= COORDINATION COMPOUNDS ====

Oxonitrates VO(NO₃)₃ and MoO₂(NO₃)₂ and Nitronium and Nitrosonium Nitratometallates as Nitrating Agents

I. V. Morozov, E. V. Karpova, D. M. Palamarchuk, A. Yu. Gavrilova, and S. I. Troyanov

Department of Chemistry, Moscow State University, Moscow, 117234 Russia

e-mail: morozov@inorg.chem.msu.ru

Received April 14, 2009

Abstract—Dissolution of vanadium in anhydrous HNO₃ followed by exposure of the solution in a dessicator over P_2O_5 gave liquid vanadyl trinitrate (I). The X-ray diffraction analysis of I was carried out for a single crystal grown on cooling the liquid in a sealed capillary. The structure is composed of VO(NO)₃ molecules in which the V atom has an unusually high C.N. 7; it coordinates the terminal O atom and three bidentate nitrate groups to form a distorted pentagonal bipyramid as the coordination polyhedron with the terminal O atom occupying one axial vertex. Using the GAMESS program package, ab initio calculation of the structure of VO(NO₃)₃ in the liquid phase was carried out. It was shown that in all three physical states, vanadyl trinitrate retains its molecular structure almost invariable. Toluene and naphthalene nitration using I and (NO₂)[Fe(NO₃)₄], NO[Cu(NO₃)₃], (NO)_{3/4}(NO₂)_{1/4}[Zr(NO₃)₅], and MoO₂(NO₃)₂ proceeds at high rates at low temperatures to give an unusually high *para*-nitrotoluene percentage in the products as compared with the *ortho*-isomer. The activity of the studied compounds in the nitration of naphthalene decreases in the series VO(NO₃)₃ > (NO)_{3/4}(NO₂)_{1/4}[Zr(NO₃)₅] > MoO₂(NO₃)₂.

DOI: 10.1134/S0036023609120109

Nitration is an important reaction of organic chemistry both for laboratory practice and for industry. The nitro derivatives formed, which are mainly aromatic, are important final products or intermediates in the production of a broad spectrum of products, in particular, explosives, construction materials, and pharmaceuticals.

Although nitration is a thoroughly studied industrial process, modern requirements to the efficiency, selectivity, and environmental safety of production processes call for nitration methods that comply with the "green chemistry" concept [1]. This refers first of all to the use of sulfuric acid-free nitration methods. Therefore, the search for alternative approaches to nitration is in progress. One of these approaches is the use of inorganic nitrates as nitrating agents. According to available publications, the use of nitrates may increase the selectivity of nitration and decrease the undesirable resinification and oxidation secondary processes.

For example, it was shown [2] that vanadyl trinitrate $VO(NO_3)_3$ is a strong and convenient nitrating agent for a series of benzene derivatives. A high yield of nitration products and minor contribution of side reactions were also noted for substrates containing electron-donating substituents, namely, anisole and *N*-methylaniline. It was suggested [2] that the reagent is simultaneously an active catalyst capable of being regenerated in the presence of nitrogen oxides.

The use of inorganic nitrates as nitrating agents has been largely constrained until now by the complexity of preparation of these compounds. The synthesis of anhydrous nitrates or oxonitrates requires most often the use of nitrogen oxides N_2O_4 or N_2O_5 in the presence of organic solvents and under conditions eliminating the access of air moisture [3]. For example, vanadyl trinitrate VO(NO₃)₃ is formed in the reaction of dinitrogen pentoxide with VOCl₃ or V₂O₅ [2, 4]. To date, the structure of this compound has been known only in the gas phase [5]. We developed a new synthetic approach that markedly simplified the synthesis of anhydrous nitrates and oxonitrates including both known and new ones [6, 7].

In this study we used new synthetic approaches to prepare a number of nitrates and oxonitrates: $VO(NO_3)_3$, $MoO_2(NO_3)_2$, $NO[Cu(NO_3)_3]$, $(NO_2)[Fe(NO_3)_4]$, and $(NO)_{3/4}(NO_2)_{1/4}[Zr(NO_3)_5]$. The structure of $VO(NO_3)_3$ in the crystalline and liquid phases was established for the first time. The obtained compounds were tested as nitrating agents in nitration of toluene and naphthalene.

EXPERIMENTAL

The following chemicals were used: analytical grade $Cu(NO_3)_2 \cdot 3H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, P_2O_5 , and V; reagent grade $ZrO(NO_3)_2 \cdot 2H_2O$, H_2MoO_4 , toluene, naphthalene, and CH_2Cl_2 .

	$v, cm^{-1}*$		Assignment [11]		
Experiment	Calculation [11]		Assignment [11]		
1630 s	1646 s	1635 s	v(NO) of bidentate NO ₃		
1610 s	1621 s	1615 s			
1202 s	1223 s	1216 m 1209 m 1196 m	$v_{as}(NO_2)$ of bidentate NO_3		
1016 s	1002 m	1014 s 1007 m	v(V=O)		
996 s	990 s	995 s	$v_s(NO_2)$ of bidentate NO_3		
965 s	968 s	962 s			
796 m	773 m	775 s	$\delta_s(VO_2N)$ of the ring, δ_s of bidentate NO ₃		
774 s	768 s				
686 w	659 w	690 w 682 w	δ (ONO) of bidentate NO ₃		
450 s	445 s	452 s	$v_{as}(VO_2)$ of bidentate NO ₃		

Table 1. IR spectrum of VO(NO₃)₃

* Designations for line intensity: s is strong, m is medium, w is weak.

Synthesis of Nitrates and Oxonitrates

Anhydrous nitric acid was synthesized by a reported procedure [8]. For preparing nitrosonium salts and anhydrous *d*-metal oxonitrates $NO[Cu(NO_3)_3],$ $(NO_2)[Fe(NO_3)_4], (NO)_{3/4}(NO_2)_{1/4}[Zr(NO_3)_5], and$ $MoO_2(NO_3)_2$, saturated solutions of the nitrate hydrates $Cu(NO_3)_2 \cdot 3H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and $ZrO(NO_3)_2 \cdot$ $2H_2O$ and α -molybdic acid in anhydrous nitric acid were prepared. For VO(NO₃)₃ preparation, vanadium metal was dissolved in anhydrous nitric acid. The resulting nitric acid solutions were placed in an evacuated dessicator over P_2O_5 . Under these conditions, nitric acid vapor reacts with P_2O_5 to give N_2O_5 , which readily passes to the gas phase and partially decomposes to N_2O_4 (NO₂) and O₂. Nitrogen oxides are taken by the starting nitric acid solution and irreversibly bind water. Over a period of 7–15 days, the liquid phase is gradually removed to give crystalline products. This synthetic method is described in detail in the literature [6, 7, 9].

No crystalline products were formed in the synthesis of $VO(NO_3)_3$ but after 10 days, the solution separated into two phases, the heavier phase colored light yellow and the lighter phase colored light brown. During the subsequent 5 days, the ligher liquid completely evaporated. The further analysis showed that the remaining viscous yellow liquid was $VO(NO_3)_3$ with HNO₃ and nitrogen oxide impurities. These were removed by the following procedure: high cooling in liquid nitrogen vapor resulted in separation, from the yellow thick liquid, of several drops of a lighter brownish liquid not miscible with the yellow liquid. These drops were removed by a pipette in a dry box.

The phase composition of the crystalline samples was determined by powder X-ray diffraction. The hygroscopic crystals were ground in a dry box, placed on a quartz holder, and tightly coated by a polystyrene film wetted with mineral oil. The measurement was carried put on a DRON 3M instrument using a CoK_{α} radiation in the 2 θ range of 5°–60°. The single-phase nature of the obtained samples was confirmed by similarity of the experimental X-ray diffraction patterns and theoretical ones calculated from single crystal X-ray diffraction data.

The yellow VO(NO₃)₃ sample was identified by comparing its IR spectrum with published data. For recording the IR spectrum, a drop of liquid VO(NO₃)₃ in a dry box was placed into a polyethylene bag and tightly sealed. The spectrum was recorded in the range of 4000–400 cm⁻¹ on a PE-1600 FTIR spectrometer. The spectrum of VO(NO₃)₃ and band assignment are summarized in Table 1.

The bands corresponding to C–C and C–H vibrations of the polyethylene film are not superimposed on the vanadyl nitrate molecule vibrations and are not given in Table 1. The obtained IR spectrum fully corresponds to published data [10].

Structure Determination for $VO(NO_3)_3$ in the Crystalline and Liquid Phases

To carry out single crystal X-ray diffraction, a liquid VO(NO₃)₃ sample was placed in a thin-walled glass capillary, which was then sealed. The X-ray diffraction experiment was carried out on a IPDS (STOE) instrument (Mo K_{α} radiation, $\lambda = 0.71073$ Å, graphite monochromator). By multiple repeating of cooling (freez-

Table 2. Crystal data, X-ray diffraction experiment parameters, and structure refinement details for $VO(NO_3)_3$

System	Monoclinic
Space group	$P2_1/c$
<i>a</i> , Å	10.079(3)
b, Å	13.203(4)
<i>c</i> , Å	5.686(2)
β, deg	102.47(2)
<i>V</i> , Å ³	738.8(4)
Ζ	4
$d_{\text{calcd}}, \text{g/cm}^3$	2.274
μ , mm ⁻¹	1.399
Crystal size, mm	$0.5 \times 0.3 \times 0.3$
Т, К	200(2)
$\theta_{\rm max}$, deg	23.8
The number of reflections, measured/inde- pendent	3475/1132
The number of reflections with $F^2 > 2\sigma(F^2)$	495
The number of reflections/least square re- finement parameters	1121/127
R_1	0.140
wR_2	0.284

Table 3. Interatomic distances (Å) and bond angles in the $VO(NO_3)_3$ molecule in the gas, liquid, and crystalline phases

	Physical state of VO(NO ₃) ₃						
Bond	ga	S	liquid	orretal			
	[11]	calcu	ci y star				
V-O(10)	1.607(7)	1.483	1.482	1.573(15)			
V–O(1)	2.154(9)	2.041	2.037	2.084(13)			
V–O(2)	1.971(5)	1.984	1.980	2.014(12)			
V–O(4)	2.154(9)	2.041	2.037	2.085(13)			
V–O(5)	1.971(5)	1.984	1.980	1.989(15)			
V-O(7)	2.258(20)	2.253	2.284	2.229(15)			
V–O(8)	1.915(7)	1.919	1.931	1.975(13)			
Angle							
O(10)VO(8)	94.5(13)	100.7	100.7	100.7(8)			
O(10)VO(2)	96.3(9)	102.5	102.7	100.6(7)			

ing)-heating (partial melting) cycles for a sample in a capillary under a stream of the X-ray diffraction unit cooling gas, $VO(NO_3)_3$ was crystallized as crystal clots rather than as a powder formed upon the primary cooling. After X-ray diffraction data had been collected,

they were processed to isolate the most intense component; as a result, the group of reflections caused by diffraction from one crystal was distinguished and reflections from other (three or four) components were discarded. The crystal data, X-ray diffraction experiment parameters, and structure refinement details for $VO(NO_3)_3$ are summarized in Table 2, and selected bond lengths and bond angles are in Table 3. The full set of crystal data is deposited with the Inorganic Crystal Structure Database (FIZ, Karlsruhe and NIST, Gaithersburg) with the registration number ICSD 420596. Note that the accuracy of determination of the geometric structure of $VO(NO_3)_3$ is not very high, due to the inevitable presence of accidental components from other crystals in the X-ray diffraction pattern. The error in V-O bond length determination was 0.012-0.015 Å, and the size of OVO angles was determined to an accuracy of 0.7°-0.8°. Nevertheless, the absolute values for the bond lengths and angles are in quite satisfactory agreement with the results of gas-electron diffraction study of VO(NO₃)₃ [11] (Table 3).

The structure of $VO(NO_3)_3$ in the liquid phase was determined by an ab initio quantum chemical calculation of the equilibrium geometry of this molecule. As the starting geometry, the geometry of gaseous vanadyl nitrate determined previously [11] from gas-electron diffraction data was used. The calculation was carried out using the PC GAMESS program package [12] by restricted Hartree-Fock method in the self-consistent field approximation, SCF/RHF. A polarized basis set comprising heavy effective potentials for the inner shells was used for the V atom and correlation-consistent polarized valence double-zeta basis sets were used for all other atoms. First, the structure of the VO(NO₃)₃ molecule in the gas phase was calculated. The reliability of this calculation was confirmed by good agreement between the geometry found for an isolated $VO(NO_3)_3$ molecule with gas-electron diffraction data (Table 3). For determining the vanadyl nitrate structure in the liquid phase, a continual model was used [13]; the dielectric constant was taken to be 80 and the solvation shell radius was assumed to be 4 Å.

Using the equilibrium geometry of the vanadyl nitrate thus obtained, the vibrational spectrum of this molecule was calculated. It has thirty-six principal vibrations of which twenty vibrations are in the IR range. All of the found vibration frequencies are real, which indicates that the stationary state is true. In Table 1, the frequencies of the strongest vibrations present in the experimental IR spectrum of liquid vanadyl trinitrate are compared with theoretical vibration frequencies multiplied by the scaling factor of 0.9. The assignment of vibration frequencies of the experimental IR spectrum corresponds to that predicted by quantum chemical calculation. The satisfactory agreement between the theoretical and experimental IR spectra indicates that the found configuration coincides with the real one.

$\begin{array}{c c} \operatorname{Run} & \\ \text{no.} & T, ^{\circ}\mathrm{C} \end{array}$		Nitrating agent (NA)	v(T): v(NA)	Product composition, mol %					<i>E</i> *	o /n **
				Т	o-MNT	<i>p</i> -MNT	2,4-DNT	2,6-DNT	$L_{\rm NA}$	0-1p-11
1	0	VO(NO ₃) ₃	4:1	50	27	23	0	0	2.0	1.2
2		$MoO_2(NO_3)_2$	2:1	54	21	25	0	0	0.92	0.84
3		$(NO_2)[Fe(NO_3)_4]$	4:1	52	23	25	0	0	1.9	0.92
4		NO[Cu(NO ₃) ₃]	3:1	30	33	37	0	0	2.1	0.89
5	50	$MoO_2(NO_3)_2$	4:1	53	20	23	3.4	0.6	2.0	0.87
6		$(NO_2)[Fe(NO_3)_4]$	4:1	25	21	23	25	6	4.2	0.91

Table 4. Reactant ratio and composition of the products of toluene nitration

Notes: * $E_{\text{NA}} = \frac{v(\text{NO}_2 -)}{v(\text{NA})}$ is the efficiency of nitrating agent.

** $o-/p--\frac{v(o-MNT)}{v(n-MNT)}$.

Toluene and Naphthalene Nitration

For nitration, suspensions of inorganic nitrate (10 wt %)in dichloromethane pre-distilled over P2O5 were prepared. For this purpose, dichloromethane was added to a weighed portion of the nitrate and the mixture was magnetically stirred in a tightly closed vessel for 10 min. In the case of vanadyl nitrate, a true solution formed, which is consistent with published data [2]. The resulting suspension of a nitrating agent (NA) was added dropwise to a stirred 10% dichloromethane solution of toluene (T) or naphthalene (N) kept at a constant temperature. The temperature of the reaction medium was maintained constant using a water bath or a cooling ice-salt mixture. The reaction was carried out for 30 min, then excess water was added, and the organic fraction was separated, washed with water to pH 7, and dried over anhydrous Na₂SO₄. The solvent was removed on a rotary evaporator and the organic products were analyzed in the reaction mixture by ¹H NMR spectroscopy. The ¹H NMR spectra were recorded on an Avance Bruker spectrometer operating at 400 Hz at 28°C in CDCl₃. The proton signals were assigned relying on published data [14].

The composition of the toluene nitration products was determined from the integral intensity ratio of the signals for aromatic protons in the ¹H NMR spectra of reaction mixtures. The 2,4-dinitrotoluene (DNT) content was determined using the HC(3) proton signal manifested as a doublet with the spin-spin coupling constant J = 2.0 Hz at about 8.80 ppm; 2,6-DNT was determined based on the doublet at 7.98 ppm, J =8.1 Hz; para-mononitrotoluene (MNT) was determined using the doublet at 8.08 ppm, J = 8.6 Hz; and ortho-MNT was determined using the doublet at 7.93 ppm, J = 8.1 Hz.

The relative content of 1,8-dinitronaphthalene (1,8-DNN) in the naphthalene nitration products was found based on the triplet at 7.75 ppm; 1,5-DNN was quantified using the triplet at 7.82 ppm, and for mononitronaphthalene, a doublet at 8.56 ppm was used.

The weights of reactant samples were 0.1 to 1 g in most of experiments, which corresponds to 1 to 50 mmol. Since the nitrating agents used are hygroscopic, all operations with these compounds (weighing, preparation of the starting suspensions or solutions) were carried out in a dry box under nitrogen, while the proper nitration reactions were carried out under conditions excluding a contact with air moisture. Toluene was nitrated at 0 and 50°C, and naphthalene was nitrated at -5° C. The starting reactant ratio and the composition of the nitration products are presented in Table 4 for toluene (runs 1-6) and in Table 5 for naphthalene (runs 7-12).

RESULTS AND DISCUSSION

It follows from Table 3 that going from the crystalline phase to liquid or gas phase is not accompanied by pronounced changes in the geometry of the $VO(NO_3)_3$. The somewhat underestimated V-O distance for the vanadyl group in the liquid and gas phases can be attributed to the lack of electron correlation corrections in the self-consistent field method.

In the $VO(NO_3)_3$ molecule, the vanadium atom has an unusually high C.N. = 7 (Fig. 1). The vanadium coordination polyhedron is a distorted pentagonal bipyramid where one axial vertex is occupied by the terminal O(10) atom, which forms the shortest V–O distance (1.573(15) Å) and the other axial vertex is occupied by the O atom of the asymmetric bidentate nitrate group, this bond being the longest (V-O(7)), 2.229(15) Å) (the indicated distances correspond to crystalline $VO(NO_3)_3$ (Table 3)). The equatorial plane is formed by the second O atom of this nitrate group and four more O atoms of two symmetrical bidentate NO₃ groups located at V–O distances of 1.975(13)–2(085) Å (cf. 2.03 Å). The distortion of the pentagonal bipyramid

Run	Nitrating agent (NA)	$\frac{\nu(N)}{\nu(NA)}$	F	$\nu(NO_2-)$			
no.	Nitrating agent (NA)		N	MNN	1,5-DNN	1,8-DNN	$L_{\rm NA} = \frac{1}{\nu({\rm NA})}$
7	VO(NO ₃) ₃	4:1	42	58	0	0	2.3
8	$(NO)_{3/4}(NO_2)_{1/4}[Zr(NO_3)_5]$	3:1	50	50	0	0	2.0
9	$MoO_2(NO_3)_2$	4:1	77	23	0	0	0.92
10	VO(NO ₃) ₃	1:3	0	0	21	79	0.67
11	$(NO)_{3/4}(NO_2)_{1/4}[Zr(NO_3)_5]$	1:3	0	70.5	7	22.5	0.43
12	$MoO_2(NO_3)_2$	1:3	0	85	5	10	0.38

 Table 5. Results of naphthalene nitration

is due to the fact that the OVO bond angles involving the same nitrate group range from 61° to 64°, which is somewhat smaller than the perfect value (for example, the angle involving axial oxygen atoms, O(10)VO(7), is 162.5(7)°). In addition, the vanadium atom is shifted from the equatorial plane toward the terminal O(10) atom: the O(10)VO(equat. plane) angles range from 94.1(7)° to 103.4(7)°. In the crystal structure of vanadyl trinitrate, each VO(NO₃)₃ molecule is surrounded by twelve other molecules and forms O…O contacts at least 2.9–3.15 Å long; the molecules are more closely packed in the (*a*0*c*) plane (four neighboring V atoms are located at 4.8 to 5.7 Å distances, while along the *b* axis two nearest V…V contacts are 6.8 Å) (Fig. 2).

Due to its molecular structure, $VO(NO_3)_3$ is soluble in organic solvents. This is favorable for high rates of nitration, which occurs by a homogeneous mechanism. This is consistent with published data [2] and is confirmed by toluene and naphthalene nitration experiments.

Toluene nitration experiments were carried out with deficiency of nitrating agents; as a result, no DNT was formed at 0° C (Table 4, runs 1–4); however, at 50°C, DNT was detected in the reaction products (Table 4, runs 5 and 6).

Attention is attracted by unusually high content of *p*-MNT in the toluene nitration products (Table 4, last column). Indeed, when $MoO_2(NO_3)_2$, $NO[Cu(NO_3)_3]$, or $(NO_2)[Fe(NO_3)_4]$ was used (Table 4, runs 2–6), the *o*-MNT to *p*-MNT ratio in the reaction products was 0.84–0.92, whereas with conventional nitrating agents, v(o-MNT)/v(p-MNT) was 1.2 to 1.6 [15, 16].

Fig. 1. Structure of the $VO(NO_3)_3$ molecule in the crystal structure of vanadyl trinitrate.





Fig. 2. Crystal structure of $VO(NO_3)_3$ projected along the *c* axis.

For stoichiometric description of the nitration, the parameter $E_{\rm NA}$ (the efficiency of a nitrating agent) characterizing the average number of nitro groups introduced in the substrate per molecule of the nitrating agent was calculated. In the case of toluene (runs 1–6), the $E_{\rm NA}$ value was found from the data of Table 4 using the relation

$$E_{\text{NA}} = \nu(\text{NO}_2\text{-})/\nu(\text{NA}) = 0.01[\chi(\text{MNT}) + 2\chi(\text{DNT})] \cdot [\nu_0(\text{T})/\nu(\text{NA})],$$

where $v_0(T)$ and v(NA) are the initial amounts of toluene and the nitrating agent, $v(NO_2)$ is the total number of nitro groups introduced in toluene, $\chi(MNT)$ and $\chi(DNT)$ are the MNT and DNT contents in the nitration products (mol %). In the naphthalene nitration experiments, the E_{NA} value was calculated in a similar way from the data of Table 5.

The parameter $E_{\rm NA}$ allows one to take into account the stoichiometric ratio between the amount of converted substrate and the nitrating agent and to compose the scheme of nitration:

$$2T + VO(NO_3)_3 \longrightarrow 2NT + VO_2(NO_3) + H_2O, \quad (1)$$

$$T + MoO_2(NO_3)_2 \longrightarrow NT + MoO_2(OH)(NO_3), \quad (2)$$

$$2T + (NO_2)[Fe(NO_3)_4] \longrightarrow 2NT + Fe(NO_3)_3 \cdot H_2O_1(3)$$

$$2T + NO[Cu(NO_3)_3] + 0.5O_2 \longrightarrow 2NT + Cu(NO_3)_2 \cdot H_2O.(4)$$

The above equations correspond to runs 1–4. The molecular formulas of inorganic products are tentative; however, in some cases, they may be close to the true formulas. For example, in the case of $MoO_2(NO_3)_2$, on going to nitration of an excess of naphthalene, the E_{NA} value remains invariable; this may be indicative of existence of rather stable hydroxymolybdenyl nitrate with the molecular formula close to $MoO_2(OH)(NO_3)$.

As temperature increases (run 5, equation (5)), $E_{\rm NA}$ increases considerably compared to that in run 2 and reaches the maximum possible value corresponding to the formation of molybdic acid:

$$2T + MoO_2(NO_3)_2 \longrightarrow 2NT + H_2MoO_4.$$
(5)

This means that nitration occurs stepwise via a number of inorganic intermediates. In the case of VO(NO₃)₃ and nitration of toluene, $E_{NA} = 2$ corresponds to the formation of polymeric VO₂(NO₃) (reaction (1)), possibly in the hydrated form, while in the case of naphthalene nitration, this value increases, indicating involvement of the last nitrate group in the nitration. According to published data [2], nitration of toluene at room temperature with a 10% solution of VO(NO₃)₃ = 1 : 1 affords a mixture of MNT and DNT, whereas the ratio T : VO(NO₃)₃ = 3 : 2 gives only MNT. This may also attest to the successive formation of several inorganic intermediates, probably, with decreasing nitrating capacity, during the process.

Naphthalene nitration experiments with excess nitrating agent revealed the sequence of relative activities of nitrating agents in which the compounds can be arranged: $VO(NO_3)_3 > (NO)_{3/4}(NO_2)_{1/4}[Zr(NO_3)_5] > MoO_2(NO_3)_2$. The highest activity is observed for vanadyl nitrate, which is soluble in organic solvents due to its molecular structure; hence, nitration occurs as a single-phase reaction in this case.

It is noteworthy that the use of acetonitrile as the solvent considerably decreases the nitrating activity of $VO(NO_3)_3$, which is in line with reported data [2]. Even in the presence of a threefold molar excess of $VO(NO_3)_3$ with respect to the substrate, most of naphthalene remain unchanged in acetonitrile.

Our experiments on toluene and naphthalene nitration by a 10% solution of VO(NO₃)₃ in dichloromethane confirmed the reported data about this compound as a potent and convenient nitrating agent. In addition, a series of nitronium and nitrosonium nitratometallates, (NO₂)[Fe(NO₃)₄], NO[Cu(NO₃)₃], and (NO)_{3/4}(NO₂)_{1/4}[Zr(NO₃)₅], and also molybdenyl nitrate MoO₂(NO₃)₂, were tested as nitrating agents. It was shown that nitration of naphthalene and toluene occurs rapidly, the resulting mixture of mononitrotoluenes being enriched in the *para*-isomer. The nitro compounds formed can be readily separated from the inorganic side products by washing with water and contain almost no oxidation products or other impurities.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 07-03-01142.

REFERENCES

- 1. Ono Noboru, *The Nitro Group in Organic Synthesis* (Willey-VCH, New York, 2001).
- M. F. A. Dove, B. Manz, J. Montgomery, et al., J. Chem. Soc., Perkin Trans. 1, 1589 (1998).
- 3. *Preparative Inorganic Reactions*, Ed. by W. Jolly (New York, 1964; Mir, Moscow, 1966), Vol. 1.
- 4. M. Schmeisser, Angew. Chem. 67, 493 (1955).

- B. A. Smart, H. E. Robertson, D. W. H. Rankin, et al., J. Chem. Soc., Dalton Trans., 473 (1999).
- K. O. Znamenkov, I. V. Morozov, and S. I. Troyanov, Zh. Neorg. Khim. 49 (2), 172 (2004) [Russ. J. Inorg. Chem. 49 (2), 172 (2004)].
- I. V. Morozov, A. A. Fedorova, D. V. Palamarchuk, and S. I. Troyanov, Izv. Akad. Nauk, Ser. Khim., No. 1, 92 (2005).
- Handbuch der Praeparative Anorganischen Chemie, Ed. by G. Brauer (Ferdinand Enke, Stuttgart, 1981; Mir, Moscow, 1985), Vol. 1.
- 9. D. V. Palamarchuk, M. I. Saidaminov, I. V. Morozov, and S. I. Troyanov, *Proceedings of IV National Crystallochemical Conference* (Chernogolovka, 2006) [in Russian].
- F. W. B. Einstein, E. Enwall, D. M. Morris, and D. Sutton, Inorg. Chem. **10**, 678 (1971).
- B. A. Smart, H. E. Robertson, D. W. H. Rankin, et al., J. Chem. Soc., Dalton Trans., 473 (1999).
- Alex A. Granovsky, *PC* GAMESS version 7.0 (Dragon) (MSU, Moscow, 2006).
- 13. M. W. Wong, M. J. Frisch, and K. B. Wiberg, J. Am. Chem. Soc. **113**, 4776 (1991).
- 14. E. Pretsch, P. Buehlmann, and C. Affolter, *Structure Determination of Organic Compounds: Tables of Spectral Data* (Springer, Heidelberg, 2000; Mir, Moscow).
- 15. J. R. Knowles, R. O. C. Norman, and G. K. Radda, J. Chem. Soc., 4885 (1960).
- The Chemical Encyclopedia, Ed. by I. L. Knunyants (Bol'shaya rossiiskaya entsiklopediya, Moscow, 1992), Vol. 3, p. 284 [in Russian].