

4. If first dissolved in 10^{-3} M alkali (potassium hydroxide or barium hydroxide) it foams freely in the alkaline range.

5. Alkaline earth ion or salt greatly promotes foaming in the alkaline range, but may minimize it on the acid side.

6. The data presented, considered in the light of previous knowledge, indicate that different proteins follow a general pattern in their foaming behavior and that this pattern is similar to that exhibited by other properties of proteins.

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The Preparation and Properties of Vanadium Nitrosyl Chlorides

BY ARTHUR GREENVILLE WHITTAKER¹ AND DON M. YOST

In connection with an investigation of vanadium tetrachloride, VCl_4 , it was observed that a beautiful, dark purple, coarsely crystalline substance forms readily when dry nitric oxide is passed through a solution of vanadium tetrachloride in carbon tetrachloride. Similar crystalline materials result when dry nitric oxide reacts with pure vanadium tetrachloride in either the liquid or vapor state. Although compounds containing the NO group have been previously studied,² the reaction products herein described do not appear to have been mentioned in the literature and are therefore new.

Experimental

The vanadium tetrachloride was prepared as described in a previous paper.³ Nitric oxide was prepared by slowly adding 50% sulfuric acid to a solution which was four formal in potassium nitrite and one formal in potassium iodide.⁴ The gas was purified and dried by passing it through successive tubes containing potassium hydroxide, calcium chloride and magnesium perchlorate.

In preparing these new compounds, three different sets of conditions were tried, yielding three different sets of principal reaction products. In all cases a number of products were formed, but the principal ones were the dark purple crystals and vanadium trichloride. Small amounts of nitrosyl chloride and vanadium oxytrichloride were always produced, however. The three sets of reaction conditions and principal products are: (1) Nitric oxide reacting with vanadium tetrachloride in the vapor phase gave the solid $V_2Cl_8(NO)_6$, and a large fraction of vanadium trichloride; (2) Nitric oxide passed into liquid vanadium tetrachloride resulted in the precipitation of the compound V_2Cl_7NO ; (3) The insoluble solid VCl_4NO was formed when nitric oxide was passed into a dilute (say 10%) carbon tetrachloride solution.

All reactions were started at room temperature, but as considerable heat is evolved the exact temperatures during reaction cannot be specified. No attempt was made to estimate the heat of reaction. The compounds were purified by subliming them from one end of a pyrex tube (50 cm. \times 2.5 cm.), which was filled with dry air or carbon dioxide at one atmosphere, to the other. Although sublimation begins at about 45°, the hot end of the tube was

maintained at 135° and the cold end at room temperature. The residue at the hot end of the tube was always vanadium trichloride. Before the crystals were removed from the tube the collection end was placed in a furnace at 50° overnight to distill any liquid away from the crystals.

Densities were determined pycnometrically; carbon tetrachloride served as the liquid. Magnetic susceptibility measurements were made by the Gouy method.

Extensive analyses of the various preparations were made using the following methods. (1) Vanadium was determined, in sulfuric acid solution, with standardized permanganate. (2) Chlorine was precipitated as silver chloride and weighed. (3) Nitrogen was determined by first oxidizing to nitrate with alkaline permanganate the nitric oxide or nitrous acid formed when the purple crystals react with water. The excess permanganate was reduced with hydrogen peroxide and the manganese dioxide filtered off. Nitrogen in the filtrate was determined by the Kjeldahl method, using aluminum metal in sodium carbonate solution as a reducing agent.

Results and Properties of the Compounds.—

The average values of the results of the analyses and of the measurements of the densities and magnetic susceptibilities are presented in Table I. As indicated there the results of the analyses were best satisfied by compounds with the empirical formulas VCl_4NO , V_2Cl_7NO and $V_2Cl_8(NO)_6$.

All the compounds gave off a colorless gas and ultimately yielded a blue solution when placed in water. The blue solution was due to vanadyl ion, VO^{++} , and the gas was identified as nitric oxide. The amount of nitric oxide liberated by each compound is indicated in Table I. In the case of V_2Cl_7NO the rate of solution was slower and it was possible to observe a brown solution in the immediate vicinity of the crystals as they reacted with water. The brown color was much like that due to VO^+ which one gets on dissolving vanadium trichloride in water.

Long, dark purple, opaque crystals were formed by each of the compounds. Microscopic examination revealed that dark purple light was transmitted by small crystals. Also, the crystals were birefringent, and they show parallel extinction. The crystals of VCl_4NO and $V_2Cl_8(NO)_6$ were needle-like, and had a tendency to form penetration twins. The crystals of V_2Cl_7NO were shorter prisms that tended to form hemispherical tufts of the prisms like pins in a pin cushion.

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(2) (a) L. Malatesta, *Gazz. chim. ital.*, **71**, 615 (1941); (b) Blanchard, *Chem. Rev.*, **21**, 3 (1937); **26**, 409 (1940).

(3) A. G. Whittaker and Don M. Yost, *J. Chem. Phys.*, **17**, 176 (1949).

(4) H. Johnston and W. F. Giaque, *THIS JOURNAL*, **51**, 3194 (1929); D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 14.

TABLE I
 SOME PROPERTIES OF THE VANADIUM NITROSYL CHLORIDES

Compound	V	Obsd. Cl.	Percentage composition		Theory Cl	NO	NO lib. by H ₂ O, %	Density at 28°	χ_m^a ($\times 10^6$) 25.3°
			NO	V					
VCl ₄ NO	23.1	62.5	11.9 ^b	22.9	63.6	13.5	13.5	2.32	2340
V ₂ Cl ₇ NO	26.8	65.8	7.8	22.6	65.6	7.8	2.5	2.50	4180
V ₂ Cl ₈ (NO) ₅	19.0	52.6	23.9 ^b	19.0	53.0	28.0	3.0	2.15	2470

^a χ_m is the molal susceptibility. ^b These results are known to be low.

Moisture in the air reacts readily with all of the preparations to give nitric oxide and vanadyl chloride. Subjected to pressure of about 0.1 mm. at room temperature, the compounds simply sublimed from a retort tube to a cold trap. Such experiments gave a rough measure of the relative volatility of the compounds. Listed in order of increasing volatility they are: V₂Cl₇NO, VCl₄NO and V₂Cl₈(NO)₅.

Efforts were made to decompose the compounds by heating them rather suddenly to 400 to 500° in an apparatus consisting of a reaction tube, a cold trap at -78°, and a pneumatic trough to catch gases that did not condense in the cold trap. The compound VCl₄NO did not appear to decompose since it could be sublimed repeatedly from one end of the reaction tube to the other without leaving a residue. The compound V₂Cl₇NO showed some decomposition in that the cold trap caught a small amount of nitrosyl chloride, and a small residue of vanadium trichloride remained. In the case of V₂Cl₈(NO)₅ decomposition took place to some extent giving NOCl and perhaps NO, some of which reacted with oxygen in the apparatus and condensed in the cold trap as a mixture of NO₂ and N₂O₃. A residue of V₂O₅ appeared to be formed. In all cases the pneumatic trough caught no significant amount of gas other than that due to expansion of the air on heating. At the elevated temperature all the compounds appeared to react slowly with oxygen in the air to give vanadium oxytrichloride.

The compounds were found to be insoluble in the dried liquids, carbon tetrachloride, *n*-butyl alcohol, ether, dioxane and nitrobenzene. All were soluble to the extent of a few per cent. in carbon tetrachloride at 100° while enclosed in a sublimation tube. Efforts to dissolve the compounds in boiling carbon tetrachloride at atmospheric pressure in a test-tube resulted in the decomposition of the compounds.

Discussion.—Unfortunately, the various preparation methods do not produce results which were clear cut. With all three some of the preparations turned out to be mixtures of two or more of the compounds. In some, but not all, cases the properties of the mixtures could be resolved into those of the components by using a simple additivity relation based on the chemical analysis and the probable pure components. As the procedure did not always yield sensible results, the existence of a fourth compound in the group

is not precluded. At any rate one or more pure samples of the above described compounds were independently produced.

The results of the magnetic susceptibility measurements deserve further mention. It is interesting that two of these compounds, namely, VCl₄NO and V₂Cl₈NO are examples of "even molecules" which are paramagnetic. For example, in the case of VCl₄NO the odd electron of the vanadium does not appear to couple with that of the NO group. Complete coupling would produce a diamagnetic substance, which is certainly not the case here.

If it is assumed that this compound obeys the Curie-Weiss law for the odd electrons per molecule, then the Curie temperature turns out to be -99°. This is not an unreasonable value. The other compounds are too complicated to make a reasonable guess as to how their paramagnetism arises.

Since these compounds are not reported elsewhere in the literature, the following names are proposed: VCl₄NO can be named vanadium nitrosyl tetrachloride, V₂Cl₇NO can be named divanadium nitrosyl heptachloride, and V₂Cl₈(NO)₅ can be named divanadium pentanitrosyl octachloride.

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Summary

1. Three new compounds are reported as resulting from reactions between vanadium tetrachloride and nitric oxide. These compounds have the empirical formulas VCl₄NO, V₂Cl₇NO and V₂Cl₈(NO)₅; they have been named vanadium nitrosyl tetrachloride, divanadium nitrosyl heptachloride, and divanadium pentanitrosyl octachloride, respectively.

2. Various properties of the compounds are reported. These include reaction with water, qualitative solubilities where no reaction takes place with the solvent, and their behavior at reduced pressure and when suddenly heated to about 450°. All the compounds have very nearly the same general appearance, and all sublime readily.

3. The density of each compound was measured, and found to be 2.32, 2.50 and 2.15 g./cc. for VCl₄NO, V₂Cl₇NO and V₂Cl₈(NO)₅, respectively.

4. The magnetic susceptibility of each compound was measured at 25.3° and found to be 2340×10^{-6} , 4180×10^{-6} and 2470×10^{-6} per

mole for VCl_4NO , $\text{V}_2\text{Cl}_7\text{NO}$ and $\text{V}_2\text{Cl}_8(\text{NO})_5$, respectively.

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The Kinetics of the Thallium(I)-Thallium(III) Exchange Reaction

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Harbottle and Dodson² and the authors³ have previously reported that the rate of the exchange reaction between thallium(I) and thallium(III) in acid solution is measurable. Harbottle and Dodson found that in perchloric acid the rate was proportional to the first power of the concentration of each reactant. They also found that the rate increased when lithium perchlorate was added, varied when the acid concentration was varied, being a maximum at about 1 f., and was greater in hydrochloric acid than in perchloric acid. The authors found the rate was greater in nitric acid than in perchloric acid, increased with increasing nitric acid concentration (1.0–1.5 f.) and decreased with increasing perchloric acid concentration (1.5–3.5 f.). This paper describes our studies of the kinetics of the thallium(I)-thallium(III) exchange reaction.

Experimental

Radioactivity.—The 3.5-year Tl^{204} was used as tracer in all experiments. Part of the Tl^{204} was produced by the n, γ reaction and was obtained from the Clinton Laboratories on allocation from the U. S. Atomic Energy Commission; part was produced by the d, p reaction in the Washington University cyclotron. The activity produced in the cyclotron was purified by solution of the bombarded metal in dilute nitric acid, oxidation with aqua regia, ether extraction of thallium(III) chloride from 6 f. hydrochloric acid containing lead(II) carrier, precipitation of thallium(III) hydroxide from copper(II) and zinc(II) carriers with ammonium hydroxide, solution of the hydroxide in nitric acid, reduction with sulfite, precipitation of added iron(III) carrier with ammonium hydroxide, oxidation of the supernatant with aqua regia, and reprecipitation and solution of thallium(III) hydroxide. Thallium(III) oxide was purified prior to irradiation in the Oak Ridge pile by solution of thallium metal in dilute nitric acid, precipitation of thallium(I) chloride, oxidation with aqua regia, ether extraction of thallium(III) chloride from 6 f. hydrochloric acid, and precipitation and reprecipitation of thallium(III) hydroxide with ammonium hydroxide. The hydroxide was dried at 150–200°. The irradiated thallium(III) oxide was dissolved in nitric acid, the solution oxidized with aqua regia to be certain all the Tl^{204} was in the plus three oxidation state, and thallium(III) hydroxide precipitated and dissolved in the appropriate acid. The specific activity of this thallium was the same as that of an aliquot further purified from added lead

and mercury carrier. Aluminum absorption curves of the radiation from either n, γ or d, p produced Tl^{204} agreed with the curve reported by Fajans and Voight.⁴ The initial half-thickness was 30 mg. per cm.², the range 310 mg. per cm.², the beta to gamma ratio about 10^4 .

Chemicals.—With the exception of the materials used in the preliminary studies of separation methods, all reaction mixtures were made up from the following solutions.

- 0.100 f. thallium(I) perchlorate (inactive)
- 0.100 f. thallium(III) perchlorate (radioactive) in 2.50 f. perchloric acid
- 5.00 f. perchloric acid
- 5.00 f. sodium perchlorate
- 5.00 f. sodium nitrate

Thallium(I) perchlorate was prepared by evaporation of a perchloric acid solution of Fisher pure thallium(I) nitrate and recrystallization of thallium(I) perchlorate three times from water. The thallium(III) perchlorate solution was prepared by solution of a mixture of active and inactive thallium(III) oxide in 9.3 f. perchloric acid and dilution. The inactive thallium(III) oxide was prepared by the method used to purify the oxide prior to neutron irradiation. Both thallium perchlorate solutions were assayed for thallium gravimetrically by precipitation of thallium(I) hexachloroplatinate(IV). The excess acid in the thallium(III) perchlorate solution was assayed by addition of excess standard sodium hydroxide, centrifugation of thallium(III) hydroxide, and back-titration with standard acid. Mallinckrodt "Analytical Reagent Grade" 60 or 71% perchloric acid and dried sodium nitrate and G. Frederick Smith anhydrous sodium perchlorate were used to prepare the remaining solutions. Mallinckrodt "Analytical Reagent Grade" ammonium hydroxide, sodium bromide, sodium chromate, sodium cyanide, and hexachloroplatinic acid (10% solution) were used in various solutions employed in the separation of the reactants.

Measurement of Radioactivity.—All precipitates were mounted by filtration on a tared, 18-mm. diameter piece of Whatman No. 42 filter paper, dried at 110°, weighed, mounted on a 2 × 2.5 in. cardboard card with scotch tape placed directly over the sample, and counted on a Geiger-Müller counter. During the filtration the filter paper was clamped between a glass chimney, 2.5 in. high and 1.4 mm. inside diameter, and a Hirsch funnel, without sides and with its surface ground flat. In order to obtain uniform deposits, the precipitate was allowed to settle on the filter paper before suction was applied. The Geiger counter⁵ had an 8 mg./cm.² dural side window, 1.0 in. in diameter. The sample was placed directly below and 0.5 cm. from the window. The counter pulses were fed directly into the discriminator of an Instrument Development Laboratories' Model 161 scaler (scale of 256). The counter was stable, had a 100 v. plateau which was flat within 1% statistical error, and had a background of 50 counts per minute inside a lead shield. The response of the counter was linear to within about 2% up to the maximum counting rate measured (3000 counts per minute).

Since samples of the same weight, composition and

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(5) The details of the construction and operation of the Geiger counter will be reported in a later publication.