given in Table 3. Since these values are obtained from \( \sqrt{\frac{1}{2}} \) values which are calculated by extrapolation of \( \sqrt{\frac{1}{2}} \) values to zero time, they are not likely to be affected by the complications associated with the surface state of the electrode.

References

Reactions of Titanium Tetrachloride & Tungsten Hexachloride with Phosphorus Trichloride & Phenylidichlorophosphine in Presence of Alkyl Chlorides
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Department of Chemistry, Kurukshetra University, Kurukshetra 132119
Received 14 August 1978; revised 9 January 1979; accepted 12 April 1979

Titanium and tungsten complexes of the type \([\text{RR'PCI}_2]_2\) \([\text{MCl}_4]\) \([\text{MCl}_4]\) have been prepared by the reaction of anhydrous metal chlorides with \(\text{PCI}_3\) or phenylidichlorophosphine in the presence of alkyl chlorides (R stands for phenyl or chloride and R' for alkyl group). When M is titanium, \(x = 2\) and \(y = 8\) and when M is tungsten, \(x = 1\) and \(y = 5\). The complexes have been characterised by IR and magnetic data.

We have earlier reported the formation of ionic complexes by the reaction of (i) trichlorophosphine with metal chloride in the presence of alkyl chlorides and (ii) phenyl dichlorophosphine with metal chloride in the presence of alkyl chlorides using anhydrous metal chlorides such as boron trichloride\(^{12}\), aluminium trichloride\(^{12}\), ferric chloride\(^{12}\), stannic chloride\(^{12}\) and niobium and tantalum pentachlorides\(^{4}\). Similar reactions have now been carried out with titanium tetrachloride and tungsten hexachloride and complexes obtained characterized on the basis of IR, magnetic and analytical data.

Titanium (IV) chloride (Fluka), anhydrous tungsten hexachloride (Alfa Inorganics) and triphenylmethylchloride (Fluka) were used as such. Phenylidichlorophosphine was prepared by the method reported by Buchner and Lockhart\(^4\). Alkyl chlorides were prepared from the respective alcohols, dried over phosphorus pentoxide and distilled before use. The phosphorus trichloride (BDH) was distilled before use. Solvents (methylene dichloride and carbon disulphide) were dried and deoxygenated before use. Because of the hygroscopic nature of the reactants and products all preparations were carried out under anhydrous conditions. To avoid oxidation of the compounds nitrogen gas was flushed into the reaction mixture.

Preparation of titanium complexes — A weighed quantity of titanium tetrachloride was dissolved in deoxygenated methylene dichloride and to this was added small excess of \(\text{PCI}_3\). The reaction mixture became a little hot and turned light yellow in colour in all the cases. Finally, alkyl chloride was added and the reaction mixture set aside. The reaction mixture turned dark yellow and after some time yellow crystalline precipitate started separating out. The order of adding the reagents was always kept the same and excess of reagents were used to minimise the chance for the formation of polymeric anions. When the separation of the precipitate had ceased, the solvent was decanted off and the precipitate washed with solvent by decantation. The product was dried under reduced pressure (1-2mm) at room temperature. Analytical data of the complexes are given in Table 1.

Preparation of tungsten complexes — To a weighed quantity of metal chloride, dissolved in deoxygenated carbon disulphide, a slight excess of phosphorus halide was added initially. The contents were shaken vigorously in order to dissolve the metal chloride. The reaction mixture became dark blue in colour. Alkyl chloride was then introduced to this mixture. The reaction mixture was allowed to stand for some time with occasional shaking. After some time, the reaction mixture turned dark green and became a little hot. Dark green precipitate started settling down. The mother liquor was removed and the solid product washed with carbon disulphide by decantation. The solid was dried at room temperature under diminished pressure (1-2mm). Elemental analyses of the products are listed in Table 1.

Analyses — Chlorine was estimated gravimetrically as AgCl. Titanium was estimated as titanium oxide (\(\text{TiO}_2\)) while tungsten as barium tungstate (\(\text{BaWO}_4\)). To estimate phosphorus, the complexes were oxidised with nitric acid and potassium permanganate solution (2%), precipitated as phosphomolybdate, dissolved in dilute ammonia and precipitated again as magnesium ammonium phosphate.

Physical measurements — Infrared spectra of the compounds were taken in nujol on a Beckman IR-20 spectrophotometer. Far IR spectra of the compounds were recorded on a Grubb-Parsons, England DM4 spectrophotometer at Indian Institute of Technology, New Delhi using polyethylene plates and nujol for sample preparation.

Magnetic susceptibilities (in the case of tungsten complexes) were recorded by Guoy method using conventional apparatus calibrated against \(\text{CuSO}_4\cdot5\text{H}_2\text{O}\).

The conductances of dilute solutions \((10^{-4}M)\) in nitromethane were measured on an Elco conductivity bridge type CM-82.
TABLE 1 - CHARACTERIZATION DATA OF THE COMPLEXES

Table showing the characterization data of the complexes.

<table>
<thead>
<tr>
<th>Reagents (g)</th>
<th>R'</th>
<th>Product</th>
<th>Found (%)</th>
<th>Calc. (%)</th>
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<tr>
<td>MC1</td>
<td>PCl3</td>
<td>R'Cl</td>
<td>M</td>
<td>P</td>
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<tr>
<td>TiCl4</td>
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<tr>
<td>2.663</td>
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<td>[Am]PCl3 [TiCl4]</td>
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<tr>
<td>2.872</td>
<td>1.2</td>
<td>0.8</td>
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<td>[Bu]PCl3 [TiCl4]</td>
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<tr>
<td>3.329</td>
<td>1.3</td>
<td>1.1</td>
<td>Cyclohexyl</td>
<td>[C6H11P]Cl3 [TiCl4]</td>
</tr>
<tr>
<td>3.414</td>
<td>1.3</td>
<td>2.7</td>
<td>Triphenyl-</td>
<td>[Ph]PCl3 [TiCl4]</td>
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</tbody>
</table>

Titanium complexes; R = Cl

<table>
<thead>
<tr>
<th>R'</th>
<th>M</th>
<th>P</th>
<th>Cl</th>
<th>M</th>
<th>P</th>
<th>Cl</th>
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</thead>
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<tr>
<td>s-Butyl</td>
<td>14.81</td>
<td>4.62</td>
<td>59.86</td>
<td>14.72</td>
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<td>t-Amyl</td>
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<td>58.71</td>
<td>14.40</td>
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<tr>
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<td>57.23</td>
<td>14.15</td>
<td>4.58</td>
<td>57.60</td>
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<td>Triphenyl-</td>
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<td>3.68</td>
<td>46.47</td>
<td>11.44</td>
<td>3.70</td>
<td>46.58</td>
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</tbody>
</table>

Tungsten complexes; R = Cl

<table>
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<th>Cl</th>
<th>M</th>
<th>P</th>
<th>Cl</th>
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</thead>
<tbody>
<tr>
<td>s-Butyl</td>
<td>30.84</td>
<td>5.02</td>
<td>53.44</td>
<td>31.10</td>
<td>5.24</td>
<td>53.99</td>
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<tr>
<td>t-Amyl</td>
<td>31.00</td>
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<td>Cyclohexyl</td>
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<td>40.87</td>
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<table>
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<th>Cl</th>
<th>M</th>
<th>P</th>
<th>Cl</th>
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<td>44.81</td>
<td>29.06</td>
<td>4.90</td>
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<tr>
<td>t-Amyl</td>
<td>28.59</td>
<td>4.68</td>
<td>44.35</td>
<td>29.06</td>
<td>4.90</td>
<td>44.83</td>
</tr>
<tr>
<td>Cyclohexyl</td>
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<td>4.59</td>
<td>44.00</td>
<td>28.43</td>
<td>4.79</td>
<td>43.86</td>
</tr>
<tr>
<td>Triphenyl-</td>
<td>27.44</td>
<td>4.70</td>
<td>42.87</td>
<td>27.91</td>
<td>4.70</td>
<td>43.06</td>
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<tr>
<td>PhPCl3</td>
<td>22.16</td>
<td>3.82</td>
<td>34.39</td>
<td>22.45</td>
<td>3.78</td>
<td>34.64</td>
</tr>
</tbody>
</table>

Depending upon the alkyl chlorides used, the compounds separated out from the solvents after a few minutes to a few days. On this basis the alkyl chlorides can be arranged in the following increasing order of reactivity: triphenylethyl chloride > t-amyl chloride > t-butyl chloride > cyclohexyl chloride > isobutyl chloride > s-butyl chloride. Bright yellow solids, in case of titanium and dark green solids in case of tungsten were obtained.

[But+ PCl3] [TiCl4] and [Bu2PhPCl3] [TiCl4] have the molar conductance values of 144 and 408 mho cm² respectively in dry nitromethane, indicating their 1 : 1 electrolyte behaviour. This has been confirmed by vibrational spectral analysis and the elemental analyses. On this basis the titanium and tungsten complexes can be formulated as [RR'PCl2][TiCl4] and [RR'PCl3][WC14] respectively, where R is phenyl or chloride group and R' is an alkyl group. Similar complexes of titanium and tungsten have been reported earlier,

The infrared spectral data (νmax in cm⁻¹) of the complexes can be discussed in terms of cation and anion spectra.

**Cation spectra** — Phosphorus in tetravalent compounds have tetrahedral structure. According to the Selection Rule," pentatomic molecules with general formula XY3Z are expected to have six vibrational modes, three A and three E, all of which are infrared and Raman active. The absorption bands ~ 790-780 in the spectra of compounds having alkyltrichlorophosphonium cation can be attributed to νP-C (alkyl).

P-Cl vibrations are observed as a strong band and a shoulder around 645-630 and 490-475 respectively. Bands ~ 215-208 are weak and can be assigned to 8R'-P-Cl. These values agree well with the literature values for such cations. The alkyl trichlorophosphonium cations, [R'PCl2]+, are expected to have distorted tetrahedral structure having C₃v symmetry. Alkylphenyldichlorophosphonium cations, [R' PhPCl]₂⁺ should be further distorted tetrahedrally having six A' and three A" vibrational modes and C₃v symmetry. Their infrared spectra show very strong bands at 1450-1435 and 1005-990 which are characteristic of P-Ph [A' (P-C)] vibrations. Seel et al. and Carbridge have also observed similar bands in the range 1450-1425 and 1010-990 respectively for P-Ph vibrations. The bands ~ 795-785 is assigned to A'vP-C (P-C alkyl). The bands in the regions 615-605 and 508-472 may be assigned to A'v,P-Cl and A'v,P-Cl respectively.
Anion spectra — The infrared active absorptions expected for the anion \([\text{TiCl}_6^{2-}\) having \(D_{	ext{sh}}\) symmetry are three \(A''\) and five \(E''\). A strong band at 400-415 can be assigned to \(A''_1\) \(\nu\text{Ti-Cl}\) terminal and at 380 to \(E''_3\) \(\nu\text{Ti-Cl}\). Weak to medium strong bands \(\sim 260-277\) are due to \(A''_2\) \(\nu\text{Ti-Cl}\) bridging frequencies. Weak bands to weak shoulders at 240 can be attributed to \(E''_2\) \(\nu\text{Ti-Cl}\) bridging vibrations. These observations are in agreement with those recorded by Creighton and Green11, for \((\text{C}_2\text{H}_5)_2\text{NiCl}_6\) and by Bullock et al.7 for \([\text{BuPCl}_3]_2\text{TiCl}_4\).

The IR spectrum of the hexachlorotungstate anion \([\text{WCl}_6^{2-}\) is, in agreement with the octahedral species. Of the total six, only two fundamentals, \(v_3\) and \(v_4\), are IR active for the octahedral species10. The bands observed \(\sim 305-300\) are assignable to \(v_3\) and are in agreement with those observed by Bullock et al.7.

Hexachlorotungstate anion shows antiferromagnetism12. Magnetic susceptibility measurements of the compounds \([\text{RPhPCl}_3] \text{WCl}_6\) and \([\text{RPhPCl}] \text{WCl}_6\) \((\text{R} = \text{Bu})\) at room temperature \(298K\) are found to be 0.54 and 0.56 B. M., respectively as expected10.

In the case of isobutyl chloride, it was observed that the phosphonium cations contain tertiary butyl group instead of isobutyl one. This may be due to the rearrangement of the carbocation when the chloride ion attacks the Lewis acid adduct. Similar type of rearrangement has been suggested in Friedel-Crafts reaction of the carbocation17, Kinnear and Perren18 have also observed the change from isobutyl to \(\text{t-butyl}\) in aluminium complexes. The IR spectrum of the complexes obtained from isobutyl chloride and \(\text{t-butyl}\) chloride are superimposable, which further confirm this rearrangement.

The authors are thankful to the CSIR, New Delhi for the award of junior/senior research fellowship to one of them (M. S. S.).

References

Solution Chemistry in Fused Phenol: Part II—Nature of Solutions of Protonic Acids & Bases in Fused Phenol

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Evidence for the formation of addition compounds of protonic acids, viz. fluorosulphuric, chlorosulphuric, disulphuric, sulphuric, p-toluenesulphonic, acetic and chloro-, dichloro-, trichloro-acetic acids, and bases viz. pyridine, \(\text{C}_6\text{H}_5\text{ON} \) morpholine, quinoline, benzylamine and aniline etc. with phenol, in the molar ratios 1:2 and 1:1 has been obtained by measuring the conductance, viscosity and density of the solutions of phenol and acids or bases at \(50^\circ\) ± 0.1°C. Fluorosulphuric acid has been developed as a titrant for the estimation of bases including amides, alkaloids and their mixtures in fused phenol.

References

PREVIOUS studies on fused phenol dealt with solubility determination, solvate formation and solvolytic reactions1-3. Protonic acids are known to form addition compounds with oxygen donors4-6. However no solid compounds have been reported in the case of phenol. It is protonated at the ring rather than at the oxygen when dissolved in fluorosulphuric acid7 while it gets sulphonated when dissolved in disulphuric acid8. Literature lacks information about the behaviour of protonic acids in phenol.

In the present investigations, an attempt has been made to study the nature of solutions of various protonic acids and bases in phenol at \(50^\circ\) ± 0.1°C (m. p. of phenol 44°C). Fused phenol has also been developed as a medium for carrying out acid-base neutralisation titrations and for the estimation of weak bases.

Phenol (BDH) was distilled twice and recrystallized from carbon tetrachloride and stored in vacuo (m. p. 44°C); it was always distilled and recrystallised before use. The fraction distilling between 163 and 165°C (590 mm) was used for all measurements. For conductance measurements, the fraction having specific conductance higher than 0.5 \(10^{-7}\) ohm\(^{-1}\) cm\(^{-1}\) was rejected.

Protonic acids, viz. fluorosulphuric acid9 and disulphuric acid9 were prepared in the laboratory by standard methods. Sulphuric acid (100%) was prepared by distilling excess of SO\(_3\) in 98% sulphuric acid till the conductance value coincided