

# PERMANGANATE OXIDATIONS IN NON-AQUEOUS SOLVENTS\*

## I. OXIDATION BY TRIPHENYLMETHYLARSONIUM PERMANGANATE

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Quaternary arsonium cations have been widely used in analysis,<sup>1</sup> mainly in the formation, with anionic complexes, of ion-association compounds which are soluble in aprotic solvents.<sup>2</sup> The triphenylmethylarsonium cation has been used to form ion-association compounds with anionic complexes of a number of metals<sup>3-7</sup> and has also been used to form ion-association compounds with the permanganate,<sup>8</sup> dichromate,<sup>9</sup> and triiodide<sup>10</sup> ions. The tetraphenylarsonium cation has been used to extract the permanganate ion into non-aqueous solvents.<sup>11,12</sup> The permanganate ion can be extracted into non-polar solvents from acid aqueous solutions containing tributylphosphate. The triphenylarsine oxide permanganic acid adduct is soluble in chloroform and nitrobenzene.<sup>13</sup>

Triphenylmethylarsonium permanganate has been isolated<sup>8</sup> and is soluble in aprotic polar solvents. It is very soluble in chloroform and nitrobenzene (saturated solutions are approximately 1M and 0.8M respectively) and is sufficiently stable in these solvents to make possible a study of oxidizing properties of the permanganate ion in non-aqueous media.

While triphenylmethylarsonium dichromate has no oxidizing properties in non-aqueous solvents,<sup>13</sup> the corresponding permanganate behaves like permanganate ion in neutral solution, being reduced in the presence of a suitable reductant to insoluble manganese dioxide.

Preliminary investigation of the oxidizing properties of the permanganate ion in chloroform showed that propan-2-ol was oxidized quantitatively to acetone. The results of a typical reaction are shown in Table 1. Kinetics of this reaction and the oxidizing properties with regard to other functional groups will be reported later.

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<sup>1</sup> Willard, H. H., and Smith, G. M., *Industr. Engng. Chem. (Anal. Ed.)*, 1939, **11**, 186, 269, 305.

<sup>2</sup> Tribalat, S., and Pidet, C., *Bull. Chem. Soc. Fr.*, 1961, 1527.

<sup>3</sup> Ellis, K. W., and Gibson, N. A., *Analyt. Chim. Acta*, 1953, **9**, 368.

<sup>4</sup> Dwyer, F. P., and Gibson, N. A., *Analyst*, 1951, **76**, 548.

<sup>5</sup> Figgis, B., and Gibson, N. A., *Analyt. Chim. Acta*, 1952, **7**, 313.

<sup>6</sup> Jasim, F., Magel, R. J., and Wilson, C. L., *Rec. Trav. Chim. Pays-Bas*, 1960, **79**, 541.

<sup>7</sup> Neeb, R., *Z. analyt. Chem.*, 1956, **152**, 158.

<sup>8</sup> Gibson, N. A., and White, R. A., *Analyt. Chim. Acta*, 1955, **12**, 413.

<sup>9</sup> Gibson, N. A., and White, R. A., *Analyt. Chim. Acta*, 1955, **12**, 115.

<sup>10</sup> Gibson, N. A., and White, R. A., *Analyt. Chim. Acta*, 1955, **13**, 546.

<sup>11</sup> Richardson, M. L., *Analyst*, 1962, **87**, 435.

<sup>12</sup> Matusek, J. M., and Sugihara, T. T., *Analyt. Chem.*, 1961, **33**, 35.

<sup>13</sup> Armstrong, R., M.Sc. Thesis, University of Sydney, 1964.

The permanganate ion in chloroform oxidized oct-1-ene, propan-1-ol, propanal, heptan-4-ol, 1-nitropropane, 2-nitropropane, and formic acid but did not oxidize t-butanol, toluene, ethyl acetate, diethyl ether, acetone, or heptan-4-one.

Approximately 90% of the triphenylmethylarsonium cation was recovered after an oxidation. Thus it was possible to oxidize a compound which was insoluble in water but soluble in a polar aprotic solvent without large quantities of the cationic species being required, by a variation of the following kind. The compound to be oxidized was dissolved in chloroform, for example, and shaken with an aqueous solution of potassium permanganate and triphenylmethylarsonium chloride. Triphenylmethylarsonium permanganate was extracted into the chloroform layer, the permanganate reduced, and the cation extracted back into the aqueous layer. The process continued until all permanganate or cation had been used or all the oxidizable material oxidized. This application could be important in preparative organic oxidations and will be reported more fully in a later publication.

TABLE I  
RESULTS OF A TYPICAL REACTION AT 50°  
Initial concentrations 0.1M with respect to both triphenylmethylarsonium permanganate and propan-2-ol

Reaction Time (min)	Acetone (M)	Propan-2-ol (M)	Acetone + Propan-2-ol	Permanganate (M)
8	0.0012	0.0978	0.0990	0.0970
60	0.0173	0.0831	0.1004	0.0732
122	0.0337	0.0651	0.0988	0.0468
223	0.0595	0.0396	0.0991	0.0165
298	0.0677	0.0306	0.0983	0.0054

### Experimental

#### Gas Chromatography

The analysis of organic compounds was carried out by gas chromatography since this enabled both a rapid and accurate method of analysis ( $\pm 1\%$ ). The gas chromatograph was a Perkin-Elmer 154C Vapour Fractometer with a katharometer detector. The flow rate of the carrier gas, helium, was 40 ml/min. Separation of acetone, propan-2-ol, and chloroform (retention times of 4.5, 5.4, and 8.0 min respectively) was obtained at 100° with a 12-ft  $\frac{1}{8}$ -in. column packed with a mixture of equal amounts of dinonyl phthalate (20% by weight on unactivated Celite) and of diethylene glycol adipate on Chromosorb W (Wilkins Instrument and Research Inc.). A peak-height calibration curve was obtained using standard solutions prepared by dilution of known volumes. For the range 0-0.2M solutions there was a linear relationship between concentration and peak height. The injection system of the gas chromatograph could not be used for the analysis of the reaction mixture because of the presence of the non-volatile cation and manganese dioxide. An external injection system with volatilization chamber (Fig. 1) was designed which could be readily flushed with solvent to remove triphenylmethylarsonium permanganate. It was necessary to clean the external apparatus after each injection as the manganese dioxide (a product of the decomposition of the permanganate at the temperature, 50°, of the volatilization chamber) and permanganate caused oxidation of the following samples. The carrier gas was diverted from the gas sampling valve through the injection system and then through the liquid injection block of the gas chromatograph. The carrier gas was able to by-pass the volatilization chamber, thus allowing the injection section to be flushed with solvent. An oil-bath was used to heat the volatilization chamber. Another similar injection system was used for analysis of mixtures

in which all the permanganate had been reduced. In this the volatilization chamber was heated by electrical tape capable of attaining a temperature of 180°. No provision was made for by-passing the injection point. Reaction mixture samples were centrifuged to remove manganese dioxide before the gas chromatograph samples were taken.

### Reagents

Ethanol was removed from the chloroform (Rhodia B.P.) by shaking with concentrated sulphuric acid and then with potassium permanganate. After washing with water the chloroform was dried with anhydrous magnesium sulphate. Propan-2-ol (B.D.H. Analytical Reagent) and fractionated acetone (C.S.R. Chemicals) were used.

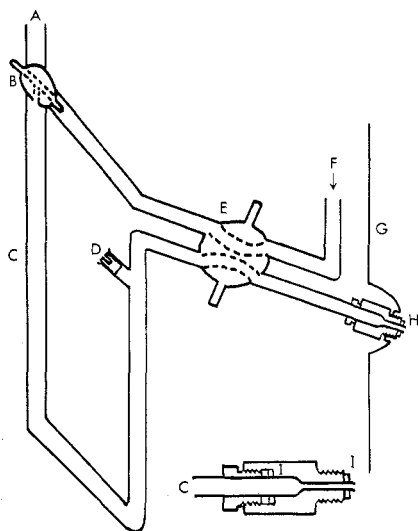


Fig. 1.—An injection system and volatilization chamber used when non-volatile compounds were present.

- A To vacuum pump;
- B 3-way tap;
- C  $\frac{1}{4}$ -in. glass tubing;
- D Injection seal, Burrell silicone seal (puncture type);
- E by-pass tap;
- F from gas sampling valve;
- G gas chromatograph;
- H injection block of gas chromatograph;
- I silicone rubber washers.

### Triphenylmethylarsonium Permanganate

Triphenylmethylarsonium permanganate was prepared by adding an aqueous solution of purified<sup>14a</sup> potassium permanganate (10% excess as an 0.02M solution) to triphenylmethylarsonium chloride (0.5% aqueous solution). The purple precipitate of triphenylmethylarsonium permanganate was filtered off after several minutes and dried under vacuum over phosphorus pentoxide. The compound decomposed on standing and decomposed explosively at 108°. Arsenic was determined,<sup>15</sup> after the destruction of the cation and reduction to  $\text{As}^{\text{III}}$ , by titration with  $\text{KBrO}_3$ . Manganese was determined (after decomposition) by titrating  $\text{Mn}^{\text{II}}$  directly with ethylenediaminetetraacetic acid<sup>14b</sup> and colorimetrically as permanganic acid.<sup>14c</sup> Permanganate was estimated<sup>8</sup> by titrating excess  $\text{Fe}^{\text{II}}$  with standard permanganate (for reproducible results it was necessary to stir the solution of triphenylmethylarsonium permanganate and excess  $\text{Fe}^{\text{II}}$  for 1 hr) (Found: C, 52.2; H, 4.4; As, 16.9; Mn, 12.5;  $\text{MnO}_4$ , 26.9. Calc. for  $\text{C}_{19}\text{H}_{18}\text{AsMnO}_4$ : C, 51.8; H, 4.1; As, 17.0; Mn, 12.5;  $\text{MnO}_4$ , 27.0%).

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<sup>14</sup> Vogel, A. I., "Quantitative Inorganic Analysis" 3rd Ed., (a) p. 282; (b) p. 434; (c) p. 788. (Longmans: London 1961.)

<sup>15</sup> Shulek, E., and Villecz, P., *Z. analyt. Chem.*, 1929, **76**, 81.