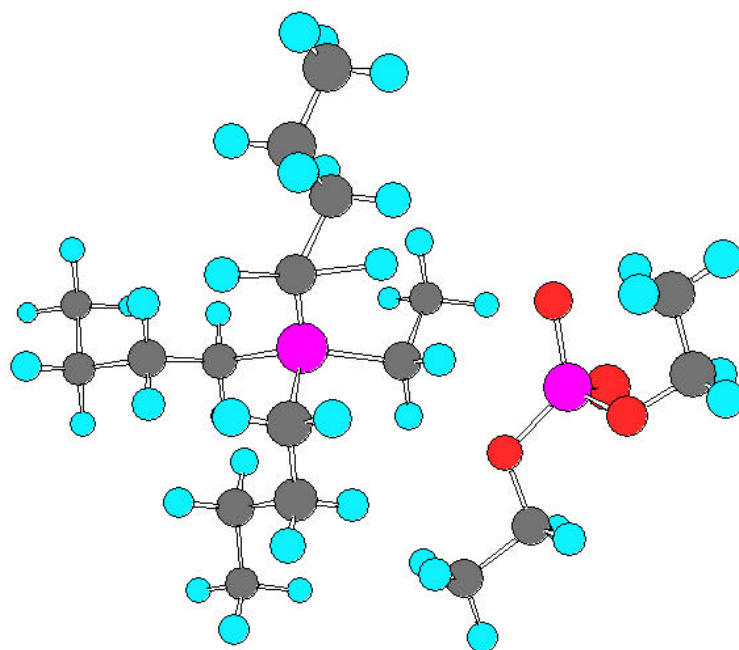


Cytec

– a Pioneer in Phosphorus Chemistry

CYPHOS® IL 169

Phosphonium Ionic Liquid



Europe: +31 765 04 1590 ; USA +1 973 703 0559 ; Canada +1 905 374 5834
www.cytec.com

Introduction:

Why consider a “phosphonium” ionic liquid?

Soon after the discovery that certain nitrogen based room temperature liquid salts were found to be useful as battery electrolytes (1a,1b,), interest in these and similar salts as novel fluids and solvents developed. There were a scant number of papers during the 1980s and early 1990s but mainly due to the efforts of the group at The Queen’s University – Belfast, headed up by Professor Ken Seddon, there has been an exponential rise in interest and number of publications in the last 7 to 8 years. (2) Indeed, almost an entire issue of Green Chemistry (3) has been devoted to ionic liquids.

Perhaps one of the most influential publications to direct industrial attention to ionic liquids was a feature article entitled “Designer Solvents” in C&E News – March 30,1998 in which Ken Seddon, Robin Rogers, Tom Welton, Helene Olivier and others elaborated on the potential of ionic liquids. While the article dealt almost entirely with nitrogen based ionic liquids, there was a brief reference by Ken Seddon which alluded to the fact that phosphonium salts are also a potential source of numerous ionic liquids. This brief reference to phosphonium ionic liquids is very much representative of the current fraction of publications relating to phosphonium based ionic liquids. With the exception of several papers and patents by George Parshall in the mid 1970s using stannate and germanate salts and John Knifton et al in the early 1990s which centre on the use of molten tetrabutylphosphonium bromide as an ionic solvent, almost the entire volume of ionic liquid literature deals with nitrogen based systems and in particular, those based on 2-methylimidazolium salts.

There was a good reason for the lack of phosphonium based ionic liquid publications – availability of the starting material! While Cytec has been commercially producing phosphine derivatives since 1971, it was not until 1990 that tributylphosphine was produced on a large commercial scale. Since that time, not only has tetrabutylphosphonium chloride and bromide become available in multi ton scales, many other trialkylphosphines and the corresponding quaternary phosphonium salts are or can be manufactured on a large scale.

The phosphonium cation contains four substituents and the various combinations along with the multitude of various available anions represents an enormous number of possible salts. Even when one restricts the cation to the generic formula – $[PR_3R']^+$, the number is still very large. Of course, not all such phosphonium salts are liquid at room temperature, but by a judicious selection of R and R’ as well as the appropriate anion, there are many phosphonium salts which are in fact liquid at room temperature and many more which fall within the broad general definition of ionic liquids as salts which are low melting – that is less than 100 °C.

There are several reasons why one might consider a phosphonium ionic liquid. The most important one for those contemplating an industrial process is availability and cost. Phosphonium salts can meet both of these demands – already Cytec is manufacturing phosphonium salts on a multi ton scale and because of the high volumes, costs will be relatively low. For commercial products, chemical inventory registration is also part of the availability equation. While, most of the possible phosphonium ionic

liquids are still not registered, several are already listed on EINECS, TSCA, EEC, AICS, PICCS and DSL.

Ionic liquids, in general, are not going to be outrageously expensive, but they will not be in the same league as toluene, 2-hydroxypropane (IPA) or tetrahydrofuran (THF). This means that to be economically viable, they must be chemically as well as thermally very stable for multiple recycle use. Even 0.5 to 1% decomposition can lead to major losses after 10 to 20 cycles. Not only will there be solvent losses but there will also be contamination of the ionic liquid solvent and/or products with decomposition byproducts.

In this regard, phosphonium salts are much more thermally stable than the corresponding ammonium salts and even have an edge on imidazolium salts. This is very important for processes which operate at temperatures greater than 100 °C. In addition to being slightly less thermally stable, the imidazolium cation contains protons which are not entirely inert. They are somewhat acidic which can result in carbene formation. Phosphonium salts, on the other hand have no such acidic protons.

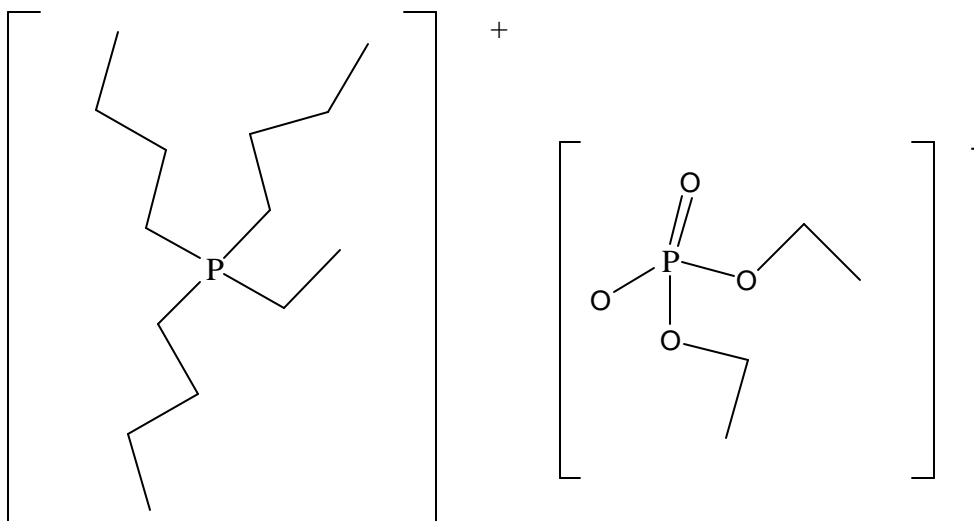
The fact that alkylphosphonium salts are, in general, less dense than water can be beneficial in product work-up steps while decanting aqueous streams which contain inorganic salt byproducts. Imidazolium salts, on the other hand are more dense than water.

Trade Name:[CYPHOS IL 169](#)

Chemical Name: Ethyl tri(butyl)phosphonium diethylphosphate

C.A.S. Number: None

Registration: None



[CYPHOS IL 169](#) – a liquid at room temperature - is manufactured directly from tributylphosphine and triethylphosphate (4,5). Consequently it is **entirely halogen free**. This can be significant for applications in which even ppm levels of halogen can be detrimental to a catalytic process.

³¹P NMR:

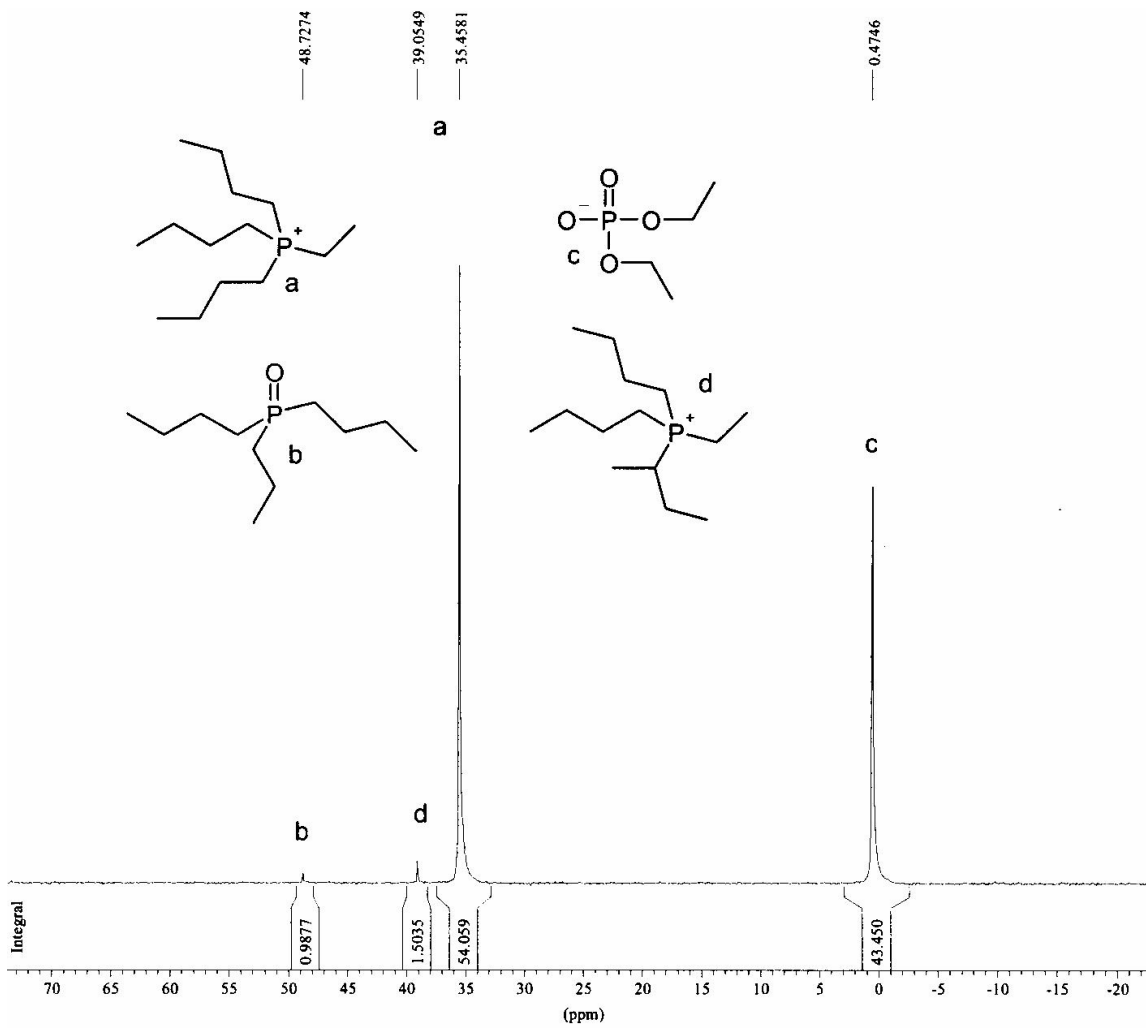
Figure 1 contains the ³¹P NMR spectrum of [CYPHOS IL 169](#). There are two main signals at 35.45 and 0.47 ppm which are due to the ethyl(tributyl)phosphonium cation (a) and diethylphosphate anion (c) respectively. The minor signal at 39.05 ppm is the result of the presence of ethyl(sec-butyl)dibutylphosphonium cation (d). The latter is formed by the reaction of sec-butyl(dibutyl)phosphine (a 3% impurity in tributylphosphine) with triethylphosphate. While the sec-butyl analogue may be considered an “impurity”, it functions equally well as an ionic liquid. The least significant signal at 48.72 ppm is from a trace of tributylphosphine oxide (b).

References:

- 1a) Fannin, A .A, Jr; King, L. A.; Levisky, J. A.; Wilkes, J. S.; J. Phys. Chem., 1984, **88**, 2610-2614
- 1b) Fannin, A. A. Jr; Floreani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; and Williams, J. L., J. Phys. Chem. 1984, **88**, 2614-2621
- 2) “Forward”, Professor Ken Seddon, Green Chemistry April, 2002.
- 3) Green Chemistry April, 2002
- 4) “Industrial Preparation of Phosphonium Ionic Liquids”; Christine Bradaric, Andrew Downard, Christine Kennedy, Allan Robertson, Yuehui Zhou; Green Chemistry, 2003, **5**, 143-152
- 5) “Phosphonium Salts”; A Robertson; WO 01/87900 A1

Figure 1:

CYPHOS IL 169 ^{31}P NMR



Important Notice: The information and statements in this data sheet are believed to be reliable but are not to be construed as a warranty or representation for which we assume legal responsibility or as an assumption of a duty on our part. Users should undertake sufficient verification and testing to determine the suitability for their own particular purpose of and information or products or vendors referred to within. **NO WARRANTY OF FITNESS FOR A PARTICULAR PURPOSE IS MADE.** Nothing in this data sheet is to be taken as permission, inducement or recommendation to practice any patented invention without a license.

Trademark Notice: The ® indicates a Registered Trademark in the United States and the TM or * indicates a Trademark in the United States. The mark may also be registered, the subject of an application for registration or a trademark in other countries.

September 16, 2004/07/03