Conversion of VOCl₃ to VOCl₂ in Liquid TiCl₄

DAVID C. LYNCH

Titanium tetrachloride, produced by chlorination of titaniferrous ores or rutile, is invariably contaminated by impurities that are also chlorinated, carried over with the TiCl₄ vapor from the chloride furnace, and condensed with the titanium tetrachloride vapor. Ultimately, many of these impurities can be separated by distillation. Unfortunately, that is not the case with vanadium, which dissolves in TiCl₄ (l) as VOCl₃ and has a normal boiling point temperature of 400 K, only 9 deg below that of the titanium tetrachloride.

Vanadium removal is essential. Titanium tetrachloride is the precursor to TiO₂ pigment used in paint. That pigment, with the right crystal structure and crystal size, has exceptional hiding power. If not removed, vanadium will appear as a yellow or brown spot. Any paint manufacturer ignoring this problem could soon be out of business.

In current practice, unsaturated animal fats are mixed with crude TiCl₄ to remove vanadium that is present at concentrations up to 2000 ppm. The fat acts as a chemical sink for vanadium, and when the fat is skimmed from the liquid, 1 pct of the titanium tetrachloride is lost. The skimmed fat (containing both vanadium and TiCl₄) is disposed of as a hazardous waste. Unfortunately, not all the fat is recovered, and that which remains tends to plug nozzles during oxidation of the chloride to form pigment.

For these reasons, there is a need to look at new processes for vanadium removal. Several reagents, “metallic copper, various salts and compounds, oils, carbonaceous organic compounds, and reactive sulfides,”[1] for removing vanadium have been proposed. Unfortunately, little has been published in the open literature regarding any success in using these reagents. However, in two patents, H₂, TiCl₃, and TiCl₄ with “white mineral oil” are reported as reducing VOCl₃ to VOCl₂. Based on normal melting and boiling point complexes with more AlF₃ and NaF to form a mixed Al-Fe oxyfluoride, however, cannot be excluded. The fundamental assumption that the activity coefficient of the dissolved species is constant over quite a wide range of solvent composition is not sufficiently robust that the matter can be pursued further.

REFERENCES

It is possible to conclude that VOCl₂ has a substantially lower vapor pressure and thus can be separated from titanium tetrachloride by distillation. Davis[2] sought to reduce VOCl₃ to VOCl₂ using hydrogen at temperatures between 873 and 1073 K. Davis claims that only direct reduction,

$$2\text{VOCl}_3 (g) + \text{H}_2 (g) \rightarrow 2\text{VOCl}_2 (s) + 2\text{HCl} (g)$$ [1]

occurs, and at temperatures below 1073 K, H₂ does not react at a sufficient rate for formation of lower titanium chlorides (TiCl₃ and TiCl₂), chlorides that can act as reducing agents for VOCl₁. Davis also claims that the rate of reaction is independent of the concentration of HCl in the vapor phase and that 30 times the stoichiometric amount of H₂ is required to drive the reaction to completion.

Boy[d][3] treated crude TiCl₄ liquid with TiCl₃ (s), white mineral oil and TiCl₄(s) with white mineral oil at 393 K. He found that both TiCl₃ and TiCl₄ in the presence of the mineral oil acted as reducing agents, with the latter combination having a greater impact. Mineral oil on its own was not found to reduce VOCl₃ to VOCl₂.*

*Mineral oil most likely acts to transport TiCl₃ and maintain and improve contact between reactants.

TiCl₃ is not only an expensive reagent, it is corrosive and both air and water sensitive. Pigment producers will not accept the difficulties of handling that reagent when already faced with the highly toxic nature of TiCl₄, and its sensitivity to air and water. Moreover, the economics of using TiCl₃ for reducing VOCl₁ is expensive at best and prohibitive when excess quantities of that reagent must be employed to get good contact between the reagent and the VOCl₁ that is present in the solution as a minor constituent.

The problem is to devise a process for removal of vanadium from TiCl₄ that improves on existing practice, is economical, can be accomplished without using expensive and difficult to handle reagents, and does not require vaporization of the crude TiCl₄ for reduction of the VOCl₁. Any additional vaporization steps beyond that required for distillation add significantly to the energy required for producing pigment.

In the present work, a relatively clean and simple process is presented for reducing VOCl₁ in crude TiCl₄ at temperatures below the normal boiling point of the tetrachloride. The process involves both direct reduction of VOCl₁ in the liquid phase at 373 K,

$$2\text{VOCl}_3 (l) + \text{H}_2 (g) = 2\text{VOCl}_2 (s) + 2\text{HCl} (g)$$ [2]

and indirect reduction,

$$2\text{TiCl}_4 (l) + \text{H}_2 (g) = 2\text{TiCl}_3 (s) + 2\text{HCl} (g)$$ [3]

$$\text{TiCl}_3 (l) + \text{VOCl}_3 (l) = \text{TiCl}_4 (l) + \text{VOCl}_2 (s)$$ [4]

through production of TiCl₃. The equilibrium constants for these reactions are large and positive, indicating the reactions are energetically favored at 373 K.[4] The issue becomes how to stimulate the physical processes involved in the reactions to achieve reasonable reaction rates at temperatures below the normal boiling point of TiCl₄.

Upon examination of Reactions [2] through [4], the author has hypothesized that the likely rate-limiting step involved in both direct and indirect reduction of VOCl₁ is the dissociation of H₂. The author has further hypothesized that ultraviolet light can be used effectively in a gas-liquid system to enhance the rate of Reactions [2] and [3]. Photons can be used to produce the radicals Cl and H. Ripping a chlorine atom from TiCl₄ is more energetically favorable than dissociation of the hydrogen molecule. It is hypothesized that TiCl₃ is formed by either H₂ reacting with Cl (the latter produced by interaction of photons with TiCl₄) or that monatomic hydrogen (produced by photon interaction with H₂) reacts directly with TiCl₄. In the former process H₂ prevents the back reaction through formation of HCl. Interaction of H₂ and/or TiCl₄ in the gas phase with ultraviolet light requires photons with sufficient energy not only to break bonds but also to impart sufficient translational motion so as to preclude recombination. If the photon has too much energy, the molecules cannot interact with the light, and no radicals (Cl and H) are produced. In the gas phase there are a limited number of quantum states by which H₂ and TiCl₄ can interact with ultraviolet light.

Accordingly, in the gas phase, there are a number of narrow bandwidths of wavelengths of light that can bring about radical production. However, by bubbling H₂ through crude TiCl₄ and simultaneously passing ultraviolet light through the liquid, the light can interact with H₂ and TiCl₄ at the bubble’s surface. The presence of the interface between the liquid and the gas offers a nearly unlimited number of quantum mechanisms for interaction between the reactants and ultraviolet light, interactions that lead to formation of monatomic chlorine and hydrogen. From a purely statistical approach based on concentration, the photons will interact with TiCl₄ and H₂ to produce TiCl₃ that is thermodynamically stable at the temperatures of interest in this study. The TiCl₃, formed on a molecular scale, will mix with the crude TiCl₄ and will be available to reduce VOCl₁, according to Reaction [4].

In the apparatus shown in Figure 1, a low-pressure hydrogen plasma is used to produce photons capable of producing both hydrogen and chlorine radicals for reaction. Flamn[6] has evaluated how energy is distributed in producing a hydrogen plasma. At any moment, over 50 pct of the energy is emitted as radiation, while 20 pct is stored in monatomic hydrogen through dissociation of H₂. Since a plasma is dynamic and bonds are being both broken and reformed