Potassium Diphenyldiselenophosphate as Analytical Reagent. Solvolysis and Spectral Properties of Potassium Diphenyldiselenophosphate in Organic Solvents.

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Summary: The possibility of using potassium diphenyldiselenophosphate as an analytical reagent in non-aqueous medium is explored.

Potassium diphenyldiselenophosphate $(PhO)_2P(Se)(Sek)$ (dsp) is an analogue of dhiophosphoric acids which have been in use for considerable time for extraction photometric determination of a number of compounds[1]. Taking into account the solvolysis and the spectral features of dsp studied here, this work looks into the possibility of using it as an analytical reagent in non-aqueous medium.

Experimental

Potassium diphenyldiselenophosphate (dsp) was synthesised by the interaction of diphenylchloroselenophosphate with potassium hydroselenide (recrystallized from benzene/acetone, m.p. 172°C decomp.). The details under this section have been reported in an earlier work[2].

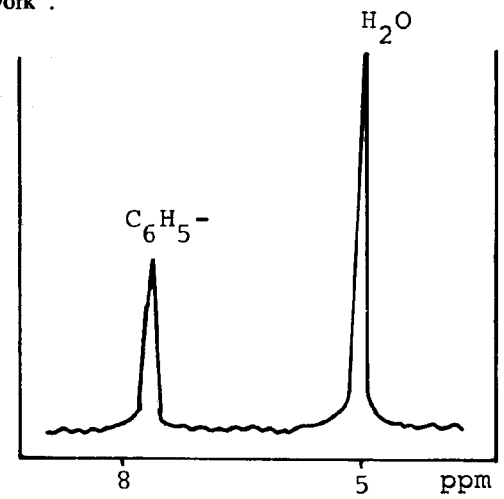


Fig. 1. PMR spectrum of potassium diphenyldiselenophosphate (dsp) in D_2O.

Results and Discussions

The PMR spectrum of dsp obtained in D_2O at 90 MHz is a singlet at δ = 2.6 ppm. with respect to water and 7.6 ppm. with respect to TMS (fig. 1). This absorption is due to the protons of the phenyl ring for which a resonance signal is observed in the region $\delta = 6.5 - 8.0$ ppm[3]. Figure 2 represents the absorption spectra of dsp in ethanol. Similar spectra have been recorded in methanol, DMF, acetonitrile and tert-butanol. The absorption spectrum above 250 nm has two absorption bands – 267 nm ($a = 2.8 \times 10^3$) and 273 nm ($a = 2.6 \times 10^3$). The solutions of potassium diethyldiselenophosphate (273 nm; $a = 1.2 \times 10^3$) and di-n-propyldiselenophosphate (262 nm; $a = 3.2 \times 10^3$) also absorb in the same region[4] The absorption at 273 nm is almost equal to the absorption at 277 nm in P_2Se_5 bands[5] attributable to the

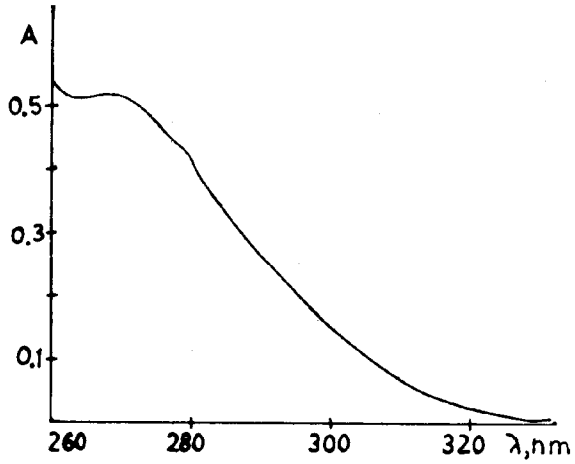


Fig. 2. Absorption spectrum of dsp in ethanol.

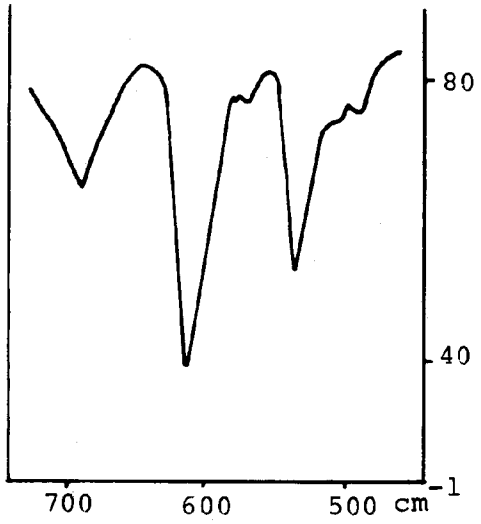


Fig. 3. IR spectrum of dsp.

transition of the P = Se bond. The absorption below 250 nm can be explained by 4p - 5s Rydberg's transition in the selenium atom by analogy to 3p - 4s transition in the sulphur atom and 4p - 5s transition in bromine atoms[6].

The IR spectrum of dsp is shown in the figure 3. Chittenden and Thomas[7] while studying compounds like $(RO)_3P(Se)$, $R(RO)_2$ PSe and (RO) (OH) (R) PSe observed two intense absorption bands in the region 600 - 450 cm^{-1} due to the vibration of ν (P = Se) bonds. In the IR spectra of potassium bis dialkyldiselenophosphate and chromium dialkyldiselenophosphate and of 0.01-diethyldiselenophosphate of a number of elements, also show two absorption bands in the region 600 - 450 cm^{-1}.

The IR spectra of potassium diphenyldiselenophosphate is characterised by the presence of two absorption bands at 610 and and 515 cm^{-1} (figure 4). According to the data obtained from literature[4,5,7] these two absorption bands can be attributed to the assymmetric ν_1 and symmetric ν_2 streching frequencies of P(Se)Se group of diphenyldiselenophosphate. The appearance of these frequencies can be explained by the presence of two resonance forms of $>P^{=Se}_{\backslash Se}-$ and $>P^{=Se}_{\backslash Se}-$ Similar resonance is observed for diethyldiselenophosphate and 0,01-dimethyldithiophosphate[8].

Potassium diphenyldiselenophosphate (dsp) is stable in most of the organic solvents like DMF, DMSO, acetonitrile acetone and alcohols. The spectral features of dsp solutions remain unchanged for a week's time. In

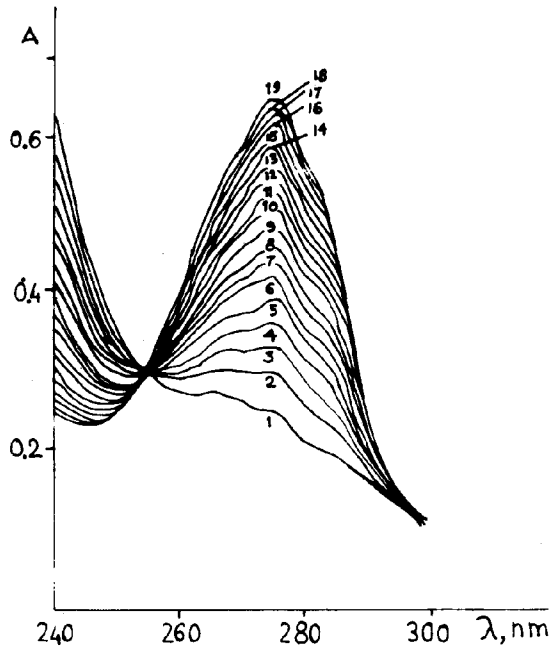


Fig. 4. Absorption spectra of ethanol solution of dsp (1×10^{-4} M) in the presence of 0.15 M HCl after 2, 4.5, 6.1, 8.3, 10.5, 12.1, 14, 15.5, 17.2, 20.47, 22.5, 25.3, 27.3, 31.1, 34.35, 40.4, 44.55, 45.26, 59.4 minutes after the mixing of the reagents.

aprotic solvents (CH_3CN, DMSO and DMF) the reagent is stable in the presence of small quantities of HCl which is added to offset the solvolysis of the salts used. However in alcohols, in the presence of HCl, the reagent fast disintegrates. Figure 4 shows change with time in the absorption spectrum of dsp in the presence of 0.15 M HCl. It can be seen that with the passage of time a product accumulates having an absorption maximum at 275 nm. The location and the nature of this spectrum is similar to the spectral characteristics of pheonl, in the ethanolic solution of dsp (λ_{max} = 275 nm; a = 2×10^3). On this basis it can be suggested that the observed processis the acid catalysed solvolysis of dsp according to the following equation:

$$C_6H_5O>P^{=Se}_{C_6H_5O\ \backslash SeK} + 2\,C_2H_5OH \rightarrow$$

$$C_2H_5O>P^{=Se}_{C_2H_5O\ \backslash Sek} + 2\,C_6H_5OH \qquad (1)$$

Similar phenomenon is observed in methanol and tert-butanol.

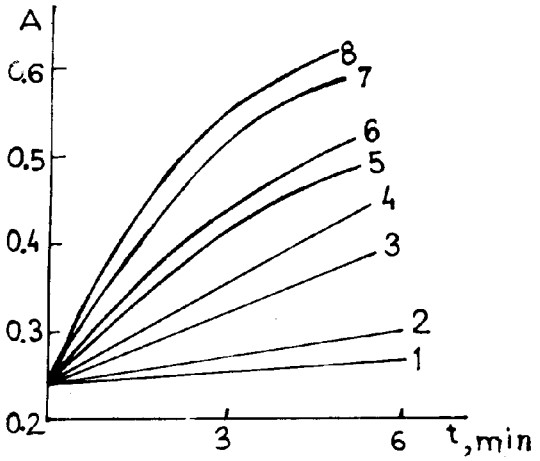


Fig. 5. Kinetics of the solvolysis of ethanol solution of dsp (1×10^{-4} M):
1- 4×10^{-4} M HCl 2- 8×10^{-4} M HCl
3- 2×10^{-3} M HCl 4- 4×10^{-3} M HCl
5- 1×10^{-2} M HCl 6- 2×10^{-2} M HCl
7- 4×10^{-2} 8- 8×10^{-2} M HCl

Figures 5 & 6 represent the kinetics of dsp dissociation in methanol in the presence of varying HCl concentration. A straight line (figure 7) from this data satisfying equations (2) & (3) representing first order kinetic reaction, shows that this prcess presents itself as pseudo monomolecular disintegration of the reagent (equation 1).

$$K_{obsd} = \frac{1}{t} \ln \frac{L_0}{L_0 - x} \qquad (2)$$

$$t = \frac{1}{K_{obsd}} \times 2.3 \log \frac{A_\infty - A_0}{A_\infty - A_x} \qquad (3)$$

where K_{obsd} – observed rate constant, L_0 and $(L_0 - x)$ – the initial reagent concentration and the concentration after time t respectively. A_0, A_∞ and A_x – the absorbance (initial, final and after time t) respectively. The rate constant K_{obsd} can be calculated either by using the initial velocities v_0 by the following equation:

$$K_{obsd} = \frac{v_0}{\Delta a\,(L_0)} \qquad (4)$$

or it can be calculated graphically through equation (3) from where K_{obsd} is equal to the tangent of the slope from the coordinates:

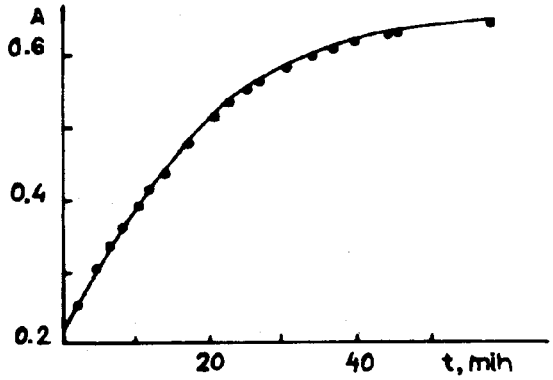


Fig. 6. Kinetics of the solvolysis of ethanol solution of dsp (1×10^{-4}) in the presence of 0.15 M HCl.

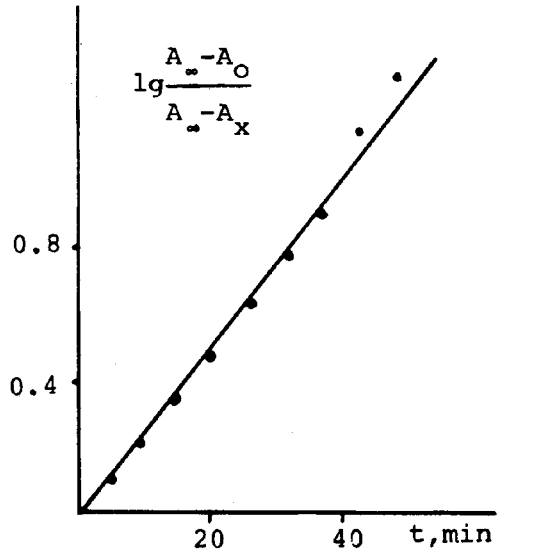


Fig. 7. The plot of the data collected from figure 6 using coordinates of equation 3.

$$\log \frac{A_\alpha - A_0}{A_\infty - A_x} - t \text{ (figure 7)}$$

The values of rate constant K_{obsd} vary with HCl concentration. The dependence of K_{obsd} on HCl concentration in methanol and ethanol ploted in figure 8 & 9 shows that this is in the form of a saturated curve. This can be explained as being due to the protonation of anionic from of the ligand according to the following scheme:

$$S^- + H^+ \overset{K_a}{\rightleftharpoons} SH$$

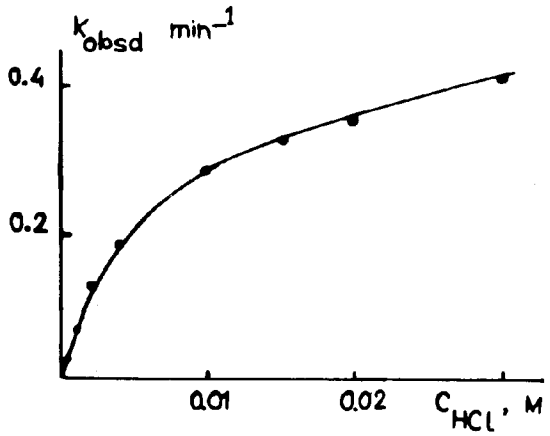


Fig. 8. Dependence of K_{obsd} on HCl concentration in methanol.

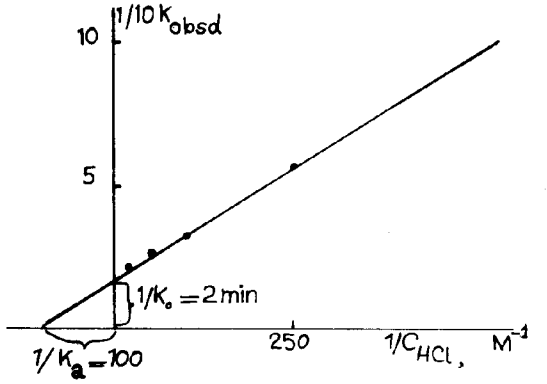


Fig. 10. The plot of figure 8 using coordinates from equation 6.

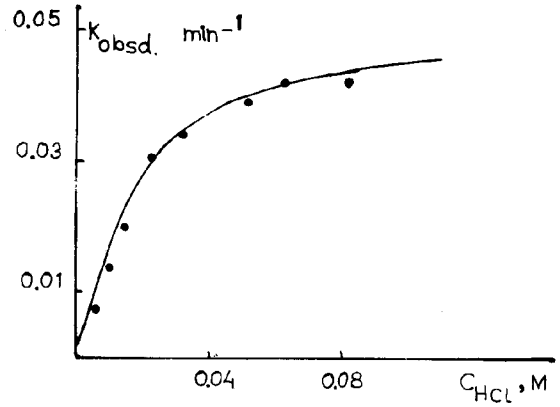


Fig. 9. Dependence of K_{obsd} on HCl concentration in ethanol.

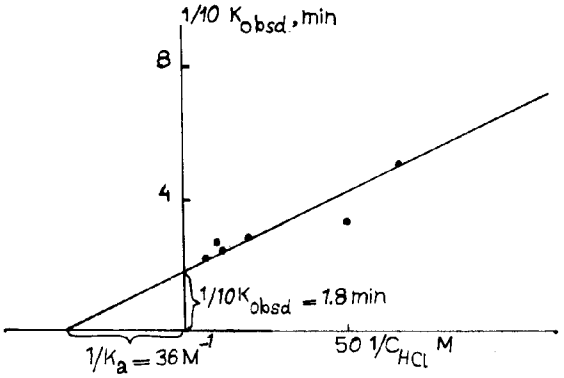


Fig. 11. The plot of figure 9 using coordinate of equation 6.

where S^- – diphenyldiselenophosphate (anion)

K_a – protonation constant.

Kinetic equation satisfying this scheme has the following form

$$K_{obsd} \frac{K_0 (HCl)}{K_a + (HCl)} \qquad (5)$$

where K_0 – rate constant of pseudo-first–order disintegration of protonic form of the reagent (K_0 includes constant concentration of the solvent). Equation (5) can be linearised easily:

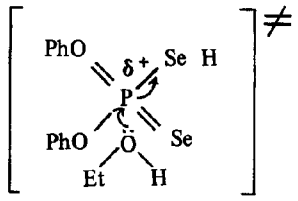
$$\frac{1}{K_{obsd}} = \frac{1}{K_0} + \frac{K_a}{K_0} \times \frac{1}{(HCl)} \qquad (6)$$

A st. line is obtained from the experimental dependence of K_{obsd} on HCl concentration from the coordinates of equation (6). The obtained data thus can be used to calculate the dissociation values of diphenyldiselenophosphoric acids (K_a in methanol and ethanol is 1×10^{-2} and 2.8×10^{-2} respectively).

In this way the kinetics of solvolysis of the reagent can be used to calculate indirectly the values of dissociation constants of diphenyldiselenophosphoric acids. The pK_a of dsp (1.5) can be compared with the pK_a values of diphenyldithiophosphoric acids[9] (pK_a =

2.66) indicating clearly thereby that diphenyldiselenophosphoric acid is stronger than its sulphur containing analogue.

Acid catalysed solvolysis (equation 1) is typical for the solvolysis of phosphoric acids[10] which is ascribed to the increase in the positive charge on the phosphorous atom due to the nucleophilic attack by the alcohol molecule:



Since the values K_0 depend upon the nature of the alcohol, it can be pointed out that the solvolysis proceeds according to S_N 2 mechanism.

Thus the results discussed in this work give us the possibility to characterise the reagent on the basis of its PMR, UV and IR spectra and its stability and dissociation constants can be thought of as being due to its solvolytic processes. It may be of interest to note here that the reagent can easily undergo solvolysis in relatively dilute acidic solutions (half disintegration period $\tau 1/2$ of the reagent in methanol containing 0.01 M HCl comes to three minutes). This must be taken into account while working with this reagent in alcohols or in water inthe presence of acids.

References

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