The Solubility and Thermal Decomposition Characteristics of Some Tetraphenylarsonium Compounds

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**Recommended Citation**

Cole, Jerry J. and Pflaum, Ronald T. (1964) "The Solubility and Thermal Decomposition Characteristics of Some Tetraphenylarsonium Compounds," *Proceedings of the Iowa Academy of Science, 71*(1), 145-150. Available at: [https://scholarworks.uni.edu/pias/vol71/iss1/23](https://scholarworks.uni.edu/pias/vol71/iss1/23)

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A spectrophotometric method for copper based upon the color formed between the reagent under consideration and the copper (1) ion is both accurate and precise.

Literature Cited

The Solubility and Thermal Decomposition Characteristics of Some Tetraphenylarsonium Compounds

JERRY J. COLE¹ AND RONALD T. PFLAUM²

Abstract. The tetraphenylarsonium perchlorate, perrhenate, permanganate, tetraphenylborate, dichromate, trichloro-cobaltate (II) and tetrachlorozincate (II) salts were isolated and characterized. The solubilities of the pure salts in water at 25° were determined using spectrophotometric methods. Thermal data were obtained for the pure salts using the technique of thermal gravimetric analysis. Results of the above studies show that tetraphenylarsonium chloride is valuable as a precipitant for perchlorate and perrhenate ions. The reagent also shows promise as a precipitant for the dichromate and tetraphenylboron ions.

Tetraphenylarsonium chloride has been widely accepted as an analytical reagent. The compound acts as a precipitant for several univalent anions and for a few divalent anions. It forms the basis for the gravimetric determination of a number of common ions (3, 4).

Although a variety of water insoluble tetraphenylarsonium salts have been investigated (4), solubility and thermal stability data have not been reported. It is the purpose of the present investigation to present such data for seven tetraphenylarsonium salts. Absorptimetric data for the tetraphenylarsonium cation were also evaluated.

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Published by UNI ScholarWorks, 1964
**Experimental Part**

**Apparatus and Reagents.**

All spectrophotometric measurements were made at 25°C. with a Cary Model 14 recording spectrophotometer, using 1-cm. matched silica cells. An automatic recording thermal gravimetric balance, described by Ostroff, Eyring, and Sanderson (1), was used to obtain thermal stability data.

Tetraphenylarsonium chloride was obtained from the G. Frederick Smith Chemical Co. and was used as received. Tetraphenylarsonium dichromate, perchlorate, permanganate, and perrhenate were prepared by the addition of freshly prepared solutions of \((C_6H_5)_4AsCl\) to solutions of the potassium salt of the respective anion. Tetraphenylarsonium tetraphenylboron was prepared in like manner from \((C_6H_5)_4AsCl\) and \(NaB(C_6H_5)_4\). The chloro complexes of cobalt and zinc were prepared by the addition of excess \((C_6H_5)_4AsCl\) to aqueous solutions, 0.1M in metal ion and 2M in chloride ion. All precipitates were isolated as amorphous solids from aqueous solution. All compounds with the exception of \((C_6H_5)_4AsMnO_4\), were obtained in crystalline form upon recrystallization from an acetone-water mixture.

Acetonitrile, obtained from the Matheson, Coleman, and Bell Division of the Matheson Co., was used without purification. Deionized water was used for all aqueous solutions. All other chemicals used were of reagent grade quality.

**Analysis of Tetraphenylarsonium Salts.**

The above described tetraphenylarsonium salts were analyzed spectrophotometrically. Absorptimetric measurements in the ultraviolet region of the spectrum were made on acetonitrile solutions of all salts with the exception of dichromate and permanganate. Accurately weighed samples of the previously dried salts were dissolved in 25 ml. portions of acetonitrile for this study. Absorptimetric data for the simple chloride salt were used as the bases of comparison for all solutions.

Absorptimetric measurements on acetonitrile solutions of tetraphenylarsonium dichromate were made at 440 mµ, the wavelength of maximum absorption of the dichromate ion. Similar solutions of the permanganate salt were measured at 525 mµ. Concentration values for the two anions were determined from previously prepared calibration curves for the two colored systems.

The cobalt and zinc chloro complexes were also analyzed by Volhard titration of chloride with standard silver nitrate and ammonium thiocyanate solutions. A 50% acetonitrile-water mixture was used as the solvent medium.
Solubility Measurements.

Solubilities of tetraphenylarsonium compounds in water at 25°C were determined from absorptimetric measurements. Saturated solutions of the salts were equilibrated at 25 ± 0.1°C in a constant temperature bath. Homogeneous samples of the salt solutions were carefully removed at regular intervals, transferred to absorption cells, and measured spectrophotometrically at 264 and 271 mµ. The dichromate and permanganate solutions were measured at 440 and 525 mµ, respectively. Equilibration was assumed when absorbance values on successive samples agreed to within ± 0.5%.

Thermal Stability Measurements.

Accurately weighed samples of the tetraphenylarsonium compounds of approximately 50 mg were subjected to thermal gravimetric analysis. All samples were heated from room temperature to 500°C in an atmosphere of dry air. The heating rate was held constant at 8-10° per minute.

Results and Discussion

It was found that tetraphenylarsonium chloride acts as a precipitant for a variety of anions. In general, large symmetrical univalent anions and a limited number of divalent anions are precipitated. Most precipitates were obtained in the pure state in easily filterable form. Most of the salt like compounds were readily crystallized from acetone-water mixtures.

The tetraphenylarsonium cation exhibits absorption characteristics which are quite similar to those of the tetraphenylboron anion (2). Absorption spectra of tetraphenylarsonium chloride solutions are shown in Figure 1. The absorbing species exhibits wavelengths of maximum absorption at 264 and 271 mµ with molar absorptivities of 3230 and 3160, respectively. Beer’s law is obeyed at both wavelengths over the concentration range of 5 x 10^{-5}M — 3 x 10^{-4}M.

In order to determine solubilities and to calculate ion product constants, it is imperative that molecular formulas be well established. The formulas of the seven compounds listed in Table I were determined from spectrophotometric and titrimetric data. The absorptimetric data presented above and calibration curves at 440 mµ and at 525 mµ for the dichromate and permanganate ions, respectively, were used in the calculations. Data from the chloride determinations were used for the chloro complexes.

Tetraphenylarsonium salts were assumed to be ionic and to dissociate completely in water to the limit of the ion product. In addition, complexed metal ions are likewise assumed to
undergo complete dissociation. Thus, the following equations are representative of the reactions involved in solubility studies:

\[(C_6H_5)_4AsClO_4 \rightleftharpoons (C_6H_5)_4As + + ClO_4^-\]
\[[(C_6H_5)_4As]_2Cr_2O_7 \rightleftharpoons 2 (C_6H_5)_4As^+ + Cr_2O_7^{2-}\]
\[[(C_6H_5)_4As]_2FenCl_4 \rightleftharpoons 2 (C_6H_5)_4As^+ + Zn^2+ + 4Cl^-\]
Figure 2. Thermal Decomposition Curves of Some Tetraphenylarsonium Compounds.

The results of solubility measurements and calculations based upon the above types of reactions are summarized in Table II. It can be seen that the sample salts have ion products which approximate those of calcium oxalate and barium carbonate.

The results of thermal gravimetric studies are shown in Figure 2 and Table II. The minimum decomposition temperature represents the lowest temperature at which a weight loss is detectable on the thermal gravimetric curve. With the exception of the permanganate salt, all compounds studied can be safely dried at 110°C. With the further exception of the dichromate and perchlorate salts, the remaining compounds are stable at least up to 250°C.

Table II. Solubilities and Minimum Decomposition Temperatures of Tetraphenylarsonium Compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility at 25°C g/100 ml x10^4</th>
<th>Ksp</th>
<th>Minimum decomp. Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO₄⁻</td>
<td>3.05</td>
<td>3.98 x 10⁻⁹</td>
<td>230ᵃ</td>
</tr>
<tr>
<td>ReO₄⁻</td>
<td>3.60</td>
<td>3.23 x 10⁻⁹</td>
<td>285</td>
</tr>
<tr>
<td>MnO₄⁻</td>
<td>4.52</td>
<td>8.10 x 10⁻⁹</td>
<td>255</td>
</tr>
<tr>
<td>B(C₅H₅)₄⁻</td>
<td>4.99</td>
<td>5.0 x 10⁻⁸</td>
<td>295</td>
</tr>
<tr>
<td>CoCl₃⁻</td>
<td>790</td>
<td>6.79 x 10⁻⁸</td>
<td>185</td>
</tr>
<tr>
<td>Cr₂O₇⁻</td>
<td>535</td>
<td>6.42 x 10⁻¹⁰</td>
<td>315</td>
</tr>
<tr>
<td>ZnCl₂⁻</td>
<td>61.7</td>
<td>3.22 x 10⁻¹⁰</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ Violent decomposition at app. 300°C
ᵇ Violent decomposition below 110°C

**SUMMARY**

The solubilities and the thermal decomposition temperatures of seven tetraphenylarsonium salts were determined. The sorptimetric characteristics of the tetraphenylarsonium ion were also ascertained. The data obtained substantiate the use of tetraphenylarsonium chloride as a precipitant for perchlorate and perrhenate ions.

**Literature Cited**