1006. *Volatile Tetranitratotitanium*(IV)*: Preparation, Infrared Spectrum, and Reaction with Saturated Hydrocarbons.*

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The highly volatile tetranitratotitanium(IV) is readily prepared by reaction of liquid dinitrogen pentoxide with hydrated titanium nitrate at 30°, followed by sublimation at 36—100°/0·02 mm. The complex melts at 58°, contains covalent nitrato-groups, and reacts with saturated hydrocarbons such as Nujol. The implications of these results on the preparation of anhydrous nitrates, the measurement of their infrared spectra, and their reaction with hydrocarbons are discussed.

Tetranitratotitanium(IV) was recognised as a volatile complex (m. p. 58·5°, subliming in a vacuum) by Schmeisser,[1] who prepared it by reaction of titanium tetrachloride with dinitrogen pentoxide. However, he gave no analytical figures and no evidence to indicate whether the nitrato-groups were ionic or co-ordinated to the metal (as one would expect from its ease of sublimation). Gutmann and Tannenburger[2] attempted to prepare the complex by reaction of titanium tetraiodide with dinitrogen tetroxide in carbon tetrachloride but isolated only a nitrato-oxide $TiO(NO_3)_2$; they considered that the tetranitrate decomposed at about 10°.

We have prepared the tetranitrato-compound by reaction of the hydrated nitrate with liquid dinitrogen pentoxide, a method which we have used previously[3] to prepare volatile

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[1] Schmeisser, *Angew. Chem.*, 1955, **67**, 493.

[2] Gutmann and Tannenburger, *Monatsh.*, 1956, **87**, 421.

[3] Field and Hardy, unpublished work.

nitrato-complexes of copper, hafnium, and zirconium; we have also used dinitrogen pentoxide to prepare the copper complex from the metal[3] and the zirconium complex from its tetrachloride.[4,5] The composition of the titanium compound, and its m. p., sublimation temperature, and infrared spectrum have been determined. The compound reacts with n-dodecane and readily nitrates and oxidises saturated paraffinic hydrocarbons such as are often used in the preparation of mulls for the measurement of infrared spectra.

EXPERIMENTAL AND RESULTS

Preparation and Sublimation.—The hydrated nitrate of titanium(IV) was prepared by dissolving hydrated titanium hydroxide in fuming nitric acid and evaporating the solution to dryness; the hydrated hydroxide was obtained by precipitation with aqueous ammonia from a solution of titanous chloride. An excess of dinitrogen pentoxide, prepared by dehydrating fuming nitric acid with phosphorus pentoxide, was distilled on to the solid hydrated titanium nitrate cooled by liquid nitrogen. The mixture was warmed to ~30° to melt the dinitrogen pentoxide, which was allowed to reflux for 2 hr. Most of the product dissolved to form a viscous, straw-coloured, liquid, lower phase. The excess of dinitrogen pentoxide was pumped off, and the yellow solid which remained was kept at 21°/0·1 mm. for 1 hr., during which the salt lost its co-ordinated oxides of nitrogen and became white. Dry helium was admitted to the tube, and a glass-wool plug was placed between the salt and a cold-finger which was about 5 cm. above the solid. The temperature was then increased; at 36°/0·03 mm. the complex started to sublime and was condensed as large, apparently cubic crystals on the water-cooled cold-finger. The crystals grew to a size of a few mm. before fusing with neighbouring crystals. Sublimation was rapid at 100°/0·02 mm. and about 2 g. was condensed in 1 hr. The apparatus was cooled, filled with dry helium, and transferred to an argon-filled dry-box for subsequent manipulation.

Properties.—*Melting point.* The finely powdered solid in a capillary tube (protected from water vapour in the air) melted at 58° ± 0·5° at approximately atmospheric pressure over a series of cycles of melting and freezing, indicating that no appreciable decomposition occurred.

Analysis. The *product* contained 16·1% of titanium (determined by ignition to titanium dioxide) and 82·6 ± 2·6% of nitrate (determined with nitron after hydrolysis in water [$Ti(NO_3)_4$ requires Ti, 16·2; NO_3, 83·3%). Only 0·1% of nitrite was found by ceric titration after hydrolysis in water.

Infrared spectra and reaction with n-dodecane. The infrared spectrum (2—15 μ) of the complex was first obtained with a Hilger H800 double-beam instrument with a rock-salt prism, for a sample in a Nujol mull, prepared in a dry-box, between silver chloride plates. The spectrum contained strong split peaks which we tentatively assigned to the co-ordinated nitrato-group at 1550—1620 (ν_4[6]), 1240—1300 (ν_1), 1009 (ν_2), and 740—770 cm^{-1} (ν_6); weak peaks for water and/or metal–OH bonds at about 3400 cm.$^{-1}$; and a strong broad band centred at about 930 cm.$^{-1}$, similar to that found in some metal oxides[3] and oxygen-bridged titanium complexes.[7] The mull was lemon-yellow after the spectrum had been determined (about 30 min.).

We suspected that the complex had reacted with a trace of water or impurity in the Nujol, or (more probably) had nitrated the Nujol and had itself decomposed to a nitrate oxide. We therefore prepared a mull with n-dodecane (99·5% pure, supplied by L. Light and Co., Colnbrook, England) which had been passed through a column of activated alumina to remove any trace of water, and measured the infrared spectrum from 2 to 15 μ as a function of time from 20 to 200 min. at 22°, in order to differentiate between the absorption peaks due to reaction products and to the complex itself.

In separate experiments $0{\cdot}5 \times 10^{-3}$ mole of the powdered titanium complex was allowed to react at about 20°, in a dry-box with an argon atmosphere (but containing some dry air from transfer operations), (*a*) for 30 min. with 1×10^{-3} mole of n-dodecane, and (*b*) for 16 hr. overnight with $0{\cdot}5 \times 10^{-3}$ mole of n-dodecane. The organic products were isolated by washing the yellow pastes with water, separating the phases by centrifugation, and vacuum-drying the upper (organic) phase; their infrared spectra was measured as above.

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[4] Field and Hardy, *Proc. Chem. Soc.*, 1962, 76.

[5] Heslop and Robinson, " Inorganic Chemistry," Elsevier, London, 2nd edn., 1963, p. 521.

[6] Addison and Gatehouse, *J.*, 1960, 613.

[7] Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.

The product after 30 minutes' reaction contained about 10 mole % of an alkyl nitrate, characterised by the sharp absorption peaks at 1635, 1278, and 860 cm.$^{-1}$. At this stage, no peaks were observed which could be ascribed to an alkyl nitrite, nitroalkane, or carboxylic acid. The frequencies and strengths of the peaks to be expected for alkyl nitrites and nitroalkanes have been reported by Brown[8] and for these compounds and carboxylic acids by Bellamy.[9] The spectra of capillary films of n-dodecyl nitrate, n-dodecyl nitrite, and 1-nitro-n-dodecane were measured in order to assist in the identifications.

The product after reaction for 16 hr. with the higher ratio of the titanium complex contained a substantial amount of a carboxylic acid (peaks at about 3078, 1710, 1410, 1279, and 940 cm.$^{-1}$) and smaller amounts ($\sim$10 mole %) of an alkyl nitrate and a nitroalkane; no significant amount of an alkyl nitrite (which would have had a strong peak at about 790 cm.$^{-1}$) was present.

DISCUSSION

Preparation of Anhydrous Nitrato-complexes of Metals.—We have demonstrated in the preparation of this complex the ease of reaction of a hydrated nitrate of a metal with liquid dinitrogen pentoxide to give an anhydrous nitrato-compound. Although Guntz and Martin[10] used a similar method (reaction of a solution of dinitrogen pentoxide in nitric acid with a hydrated nitrate) in 1909 to prepare the anhydrous nitrates of cobalt, copper, manganese, and nickel, the wider applicability of the method has not been generally realised. This method has, however, two main advantages over the use of an anhydrous metal chloride;[1] first, a hydrated nitrate can usually be prepared more easily and cheaply than an anhydrous metal chloride, and secondly, there can be no complication from retention of chloride in the product or formation of a nitrosonium chloro-complex, as was found by Reihlen and Hake[11] and Partington and Whynes[12] when they treated titanium tetrachloride with liquid dinitrogen tetroxide.

Reaction of Tetranitratotitanium(IV) *with n-Dodecane.*—Tetranitratotitanium(IV) reacts rapidly with n-dodecane at room temperature, and the infrared spectra of the mixture and the organic product indicate that an alkyl nitrate, a nitroalkane, and a carboxylic acid are formed. The titanium product was probably a nitrate oxide with some form of oxygen-bridging (indicated[7] by a broad absorption band centred on 917 cm.$^{-1}$) but it still contained co-ordinated nitrato-groups. There may also have been some contribution from titanium–oxygen double bonds (strong peak at 1007 cm.$^{-1}$, in the region where such a bond would be expected to absorb,[7] but ν_2 of the co-ordinated nitrato-group also absorbs in this region).

A radical mechanism, such as is generally accepted[13] for the nitration of saturated paraffins, seems likely in this reaction. Addison[14] has suggested that the NO_2 radical can be produced from the dissociation $MO{\cdot}NO_2 \longrightarrow MO{\cdot} + {\cdot}NO_2$ and that this explains the solution properties of beryllium nitrates and the vigorous reaction of anhydrous dinitratocopper(II) with diethyl ether.

The distribution of the products found by us differs from that obtained in the nitration of long-chain saturated hydrocarbons with aqueous nitric acid or with hydrated metal nitrates. Nitration with nitric acid at high temperatures (in sealed tubes) generally gives nitroalkanes, polynitroalkanes, and carboxylic acids.[15] However, the products of the initial reaction of the titanium complex with n-dodecane are the same as those reported by Titov and Schitov[16] for the reaction of paraffins with dinitrogen pentoxide below 0°.

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[8] Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 6341.

[9] Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, London, 1954.

[10] Guntz and Martin, *Bull. Soc. chim. France*, 1909, **5**, 1004; 1910, **7**, 313.

[11] Reihlen and Hake, *Annalen*, 1927, **452**, 47.

[12] Partington and Whynes, *J.*, 1949, 3135.

[13] Topchiev, " Nitration of Hydrocarbons and Other Organic Compounds," Pergamon Press, London, 1959.

[14] Addison, " The Significance of NO_2 Free Radicals in the Reactions of Dinitrogen Tetroxide and Metal Nitrates," Amer. Chem. Soc. Special Publ., No. 36, 1962, p. 131.

[15] Groggins, " Unit Processes in Organic Synthesis," McGraw-Hill, New York, 1947, p. 6.

[16] Titov and Schitov, *Doklady Akad. Nauk S.S.S.R.*, 1951, **81**, 6, 1085.

The nitration of hydrocarbons with inorganic nitrates has been studied by Konovalov,[17] Topchiev,[13] and Asinger and his co-workers.[18] In general, hydrated metal nitrates, either solid or in aqueous solution, when heated with the hydrocarbon in sealed tubes at 100—150°, gave a mixture of nitroalkanes and oxidation products. Topchiev [13] found that aromatic hydrocarbons (benzene, toluene, xylene, mesitylene) were not nitrated when heated with the anhydrous nitrate of K, Na, NH_4, Ba, Pb, or Ag. However, in the presence of a metal chloride, *e.g.*, aluminium chloride, these salts reacted at 30—40°. These nitrates are probably not effective as nitrating agents on their own because they are predominantly ionic nitrates (as deduced from their infrared spectra [19]) and are unable to release NO_3 or NO_2 as radicals.

Infrared Spectrum of Tetranitratotitanium(IV).—Our work stresses the desirability of (i) using a mulling agent more stable than saturated hydrocarbons (Nujol, etc.) for the measurement of spectra of reactive covalent nitrates, (ii) rapid measurement of spectra before significant decomposition can occur, or (iii) measurement of the spectra as a function of time in order to determine which peaks are due to products of decomposition or reaction. The last method appears to be necessary until a suitable mulling agent or technique is devised; pressed discs of potassium bromide or silver chloride could possibly be used but they may also undergo reaction and may give modified spectra in some cases; fluoro- and chloro-hydrocarbons would probably be more suitable but those commonly available, *e.g.*, Fluorube oil and hexachlorobutadiene, absorb over important ranges of frequency.

The frequencies (cm.$^{-1}$) and strengths of the principal peaks in the infrared spectrum of tetranitratotitanium(IV), corrected by method (iii), are ν_4 1628vs, ν_1 1225s, ν_2 988s, and $\nu_6(\nu_3)$ 784—773 (split).

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[17] Konovalov, *Zhur. russk. Khim. obshchei*, 1906, **39**, 109.
[18] Asinger, Geiseler, and Wirth, *Chem. Ber.*, 1957, **90**, 1987.
[19] Ferraro, *J. Mol. Spectroscopy*, 1960, **4**, 99.