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Spectrophotometric Investigations of Some Complexes of Ruthenium. IV. Ruthenium Reactions with Thiosemicarbazide, 4-Phenylthiosemicarbazide and Diphenylthiocarbazide[1]

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A spectrophotometric investigation revealed that the orange colored complex formed by the reaction of ruthenium with thiosemicarbazide was $Ru(SC(NH)NHNH_2)^{+2}$. 4-Phenylthiosemicarbazide reacted similarly with ruthenium to give the bright red $Ru(SC(NC_6H_5)NHNH_2)^{+2}$. Both the thiosemicarbazide and the 4-phenylthiosemicarbazide behaved as weak acids, liberating a hydrogen ion for each molecule of ligand which entered the complex. At unit ionic strength the thiosemicarbazide complex was found to have a formation constant of 5.6 ± 0.2, while the constant for the 4-phenylthiosemicarbazide complex was 45 ± 2. Diphenylthiocarbazide in the presence of ruthenium was oxidized to dithizone, which in turn complexed the ruthenium giving a deep-violet colored solution.

Ruthenium reacts with a number of thiourea derivatives of the type $HSC(NR)NR_2$, in which the R's can be hydrogen, alkyl, aryl or NHR radicals, to give complexes which range in color from red through blue. The reactions of ruthenium(IV) perchlorate with a few of these complexing agents have been studied spectrophotometrically to determine the formulas and formation constants of the complexes involved.[2a–c] In the present paper the reactions of $Ru(ClO_4)_4$ with thiosemicarbazide, 4-phenylthiosemicarbazide, and diphenylthiocarbazide are described. Preliminary investigation of these reactions suggested that the complexes were not highly stable and that, as had been observed with other organic complexing agents,[2a–c] the Ru(IV) was being reduced to Ru(III) at the expense of the ligand. For these reasons the method used for the interpretation of the spectrophotometric data was that which was described for similar cases.[2a,b]

Experimental

Absorption Measurements.—A Beckman model DU and a Cary automatic recording spectrophotometer were used for the optical density measurements. Matched silica cells of 1.00 and 2.00 cm. optical length were used. The results are expressed in terms of optical density, D, defined by the relationship $D = \log_{10} I_0/I$, in which I_0 and I are the incident and transmitted light intensities, respectively.

Materials.—The preparation and standardization of the $Ru(ClO_4)_4$ solution have been given in a previous paper.[2a] The thiosemicarbazide, 4-phenylthiosemicarbazide, and diphenylthiocarbazide, recrystallized Eastman Organic Chemicals #1275, #5426 and #3110, respectively, were weighed out directly to provide solutions of the desired concentrations. The $LiClO_4$ and $HClO_4$, used to maintain constant ionic strength and hydrogen ion concentration, were from G. Frederick Smith Chemical Co. Throughout the investigation particular care was taken to avoid iron contamination.

Technique.—An extensive investigation of these as well as other systems of ruthenium has shown that the attainment of equilibrium is very slow, requiring days at room temperature. However, at higher temperatures equilibrium is attained much more rapidly. A number of different temperatures have been investigated and found satisfactory. The procedure followed in general consisted of heating a solution for a specified length of time in a constant temperature hot water-bath, and then cooling the solution rapidly in ice to 25°. Immediately after preparation each solution was scanned as quickly as possible on the spectrophotometer. The same absorption spectrum was obtained for a given complexing agent and concentration regardless of the temperature to which the solution was heated to produce equilibrium. This indicates that the constant calculated is the one for 25°; or that there is little difference in the constant over this temperature range (ΔH is small).

Results

Thiosemicarbazide.—The reactions of ruthenium(III) and/or ruthenium(IV) chloride with thiosemicarbazide to form a red to green colored solution has been reported.[3] However in the present experiments, when $Ru(ClO_4)_4$ reacted with thiosemicarbazide, neither of these colors was observed; the solutions varied in color from orange-brown to yellow.

The temperature study revealed that a minimum period of 30 minutes in a boiling water-bath was sufficient to produce equilibrium, while heating periods longer than one hour produced a turbidity. In this investigation, all solutions were heated exactly 35 minutes in the water-bath, then cooled in ice until the temperature of the solution reached 25 ± 1°. Immediately after preparation, each solution was scanned as quickly as possible on the spectrophotometer. It was found that the colored solution, after preparation, showed no signs of fading in 2.5 hours.

In all solutions used for the determination of the formulas and stability constants, the ruthenium concentration was maintained constant at 5.585×10^{-5} M, the perchloric acid concentration constant at 0.127 M, and the ionic strength constant at 1.0. Solutions were prepared by mixing necessary quantities of a solution of $Ru(ClO_4)_4$ and a freshly prepared solution of thiosemicarbazide to give the final desired concentrations. Equilibrium was attained by the previously described heating and cooling procedure. More than eighty solutions which contained ratios of ligand to ruthenium from 3600 to 2 were so prepared and scanned.

A typical constant wave length plot of the optical density as a function of the thiosemicarbazide to ruthenium ratio is given in Fig. 1. This shows clearly that the optical density of the solution does not change for ratios of ligand to ruthenium greater than 2800 (the line labeled d_1 in Fig. 1).

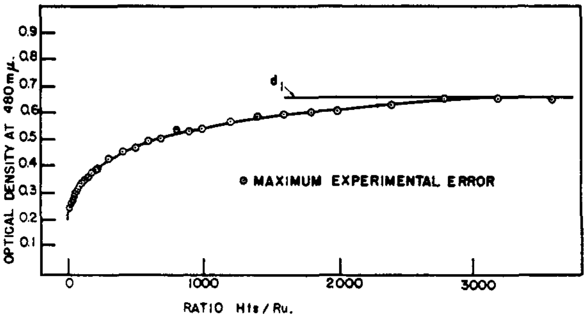

Fig. 1.—Optical densities at 480 mμ of various solutions with excess thiosemicarbazide present: $[Ru] = 5.585 \times 10^{-5}$ M; $[HClO_4] = 0.127$ M; $\mu = 1.0$; cell length = 2.00 cm.; circles, experimental points; curve, calculated on the basis of $Ru(ts)_1^{+2}$.

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[1] Work performed in the Ames Laboratory of the Atomic Energy Commission.

[2] R. P. Yaffe and A. F. Voigt, THIS JOURNAL, (a) **74**, 2500 (1952); (b) **74**, 2503 (1952); (c) **74**, 3163 (1952).

[3] B. Steiger, *Mikrochemie*, **16**, 193 (1934).

Hence the absorption spectrum of the last complex is known from experimental data. It was found that this complex (Fig. 2A) obeyed Beer's law over all wave lengths investigated.

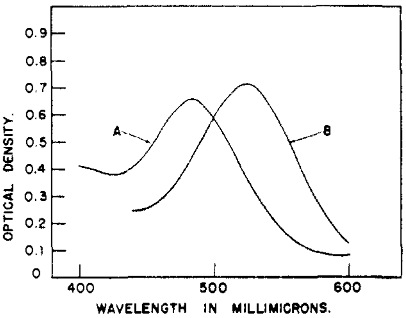

Fig. 2.—Absorption spectra of $Ru(ts)_1^{+2}$ and $Ru(pts)_1^{+2}$: $[Ru] = 5.585 \times 10^{-5}$ *M;* $[H^+] = 0.127$ *M;* $\mu = 1.0$; cell length = 2.00 cm.; A, $Ru(ts)_1^{+2}$; B, $Ru(pts)_1^{+2}$.

The method used to interpret the data was that presented in previous papers.[2a,b] Assuming only one complex to be present, the following equation may be written

$$Ru^{+3} + n\text{Hts} \rightleftarrows Ru(ts)_n^{3-n} + nH^+ \qquad (1)$$

where Hts is used as an abbreviation for thiosemicarbazide. The non-thermodynamic equilibrium constant then becomes

$$K_n = \frac{[Ru(ts)_n^{3-n}][H^+]^n}{[Ru^{+3}][Hts]^n} \qquad (2)$$

If the ligand is present to a sufficiently large excess, so its equilibrium concentration is essentially equal to its total analytical concentration, then the method developed previously may be applied, and equation (3) derived.

$$D = d_0 + \frac{K_n[Hts]^n(d_1 - D)}{[H^+]^n} \qquad (3)$$

in which d_0, and d_1 are the optical densities of the uncomplexed ruthenium and the complex, respectively. The optical density, D, was corrected for the very slight color of ligand. Various values of n were tried in equation (3), and the experimentally determined optical density, D, was plotted against $[Hts]^n[H^+]^{-n}(d_1 - D)$. With the correct choice of n, this should yield a straight line, the slope of which is K, and the intercept, d_0. Values of n equal to one-half, three-halves, two, three and four were tried unsuccessfully. Only a choice of n equal to one made the data interpretable. Thus the only complex present was a one-to-one complex, $Ru(ts)_1^{+2}$. The entire system was analyzed on the assumption that two complexes were present. With this assumption the value of the equilibrium constant for the second complex approached zero in the series of successive approximations used in the calculation. Thus if higher complexes are present, they exist at concentrations too small to be detected by this spectrophotometric method.

This graphical technique to evaluate the equilibrium constant K was applied to data obtained at eleven different wave lengths, at 10 mμ intervals from 430 to 530 mμ. These eleven values of the equilibrium constant were averaged to give a mean value of $K = 5.6$ with a standard deviation of 0.2, at unit ionic strength.

By use of this equilibrium constant, the absorption spectrum of the uncomplexed ruthenium was calculated from equation (3). This absorption spectrum was found to be essentially that of ruthenium(III) perchlorate, rather than ruthenium(IV) perchlorate, which substantiated the preliminary hypothesis that Ru(IV) was being reduced to Ru(III).

Although the equation and equilibrium constant in the ruthenium–thiosemicarbazide system have been written as functions of the hydrogen ion concentration, this assumption must be proved. To test this dependence, the above procedure was repeated at 0.254 *M* instead of 0.127 *M* $HClO_4$. The results of these measurements and calculations are given in Table I.

TABLE I

COMPARISON OF K IN 0.127 M AND 0.254 M $HClO_4$

$HClO_4$ *M*	Assuming hydrogen ion dependence	Not assuming hydrogen ion dependence
	$K = \frac{[Ru(ts)_1^{+2}][H^+]}{[Ru^{+3}][Hts]}$	$K = \frac{[Ru(Hts)_1^{+2}]}{[Ru^{+3}][Hts]}$
0.127	5.6 ± 0.2	44.4 ± 1.7
.254	5.9 ± .4	23.4 ± 1.6

From Table I it is seen that the assumption of hydrogen ion dependence gives agreement in the equilibrium constant at the two acidities, whereas the assumption of no dependence does not. Therefore it must be concluded that thiosemicarbazide is behaving as an acid, each molecule releasing a proton on formation of the ruthenium complex. This behavior was anticipated since it has been reported[4] that thiosemicarbazide and its derivatives react with metal ions to bind them by substitution of the sulfhydryl hydrogen.

4-Phenylthiosemicarbazide.—The reaction of ruthenium(III) and ruthenium(IV) with 1-phenylthiosemicarbazide to form a bright red color, suitable for the colorimetric determination of ruthenium, has been reported by several investigators.[3,5] With 4-phenylthiosemicarbazide the reaction is virtually identical, ruthenium again reacting to give a bright red color.

A temperature study of the ruthenium-4-phenylthiosemicarbazide system revealed that a minimum period of 25 minutes in a 70 ± 1° bath was required to produce equilibrium, while heating periods longer than 40 minutes produced a turbidity. In this study all solutions were heated exactly 35 minutes in the water-bath, then cooled in ice until the temperature of the solution reached 25 ± 1°. Immediately after preparation, each solution was scanned as quickly as possible on the spectrophotometer. It was found that the colored solutions, after preparation, showed no signs of fading in two hours.

The solutions used for the determination of the formulas and formation constants contained constant concentrations of ruthenium (5.585×10^{-5} *M*), and of perchloric acid (0.127 *M*) and had a constant ionic strength of 1.0. In addition these solutions contained 50% by volume of ethanol which was necessitated by the limited solubility of the complexing agent. More than seventy solutions which contained ratios of ligand to ruthenium from 900 to 2 were so prepared and scanned.

A typical constant wave length plot of the optical density as a function of the 4-phenylthiosemicarbazide to ruthenium ratio is given in Fig. 3. This shows clearly that the optical density of the solution does not change for ratios of ligand to ruthenium greater than 500 (the line labeled d_1 in Fig. 3).

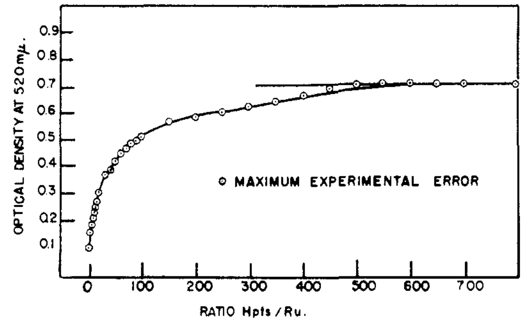

Fig. 3.—Optical densities at 520 mμ of various solutions with excess 4-phenylthiosemicarbazide present: $[Ru] = 51585 \times 10^{-5}$ *M;* $[HClO_4] = 0.127$ *M;* [ethanol] = 50%; $\mu = 1.0$; cell length, 2.00 cm.; circles, experimental points; curve, calculated on the basis of $Ru(pts)_1^{+2}$.

Hence the adsorption spectrum of the last complex (Fig. 2B) is known from experimental data. It was found that this complex obeyed Beer's law over all wave lengths investigated. A comparison of the two excess curves (Figs. 1 and 3) reveals that these are very similar in the two systems, and suggests that the 4-phenylthiosemicarbazide complex is more stable than the thiosemicarbazide complex. A com-

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(4) V. Harlay, *Compt. rend.*, **202**, 324 (1936).

(5) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1944.

parison of the two absorption spectra in Fig. 2 reveals that the spectra of the two complexes are similar, with the phenyl derivative shifting the maximum toward longer wave lengths.

By use of the method of analysis described for the thiosemicarbazide complex, the 4-phenylthiosemicarbazide data were interpreted. It was found that only one complex was present, a one-to-one complex, $Ru(pts)_1^{+2}$ as equation 4 illustrates

$$Ru^{+3} + Hpts \rightleftharpoons Ru(pts)_1^{+2} + H^+ \qquad (4)$$

where Hpts is used as an abbreviation for 4-phenylthiosemicarbazide. No evidence was found for the presence of higher complexes.

The graphical technique to evaluate the equilibrium constant was carried out at eight different wave lengths at 10 mμ intervals from 490 to 560 mμ. These eight values of the equilibrium constant were averaged to give a mean value $K = 45$ with a standard deviation of 2, at unit ionic strength and 50% ethanol.

$$K = \frac{[Ru(pts)^{+2}][H^+]}{[Ru^{+3}][Hpts]} = 45 \pm 2 \qquad (5)$$

Calculations using this equilibrium constant, showed the absorption spectrum of the uncomplexed ruthenium to be that of ruthenium(III) perchlorate, substantiating the hypothesis that Ru(IV) was being reduced to Ru(III) by the ligand.

To test the hydrogen ion dependence, the entire system was studied at 0.254 M $HClO_4$ instead of 0.127 M. The results in Table II show that the 4-phenylthiosemicarbazide, like thiosemicarbazide, is behaving as an acid, each molecule releasing a proton on formation of the ruthenium complex.

TABLE II

COMPARISON OF K IN 0.217 AND 0.254 M $HClO_4$

	Assuming hydrogen ion dependence	Not assuming hydrogen ion dependence
$HClO_4$, M	$K = \frac{[Ru(pts)^{+2}][H^+]}{[Ru^{+3}][Hpts]}$	$K = \frac{[Ru(Hpts)^{+3}]}{[Ru^{+3}][Hpts]}$
0.127	45 ± 2	354 ± 13
.254	48 ± 3	196 ± 12

The turbidity observed in these systems following long periods of heating was considered from its appearance to be due to free sulfur or some similar oxidation or decomposition product of the complexing agents. The possibility also existed that the turbidity was due to a precipitate containing ruthenium. In order to decide between these two possibilities ruthenium solution containing Ru^{106} (and its 30 second Rh^{106} daughter) was treated with a 400-fold excess of 4-phenylthiosemicarbazide. In order to obtain an appreciable amount of precipitate, the solution was boiled for four hours, the turbidity then being much heavier than in the normal experiments. The precipitate was filtered off and washed twice with a small amount of water. From an original counting rate of 34,000 counts per minute in 48 ml. of solution, 138 counts per minute were obtained in the precipitate or 0.4%. Since the washing had not been very thorough in order to avoid dissolving any precipitate of medium solubility, the conclusion can be made that the precipitate is essentially inactive and does not contain ruthenium. Since the turbidities in the other systems had the same appearance it is considered quite unlikely that they contain ruthenium other than that which may be adsorbed on the solid.

Diphenylthiocarbazide.—Ruthenium has been reported to react with diphenylthiocarbazide to give a deep violet colored solution.[8] A spectrophotometric investigation of this reaction revealed that in the presence of Ru(IV), diphenylthiocarbazide is rapidly oxidized to diphenylthiocarbazone, usually known as dithizone. The formation of dithizone could be observed spectrophotometrically, since it has a characteristic absorption spectrum[5] with peaks at approximately 450 and 620 mμ. The ruthenium reacted with the dithizone to give the reported violet solution, the spectrum of which showed peaks due to both the dithizone and the complex. The same color resulted when dithizone (Eastman Organic Chemical #3092) was treated with ruthenium.

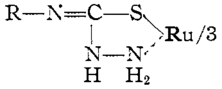
The behavior of diphenylthiocarbazide is not unexpected, since it is known to be very easily oxidized. Also the corresponding oxygen-containing reagent, diphenylcarbazide, is reported by Sandell[5] to complex several heavy metal cations in reactions in which the reagent is first oxidized to the diphenylcarbazone.

Since the reaction of ruthenium with diphenylthiocarbazide was not clear cut, the investigation was terminated.

Conclusions

Table III summarizes the reactions of ruthenium with five complexing agents. In all cases but thiocyanate which is the ion of a strong acid, the complexing action involves the release of a proton. Most probably this hydrogen is lost from the sulfhydryl group, since this is the most acidic position in the molecules.

A study of the structures of metal complexes of thiosemicarbazide, and of a number of its derivatives, has quite conclusively shown that chelation occurs between the sulfur and the hydrazine group.[6,7] It seems reasonable that the ruthenium complexes with thiosemicarbazide and 4-phenylthiosemicarbazide involve chelate rings of the same type (I).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As has been pointed out previously, a five-membered chelate ring is probable in the dithioöxamide[2c] and a four-membered chelate ring in the thiourea complexes.[2b] Very little can be said about the relative stabilities of the complexes since the solu-

TABLE III

SUMMARY OF RUTHENIUM REACTIONS

Ligand	Formulas of complexes	Formation constants	Color	Solvent	Ionic strength
CNS^-	$Ru(CNS)^{+2}$	60 ± 1	Deep-blue	Water	1.0
HS—C=NH NH_2	$Ru(SC(NH)NH_2)^{+2}$ $Ru(SC(NH)NH_2)_3$	16.3 ± 0.5 5.3 ± 0.1	Blue-green	Water	3.0
HS—C=NH H_2N—C=S	$Ru(SC(NH)CSNH_2)^{+2}$ $Ru(SC(NH)CSNH_2)_3$	930 ± 30 8300 ± 200	Blue-green	Water–50% acetic acid	1.0
HS—C=NH H_2NHN	$Ru(SC(NH)NHNH_2)^{+2}$	5.6 ± 0.2	Orange-brown	Water	1.0
HS—C=N—C_6H_5 H_2NHN	$Ru(SC(NC_6H_5)NHNH_2{}^{+2}$	45 ± 2	Red	Water–50% ethanol	1.0

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(6) K. A. Jensen, *Z. anorg. allgem. Chem.*, **221**, 6 (1934); **221**, 11 (1934).

(7) K. A. Jensen and E. Rancke-Madsen, *ibid.*, **219**, 243 (1934).

bilities of the various ligands necessitated the use of different solvents. However, in all the systems studied, the free energy changes which occur when the complexes are formed are small, and the differences among them even smaller so that one is not justified in trying to relate these differences to structural differences in the various complexes.

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[CONTRIBUTION FROM THE LABORATORY DIVISION, ENGINEERING DEPARTMENT, U. S. NAVAL GUN FACTORY]

Preparation of Vanadium Monoxide

BY MIKKEL FRANDSEN

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A compressed, intimate mixture of vanadium trioxide and finely divided vanadium is heated in a vacuum at 1750° for one hour. Evidences of conversion are changes in physical and chemical properties, chemical analysis and X-ray examination. Vanadium monoxide has a specific gravity of 5.55 (25°/4), hardness 8-9 on the Mohs scale, and a medium gray color. It dissolves slowly in hot dilute hydrochloric acid, forming a violet or blue solution; hydrofluoric acid acts faster, and nitric acid dissolves it readily under evolution of nitric oxide.

Vanadium monoxide, VO, was prepared from vanadium pentoxide containing 99.80% V_2O_5, 0.08% SiO_2 and spectroscopic traces, or less than 0.01% of manganese, copper and calcium.

The pentoxide, contained in a porcelain boat and placed in a tubular electric furnace, was reduced in a current of purified hydrogen, first for one hour slightly below the melting point, 658°, and subsequently for one hour at 1000°. Complete reduction to vanadium trioxide, V_2O_3, is thereby obtained, as shown by the weight loss, determined after cooling in hydrogen.

Vanadium trioxide was then further reduced to metallic vanadium with calcium hydride, 100 mesh, 87.7% CaH_2, by the method of Meerson, Kats and Khokhlova.[1] The mixed powders, with 50% excess of calcium hydride, were pressed into an armco iron boat and heated in a hydrogen atmosphere for one hour at 1025–1175°. The reaction product was freed from calcium and magnesium compounds with cold, dilute hydrochloric acid (1:10), washed with water, and dried in a vacuum. It consisted of fine, gray particles, size one micron or less, mostly metallic vanadium as shown by the percentage analysis: 87.59 V (not including V in VO), 11.00 VO, 0.98 H_2, 0.28 C, 0.10 Fe and 0.01 Mn.

To convert this product into the monoxide it was thoroughly mixed with an amount of vanadium trioxide, 200 mesh, calculated from the equations

$$V + V_2O_3 = 3VO; \quad C + V_2O_3 = 2VO + CO;$$
$$2VH_x + 2V_2O_3 = 6VO + XH_2$$

By compressing the mixture in a steel cylinder at 70,000 lb./sq. in., the particles were brought in close contact. The resulting disc was placed in a covered platinum crucible supported by a fireclay crucible, and surrounded with an inverted 3 inch Pyrex tube connected to a liquid air trap and a vacuum pump. Under vacuum the crucible was heated with a water cooled induction coil until the platinum started to melt (1755°), and held at this temperature for about one hour, before being allowed to cool to room temperature. During the heating period the Pyrex tube was cooled with a strong air blast. A dark deposit of negligible weight was formed on the inside walls of the Pyrex tube; by spectrographic analysis it was found to contain gold, silver, copper, platinum and vanadium; all but the last one coming from the platinum itself.

The melting points of vanadium and vanadium trioxide are 1710 and 1970°, respectively. The vanadium was, therefore, melted with some attending vaporization, favoring contact and reaction with the solid trioxide.

The yield was a gray, porous, sintered disc of smaller dimensions than the original. Changes in some physical properties, given in Table I, indicate the formation of a new compound. The color changed from dark gray to medium gray.

TABLE I

PHYSICAL PROPERTIES

	Color	Specific gravity	Hardness Mohs scale
Mixture	Dark gray	5.13	V: 6-7
Yield	Medium gray	5.55 (25/4)	8-9

The specific gravity of the yield was determined by the pycnometer method at 25°. The hardness of the product is remarkable, exceeding that of metallic vanadium. It was determined with Vickers and Rockwell testers, and converted to the Mohs scale.

By chemical and spectrographic analysis the composition was found to be 99.68% VO, 0.13% SiO_2, 0.10% FeO, 0.03% CaO, 0.02% Al_3O_3, 0.01% CoO, less than 0.01% Pt, Cu, Ag, Sn.

X-Ray examination confirms the composition VO.

The powdered yield dissolves slowly in warm dilute hydrochloric acid, forming a blue or violet solution, characteristic of a hypovanadous salt. Vanadium trioxide gives a green solution under the same conditions. The yield dissolves faster in hydrofluoric acid, and readily in nitric acid with evolution of nitric oxide.

WASHINGTON 25, D. C.

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(1) G. A. Meerson, G. A. Kats and A. V. Khokhlova, *J. Applied Chem.* (*U.S.S.R.*), **13**, 1770 (1940), [*C. A.*, **35**, 4712 (1941)].