Notes

The amount of carbon tetrachloride extracted is increased by adding more carbon tetrachloride to the two-phase systems. The concentrations of methanol, tin, and chloride in the carbon tetrachloride-rich layer, obtained by adding 50 ml of carbon tetrachloride to a solution at the "Opaque Point" increases as the initial salt concentration is lowered. This means that the extraction coefficient (components in CC1₄ layer/components in methanol layer) actually increases as the total salt concentration is decreased. Simultaneously the concentration of carbon tetrachloride in the methanol-rich layer is increased.

A plot of the specific conductance versus the salt concentration at the "Opaque Point" is defined by the linear relation, specific conductance $= 0.120 + 0.65 \times 10^{-4}$ salt conc. A plot of the corresponding methanol concentration versus the salt concentration gives a monotonic increasing curve (Fig. 1).



FIG. 1.—Plots of the methanol concentration (-O—), and specific conductance (-X—) vs. salt concentration in solutions at a 15°C "Opaque Point". Resistances were measured at 25°C.

For the methanol-rich layers formed by adding 50 ml of carbon tetrachloride to "Opaque Point" solutions containing 50 ml of salt-methanol solution, there exists a linear relation between the tin concentration and the specific conductance thus:

Specific conductance = $0.069 + 0.61 \times 10^{-4}$ tin conc. Plots with the corresponding methanol concentration again define a monotonic increasing function.

These data do suggest that specific interactions between tin(IV) species and the methanol molecules actually prevent miscibility with carbon tetrachloride.

Acknowledgements—Financial support from the Research Corporation is gratefully acknowledged. Thanks are also due to Mr. GEORGE E. MCALONIE for assistance with calculations.

Chemistry Department New York State University College of Education 135 Western Avenue, Albany 3, New York P. A. D. DE MAINE M. M. DE MAINE

The preparation of mononitratodioxovanadium(V), VO₂NO₃

(Received 22 January 1960; in revised form 1 March 1960)

THE recent series of papers by ADDISON and his school⁽¹⁾ concerning anhydrous liquid dinitrogen tetroxide as a preparative solvent for metal nitrates prompted an attempt to prepare a nitrate of

⁽¹⁾ C. C. ADDISON et al., J. Chem. Soc. S211, S218 (1949); 1289, 1294, 1298, 1303, 2829, 2833, 2838, 2843 (1951); 1390, 1399, 4079 (1952); 1319, 1869, 1874, 2631 (1953); 1138, 1143 (1954); 1941, 2705, 2709, 3900 (1956); 3099 (1958).

Notes

vanadium. Vanadium nitrates are unknown in the solid state, but they are believed to exist in decinormal solutions of vanadium in strong nitric acid.⁽²⁾ The exact species in which vanadium occurs in these solutions is not definitely known, but it is hypothesized that it is present as either $VO(NO_3)_a$ or VO₂NO₃, both of which are possible in strongly acidic solutions.

A solid, brick-red, free-flowing oxynitrate of vanadium which corresponds to the formula VO₂NO₃ has been prepared by the reaction of chips of electrolytic vanadium with excess liquid dinitrogen tetroxide at O°C using an acetonitrile catalyst according to the equation:

$$V + 2N_2O_4 \xrightarrow{CH_3CN} VO_2NO_3 \uparrow + 3 NO \uparrow$$
(1)

The choice of acetonitrile as the catalyst was one of convenience, and it is one of the electron donor catalysts described by ADDISON.⁽¹⁾

The properties of dinitrogen tetroxide have been completely described elsewhere.^(1,3,4,5) Dinitrogen tetroxide supplied by the Matheson Company was used for all preparations. The cylinder was fitted with stainless steel couplings and connected to the all-glass apparatus described below. Eastman-Kodak "White Label" acetonitrile was used as the catalyst. Electrolytic vanadium chips prepared by the Union Carbide Metals Company were used as the vanadium source.

The all-glass apparatus consisted of a 250 ml Pyrex three-necked flask fitted with 24/40 \$ female joints. The centre connexion was fitted with a cold-finger condenser which led to a vacuum pump via an intermediate liquid nitrogen trap. One of the side connexions served as the inlet for the dinitrogen tetroxide and argon, both of which were first passed through a calcium chloride tube to ensure anhydrous conditions. The remaining connexion was fitted with a separatory funnel through which the acetonitrile catalyst was added.

A typical preparation involved the following steps: 5 g of peasized electrolytic vanadium chips were placed in the flask and the entire system was purged with dry argon for about 40 min. The flask and cold finger were cooled with ice so that the temperature was maintained at 0 to 5°C during the course of the preparation. Dinitrogen tetroxide (liquid range -9.3 to $+21.8^{\circ}$ C.) was then introduced into the flask and allowed to liquefy until 75-100 ml of the brownish liquid were present in the flask. Then about 5-8 ml of acetonitrile were added, and a brick-red precipitate formed. The reaction mixture was allowed to stand for 5-6 hr, after which the excess solvent and catalyst were removed under vacuum. The resulting brick-red powder was found to be unstable in moist air and was, therefore, handled in a dry box. The yield was 91 per cent based on vanadium according to equation (1). Chemical analysis gave the following results: Found: V, by the ferrous sulphate method,⁽⁶⁾ 35.6% NO₃: by the nitron method,⁽⁷⁾ 41.9%. Calc. for VO₂NO₃: V, 35.2%; NO₃, 42.8%.

The product was found to be very soluble in water, producing an orange-coloured solution which, when the concentration was at least 730 mg/100 ml water, formed a deep brown gel within 24 hr of the solution preparation. Less concentrated solutions were stable indefinitely. Exposure of the salt to moist air caused a slow change to a brown gel similar to that described above. The freshly prepared solution gave a positive qualitative test for nitrate with brucine. Attempts to recover the original brick-red powder from aqueous solution proved futile. Rapid evaporation by heating, as well as slow crystallization, produced vanadium pentoxide with loss of nitrate. The brick-red powder was found to be insoluble in the more common organic solvents. Heating the brick-red powder at 350°C either in vacuo, or in an argon stream for 6 hr caused decomposition which proceeded via the equation:

$$2\mathrm{VO}_2\mathrm{NO}_3 \to \mathrm{V}_2\mathrm{O}_5 + \mathrm{N}_2\mathrm{O}_5 \uparrow \tag{2}$$

The tan powder remaining was found to be vanadium pentoxide by analysis. A solution formed by collecting the evolved gas in distilled water gave a positive qualitative test for nitrate with brucine, indicating that dinitrogen pentoxide or its decomposition products, nitrogen dioxide and oxygen, was the gas and/or gases evolved.

- (2) G. JANDER and K. F. JAHR, Z. Anorg. Chem. 212, 1 (1933).
 (3) P. GRAY and P. RATHBONE, J. Chem. Soc. 3550 (1958).
 (4) P. Gravand A. D. Yarabar, G. Chem. Soc. 3550 (1958).
- (4) P. GRAY and A. D. YOFFE, Chem. Rev. 55, 1069 (1955).
- ⁽⁵⁾ I. C. HISATSUNE and R. V. FITZSIMMONS, Spectrochim. Acta 206 (1959).
- ⁽⁶⁾ H. H. WILLARD and H. DIEHL, Advanced Quantitative Analysis p. 247. D. Van Nostrand, New York (1943).
- ⁽⁷⁾ F. J. WELCHER, Organic Analytical Reagents Vol. III, p. 138. D. van Nostrand, New York (1947).

Notes

Qualitative infra-red studies indicate that both nitrate ions and vanadium-oxygen linkages are present in the brick-red powder. MILLER and WILKINS⁽⁸⁾ found that ten inorganic nitrates showed common absorptions in the ranges 7.25-7.41 μ and 11.90-12.25 μ when examined in potassium bromide disks. Under the same conditions the monitratodioxovanadium (V) exhibited a very strong absorption at 7.25 μ and a very weak absorption at 12.19 μ , indicating the presence of ionic nitrate. Under identical conditions vanadyl sulphate, (VOSO4); vanadium pentoxide; bis-(acetylacetonate)monoxovanadium (IV), $(VO(acac)_2)$; and monoitratodioxovanadium (V) showed common absorptions in the 9.8–10.0 μ range, which is apparently characteristic of the vanadium-oxygen linkage. This has recently been verified.⁽⁹⁾ The brick-red powder had a specific gravity of 2.055 at 25°C as determined by the pycnometer method. No diffraction pattern could be obtained, indicating that the compound was amorphous. Examination of the compound under polarized light revealed that it had but one index of refraction (which was greater than 1.78). Therefore, it is isotropic, further evidence of its amorphous character.

The molecular weight of the compound was determined in water at 25°C by the isopiestic method using copper (II) nitrate as a standard and was found to be 150 compared to 144.96 calculated for the formula VO₂NO₃. Only cursory magnetic measurements were made. The compound was found to be slightly diamagnetic at room temperature (25°C) and with a molar susceptibility of $+116 \times 10^{-6}$ c.g.s.u. at liquid nitrogen temperatures (-195° C). The latter figure corresponds to a magnetic moment of 0.08 Bohr magnetons (B.M.) versus the expected zero B.M. for a compound with no unpaired electrons.

Acknowledgement-The authors are indebted to Professor W. C. FERNELIUS of the Pennsylvania State University for his many stimulating suggestions.

Metals Research Laboratories Union Carbide Metals Company Division of Union Carbide Corporation Niagara Falls, New York

JOHN A. PANTONIN* ALBERT K. FISCHER[†] EDWARD A. HEINTZ[‡]

* Present address: The Enrico Fermi Institute for Nuclear Studies, University of Chicago, Chicago 37, Illinois.

† Present address: Research Laboratory, Union Carbide Technical Center, South Charleston, West Virginia. ⁺ To whom all correspondence should be sent. ⁺ To whom all correspondence should be sent.

(8) F. A. MILLER and C. H. WILKINS, Analyt. Chem. 24, 1253 (1952).

⁽⁹⁾ C. G. BARRACLOUGH, J. LEWIS and R. S. NYHOLM, J. Chem. Soc. 3552 (1959).