The formation of aryloxenium ion in the reaction of *N*-nitro-*O*-(4-nitrophenyl)hydroxylamine with strong acids*

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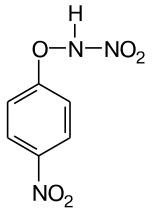
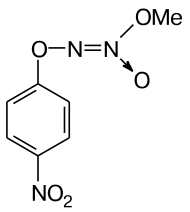
The reaction of *N*-nitro-*O*-(4-nitrophenyl)hydroxylamine (**1**) with conc. H_2SO_4 affords 4-nitropyrocatechol and that with conc. sulfonic acids (RSO_3H where R = Me, CF_3) affords 2-hydroxy-5-nitrophenyl-R-sulfonates in yields of 80—85%. These reactions are assumed to proceed through an intermediate (phenoxy)oxodiazonium ion $[NO_2C_6H_4O—N=N=O]^+$, which eliminates the N_2O molecule to form the aryloxenium ion $[NO_2C_6H_4O]^+$. The latter reacts with acid anions at the *ortho*-carbon atom of the phenyl ring. The thermodynamical parameters of the elementary reactions resulting in the formation of the (phenoxy)oxodiazonium ion $[NO_2C_6H_4O—N=N=O]^+$ and aryloxenium ion $[NO_2C_6H_4O]^+$ were calculated in the B3LYP/6-311+G(d) study of the combined molecular system (nitrohydroxylamine **1** + $[H_3SO_4]^+$). The reaction of nitrohydroxylamine **1** with aqueous solutions of strong acids (~70% H_2SO_4, CF_3SO_3H) affords mainly 4-nitrophenol. It appears that the mechanism of this reaction does not involve the formation of the aryloxenium ion.

Key words: hydroxylamines, nitramines, oxodiazonium ion, B3LYP/6-311+G(d) density functional method, ^{15}N NMR.

In the previous work,[1] we have obtained *N*-nitro-*O*-(4-nitrophenyl)hydroxylamine (**1**), which is the first nitrohydroxylamine isolated in the H form, and its *O*-methyl derivative **2**. The ^{15}N-labeled compounds ^{15}N-**1** and ^{15}N-**2** (degree of enrichment is 92%) have also been prepared.



1



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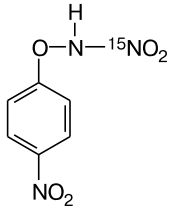
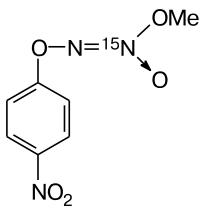


^{15}N-**1**

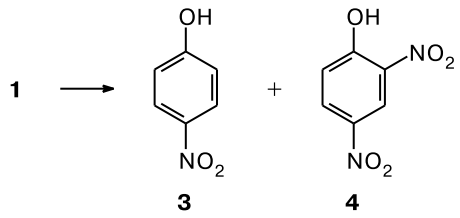


^{15}N-**2**

* Dedicated the 80-th anniversary of the academician of the Russian Academy of Sciences O. M. Nefedov.

While the nitrohydroxylamine derivative **2** is a relatively stable compound, the stability of the H-form **1** depends significantly on its environment. Compound **1** decomposes rapidly in solid and non-polar solvents at room temperature to form 4-nitrophenol (**3**). 2,4-dinitrophenol (**4**) is produced in small amounts as a secondary reaction product (Scheme 1). The stability of **1** increases considerably in basic (Et_2O, dioxane) and protic solvents (H_2O, MeOH). For example, in water the first signs of decomposition emerged only after 6 days.

Scheme 1



3 **4**

It has been established[1] that for the H-form **1** there exists a fast (NMR-time scale) equilibrium between the nitramine (**1**) and isonitramine (**1′**) forms, the contents of both forms in the equilibrium mixture being comparable

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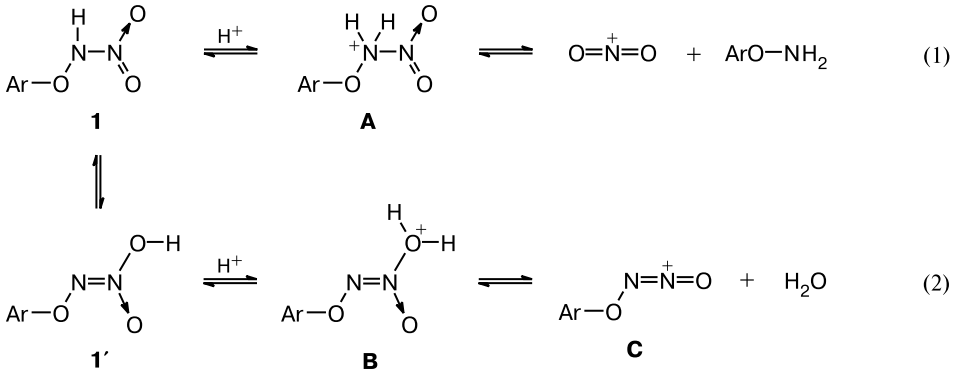
Scheme 2



Ar = 4-$NO_2C_6H_4$

(Scheme 2). It was assumed[1] that decomposition of **1** starts from autoprotolysis, which can proceed either at the N atom (intermediate **A**) followed by the formation of the nitronium cation or at the O atom (intermediate **B**) followed by the elimination of the H_2O molecule and formation of the (phenoxy)oxodiazonium ion **C**. It seems impossible to select one of these reaction pathways at the present time, although we consider the second one as a more probable.

In the present work, we studied the behavior of nitrohydroxylamine **1** in strong acids (H_2SO_4, CF_3SO_3H, $MeSO_3H$, and HSO_3F).

Results and Discussion

Decomposition of nitrohydroxylamine 1 in aqueous solutions of strong acids. The solubility of compound **1** in aqueous solutions of strong acids is very low. For example, when being in the form of suspension in conc. HCl (35%) at 20 °C the substance undergoes no changes for two days. In 70% H_2SO_4 and 73% CF_3SO_3H, nitrohydroxylamine **1** dissolves slowly and decomposes (Table 1). The main decomposition products of **1** in aqueous solutions of strong acids are nitrophenol **3** and dinitrophenol **4** (see Scheme 1, Table 1, the same products have been observed[1] upon decomposition of **1** in $CHCl_3$). As in $CHCl_3$, a pronounced induction period was observed. For example, in the case of 73% CF_3SO_3H the reaction at 0 °C proceeds as follows. During the first 50 min, the substance was in the form of suspension without noticeable signs of decomposition. Then, the substance dissolved completely for 1—2 min and the most of compound **1** transformed into nitrophenols **3** and **4**, thanks to which the reaction mixture became yellow. After 40 min, the reaction completed, *i.e.*, there was no nitrohydroxylamine **1** in the reaction mixture (TLC control).

When the decomposition temperature of **1** in 73% CF_3SO_3H was increased to 20 °C, the induction period, during which the substance was in suspension, decreased to 10 min and the complete decomposition time decreased to 30 min. When performing the decomposition reaction in 73% CF_3SO_3H at 40 °C, no induction period was observed and the decomposition rate decreased to 10 min.

The decrease in the acid strength retarded decomposition. For example, in 70% H_2SO_4 compound **1** decomposed completely at 40 °C for 30 min. In a weaker 97% $MeSO_3H$, it dissolved immediately after mixing, but the complete decomposition at 20 °C occured for 2 days. In $MeSO_3H$, there was no induction period, *viz.*, virtually no decomposition products were observed for ~30 min (TLC control).

The influence of nitrating and nitrosating agents on decomposition of **1** in 73% CF_3SO_3H is shown in Table 2. Both particles almost eliminate the induction period even at low concentrations.

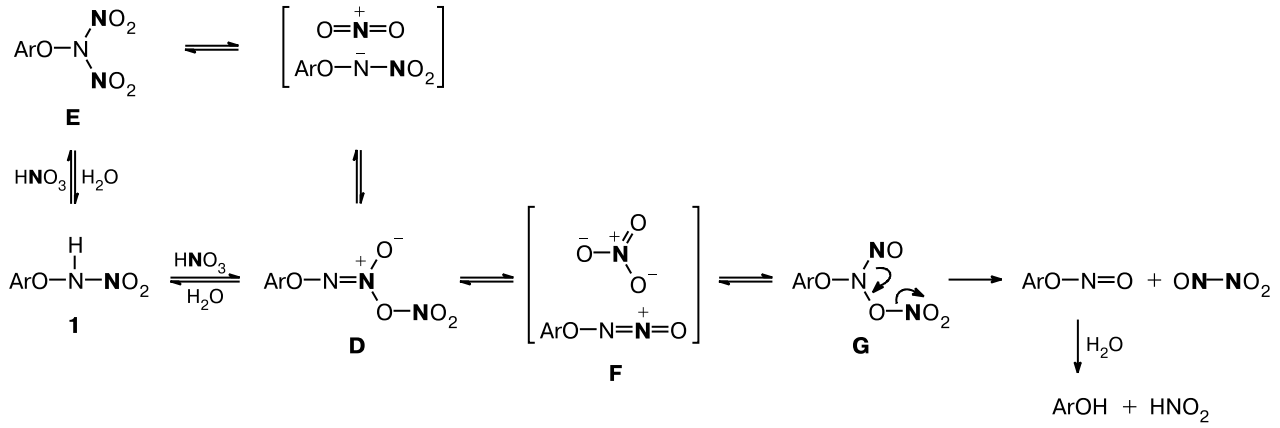
The proposed decomposition scheme of compound **1** in aqueous solutions of strong acids consists of three main steps. The first step is initiation. When protonation pro-

Table 1. The yields of nitrophenols **3** and **4** upon decomposition of nitrohydroxylamines **1** and ^{15}N-**1** in aqueous solutions of acids[a]

Acid (*C* (%))	Acid : H_2O (mol/mol)	*T*/°C	*t*[b]	Yield (%)	
				3	**4**
$MeSO_3H$ (97)	1 : 0.16	20	2 day	57	29
H_2SO_4 (70)	1 : 2.3	40	30 min	63	21
CF_3SO_3H (73)	1 : 3	40	10 min	62	24
CF_3SO_3H (73)	1 : 3	20	30 min	64	26
CF_3SO_3D (71)[c]	1 : 3	20	30 min	69	16
CF_3SO_3H (73)	1 : 3	0	1.5 h	72	12

[a] The product yields were determined by ^{1}H NMR spectroscopy (the conversion of compound **1** was 100%).
[b] The complete decomposition time of compound **1** (TLC control).
[c] Compound ^{15}N-**1** was used for the reaction in 71% CF_3SO_3D. The reaction was performed in a sealed NMR tube with addition of CD_3OD (8 vol.%).

Scheme 3



Note. Hereinafter, the labeled ^{15}N atoms are bold.

ceeds at the nitrogen atom, nitric acid forms at the initiation step (see Scheme 2, reaction 1), which reacts with **1** at the second step to form three nitrosating particles (Scheme 3). At the third step, nitrosating particles react with **1** to form N_2O and HNO_3 (Scheme 4) and, then, the second step occurs again. It appears that a small amount of $ArONH_2$ that formed from **1** at the initiation step (see Scheme 2, reaction 1) transforms into nitrophenol **3** and N_2O under the action of nitrosating particles.

The overall decomposition of nitrohydroxylamine **1** is represented in Scheme 5.

Scheme 4

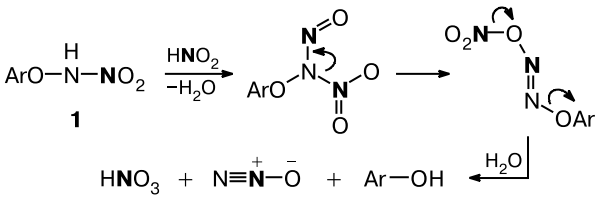
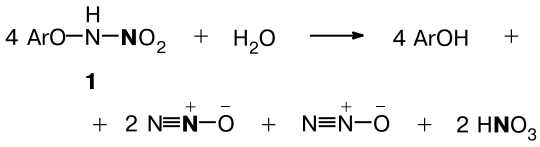


Table 2. The yields of nitrophenols **3** and **4** in the reaction of nitrohydroxylamine **1** with nitrating and nitrosating agents in 73% CF_3SO_3H at 0 °C[a]

Reagent	t_1/min[b]	t_2/h[c]	**1** : Reagent (mol/mol)	Yield (%)	
				3	**4**
—[d]	50	1.5	1 : 0	72	12
HNO_3	5	1.15	1 : 0.1	72	12
HNO_3	1	1	1 : 1	64	20
$NaNO_2$	5	1.15	1 : 0.1	72	13
$NaNO_2$	0	1	1 : 1	37	55

[a] The product yields were determined by ^1H NMR spectroscopy. The conversion of compound **1** was 100%.
[b] The time from mixing of nitrohydroxylamine **1** with the acid to the emergence of first traces of compounds **3** and **4** (TLC control).
[c] The complete decomposition time of nitrohydroxylamine **1** (TLC control).
[d] Decomposition of nitrohydroxylamine **1** without addition of reagents.

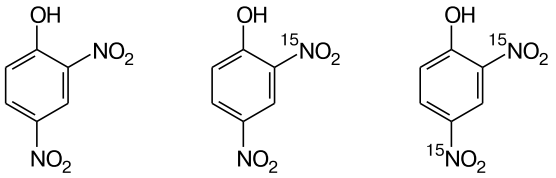
Scheme 5



Let us consider in more detail the reactions shown in Scheme 3. Intermediate **D** can form in two ways: nitration of **1** directly at the O atom or nitration of **1** at the N atom to form the intermediate compound **E** followed by its rearrangement. The key step of the process is rearrangement of compound **D** into **G**, which can occur *via* the ion pair **F** composed of (phenoxy)oxodiazonium and nitrate ions.

The reaction of the labeled compound ^{15}N-**1** with 71% CF_3SO_3D (the molar ratio CF_3SO_3D : D_2O is 1 : 3) confirms the overall decomposition equation (see Scheme 5). The reaction was performed in a sealed NMR tube and the products were determined according to the ^{14}N and ^{15}N NMR spectra. The composition of products coincides virtually with the composition of the products that formed upon decomposition of ^{15}N-**1** in $CHCl_3$ (see Ref. 1). The ^{15}N NMR spectrum displays only the signals for $H^{15}NO_3$ and $N^{15}NO$. The analysis of the ^{14}N NMR spectrum (with regard to details, see Ref. 1) shows that the ratio of the nitrous oxide labeled at the central nitrogen atom ($N^{15}NO$) to the unlabeled nitrous oxide taking into account the degree of enrichment is ~2 : 1. Note that the ^{14}N NMR spectrum displays also the signal for the unlabeled HNO_3 that formed from compound **1** being present in the labeled

sample of ^{15}N-**1** (the degree of enrichment with ^{15}N is 92%). After recording the spectrum, nitrophenol **3** and dinitrophenol **4** were isolated from the reaction mixture in yields of 69% and 16%, respectively (see Table 1). It was defined by mass spectrometry that when taking into account the degree of enrichment, the molar ratio of compound **4** with the unlabeled nitro groups, one labeled nitro group (^{15}N-**4**), and two labeled nitro groups ($^{15}N_2$-**4**) is 1 : 2.2 : 0.1. We have also observed[1] the formation of a small amount of $^{15}N_2$-**4** labeled on two nitro groups upon decomposition of **1** in $CHCl_3$ (see Refs 2 and 3).



4 ^{15}N-**4** $^{15}N_2$-**4**

The special experiments showed that under the conditions analogous to the decomposition conditions of nitrohydroxylamine **1** (73% CF_3SO_3H, 0 °C, 1.5 h), nitrophenol **3** reacts with nitrating and nitrosating agents in 73% CF_3SO_3H to form dinitrophenol **4** and some amount of unidentified products, the nitrosating agents reacting faster than the nitrating ones (Table 3). Consequently, the ratio of **4** to ^{15}N-**4** being equal to ~2 : 1 suggests that the labeled and unlabeled nitrosating agents were also in the ratio of 2 : 1.

Note that by comparison of the data from Tables 2 and 3, it is seen that compound **1** reacts with nitrating and nitrosating agents considerably faster than compound **3**.

Thus, one can state that the main decomposition steps of nitrohydroxylamine **1** in $CHCl_3$ (see Ref. 1) and abovementioned acids (see Table 1) proceeds according to the identical schemes. At the same time, there can be differences in the initiation steps: it is most likely that denitration plays a key role upon decomposition in these acids (see Scheme 2, reaction 1).

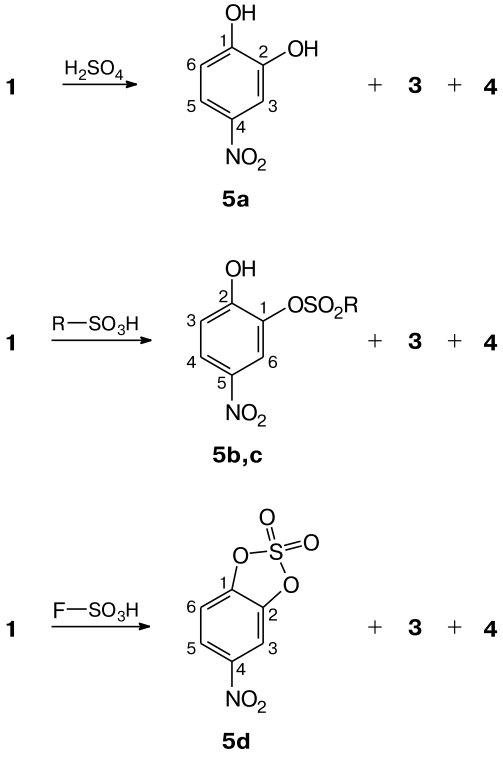
Table 3. The reaction of nitrophenol **3** with nitrating and nitrosating agents in 73% CF_3SO_3H to form dinitrophenol **4**[a]

Reagent	**3** : Reagent (mol/mol)	Conversion of **3** (%)[b]	Yield of **4**
HNO_3	1 : 1	3	65
$NaNO_2$	1 : 1	8	96
$NaNO_2$: HNO_3 (1 : 1)	1 : (1 : 1)	13	67

[a] The reaction temperature is 0 °C and the reaction time is 1.5 h.
[b] Determined by ^{1}H NMR spectroscopy.

The reaction of 1 with strong concentrated acids. Upon the reaction of compound **1** with strong concentrated acids, the composition of organic reaction products changes dramatically. For example the reaction of **1** with concentrated H_2SO_4, RSO_3H (R = Me, CF_3), and HSO_3F affords 4-nitropyrocatechol **5a** and its sulfo derivatives **5b—d** in high yields (Scheme 6, Table 4). Nitrophenols **3** and **4**, which formed in slight amount, are side products.

Scheme 6



R = Me (**b**), CF_3 (**c**)

The reaction of **1** with 100% H_2SO_4 at 10 °C results in the fast formation of pyrocatechol **5a** in 79% yield. Nitrophenol **3** forms in a yield of 11% (see Scheme 6, Table 4). Upon dilution of sulfuric acid to 85% (the molar ratio H_2SO_4/H_2O is 1 : 1), the yield of compound **5a** does not change virtually, but the reaction rate decreased and 100% conversion of **1** at 20 °C took 2 h. At 40 °C, the same reaction proceeds for 5 min and the yield of 4-nitropyrocatechol **5a** even increased slightly. Further dilution of the acid decreases the yield of compound **5a** and increases the yield of **3** and, if the water content is more than 2 moles per 1 mole of H_2SO_4, 4-nitropyrocatechol **5a** does not form at all (see Table 1).

The reaction of **1** with a weaker acid, *viz.*, 100% $MeSO_3H$, proceeds much slower than that with H_2SO_4. Nevertheless, sulfonate **5b** forms in a high yield (see Scheme 6, Table 4). However, the addition of

Table 4. The reaction of nitrohydroxylamines **1** and ^{15}N-**1** with strong concentrated acids[a]

Run	Acid (*C* (%))	Acid : H_2O (mol/mol)	*T*/°C	*t*[b]	**5**	Yeild (%)		
						5	**3**	**4**
1	H_2SO_4 (100)	1 : 0	10	<5 min	**a**	79	11	3
2	H_2SO_4 (96)	1 : 0.23	0	<5 min	**a**	79	8	3
3	H_2SO_4 (93)	1 : 0.35	20	5 min	**a**	83	6	0
4	H_2SO_4 (85)	1 : 0.96	20	2 h	**a**	74	12	0
5	H_2SO_4 (85)	1 : 0.96	40	5 min	**a**	87	6	0
6	H_2SO_4 (75)	1 : 1.8	40	20 min	**a**	58[c]	37[c]	0
7	$MeSO_3H$ (100)	1 : 0	20	3 day	**b**	82	8	0
8	CF_3SO_3H (100), $CHCl_3$[d]	1 : 0	0	1 h	**a**	13	6	0
					c	73		0
9	CF_3SO_3H (97)	1 : 0.25	0	5 min	**c**	85	5	0
10	CF_3SO_3D (97)[e]	1 : 0.23	0	5 min	**c**	88	3	5
11	CF_3SO_3H (89)	1 : 1	40	5 min	**c**	87	9	<1
12	CF_3SO_3H (88)	1 : 1.2	40	5 min	**c**	46	25	19
13	CF_3SO_3H (85)	1 : 1.5	40	10 min	**c**	12	53	32
14	CF_3SO_3H (81)	1 : 1.9	40	10 min	**c**	12	66	19
15	HSO_3F (97)	1 : 0.17	0	5 min	**a**	3	6	0
					d	82		0

[a] The product yields were determined by ^{1}H NMR spectroscopy. The conversion of compound **1** was 100%.
[b] The complete decomposition time of compound **1** (TLC control).
[c] The conversion of compound **1** was 70%.
[d] A solution of 100% CF_3SO_3H (20 equiv.) in $CHCl_3$.
[e] Compound ^{15}N-**1** was used for the reaction in 97% CF_3SO_3D. The reaction was performed in a sealed NMR tube with addition of CD_3OD (8 vol.%).

0.16 mol.% of water terminates this process completely (see Table 1).

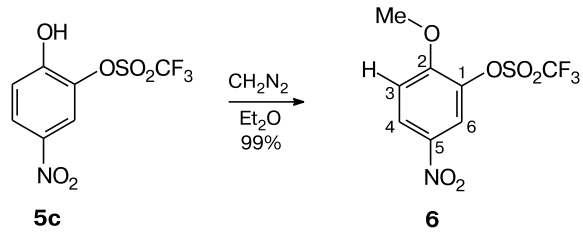
The reaction of **1** with CF_3SO_3H containing no more than 11% of water (the molar ratio CF_3SO_3H/H_2O is 1 : 1) affords sulfonate **5c** in a good yield (see Scheme 6, Table 4). The reaction of **1** with 20 equiv. of 100% CF_3SO_3H in $CHCl_3$ proceeds considerably slower than in the case where pure CF_3SO_3H was used. This is likely due to the fact the acid decomposition rate of **1** depends strongly on the acid concentration. If the molar ratio of water to CF_3SO_3H is more than 1 : 1, the yield of sulfonate **5c** decreases, and, if the water content is more than 2 moles per 1 mole of CF_3SO_3H, the sulfonate does not form at all (see Table 1).

The reaction of **1** with 97% FSO_3H affords the cyclic sulfate **5d** in a yield of 82% and a small amount of nitrophenol **3** (6%) (see Scheme 6, Table 4).

Sulfonates **5b—c** and sulfate **5d** were obtained for the first time and their structures were confirmed by ^{1}H, ^{13}C, ^{14}N, and ^{19}F spectroscopy. The position of the sulfo group in products **5b—c** was confirmed by the NOESY experiment for compound **6**, which is the methylation product of sulfonate **5c** at the hydroxyl group using diazomethane (Scheme 7). The NOESY spectrum displayed interaction of the OMe protons with H(3).

To explain the formation of 4-nitropyrocatechol **5a** and its sulfoderivatives **5b—d** in the strong concentrated acid medium, we proposed the following reaction scheme.

Scheme 7

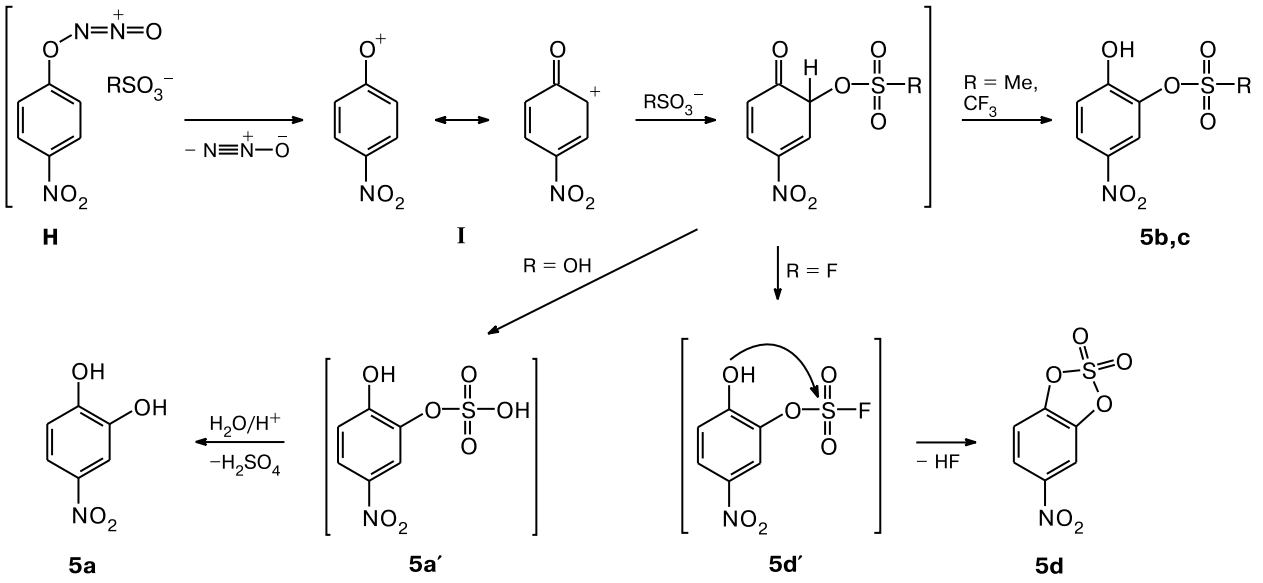


5c **6**

At the first step, the protonation of the isonitramine form **1′** at the O atom followed by water elimination (see Scheme 2, reaction 2) results in ion pair **H** composed of the (phenoxy)oxodiazonium ion and weak nucleophilic anion (RSO_2O^-, R = Me, OH, CF_3, F), which is incapable of reacting at the terminal nitrogen atom of the cation $-N{=}N{=}O^+$ (Scheme 8). This cation evolves the N_2O molecule to form the *p*-nitrophenyloxenium ion **I**, which can react as an ambident cation with the RSO_2O^- anion at the *ortho*-carbon atom of the phenyl ring to form finally compounds **5a—d**. The aryloxenium ions of type **I** have been discussed earlier.[4,5]

The *O*-methyl derivative **2** is a model of the isonitramine form **1′** and could also form the (phenoxy)oxodiazonium ion **C** after protonation and elimination of methanol (Scheme 9). Note that at least at the first reac-

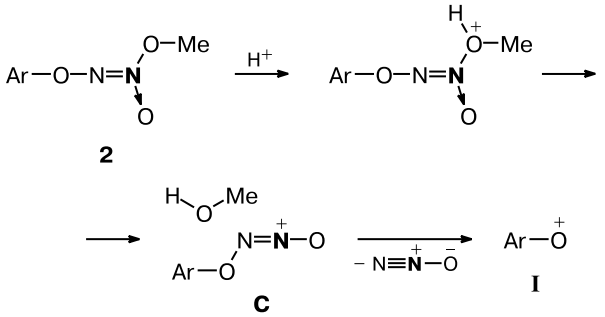
Scheme 8



R = Me (**b**), CF_3 (**c**)

tion steps, compound **2** cannot undergo denitration to form HNO_3.

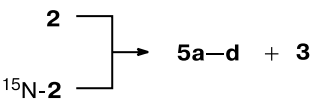
Scheme 9



R = Me (**b**), CF_3 (**c**)

O-Methyl derivative **2** was introduced into the reactions with the same acids, with which nitrohydroxylamine **1** reacted (Scheme 10, Table 5), to result in 4-nitropyrocatechol **5a** and its sulfo derivatives **5b**—**d** in high yields, as well as a small amount of nitrophenol **3** as a side product.

Scheme 10



The reaction rate of the *O*-methyl compound **2** with concentrated acids is defined by their strength and water content. For example, the reaction of **2** with very concentrated acids (97% CF_3SO_3H and 97% HSO_3F) occured over the same period as the reaction of **1** with these acids. At the same time, the reaction of **2** with 20 equiv. of 100% CF_3SO_3H in $CHCl_3$ occured under much more severe conditions than those for **1**. This is likely due to the fact that the acid decomposition rate of **2** depends on the acid concentration stronger than that of **1**. In a weaker 100% H_2SO_4, complete decomposition of **2** occurs slower than that of **1** and completed in 10 min. In a yet weaker 100% $MeSO_3H$, the decomposition rate of **2** is severalfold less than that of **1**. Successive dilution of H_2SO_4 to the concentrations of 96, 93, and 85% results in a dramatic delay of decomposition of **2** compared to **1**. When the molar ratio of acid : H_2O is equal to 1 : 1, the solubility of compound **2** decreases considerably and the portion of **2** is in the heterogeneous phase, which leads to a great increase in the reaction time. The increase in the temperature to 70 °C increases the solubility of **2** and accelerates considerably the reaction, the yield and ratio of the products changing slightly.

In a yet more diluted solutions of acids (50—70% H_2SO_4 and CF_3SO_3H), the reaction of **2** proceeds quite slow even at 70 °C. This is due the fact decomposition occurs in the heterogeneous medium and compound **2** dissolves slowly as the reaction proceeds. It is interesting that in contrast to nitrohydroxylamine **1**, decomposition of compound **2** in such diluted acid solutions even so results in small amounts of 4-nitropyrocatechol **5a** (see Table 5).

In general, the reaction rate of the *O*-methyl compound **2** with strong acids is lower than that of compound **1**, although the direct comparison of the reaction rates of these compounds with acids can be performed only up to

Table 5. The reaction of compounds **2** and ^{15}N-**2** with strong acids[a]

Run	Acid (*C* (%))	Acid : H_2O (mol/mol)	*T*/°C	*t*[b]	Conversion of **2** (%)	**5**	Yield (%)	
							5	**3**
1	H_2SO_4 (100)	1 : 0	10	10 min	100	**a**	91	4
							(57)[e]	—
2	H_2SO_4 (96)	1 : 0.23	0	3 h	100	**a**	87	4
3	H_2SO_4 (93)	1 : 0.35	20	4 h	100	**a**	86	4
4	H_2SO_4 (85)	1 : 0.96	20	5 day	79	**a**	84	8
5	H_2SO_4 (85)	1 : 0.96	70	30 min	89	**a**	83	10
6	H_2SO_4 (70)	1 : 2.3	70	14 h	66	**a**	35	56
7	H_2SO_4 (50)	1 : 5.4	70	14 h	50	**a**	10	72
8	$MeSO_3H$ (100)	1 : 0	70	8 h	97	**b**	88	5
							(50)[e]	—
9	$MeSO_3H$ (100)	1 : 0	20	11 day	56	**b**	84	4
10	CF_3SO_3H (100)	1 : 0	0	5 min	100	**c**	86	3
11	CF_3SO_3H (100), $CHCl_3$[c]	1 : 0	61	1.3 h	95	**a**	10	7
						c	73	
12	CF_3SO_3H (97)	1 : 0.25	0	5 min	100	**c**	86	3
							(56)[e]	—
13	CF_3SO_3D (97)[d]	1 : 0.23	0	5 min	100	**c**	92	2
14	CF_3SO_3H (89)	1 : 1	30	5 day	66	**c**	86	6
15	CF_3SO_3H (89)	1 : 1	70	30 min	100	**c**	82	5
16	CF_3SO_3H (70)	1 : 3.6	70	9 h	72	**c**	28	58
17	CF_3SO_3H (50)	1 : 8.3	70	9 h	54	**c**	7	85
18	HSO_3F (97)	1 : 0.17	0	5 min	100	**d**	70[e]	—

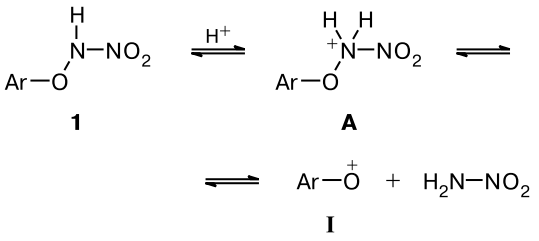
[a] The conversion of compound **2** and product yields were determined by ^{1}H spectroscopy.
[b] The decomposition time of compound **2**.
[c] A solution of 100% CF_3SO_3H (20 equiv.) in $CHCl_3$.
[d] Compound ^{15}N-**2** was used for the reaction in 97% CF_3SO_3D. The reaction was performed in a sealed NMR tube with addition of CD_3OD (8 vol.%).
[e] The yields are given for the isolated product (nitrophenol **3** was not isolated).

the molar ratio acid/H_2O of 1 : 1, at which the decomposition reactions of both compounds can be performed in a homogeneous solution. For the preparation of products **5a**—**d**, the reactions of the *O*-methyl compound **2** are more convenient than the corresponding reaction of **1** due to a low thermal stability of the latter and its tendency to self-decomposition.

The reaction of the labeled samples ^{15}N-**1** and ^{15}N-**2** with 97% CF_3SO_3D (the molar ratio CF_3SO_3D : D_2O is 1 : 0.2) confirms the proposed mechanism of the formation of products **5a**—**d** through the intermediate (phenoxy)oxodiazonium ion (see Schemes 8 and 9, Tables 4 and 5, the reaction with 97% CF_3SO_3D). The reactions were performed in a sealed NMR tube and the products were determined according to the ^{14}N and ^{15}N NMR spectra. The ^{15}N NMR spectrum displays only the signal for N^{15}NO and contains no signals for the labeled nitrogen molecules and H$^{15}NO_3$. The ^{14}N NMR spectrum displays the signal for the terminal nitrogen atom of N^{15}NO and low signals for the unlabeled N_2O corresponding to the degree of enrichment of the samples ^{15}N-**1** and ^{15}N-**2** with the ^{15}N label.

By analyzing the alternative formation mechanisms of the *p*-nitrophenyloxenium ion **I** from nitrohydroxylamine **1**, one can suggest the scheme including the protonation of **1** at the nitrogen atom followed by elimination of the nitramide molecule (Scheme 11). The similar mechanism has been proposed earlier to explain the formation of the phenyloxenium ion from *N*-sulfonyl-*O*-phenylhydroxylamines in the acid medium.[5]

Scheme 11



To decide between the proposed generation mechanisms of cation **I** from compound **1**, we performed theoretical studies.

Theoretical study of the generation of the oxenium ion I from nitrohydroxylamine 1 in H_2SO_4. The main purpose of

the theoretical studies was to confirm the formation of the (phenoxy)oxodiazonium ion $[ArO—N=N=O]^+$ (**C**) as a kinetically independent particle upon the reaction of compound **1** with conc. H_2SO_4.

By the B3LYP/6-311+G(d) density functional method,[6,7] we studied the potential energy surface (PES) of the combined molecular system {isonitramine form **1′** + + $[H_3SO_4]^+$} (Scheme 12).

Scheme 12

$$\mathbf{1'} + [H_3SO_4]^+ \longrightarrow \underset{\mathbf{7}}{\{[ArO—N=N=O]^+ \cdot H_2O \cdot H_2SO_4\}}$$

ΔH = –4.4 kcal mol^{-1}

Since the reacition under consideration proceeds in concentrated H_2SO_4, we studied also PES for the combined molecular system $\{[ArO—N=N=O]^+ \cdot 3\ H_2SO_4\}$ (**8**) (Scheme 13). The simulation of solvation was performed within the supramolecular approach taking clear account of three H_2SO_4 molecules without consideration of the H_2O molecule, which in a strong-acid medium transforms readily into the $[H_3O]^+$ ion and leaves the internal solvation sphere of the (phenoxy)oxodiazonium ion **C**.

Scheme 13

$$\underset{\mathbf{8}}{\{[ArO—N=N=O]^+ \cdot 3\ H_2SO_4\}} \longrightarrow \underset{\mathbf{9}}{\{[ArO]^+ \cdot N_2O \cdot 3\ H_2SO_4\}}$$

ΔH = –42.1 kcal mol^{-1}, ΔG = –45.4 kcal mol^{-1}

To confirm the local minima on the PES, the vibrational spectra of the particles under study were calculated.

Let us consider the reacion in Scheme 12. Taking into account a high acidity of the medium under consideration, the protonated molecule of sulfuric acid $[H_3SO_4]^+$ was regarded as a protonating agent. It has been shown earlier[8,9] that the $[H_3SO_4]^+$ ions can exist in 100% sulfuric acid as complexes containing one or two H_2SO_4 molecules.

The study of the PES of the combined molecular system (isonitramine form **1′** + $[H_3SO_4]^+$) (see Scheme 12) showed that upon approximation of molecule **1′** and the $[H_3SO_4]^+$ cation, elongation of the N···OH_2 bond occurs, which is accompanied by the activationless formation of complex **7** consisting of the (phenoxy)oxodiazonium ion $[ArO—N=N=O]^+$ (**C**), the H_2O molecule, and the H_2SO_4 molecule (Fig. 1, Table 6), where the distance N···OH_2 is 2.03 Å. The formation of this complex is a low exothermic reaction. As it follows from the computed effective Mulliken charges, the –N=N=O fragment in the (phenoxy)-

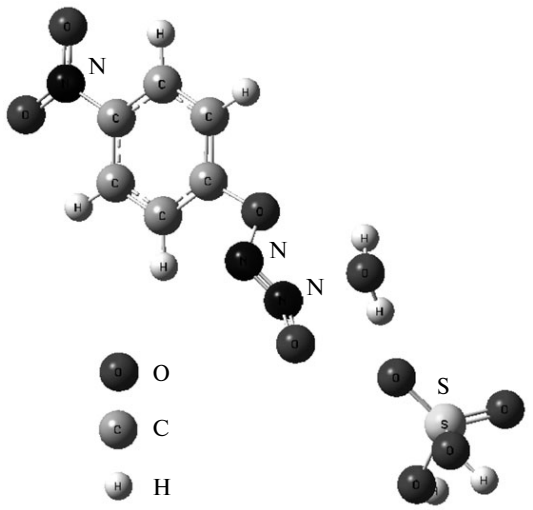


Fig. 1. DFT/B3LYP optimized geometry of complex **7** obtained in the study of the PES of the combined molecular system {isonitramine form **1′** + $[H_3SO_4]^+$}.

oxodiazonium ion $[ArO—N=N=O]^+$ (**C**) (see Fig. 1) is characterized by the positive net charge (0.35 e).

Let us consider the reaction in Scheme 13. The study of the combined molecular system $\{[ArO—N=N=O]^+ \cdot 3\ H_2SO_4\}$ (**8**) (see Scheme 13, Fig. 2, Table 6) allowed localization of a minimum on the PES, which confirms that the $[ArO—N=N=O]^+$ ion (**C**) can exists as a kinetically independent particle. In addition, we revealed the minimum corresponding to the complex $\{[ArO]^+ \cdot N_2O \cdot 3\ H_2SO_4\}$ (**9**) (see Scheme 13, Fig. 3). The performed calculations of the thermodynamic parameters of these complexes show that the reaction is extremely exothermic. However, the complexity of the combined molecular system $\{[ArO—N=N=O]^+ \cdot 3\ H_2SO_4\}$ (**8**) did not allow us to localize the transition state related to the decomposition coordinate and to estimate the activation barrier of this process.

Table 6. Selected geometry parameters (bond lengths (*d*) and angles (ω)) of the O—N=N=O fragment in the complex $\{[ArO—N=N=O]^+ \cdot H_2O \cdot H_2SO_4\}$ (**7**) (see Fig. 1) and complex $\{[ArO—N=N=O]^+ \cdot 3\ H_2SO_4\}$ (**8**) (see Fig. 2) (B3LYP/6-311+G(d))

Complex	*d* (O—N)	*d* (N—N)	*d* (N—O)	ω (N—N—O) /deg	*d* (N···O) /Å
	Å				
7	1.35	1.21	1.16	145.6	2.03[a]
8	1.40	1.18	1.16	159.6	2.37[b]

[a] The distance between the central nitrogen atom of the —N=N=O fragment and the oxygen atom of the H_2O molecule in the complex.

[b] The distance between the central nitrogen atom of the —N=N=O fragment and the oxygen atom of the H_2SO_4 molecule in the complex.

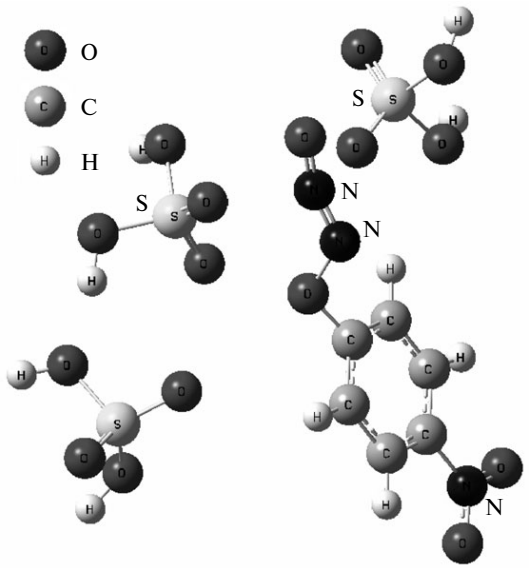


Fig. 2. DFT/B3LYP optimized geometry of complex **8** obtained in the study of the PES of the combined molecular system {isonitramine form **1**´ + $[H_3SO_4]^+$ + 2 H_2SO_4}.

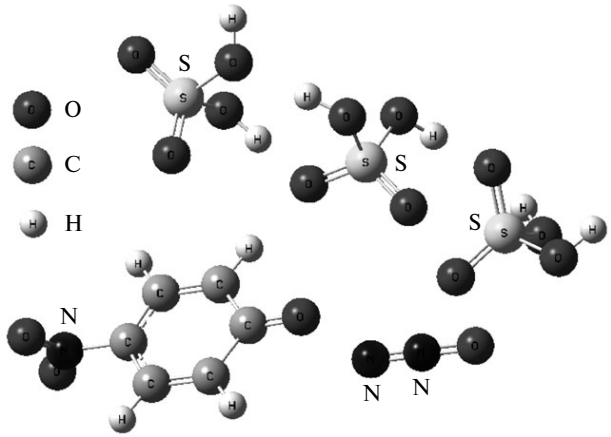


Fig. 3. DFT/B3LYP optimized geometry of the oxenium ion **I** in complex **9**. The distance between the O atom of the oxenium ion **I** and the terminal N atom of the N_2O molecule in complex **9** is 2.9 Å.

We performed also the study of the complex {nitramine form **1** + $[H_3SO_4]^+$} as an alternative intermediate in the reaction with H_2SO_4 (see Scheme 11).

As noted above for the H-form **1**, there exists a fast (NMR-time scale) equilibrium between nitramine **1** and isonitramine **1**´ forms, the contents of both forms in the equilibrium mixture being comparable (see Scheme 2). Therefore, we studied the PES of the combined molecular system {nitramine form **1** + $[H_3SO_4]^+$} in order to establish the existence possibility of the $[ArO—NH_2—NO_2]^+$ ion (**A**) and the possibility of its decomposition to eliminate the NH_2NO_2 molecule and to form the oxenium ion $[ArO]^+$ (**I**) (see Scheme 11).

By the study of the PES of the molecular system (Fig. 4), it was found that upon protonation of **1** with $[H_3SO_4]^+$ at the nitrogen atom of hydroxylamine, there occur elongation of the N···NO_2 bond and activationless formation of complex **10** consisting of the $ArONH_2$ molecule, nitronium ion, and H_2SO_4 molecule (see Fig. 4), where the distance N···NO_2 is 1.78 Å. Note that the hypothetic formation reaction of the oxenium ion $[ArO]^+$ (**I**) and the NH_2NO_2 molecule from the complex {$ArONH_2 \cdot [NO_2]^+ \cdot H_2SO_4$} (**10**) is endothermal (ΔH = = +18.6 kcal mol^{-1}). At the same time, the formation of the oxenium ion $[ArO]^+$ (**I**) upon protonation of the isonitramine form **1**´ is exothermal (ΔH is about −40 kcal mol^{-1}). Thus, the second pathway of the formation of $[ArO]^+$ (**I**) upon protonation of the nitramine form **1** at the nitrogen atom of hydroxylamine cannot occur due to a more thermodynamically favorable denitration process.

When 75—96% H_2SO_4 (but not 100% H_2SO_4) was used, the $[H_3O]^+$ hydroxonium ion can act as a protonating particle. However, when considering the comparable proton affinities of the water and sulfuric acid molecules,[10] the thermodynamics of the formation of $[ArO]^+$ (**I**) from **1**´ changes within the range of 3 kcal mol^{-1}.

Thus, by the B3LYP density functional study of the combined molecular systems {isonitramine form **1**´ + + $[H_3SO_4]^+$} and {nitramine form **1** + $[H_3SO_4]^+$} and localizatioin of some stationary points on the PES, we showed that the formation pathway of the oxenium ion **I** from the isonitramine form **1**´ is the most thermodynamically favorable and confirmed the existence possibility of the (phenoxy)oxodiazonium ion $[ArO—N=N=O]^+$ (**C**) as a kinetically independent particle. The thermodynamical parameters of elementary reactions resulting in the formation of intermediate $[ArO]^+$ (**I**) were calculated.

It was interesting to compare the stability of the nonsolvated oxodiazonium ion studied earlier[11], wherein the −N=N=O fragment is linked with the C atom, with the nonsolvated (phenoxy)oxodiazonium ion $[ArO—N=N=O]^+$

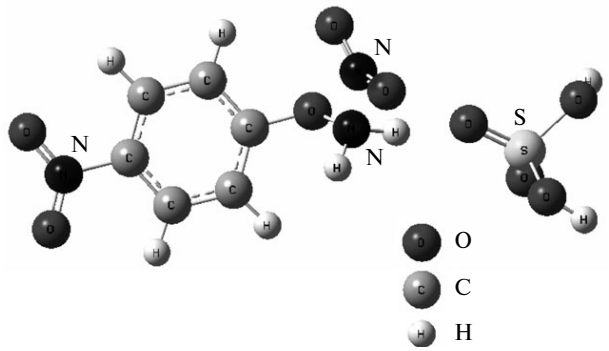


Fig. 4. DFT/B3LYP optimized geometry of complex **10** obtained in the study of the PES of the combined molecular system {nitramine form **1** + $[H_3SO_4]^+$}. The distance N···NO_2 in complex **10** is 1.78 Å.

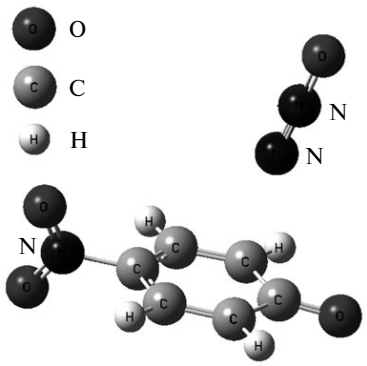


Fig. 5. DFT/B3LYP optimized geometry of the oxenium ion **I** in the complex $\{[ArO]^+ + N_2O\}$. The distance $\{[ArO]^+...NNO\}$ is 3.6 Å.

(**C**) where the —N=N=O fragment is linked with the O atom. When studying the PES of the free (phenoxy)-oxodiazonium ion $[ArO—N=N=O]^+$ (**C**) (Fig. 5), we found the activationless pathway of its decomposition to eliminate the N_2O molecule and to form the oxenium ion $[ArO]^+$ (**I**). Thus, the calculations show that the cation with the O—N=N=O fragment is less stable than that with the C—N=N=O fragment, which has been localized by us on the PES as a minimum.

Experimental

^1H, ^{13}C, and ^{14}N NMR spectra were recorded on Bruker AM-300 (300.13, 75.5, and 21.5 MHz) and Bruker DRX-500 (500.13, 125.76, and 36.14 MHz) instruments, respectively. ^{15}N NMR spectra were recorded on a Bruker DRX-500 (50.70 MHz) instrument. Chemical shifts are given relative to $SiMe_4$ (^1H, ^{13}C) or $MeNO_2$ (^{14}N, external standard, upfield chemical shifts are negative). IR spectra were recorded on a Specord M-80 spectrometer. Mass spectra were recorded on a Kratos MS-300 (EI, 70 eV) instrument. The course of reactions was monitored by thin-layer chromatography (Silufol UV-254 and Merck 60 F_{254}). CF_3SO_3D and its solutions in D_2O were prepared by heating the corresponding amounts of $(CF_3SO_3)_2O$ and D_2O at 60 °C for 2 h. A solution of nitrohydroxylamine **1** in diethyl ether (see Ref. 1), the *O*-methyl derivative **2** (see Ref. 1), labeled samples ^{15}N-**1** and ^{15}N-**2** (see Ref. 1), a solution of diazomethane in diethyl ether (see Ref. 12) were prepared according to known procedures. The yields of reaction products were determined by ^1H NMR spectroscopy.

The reaction of nitrohydroxylamine 1 with acids (general procedure). To prepare a solid sample of nitrohydroxylamine **1**, the standard procedure was used, which consists in evaporation to dryness of a solution of **1** (10 mg, 0.05 mmol) in Et_2O (1 mL) in a one-neck flask under reduced pressure (1 Torr) at 0 °C for 5 min. Subsequent manipulations were performed in the same flask. The acid* (see Tables 1 and 4) was added with vigorous stirring in single portion at 0 °C. The reaction temperature and time are given in Tables 1 and 4. After completion of the reaction, the mixture was poured into ice water (3 mL) and extracted with CH_2Cl_2 (5×2 mL) and AcOEt (2×3 mL). The AcOEt extract was washed with water (1 mL). The organic extracts were combined, washed with a saturated aqueous solution of NaCl (2 mL), dried with $MgSO_4$, and evaporated *in vacuo*. The product yields were determined by ^1H NMR spectroscopy (see Tables 1 and 4).

Decomposition of ^{15}N-1 in 71% CF_3SO_3D. Nitrohydroxylamine ^{15}N-**1** (20 mg, 0.10 mmol) crushed at 0 °C was placed under argon into an NMR tube cooled to −30 °C. A mixture of CF_3SO_3D (a 71% solution in D_2O, 0.55 mL) and CD_3OD (0.05 mL) precooled to −20 °C was added. The cooled tube was sealed, heated to 20 °C, and kept for 30 min by shaking at times. The ^{14}N and ^{15}N NMR spectra were recorded. ^{14}N NMR ($CF_3SO_3D/D_2O/CD_3OD$), δ: −11 (the NO_2 groups of **3** and **4**, $\Delta\nu_{1/2}$ = 900 Hz), −40 (HNO_3, $\Delta\nu_{1/2}$ = 40 Hz; the signal coincides with the signal for the knowing sample of HNO_3 in the same solvent mixture), −149 (the central N atom in NNO, $\Delta\nu_{1/2}$ = 30 Hz), −232 (the terminal N atom in NNO and $N^{15}NO$, $\Delta\nu_{1/2}$ = 30 Hz). The molar ratio NNO : $N^{15}NO$ equal to 0.3 : 0.7 was determined by the integral intensity ratio of the signals for the central and terminal N atoms taking into account the integral intensities of the corresponding signals for the knowing sample of N_2O in the same solvent mixture. ^{15}N NMR ($CF_3SO_3D/D_2O/CD_3OD$), δ: −17.7, −19.3, −21.1 ($C—^{15}NO_2$ groups), −43.4 ($H^{15}NO_3$), −152.9 (t, the central N atom in $N^{15}NO$, $^1J(^{14}N—^{15}N)$ = 6 Hz, *cf.* Ref. 13).

After recording the NMR spectra, the tube was unsealed and the reaction mixture was poured into ice water (3 mL) and extracted with CH_2Cl_2 (4×3 mL). The extracts were combined, washed with a saturated aqueous solution of NaCl (1 mL), dried with $MgSO_4$, and evaporated *in vacuo*. The product yields were determined by ^1H NMR spectroscopy (see Table 1). The reaction products were separated by preparative TLC on silica gel (the eluent was $CHCl_3$) to yield 4-nitrophenol (**3**) (8 mg) and 2,4-dinitrophenol (**4**) (3 mg). The resulted dinitrophenol **4** was analyzed by mass spectrometry. MS, *m/z* (the ratio of integral intensities): 287, 288, 289 $[M]^+$ (1 : 2.0 : 0.1). Taking into account the degree of enrichment, the molar ratio of compound **4** with the unlabeled nitro groups, one labeled nitro group (^{15}N-**4**), and two labeled nitro groups ($^{15}N_2$-**4**) is 1 : 2.2 : 0.1.

The reaction of 1 with HNO_3 in 73% CF_3SO_3H. To the sample of nitrohydroxylamine **1** prepared according to the standard procedure, a precooled to 0 °C solution of HNO_3 (the amount is given in Table 2) in 73% CF_3SO_3H (0.5 mL) was added with stirring at 0 °C. The reaction mixture gained an intense yellow color as compound **1** dissolved for 1—5 min. The reaction mixture was stirred at 0 °C for the time given in Table 2, poured into ice water (2 mL), and extracted with CH_2Cl_2 (5×3 mL). The organic extracts were combined, washed with a saturated aqueous solution of NaCl (1 mL), dried with ($MgSO_4$), and evaporated *in vacuo*. The product yields were determined by ^1H NMR spectroscopy (see Table 2).

The reaction of 1 with $NaNO_2$ in 73% CF_3SO_3H. To the sample of **1** prepared according to the standard procedure, a precooled to 0 °C solution of $NaNO_2$ (the amount is given in Table 2) in 73% CF_3SO_3H (0.5 mL) was added with stirring at 0 °C. The reaction mixture gained an intense yellow color as compound **1** dissolved for 0—5 min. The reaction mixture was stirred at 0 °C for the time given in Table 2 and treated as desribed in the previous procedure.

* The acid was cooled to 0 °C prior to addition in the reactions performed at 0 °C.

The reaction of nitrophenol (3) with HNO_3 in 73% CF_3SO_3H. A precooled to 0 °C solution of HNO_3 (0.003 mL, 0.07 mmol) in 73% CF_3SO_3H (0.5 mL) was added with vigorous stirring to nitrophenol **3** (10 mg, 0.07 mmol) in single portion. The reaction mixture was stirred for 1.5 h at 0 °C, poured into ice water (2 mL), and extracted with CH_2Cl_2 (5×3 mL). The extracts were combined, dried with $MgSO_4$, and evaporated *in vacuo*. The conversion of nitrophenol **3** and the yield of dinitrophenol **4** were determined by ^{1}H NMR spectroscopy (see Table 3).

The reaction of nitrophenol (3) with $NaNO_2$ 73% CF_3SO_3H. A precooled to 0 °C solution of $NaNO_2$ (5 mg, 0.07 mmol) in 73% CF_3SO_3H (0.5 mL) was added with vigorous stirring to nitrophenol **3** (10 mg, 0.07 mmol) in single portion. The reaction mixture was stirred for 1.5 h at 0 °C and then treated as descibed in the previous procedure.

The reaction of nitrophenol (3) with the system $NaNO_2/HNO_3$ = = 1 : 1 in 73% CF_3SO_3H. A precooled to 0 °C solution of HNO_3 (0.003 mL, 0.07 mmol) in 73% CF_3SO_3H (0.25 mL) was added with vigorous stirring to nitrophenol **3** (10 mg, 0.07 mmol) in single portion. A cooled to 0 °C solution of $NaNO_2$ (5 mg, 0.07 mmol) in 73% CF_3SO_3H (0.25 mL) was then added. The reaction mixture was stirred for 1.5 h at 0 °C, poured into ice water (2 mL), and extracted with CH_2Cl_2 (5×3 mL). The extracts were combined, dried with $MgSO_4$, and evaporated *in vacuo*. The conversion of nitrophenol **3** and the yield of dinitrophenol **4** were determined by ^{1}H NMR spectroscopy (see Table 3).

The reaction of 1 with 100% CF_3SO_3H in $CHCl_3$. To the sample of **1** prepared according to the standard procedure, precooled to 0 °C $CHCl_3$ (2 mL) was added with stirring at 0 °C and the reaction mixture was stirred at 0 °C until compound **1** was dissolved completely. The resulted solution of **1** was added with vigorous stirring in single portion to a solution of 100% CF_3SO_3H (0.085 mL, 0.94 mmol) in $CHCl_3$ (10 mL) at 0 °C under an argon atmosphere. The reaction mixture was stirred at 0 °C for 1 h and washed with water (3×3 mL). The combined aqueous layer was extracted with AcOEt (2×3 mL). The combined organic layer was washed with a saturated aqueous solution of NaCl (3 mL), dried with $MgSO_4$, and evaporated *in vacuo*. The product yields were determined by ^{1}H NMR spectroscopy (see Table 4).

The reaction of the *O*-methyl compound 2 with strong acids (general procedure). Method *A* (was used upon spectral determination of the yields of **5a—d**). Compound **2** (10 mg, 0.047 mmol) was added with vigourous stirring in small portions to the acid (1 mL) (see Table 5). The reaction temperature and time are given in Table 5. After completion of the reaction, the mixture was poured into ice water (3 mL) and extracted with CH_2Cl_2 (5×2 mL) and AcOEt (2×3 mL). The AcOEt extract was washed with water (1 mL). The organic extracts were combined, washed with a saturated aqueous solution of NaCl (2 mL), dried with $MgSO_4$, and evaporated *in vacuo*. The conversion of **2** and product yields were determined by ^{1}H NMR spectroscopy (see Table 5).

Method *B* (was used upon isolation of compounds **5a—d**). Compound **2** (60 mg, 0.28 mmol) was added with vigorous stirring in small portions to the corresponding 97% or 100% acid (1.5 mL) (see Table 5) at 0 °C. The reaction temperature and time are given in Table 5. After completion of the reaction, the mixture was poured into ice water (5 mL) and extracted with CH_2Cl_2 (5×5 mL) and AcOEt (2×5 mL)*. The AcOEt extract was washed with water (2 mL). The organic extracts were combined, washed with a saturated aqueous solution of NaCl (3 mL), dried with $MgSO_4$, and evaporated *in vacuo*. Product **5a** was purified by column chromatography on silica gel (the eluent was petroleum ether—acetone (1 : 1)). Products **5b—d** were purified by the preparative TLC on silica gel: the eluent was $CHCl_3$—AcOEt (8 : 1) for **5b**, $CHCl_3$ and then $CHCl_3$—AcOEt (8 : 1) for **5c**, and $CHCl_3$ for **5d**.

4-Nitropyrocatechol (5a). The yield was 25 mg (57%), m.p. 174—176 °C (from $CHCl_3$) (*cf.* Ref. 14: m.p. 176 °C); identical to the earlier obtained product[15,16] (^{1}H NMR and IR spectra).

2-Hydroxy-5-nitrophenyl methylsulfonate (5b). The yield was 33 mg (50%), m.p. 136—138 °C (from hexane). Found (%): C, 36.16; H, 3.07; N, 5.93. $C_7H_7NO_6S$. Calculated (%): C, 36.05; H, 3.03; N, 6.01. IR (KBr), ν/cm^{-1}: 1160 s, 1184 s, 1224 m, 1300 s, 1344 s, 1440 w, 1508 s, 1528 s, 1600 m, 3340 s. ^{1}H NMR (acetone-d_6), δ: 3.42 (s, 3 H, CH_3); 7.28 (d, 1 H, H(3), J = 8.8 Hz); 8.16 (d.d, 1 H, H(4), J = 8.8 Hz, J = 3.0 Hz); 8.20 (d, 1 H, H(6), J = 3.0 Hz). ^{13}C NMR (acetone-d_6), δ: 38.7 (CH_3); 118.2 (C(3) or C(6)); 121.2 (C(6) or C(3)); 124.9 (C(4)); 137.5 (C(1)); 141.0 (C(5)); 156.9 (C(2)). The spectral signals were assigned by calculations according to the additive scheme.[17] ^{14}N NMR (acetone-d_6), δ: −14 (NO_2, $\Delta\nu_{1/2}$ = 150 Hz). MS, m/z: 233 $[M]^+$.

2-Hydroxy-5-nitrophenyl trifluoromethylsulfonate (5c). The yield was 45 mg (56%), m.p. 106—108 °C. Found (%): C, 29.39; H, 1.35; N, 4.94. $C_7H_4F_3NO_6S$. Calculated (%): C, 29.28; H, 1.40; N, 4.88. IR (KBr), ν/cm^{-1}: 1136 m, 1164 m, 1216 s, 1284 m, 1312 m, 1344 s, 1428 s, 1508 m, 1528 m, 1608 m, 3340 s. ^{1}H NMR ($CDCl_3$), δ: 7.20 (d, 1 H, H(3), J = 9.5 Hz); 8.18—8.22 (m, 2 H, H(4), H(6)). ^{13}C NMR ($CDCl_3$), δ: 117.8 (C(3) or C(6)); 118.6 (q, CF_3, ^1J (^{13}C—^{19}F) = 320 Hz); 119.3 (C(6) or C(3)); 125.4 (C(4)); 136.6 (C(1)); 140.8 (C(5)); 154.2 (C(2)). The spectral signals were assigned by calculations according to the additive scheme.[17] ^{14}N NMR ($CDCl_3$), δ: −16 (NO_2, $\Delta\nu_{1/2}$ = 300 Hz). ^{19}F NMR ($CDCl_3$), δ: −74.0. MS, m/z: 287 $[M]^+$.

5-Nitro-1,3,2λ^6-benzodioxathiol-2,2-dione (5d). The yield was 43 mg (70%), m.p. 50—52 °C (*cf.* Ref. 18: m.p. 68 °C (from EtOH). Found (%): C, 33.11; H, 1.34; N, 6.52. $C_6H_3NO_6S$. Calculated (%): C, 33.19; H, 1.39; N, 6.45. IR (KBr), ν/cm^{-1}: 1060 w, 1120 w, 1216 s, 1348 s, 1432 s, 1480 m, 1540 s. ^{1}H NMR ($CDCl_3$), δ: 7.43 (d, 1 H, H(6), J = 8.8 Hz); 8.17 (d, 1 H, H(3), J = 1.5 Hz); 8.25 (d, 1 H, H(5), J = 8.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 108.2; 112.1; 121.7; 130.3; 142.1; 146.3. ^{14}N NMR ($CDCl_3$), δ: −19 (NO_2, $\Delta\nu_{1/2}$ = 110 Hz). MS, m/z: 217 $[M]^+$.

2-Methoxy-5-nitrophenyl trifluoromethylsulfonate (6). A solution of diazomethane in Et_2O (3 mL) prepared from *N*-methyl-*N*-nitrosourea (0.1 g) was added dropwise at 20 °C to a stirred solution of trifluoromethylsulfonate **5c** (30 mg, 0.1 mmol) in Et_2O (3 mL) until gas evolution was terminated and the solution became pale-yellow. The solvent was removed *in vacuo*. The residue was brought on a silica gel column (d = 10 mm, h = 20 mm) and eluted with a $CHCl_3$/AcOEt (8 : 1) mixture. The eluate was evaporated *in vacuo* to yield compound **6** (31 mg, 99%) as a light-yellow oil. Found (%): C, 32.01; H, 1.96; N, 4.75; $C_8H_6F_3NO_6S$. Calculated (%): C, 31.90; H, 2.01; N, 4.65; ^{1}H NMR ($CDCl_3$), δ: 4.06 (s, 3 H, CH_3); 7.17 (d, 1 H, H(3), J = 8.8 Hz); 8.16 (d, 1 H, H(6), J = 2.2 Hz); 8.30 (d.d, 1 H, H(4), J = 8.8 Hz, J = 2.2 Hz). The positions of the substituents in the aromatic ring were confirmed by the NOESY (^{1}H—^{1}H) experiment. ^{13}C NMR ($CDCl_3$), δ: 57.1 (CH_3); 118.7 (q, CF_3, ^1J (^{13}C—^{19}F) = 320 Hz); 112.5

* Only upon the preparation of products **5a** and **5c**.

(C(3)); 119.0 (C(6)); 125.4 (C(4)); 137.8 (C(1)); 140.9 (C(5)); 156.8 (C(2)). The spectral signals were assigned by the HSQC and HMBC experiments. ^{14}N NMR ($CDCl_3$), δ: −17 (NO_2, $\Delta\nu_{1/2}$ = 160 Hz). ^{19}F NMR ($CDCl_3$), δ: −74.3. MS, *m*/*z*: 301 $[M]^+$.

The reaction of 2 with 100% CF_3SO_3H in $CHCl_3$. A solution of compound **2** (10 mg, 0.047 mmol) in $CHCl_3$ (0.5 mL) was added with vigorous stirring at once to a solution of 100% CF_3SO_3H (0.085 mL, 0.94 mmol) in $CHCl_3$ (7 mL) at 20 °C. The reaction mixture was refluxed (61 °C) for 1.3 h and then AcOEt (10 mL) was added. The resulted mixture was washed with water (3×3 mL). The combined aqueous layer was extracted with AcOEt (2×3 mL). The combined organic extracts were washed with a saturated aqueous solution of NaCl (2 mL), dried with $MgSO_4$, and evaporated *in vacuo*. The conversion of **2** and product yields were determined by ^{1}H NMR spectroscopy (see Table 5).

Decomposition of ^{15}N-1 or ^{15}N-2 in 97% CF_3SO_3D (general procedure). The crushed at 0 °C compound ^{15}N-**1** (20 mg, 0.10 mmol) or ^{15}N-**2** (20 mg, 0.09 mmol) was placed into an NMR tube cooled to −30 °C under argon. A mixture of CF_3SO_3D (a 97% solution in D_2O) (0.55 mL) and CD_3OD (0.05 mL) precooled to −30 °C was added to the tube in single portion. The cooled tube was sealed, heated to 0 °C, and kept for 5 min with periodic shaking. The tube was then heated to 20 °C and the ^{14}N and ^{15}N NMR spectra were recorded. ^{14}N NMR (CF_3SO_3D/ /D_2O/CD_3OD), δ: −148 (the central N atom in NNO, $\Delta\nu_{1/2}$ = = 20 Hz), −232 (the terminal N atom in NNO and $N^{15}NO$, $\Delta\nu_{1/2}$ = 20 Hz). ^{15}N NMR (CF_3SO_3D/D_2O/CD_3OD), δ: −148.5 (the central N atom in $N^{15}NO$).

After recording the NMR spectra, the tube was unsealed and the reaction mixture was poured into ice water (3 mL) and extracted with CH_2Cl_2 (4×3 mL). The extracts were combined, washed with an aqueous solution of NaCl (1 mL), dried with $MgSO_4$, and evaporated *in vacuo*. The product yields were determined by ^{1}H NMR spectroscopy (see Table 4, Run *10* and Table 5, Run *13*).

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