ATRANES

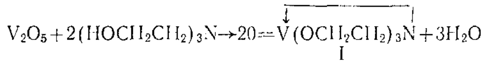
XXVII.* 1-HYDROXYVANAD(IV)ATRANE-3,7,10-TRIONIC ACID AND ITS DERIVATIVES

M. G. Voronkov and S. V. Mikhailova

UDC 547.89'258.81:541.49

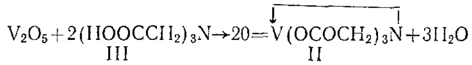
A method was developed for the preparation of the previously unknown heterocyclic, chelated mixed anhydride of aminotriacetic acid and vanadic acid – 1-hydroxyvanad(IV)atrane-3,7,10-trionic acid ($H^+[\overrightarrow{N(CH_2COO)_3V}-O]^-$ – based on the reaction of aminotriacetic acid with V_2O_5, HVO_3, and V_2O_3. A number of ammonium salts of 1-hydroxyvanad(IV)atrane-3,7,10-trionic acid were obtained.

Previously one of us and Lapsin' [2-5] described 1-oxovanadatranes (I), which were formed by the reaction of tris(2-hydroxyalkyl)amines with vanadium pentoxide via the scheme



$$V_2O_5+2(HOCH_2CH_2)_3N\rightarrow 2O{=}\underset{\text{I}}{V}(OCH_2CH_2)_3N+3H_2O \quad (1)$$

The aim of the present study was the synthesis of the previously unknown, similarly constructed 1-oxovanadatrane-3,7,10-triones (II) starting from aminotriacetic acid (III):



$$V_2O_5+2\underset{\text{III}}{(HOOCCH_2)_3N}\rightarrow 2O{=}\underset{\text{II}}{V(OCOCH_2)_3N}+3H_2O \quad (2)$$

$$HVO_3+\text{III}\rightarrow\text{II}+2H_2O \quad (3)$$

$$NH_4VO_3+\text{III}\rightarrow\text{II}+2H_2O+NH_3 \quad (4)$$

Up until now, only complexes of III with V^{3+} and V^{4+} that simultaneously contain Na or Mg ions [6-9] and have structures of the $[N(CH_2COONa)_2(CH_2COO)]_3V$, $[N(CH_2COO)_2Mg(CH_2COO)]_3V$, and $[N(CH_2COO)_2Mg(CH_2COO)]_2V{=}O$ type, obtained by heating aqueous solutions of aminotriacetic acid with Na_2CO_3 or MgO with the addition of V_2O_3 or V_2O_4, were known.

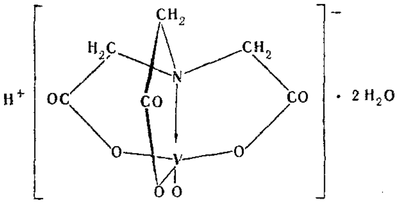
We tried to accomplish reactions (2), (3), and (4) by heating a mixture of the reagents in water, after which the water was removed by distillation in a rotary vacuum evaporator.

The reaction of III with V_2O_5 and HVO_3 could also be carried out at room temperature by prolonged mechanical shaking or stirring of an aqueous suspension of the reagents until they dissolved completely. In all cases, however, the reaction product turned out to be a substance of the $C_6H_{11}NO_9V$ composition rather than the expected 1-oxovanadatrane-3,7,10-trione (II); this product can be assigned the 1-hydroxyvanad(IV)atrane-3,7,10-trionic acid dihydrate (IV) structure:

---

*See [1] for communication XXVI.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1606-1611, December, 1971. Original article submitted March 25, 1971.



IV

Compound IV was obtained as blue crystals that are stable on storing in air and soluble in water, aqueous solutions of ammonia and amines (best above 40°C), dimethylformamide, dimethyl sulfoxide, and mono-, di-, and triethanolamines. Compound IV is insoluble in the usual organic solvents (hydrocarbons, alcohols, ethers, dioxane, acetone, chloroform, etc.).

Aqueous solutions of IV give a strongly acid reaction ($pK_a = 3.9$). The potentiometric titration curve of IV (Fig. 1) is complex. Three discontinuities with equivalence points at pH 4.3, 6.2, and 8.7 are observed on it. The first discontinuity corresponds to the formation of a salt, while the second and third are connected with salt formation accompanied by disruption of the atrane structure.

The presence of two molecules of water of crystallization in the IV molecule is confirmed by derivatography (Fig. 2). One of them is split out at 155°, the second is split out at 195-290°.

The molecular weight of IV, determined cryoscopically in water, is 233, while the molecular weight of anhydrous IV ($C_6H_7NO_7V$) is 256.1.

The structure of IV is confirmed by the results of IR and ESR spectroscopy (Figs. 3 and 4, respectively).

In our opinion, the stretching vibrations of the $(V=O)^-$ group are represented in the IR spectrum of IV by the strong absorption band at 995 cm^{-1} (Table 1). The absence of absorption at 1700-1750 cm^{-1} indicates that the IV molecule does not contain un-ionized COOH groups [10-12]. All of the CH_2COO groups in IV are equivalent and are bonded to the metal atom, which is confirmed by the presence of only two very strong absorption bands at 1575 cm^{-1} (hydrated COO^-) and 1620 cm^{-1} (COOV).

As in the IR spectra of HVO_3 and V_2O_4, the spectra of IV and its salts contain an absorption band at 560-580 cm^{-1} that can be ascribed to ν^{V-O} vibrations. It can be assumed that the band at 420 cm^{-1} is related to either the vibrations of the $N \rightarrow V$ bond or to the vibrations of the VO_3 group. The water of crystallization in IV is represented in the IR spectrum by a broad absorption band at 3400-3500 cm^{-1}.

The ESR spectrum* of IV has a hyperfine structure (hfs) (Fig. 4). The hfs components have different widths and are asymmetrical with respect to the center of the spectrum, which indicates axial symmetry of the environment of the paramagnetic particles [13, 14]. The hfs of the ESR spectra has the shape characteristic for tetravalent vanadium with the $3d^1$ configuration and is caused by interaction of the unpaired electron with the nucleus of the vanadium atom (V^{51}), the spin (i) of which is 7/2.

The structure of IV is also confirmed by its blue color, which is usually peculiar only to tetravalent vanadyl compounds, and also by the synthesis of IV from III and V_2O_4 (94% yield):

$$V_2O_4+2(HOOCCH_2)_3N \rightarrow 2IV+2H_2O \qquad (5)$$

Thus, in the reaction of III with V_2O_5, HVO_3, and NH_4VO_3, V^{5+} is reduced to V^{4+} by aminotriacetic acid, apparently via the scheme

$$3V_2O_5+N(CH_2COOH)_3 \rightarrow 3V_2O_4+NH_3+3CO_2+3CH_2O \qquad (6)$$

Similarly, HVO_3 and NH_4VO_3 oxidize III. Thus the formation of IV should be represented by the schemes

$$3V_2O_5+7N(CH_2COOH)_3 \rightarrow 6IV+3CO_2+3CH_2O+NH_3+6H_2O \qquad (7)$$

$$6HVO_3+7N(CH_2COOH)_3 \rightarrow 6IV+3CO_2+NH_3+12H_2O \qquad (8)$$

$$6NH_4VO_3+7N(CH_2COOH)_3 \rightarrow 6IV+3CO_2+3CH_2O+7NH_3+9H_2O \qquad (9)$$

The formation of CO_2 and CH_2O in reactions (7), (8), and (9) actually does occur.

---

*The hfs constant (a) for the spectra obtained is 114 Oe, and the spectroscopic splitting factor (g) is 1.9855 ± 0.0003. We thank R. A. Gavar for recording the ESR spectra.

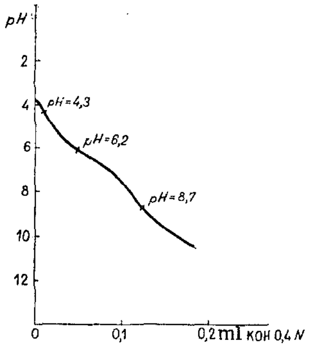


Fig. 1

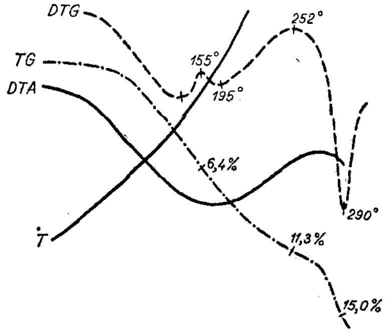


Fig. 2

Fig. 1. Potentiometric titration curve of 1-hydroxyvanadatrane-3,7,10-trionic acid for titration with 0.4 N KOH.

Fig. 2. Derivatogram of 1-hydroxyvanadatrane-3,7,10-trionic acid (heating rate 12 deg/min): T) heating curve; TG) thermogravimetric curve; DTA) differential heating curve; DTG) derivative curve.

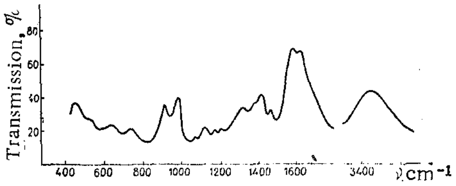


Fig. 3

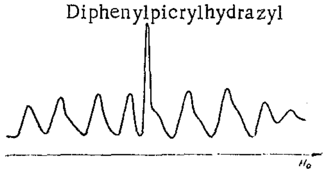


Fig. 4

Fig. 3. IR spectra of 1-hydroxyvanad(IV)atrane-3,7,10-trionic acid.

Fig. 4. ESR spectrum of 1-hydroxyvanad(IV)atrane-3,7,10-trionic acid.

The ammonia formed in reactions (7)-(9) reacts with IV to form its ammonium salt (V). The product of reactions (7) and (8) is therefore a mixture of IV and V (in a molecular ratio of 5 : 1 if the reaction mixture is heated for 3 to 4 h), and only V is formed in reaction (9). Thus, in final form, the reaction of III with V_2O_5, HVO_3, and NH_4VO_3 should be represented by the schemes*

$$3V_2O_5+7N(CH_2COOH)_3\rightarrow 5IV+V+3CO_2+3CH_2O+6H_2O \qquad (10)$$

$$6HVO_3+7N(CH_2COOH)_3\rightarrow 5IV+V+3CO_2+3CH_2O+9H_2O \qquad (11)$$

$$6NH_4VO_3+7N(CH_2COOH)_3\rightarrow 6V+3CO_2+3CH_2O+NH_3+9H_2O \qquad (12)$$

It is interesting that IV is also formed in the reaction of III with V_2O_3. Air oxygen or even the aminotriacetic acid itself is apparently the oxidizing agent in this case.

Anhydrous IV was obtained in an attempt to prepare 1-oxovanadatrane-3,7,10-trione (II) by the reaction of III with tri-n-amyl vanadate in dimethylformamide via the scheme

$$OV(OC_5H_{11})_3+(HOOCCH_2)_3N\rightarrow I+3C_5H_{11}OH \qquad (13)$$

The IR absorption spectra of anhydrous IV coincide completely with the spectra of the dihydrate of IV. Only the band at 3450 cm^{-1}, which is related to the stretching vibrations of aqueous hydroxyl groups, is absent.

Compound I could not be obtained by the oxidation of IV with hydrogen peroxide.

Crystalline ammonium salts with azure blue, or green colors are formed from IV and aqueous solutions of ammonia and amines (Table 2). They are hygroscopic and deliquesce in air. These salts can also be obtained by the reaction of III with NH_4VO_3 (the method for the synthesis of V) or with V_2O_5 and

---

*It must be assumed that the CH_2O formed is also further oxidized by V_2O_5 or HVO_3.

TABLE 1. Frequencies and Assignment of the IR Absorption Maxima of IV

$IV \cdot 2H_2O$	IV	Assignment
420 s	425 s	$N \leftarrow V$ or VO_3
565 w	575 m	
630 m	635 m	
710 w	710 m	
765 m	780 m	
910 s	910 s	δ COO$^-$
995 s	985 s	$\nu(V=O)^-$
1085 w	1070 w	C—O
1130 m	1130 m	ν C—N
1220 w	1220 w	
1320 m	1320 w	
1355 m	1365 s	
1420 s	1430 s	
1470 m	1460 m	ν COO$^-$
1575 vs	1575 vs	ν_{as} hydrated COO$^-$
1630 vs	1650 vs	ν_{as} COOV
3450 s		ν H_2O

Note: s is strong, w is weak, m is medium, and vs is very strong.

TABLE 2. Ammonium Salts of $IV[R_3NH]^+[N(CH_2COO)_3V-O] \cdot nH_2O$

NR_3	n	Color	Empirical formula	Found, %				Calc., %				Yield, %
				C	H	N	V	C	H	N	V	
NH_3	2	Green	$C_6H_{15}N_2O_9V$	23,13	5,16	9,31	16,70	23,23	4,87	9,03	16,42	86,0
$C_2H_5NH_2$	2	Blue	$C_8H_{18}N_2O_9V$	28,65	6,53	7,65	14,92	28,48	5,38	8,31	15,11	90,0
$(C_2H_5)_2NH$	0	Blue	$C_{10}H_{18}N_2O_7V$	37,11	5,31	8,69	14,10	36,48	5,51	8,50	15,47	83,0
$(C_2H_5)_3N$	0	Dark-blue	$C_{12}H_{22}N_2O_7V$	40,48	5,91	7,70	15,65	40,34	6,20	7,84	14,25	96,0
C_5H_5N	1	Blue	$C_{11}H_{14}N_2O_8V$	37,41	4,41	7,31	13,95	37,40	3,99	7,93	14,42	78,0
$C_5H_{10}NH$	3	Azure	$C_{11}H_{24}N_2O_{10}V$	33,72	6,49	7,55	11,70	33,42	6,12	7,08	12,88	80,0

HVO_3 in the presence of ammonium hydroxide or the appropriate amine. (As already mentioned, ammonium salt V is partially formed in the reaction of the indicated reagents in the absence of ammonia.)

Compound IV forms a precipitate of a grayish-blue salt with aqueous mercuric acetate, while lead acetate solution gives a brown salt.

EXPERIMENTAL

Starting Reagents. Aminotriacetic acid (III) was obtained by the method in [15] and purified by recrystallization from water. Vanadium pentoxide and tetroxide were chemically pure preparations. Vanadium trioxide was obtained by the reaction of NH_4VO_3 with hydrazine hydrate.

Analysis. Carbon and hydrogen were determined by combustion in oxygen of a single weighed sample both without a catalyst and in the presence of chromium oxide. The metal was determined as the oxide remaining after calcination of the substance in a stream of oxygen at 1000°.

The IR spectra of KBr pellets were recorded with a UR-10 spectrometer. The ESR spectra of a 0.1 M aqueous solution of IV were obtained with an RÉ-1301 spectrometer. A sample of polycrystalline diphenylpicrylhydrazine (D = 2.0036) [16] was used to determine the spectroscopic g factor. The derivatograms were recorded with a derivatograph of the system in [17].

Reaction of Aminotriacetic Acid with V_2O_4. A 1.65-g (0.01 mole) sample of V_2O_4 was added to a hot solution of 3.82 g (0.02 mole) of III in 200 ml of water. The mixture was refluxed for 3 h until the V_2O_4 had dissolved completely. The resulting blue solution was filtered, and the water was removed from it in a rotary vacuum evaporator. The residual blue crystals were washed with absolute alcohol and ether and dried in vacuo to give 2.8 g (94%) of IV. Found: C 24.50; H 4.29; N 5.12; V 17.32%. $C_6H_{11}NO_9V$. Calculated: C 24.60; H 3.78; N 4.80; V 17.40%.

Reaction of Aminotriacetic acid with V_2O_3. A 6.4-g (0.043 mole) sample of freshly prepared vanadium trioxide was added to a hot solution of 16.4 g (0.086 mole) of III in 2 liter of water. The mixture was refluxed for 4 h until all of the V_2O_3 had dissolved. The resulting blue solution was cooled and filtered, and the water was removed from it in a rotary vacuum evaporator at 40°. The blue crystals in the residue were washed with absolute alcohol and ether and dried in vacuo or dissolved in water and precipitated from solution by the addition of alcohol and similarly dried to give 18.0 g (80.5%) of IV. Found: C 24.82: H 3.45; N 5.02; V 17.90%. $C_6H_{11}NO_9V$. Calculated: C 24.60; H 3.78; N 4.80; V 17.40%.

Compound IV was also formed by vigorous shaking of V_2O_3, V_2O_4, or V_2O_5 with III in water in the cold for 5 h until a homogeneous blue solution was formed. The water was then removed in a rotary vacuum evaporator. The yield of IV in this case was just as high (up to 98%).

Reaction of Aminotriacetic Acid with V_2O_5. A 1.81-g (0.01 mole) sample of vanadium pentoxide was added to a hot solution of 3.8 g (0.02 mole) of III in 200 ml of water. The mixture was refluxed for 6 h until the V_2O_5 had dissolved completely. The resulting dark-blue solution was filtered, and the water was removed from it in a rotary vacuum evaporator. The residual shiny blue crystals were washed with absolute alcohol and ether and dried in vacuo to give 2.3 g (80.0%) of product. Found: C 24.52: H 3.28: N 5.12: V 16.89%. $C_6H_{11}NO_9V$. Calculated: C 24.60; H 3.78; N 4.80; V 17.40%.

Reaction of Aminotriacetic Acid with HVO_3. A 0.99-g (0.01 mole) sample of vanadic acid was added to a hot solution of 1.91 g (0.01 mole) of III in 200 ml of water. The mixture was refluxed for 5 h until the HVO_3 had dissolved completely. The resulting dark-blue solution was filtered, and the water was removed from it in a rotary vacuum evaporator. The residual blue crystals were washed with absolute alcohol and ether and dried in vacuo to give 2.6 g (90.0%) of product. Found: C 24.65; H 3.92; N 4.95; V 18.60%. $C_6H_{11}NO_9V$. Calculated: C 24.60: H 3.78; N 4.80; V 17.40%.

Reaction of Aminotriacetic Acid with Tri-n-amyl Vanadate. A 3.3-g (0.01 mole) sample of tri-n-amyl vanadate was dissolved in 15 ml of dimethylformamide, and this solution was added dropwise with stirring to a solution of 1.91 g (0.01 mole) of aminotriacetic acid in 40 ml of dimethylformamide. The mixture was heated on a water bath at 60-70° for 30 min, during which the solution turned blue. The temperature was then raised gradually to 100°, and heating was continued for 1 h with gradual raising of the temperature to 130°. The resinous blue precipitate that formed was separated by suction filtration, washed with alcohol, and recrystallized from dimethylformamide–alcohol (2 : 1) to give 2.2 g (86.0%) of blue crystals. Found: C 28.9; H 2.96; N 5.31; V 18.35%. $C_6H_7NO_7V$. Calculated: C 28.2; H 2.68; N 5.46; V 19.7%.

Ammonium Salt of 1-Hydroxyvanad(IV)atrane-3,7,10-trionic Acid (V). A 0.99-g (0.01 mole) sample of HVO_3 was added to a solution of 1.91 g (0.01 mole) of III in 20 ml of 20% ammonium hydroxide, and the mixture was refluxed for 4 h. The resulting green solution was evaporated in a rotary vacuum evaporator, and the residual green crystals were worked up in the usual manner to give 2.6 g (86%) of product.

Salts of 1-Hydroxyvanad(IV)atrane-3,7,10-trionic Acid with Mono-, Di-, and Triethylamines. A 1.91-g (0.01 mole) sample of III was dissolved in 40 ml of a 10% aqueous solution of the appropriate amine, 0.99 g (0.01 mole) of HVO_3 was added, and the mixture was refluxed for 2 h. The resulting dark-green (yellow in the case of triethylamine) solution was filtered, and the solvent was removed in a rotary vacuum evaporator. The residual dark-blue or green resinous mass was dried in vacuo over concentrated H_2SO_4 for 10 days, after which it was suspended in absolute ethanol. The salt crystals isolated were purified by precipitation from aqueous solution by the addition of ethanol. The yields and colors are presented in Table 2.

Salt of 1-Hydroxyvanad(IV)atrane-3,7,10-trionic Acid with Pyridine. A 1.91-g (0.01 mole) sample of III was dissolved in 10 ml of pyridine–water (1 : 5), 0.99 g (0.01 mole) of HVO_3 was added, and the mixture was refluxed until the solid had dissolved completely. The solution became green in the process. The water and excess pyridine were removed in a rotary vacuum evaporator. The residual blue crystals were washed with absolute alcohol and ether and dried in vacuo. The crystals were very hygroscopic and deliquesced in air. They were also soluble in water. (The resulting solution was greenish-blue.) The yield was 2.8 g (78.0%).

Salt of 1-Hydroxyvanad(IV)atrane-3,7,10-trionic Acid with Piperidine. A 1.91-g (0.01 mole) sample of III was dissolved in 40 ml of 20% aqueous piperidine, 0.99 g (0.01 mole) of HVO_3 was added, and the mixture was refluxed for 2 h. The light-yellow solution that formed was evaporated in a rotary vacuum evaporator, and the residual dark-brown resinous mass was dried in vacuo over concentrated H_2SO_4. The light-brown crystals that were isolated were suspended in hot ethanol, suction-filtered, washed with alcohol, and dried in vacuo to give 2.6 g (80.0%) of product.

LITERATURE CITED

1. M. G. Voronkov and S. V. Mikhailov, Khim. Geterotsikl. Soedin., 610 (1971).
2. M. G. Voronkov and A. F. Lapsin', Khim. Geterotsikl. Soedin., 357 (1966); 35 (1967); No. 2, 348 (1970).
3. M. G. Voronkov, Vestnik Akad. Nauk SSSR, 38, 48 (1968).
4. M. G. Voronkov (Woronkow), G. I. Seltshan (Seltšchan), A. F. Lapsin' (Lapsina), and V. A. Pestunovich (Pestunovitsch), Z. Chem., 8, 214 (1968).
5. V. A. Pestunovich and M. G. Voronkov, Khim. Geterotsikl. Soedin., No. 2, 348 (1970).
6. H. Hahl and W. Kropp, U. S. Patent No. 1,517,003 (1924); Chem. Abstr., No. 1, 1105 (1925).
7. H. Hahl and W. Kropp, Austrian Patent No. 101,685 (1925); Chem. Abstr., No. 1, 3184 (1926).
8. H. Hahl and W. Kropp, U. S. Patent No. 1,695,147 (1925); Chem. Abstr., No. 1, 2556 (1929).
9. H. Hahl and W. Kropp, U. S. Patent No. 1,537,441 (1925); Chem. Abstr., No. 2, 581 (1925).
10. K. Wuethrich, Helv. Chim. Acta, 48, 779 (1965).
11. J. Selbin, Coord. Chem. Rev., 1, 293 (1966).
12. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley (1970).
13. H. M. McConnel, J. Chem. Phys., 25, 709 (1956).
14. R. N. Rogens and G. E. Pake, J. Chem. Phys., 33, 1107 (1960).
15. Yu. Bankovskii and A. Levin'sh, Izv. Akad. Nauk Latv. SSR, 107 (1957).
16. D. Ingraham, Electron Paramagnetic Resonance in Free Radicals [Russian translation], Inostr. Lit., Moscow (1961).
17. F. Paulik, I. Paulik, and L. Erdey, Z. Anal. Chem., 160, 241 (1958).