and melted at 82-85°. Resublimation raised the melting point to 89-91°.

The infrared spectrum of benzyldiphenyl-*N*-(*t*-butyl) phosphinimine supports the presence of the $N=P$ linkage which occurs at 1300 cm.$^{-1}$. A solution of the phosphinimine in practical cyclohexane on standing overnight in a humid atmosphere yielded white needles (m.p. 186-189°). This product, which crystallized from aqueous ethanol as fine needles (m.p. 191-192°), was identified as benzyldiphenylphosphine oxide by its infrared spectrum and by mixed melting points (191-193°) with a known sample of the compound.

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Reaction of Titanium Tetrachloride with Some Aromatic Hydroxy Compounds

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Titanium tetrachloride reacts in a 1:2 ratio with phenol, *o*-bromophenol, *p*-bromophenol, *p*-chlorophenol, *p*-nitrophenol, *p*-cresol, and *β*-naphthol to form the dichlorodisubstituted titanates.

A RECENT literature survey by Shiihara (*9*) indicates that there has been numerous studies made on the reaction of titanium tetrachloride with various classes of organic compounds. A lesser amount of work has been done on the reaction of hydroxy aromatic compounds with titanium tetrachloride.

One of the first reactions of a phenol compound with titanium tetrachloride was reported by Luchinskii (*6*). He reported the reaction of titanium tetrachloride with phenol to form $TiCl_3(OC_6H_5)$, which could be used for the colormetric determination of either compound. Luchinskii (*5*) also reported the reaction of titanium tetrachloride with *o*-chlorophenol, *p*-chlorophenol, and *p*-nitrophenol to form the dichlorodisubstituted titanates which were all easily hydrolyzed, dark red compounds.

This paper reports the preparation and some of the properties, including infrared spectra, of the dichlorodissubstituted titanates obtained from the reaction of a 1:2 ratio of titanium tetrachloride and phenol (m.p. 41°), *o*-bromophenol (m.p. 4-5°), *p*-bromophenol (m.p. 63.5°), *p*-chlorophenol (m.p. 39-40°), *p*-nitrophenol (m.p. 114°), *p*-cresol (m.p. 32-34°), and *β*-naphthol (m.p. 122°).

The compounds formed are dark red powdery solids with the exception of *p*-nitrophenol, which is bright orange, and *β*-naphthol, which is black-red. They are insoluble in most common organic solvents, although they dissolve in absolute ethyl alcohol readily. They are very hygroscopic and decompose in basic solution to form the corresponding phenol, titanium dioxide, and hydrogen chloride.

It has not been possible to prepare the dark red $TiCl_2(p\text{-}OC_6H_4NO_2)_2$ reported by Luchinskii (*5*) or the ruby-red crystals from the reaction of titanium tetrachloride with the corresponding phenol as reported by Reeves (*7*). The dichlorobis-(*β*-naphthoxy) titanate reported by Funk and Rogler (*12*) has been isolated in our laboratories.

The reactions were run in either carbon tetrachloride or chloroform solutions. Changing the solvent to benzene did not produce any solvent addition products as reported by Funk and his co-workers (*3*) in the preparation of $Ti(p\text{-}OC_6H_4Cl)_4 \cdot p\text{-}HOC_6H_4Cl \cdot C_6H_{12}$ and $TiCl_2(p\text{-}OC_6H_4CH_3)_2 \cdot 2\ p\text{-}HOC_6H_4CH_3$. Solvent addition is possible and aromatic complexes have been observed in our laboratories (*8*).

There was evolution of hydrogen chloride during the reactions, but not noticeable heat was generated. Upon hydrolysis in a dilute nitric acid-ethyl ether solution, the phenol was quantitatively regenerated (*2*).

$$\mathrm{TiCl_2(OC_6H_5)_2} \xrightarrow[\text{dilute HNO}_3]{\text{ethyl ether}} \underset{\text{water}\quad\text{layer}}{\mathrm{Ti(OH)_4 + Cl^-}} + \underset{\text{ether layer}}{\mathrm{C_6H_5OH}}$$

Empirical formulas of the compounds are listed in Table I. They were determined from the titanium, phenol, and

Table I. Some Properties of the Solid Products Formed from Titanium Tetrachloride and Some Aromatic Hydroxy Compounds

Empirical Formula	M.P., °C.	%, Titanium Calcd.	%, Titanium Found	%, Chloride Calcd.	%, Chloride Found	%, Phenol Calcd.	%, Phenol Found
$TiCl_2(OC_6H_5)_2$	130-135	15.8	14.1	23.2	20.2	61.0	59.7
$TiCl_2(o\text{-}OC_6H_4Br)_2$	70-75	10.4	11.1	15.3	16.3	74.3	78.0
$TiCl_2(p\text{-}OC_6H_4Br)_2$	95-98	10.4	10.3	15.3	15.8	74.3	73.5
$TiCl_2(p\text{-}OC_6H_4Cl)_2$	108-116	12.8	11.7	19.0	18.1	68.2	67.0
$TiCl_2(p\text{-}OC_6H_4NO_2)_2$	102-107	12.2	12.5	18.0	17.5	69.8	71.6
$TiCl_2(p\text{-}OC_6H_4CH_3)_2$	80-87	14.4	15.0	21.3	20.8	64.3	64.1
$TiCl_2(\beta\text{-}OC_{10}H_7)_2$	145-150	11.9	11.9	17.5	17.1	70.6	68.6

chloride analysis of the hydrolysis products in dilute nitric acid-ethyl ether solution.

Infrared spectrograms of the products were obtained using the potassium bromide technique. During the formation of the pellets, some hydrolysis occurred and part of the product formed titanium dioxide and the corresponding phenol. The titanium dioxide gave a broad peak between 2.9 to 3.2μ and a very broad shoulder around 10μ (*1*). Enough of the product remained so that some of the peaks reported by Johannesen and co-workers (*4*) and Kambara (*10*) could be observed. The Ti-Cl bond (*4*) around 10.2μ has been observed as well as the Ti-O-C bond (*10*) found in the 8.5 to 9.5μ wave length range.

A change in the adsorption peaks of the phenol products around 7.5 to 9.1μ was noted. A new peak was formed at 7.75μ. A double peak between 8.0 and 8.5 has been replaced by a single peak at 8.15μ. There is also a formation of new peaks at 8.5 and 8.95μ which are probably due to the Ti-O-C bonds. No bonds were observed around the 10 and 11μ bands because of the TiO_2 present.

The spectrogram of the *o*-bromophenol product showed that there are two new peaks formed at 8.85 and 9.3μ. There were no new peaks observed for the Ti-Cl bond because of the TiO_2 present.

The spectrogram of the *p*-bromophenol showed that a new double peak has formed around 18μ which is not evident in *o*-bromophenol itself. There was no Ti-Cl bond observed because of the TiO_2 present.

The spectrogram of the *p*-chlorophenol product showed that the double peak around 8.0 and 8.5μ has disappeared and a single peak appeared at 8.1μ. A second new peak was observed at 8.55μ. There were no Ti-Cl peaks observed because of the TiO_2 present.

The *p*-nitrophenol did not show any new adsorption peaks formed.

The spectrogram of the β-naphthol product showed a moderately strong peak formed at 8.67μ which may indicate a Ti-O-C bond and another peak formed at 10.23μ which would indicate a Ti-Cl bond.

The spectrogram of the *p*-cresol product showed a very weak peak at 9.35μ which may indicate a Ti-O-C bond.

EXPERIMENTAL

The chemically pure liquid phenols were purified by distillation. The solid phenols were chemically pure and used as such. The titanium tetrachloride was purified by distillation in a dry atmosphere. Reagent grade carbon tetrachloride and chloroform were first dried over calcium sulfate and then distilled.

Infrared analyses were run on the compounds in carbon tetrachloride using the KBr technique on a Beckman IR-5 Double-beam Recording Spectrophotometer.

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Buffer Systems of Natural Fresh Waters

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NATURALLY OCCURRING bodies of fresh water of significant size, such as lakes, rivers, and large streams, are commonly observed to vary but slightly in hydrogen ion concentration, the range of $[H^+]$ generally being $10^{-6.5}$ to $10^{-8.5}$. The relative constancy of pH in a natural water is attributed primarily to the presence in the water of dissolved CO_2, bicarbonate, and carbonate. Since the total concentration of dissolved carbonate species seldom exceeds a few millimoles per liter, however, additional buffering action for the maintenance of nearly neutral pH conditions must be contributed by the numerous other chemical, physical, and biological activities of the waters. Therefore, in addition to a detailed consideration of the role of the carbonate system, a comprehensive, integrated concept of the nature and interplay of the various capacity factors of other principal buffer systems indigenous to fresh waters is presented.

CARBONATE EQUILIBRIA

Prior to the discussion of the modes of action of buffer systems in fresh waters, the equilibria of the carbonate system is considered, and a method is described by which representation of such equilibria may be greatly facilitated. For a simple aqueous solution of carbonate species, the interdependent nature of the equilibrium concentrations of the solute components ($H_2CO_3^*$, HCO_3^-, $CO_3^{=}$, H^+, and OH^-) can be described completely by five fundamental equations ($H_2CO_3^*$ refers to the sum of CO_2 and H_2CO_3). This system of equations is composed of the three mass law relationships—defining the first and second acidity constants of $H_2CO_3^*$, K_1 and K_2, and the ion product of water, K_w—and any two equations that describe the compositional nature of the solution—e.g., a concentration and an electroneutrality or proton condition.

Simultaneous graphical representation of this system of equations in logarithmic form provides a convenient means for surveying the equilibrium relationships and their respective dependencies upon pH (*1, 7*). Figure 1 is a logarithmic equilibrium diagram for a simple aqueous carbonate system. For the construction of Figure 1, it has been assumed that the total concentration, C_T, of carbonate species is constant at 0.001M, that all activity coefficients are constant, and that the equilibrium constants valid at the appropriate temperature have been corrected for activity. Diagrams such as Figure 1 can be used expediently for