/K_{BH^+}). \quad (3)$$

Because there are no published X_0 data for HBr, we used the parameter $X_0 = -H_0 - \log C_{H^+}$, which is similar in meaning, for all acids. For the same reason, the X_0 values referring to 25°C were used. The second term of the left-hand side of Eq. (3) can be neglected because it was shown above that $C_{BH^+} \ll C_B$ in the solutions of all of the acids. The transformation of Eq. (3) into linear form gives the expression

$$\log[k_1/(C_H + C_{Nu})] = m^{\neq} m^* X_0 + \log(k/K_{BH^+}). \quad (4)$$

In concentrated HBr and HCl solutions, Br^- and Cl^- act as the strongest nucleophiles, whereas water is the strongest nucleophile in the H_2SO_4 and $HClO_4$ solutions. The water concentration in solutions of strong acids is unknown, so C_{Nu} for H_2SO_4 and $HClO_4$ was obtained by multiplying the activity of water by its concentration in neat water at 80°C (53.94 mol/l). The water activity at 80°C in the H_2SO_4 and $HClO_4$ solutions was obtained by extrapolation [42] of data available from the literature [30, 43]. Figure 2 demonstrates the validity of Eq. (4). In Fig. 2, the point corresponding to the hydrolysis of compound **I** in $HClO_4$ lies on the straight line for H_2SO_4. This confirms that water is correctly chosen as the nucleophile for the description of the hydrolysis mechanism in these acids, in which the protonated molecule of **I** is involved in the rate-determining step. The values of $m^{\neq} m^*$ and $\log(k/K_{BH^+})$ at 80°C calculated via Eq. (4) using the least squares method with 95% confidence probability are listed in Table 3.

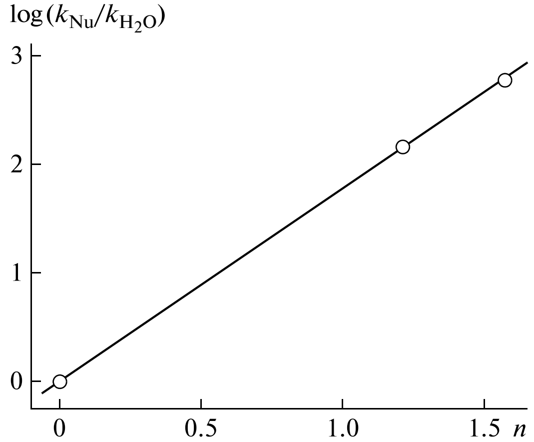


Fig. 3. Applicability of the Swain–Scott equation (5) to the S_N2 reactions of protonated compound **I** with Br^-, Cl^-, and H_2O.

Accepting $pK_{BH^+} \approx -6$, one can estimate the true values of the rate constants k of the S_N2 reactions (Table 3). The Swain–Scott correlation can be applied to these reactions in aqueous media [40]:

$$\log(k_{Nu}/k_{H_2O}) = ns, \quad (5)$$

where n is the nucleophilicity factor and s is the substrate constant. Figure 3 indicates that the Swain–Scott equation is applicable to the S_N2 reactions of protonated compound **I** at 80°C under the condition that K_{BH^+} is the same in all acids. The numerical values of n for the Cl^- and Br^- anions were taken from [40]. The substrate constant s is 0.72. As a rule, s is close to unity for typical S_N2 reactions at 25°C [40]. It is likely that the deviation from this rule observed for the reaction examined here is due to the fact that the measurements were taken at 80°C rather than 25°C. This is confirmed by the substantial difference between the

Table 4. Yields of the gaseous hydrolysis products of compounds **I**, **II**, and **IV** in strong acids based on the fraction of the reacted substance

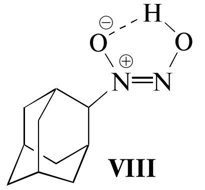
Compound	Acid	Concentration of acid, %	T, °C	Yield, mole fractions
I	HBr	24.25	80	$(N_2 + NO)$—0.62, N_2O—0.45, CH_3Br—0.64
		30.03	80	N_2—0.44, NO—0.05, N_2O—0.43, CH_3Br—0.95
		39.30	80	$(N_2 + NO)$—0.63, N_2O*, CH_3Br—1.12
		45.10	80	N_2—0.34, NO—0.05
		47.59	70	$(N_2 + NO)$—0.55, N_2O—0.42, CH_3Br—0.93
		47.59	80	N_2—0.19, NO—0.10
		47.59	90	$(N_2 + NO)$—0.55, N_2O—0.46, CH_3Br—1.05
	HCl	16.36	80	$(N_2 + NO)$—0.16, N_2O—0.71, CH_3Cl—1.21
		19.34	80	N_2—0.005, NO—0.05, N_2O—0.78, CH_3Cl—1.34
		22.34	80	$(N_2 + NO)$—0.06, N_2O—0.87, CH_3Cl—1.75
		25.26	80	$(N_2 + NO)$—0.05, N_2O—0.91, CH_3Cl—1.53
		28.25	80	$(N_2 + NO)$—0.04, N_2O—0.95, CH_3Cl—0.99
	H_2SO_4	64.16	119.8	$(N_2 + NO)$—0.02, N_2O—0.98, CO_2—0.01
II	HBr	47.01	80	$(N_2 + NO)$—0.19, N_2O—0.45, CH_3Br—0.63
IV	HBr	47.59	50	$(N_2 + NO)$—0.53, N_2O—0.31, CH_3Br—0.15

* No data.

activation energies of the first steps of compound **I** hydrolysis in 47.59% HBr and in 64.16% H_2SO_4.

An analysis of the reaction products (Table 4) confirms the proposed scheme. For the hydrolysis of compound **I** in HBr and HCl, the yield of MeBr and MeCl expressed in mole fractions is higher than unity in several cases. This is due to the formation of methanol upon the decomposition of the intermediate. The rapidly reachable equilibrium between methanol and methyl halide depends on the nature of the acid (the MeCl yield is higher than the MeBr yield) and on the acid concentration. The methyl halide yield and, accordingly, the total yield of gaseous products (α_∞, Table 4) decrease with a decreasing acid concentration. The temperature effect on this equilibrium is determined to a considerable extent by the fact that the solubility of methyl halide in the acid is temperature-dependent. Probably, it is the shift of this equilibrium upon cooling the reaction vessel to 20°C that is responsible for the gradual decrease in the pressure of the hydrolysis products over 1–2 h before stabilization. The contribution from the first hydrolysis step of compound **I** to the total MeBr yield can be estimated from the ratio of the MeBr yields in the hydrolysis of compounds **I** and **II** under similar conditions, and this contribution is 60%.

The NO content of the hydrolysis products of compound **I** indicates the intermediate formation of hydroxy-NNO-azoxymethane (**IV**). However, the measured rate constant k_1 of **IV** decomposition is 3.2 times higher than the hydrolysis rate constant k_2 of compound **I** under the same conditions; i.e., compound **IV** is unlikely to be the primary intermediate in the acidic hydrolysis of compound **I**. We found a single example of kinetic study of hydroxy-NNO-azoxy compound acidic hydrolysis—the hydrolysis of 2-(hydroxyl-NNO-azoxy)adamantane (**VIII**) [45],



VIII

However, the measurements in that work were carried out at 25°C in 0.5–2.5 M $HClO_4$ solutions ($k = 1.5 \times 10^{-6}$ l mol^{-1} s^{-1}).

It is likely that the molecule of **I** is protonated at the N atom. The rate-determining step yields intermediate **V**, which partly decomposes to yield N_2O and partly isomerizes via transprotonation to turn into **IV**. The decomposition of the latter yields NO along with N_2O. The constant k_2 refers to the totality of possible parallel and consecutive reactions of the intermediates. The total fraction of N-containing gases resulting from all reactions is close to unity. However, the proportions of these gases depend strongly on the nature and concentration of the acid, which is likely due to the strong effect of these factors on the relative contributions from the different parallel decomposition routes of intermediate **VII** (Scheme 2).

CONCLUSIONS

The kinetics of methoxy-NNO-azoxymethane hydrolysis in strong acids was studied by a manometric method. The attack of a nucleophile on the carbon atom of the methoxy group of the protonated molecule of **I** is the rate-determining step of the reaction. The resulting methyldiazene dioxide decomposes via a complicated mechanism to yield N_2, NO, and N_2O.

The rate constants of the S_N2 reactions of protonated methoxy-NNO-azoxymethane with Br^-, Cl^-, and H_2O are described well by the Swain–Scott equation at a substrate constant of $s = 0.72$.

The basicity of methoxy-NNO-azoxymethane is low ($pK_{BH^+} \approx -6$).

When treating alkoxy-NNO-azoxy compounds with strong acids at elevated temperatures, it is desirable to avoid the presence of the strong nucleophiles Br^-, Cl^-, and I^- in the reaction mixture.

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