# Physicochemical investigation of the reactions of some organo-phosphine derivatives with cyanogen halides

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The organo-phosphines $CH_3P(C_6H_5)_2$, $(CH_3)_2PC_6H_5$ and $[(C_2H_5)_2N]_3P$ react with $CNX(X = I$ and Br) in methyl cyanide solution to give two adducts, a 1:1 of ionic nature and 2:1 non-electrolyte, namely $R_3PCNI$ and $R_3P(CN)_2$ respectively with CNI, whereas cyanogen bromide gives only one type of adduct of composition $R_3PCNBr$. Conductometric titration studies and molar conductance measurements show that the 1:1 adducts are very strong electrolytes. In contrast, the 2:1 adduct formed in the case of CNI is a non-electrolyte.

Although the preparation of new phosphorous compounds of the type $R_3P(CN)X$ (R = alkyl or aryl, X = Br or I) have been reported[1-5], the reaction of cyanogen halides with group VB elements has not been thoroughly investigated. By analogy with the reactions of halogens and inter-halogens with phosphines which give conducting species in aprotic solvents[6-8], it is of interest to study similar systems using pseudo-halogen halides instead of halogens.

In view of the success achieved in the previous work from studying different phosphine-halogen systems by conductometric titration[9,10] a similar technique is used to study the behaviour of $CH_3P(C_6H_5)_2$, $(CH_3)_2PC_6H_5$ and $[(C_2H_5)_2N]_3P$ - CNX systems.

## Materials and Methods

Methyl cyanide (Fluka, Puriss P.a.) was purified by somewhat modified method as described by Goetzee et al.[11]. The solvent was successively treated with $NaOH$, $CaCl_2$, and $P_2O_5$. After refluxing, the solvent was distilled to collect the middle cut during each distillation, dried and further distilled on the vacuum line to remove traces of any drying agent left over. This solvent was used for conductance measurements. For spectroscopic purposes, Fluka spectroscopic grade was used after drying over molecular sieve and then freeze dried.

Cyanogen iodide (CNI) (Fluka) was recrystallized twice from chloroform (mp. 146-147°C). Cyanogen bromide (CNBr) (Fluka) was always redistilled before use (mp. 51-52°C).

### Adduct preparations

The adducts $R_1R_2R_3P(CN)X$ (X = Br,I) were prepared by addition of solutions of cyanogen halides dissolved in petroleum ether (7-10 ml) to solution of $R_1R_2R_3P$ in a 1:1 mole ratio of CNX:phosphine. The resulted coloured oils were triturated with dry ether. The crystals obtained were washed with dry ether and then vacuum dried. All adducts decomposed in the range of 120-130°C during the determination of their melting points. The adducts $R_1R_2R_3P(CN)_2$ were isolated as white crystals when pet.ether solutions of CNX (X = Br,I) were added to $R_1R_2R_3P$ in 2:1 mole ratio of CNX:phosphines dissolved in pet.ether. The adducts prepared by similar methods were $CH_3P(C_6H_5)_2(CN)_2$, $(CH_3)_2PC_6H_5(CN)_2$, $[(C_2H_5)_2N]_3P(CN)_2$ and their respective mps were 108-110°, 103-104° and 114-115°C. Fluka ampuled samples of phosphines were used without any further purifications. The results of the elemental micro analyses of the various adducts (Alfred Bernhardt, West Germany) are given in Table 1.

For avoiding contact with moisture, all the work was carried out in dry box ($P_2O_5$). Dry nitrogen was flushed frequently so as to maintain an inert atmosphere.

A conductometric cell was placed in the dry box, on a magnetic stirrer, and was fitted with a dropping burette. The conductance of the solution, placed in the cell, was measured by using a Wayne Kerr B641 Autobalance Universal Bridge. The bridge was placed outside the dry box. The titrations were performed by varying the molar ratios of the reactants and the conductance values were recorded.

Intra-red spectra were recorded on Pye Unicam SP1000 infrared spectrophotometer. Ultraviolet spectra were recorded on Perkin-Elmer spectrophotometer, Hitachi 2000.

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Table 1—Elemental analyses of the adducts

| Adduct | Found | | | | Calc. | | | |
|---|---|---|---|---|---|---|---|---|
| | %C | %H | %N | %P | %C | %H | %N | %P |
| $CH_3P(C_6H_5)_2CNI$ | 47.02 | 3.96 | 4.08 | 9.02 | 47.59 | 3.68 | 3.96 | 8.78 |
| $CH_3P(C_6H_5)_2CNBr$ | 54.26 | 4.02 | 4.81 | 10.72 | 54.90 | 4.25 | 4.58 | 10.13 |
| $(CH_3)_2PC_6H_5CNI$ | 37.81 | 3.84 | 4.62 | 11.03 | 37.24 | 3.79 | 4.83 | 10.69 |
| $(CH_3)_2PC_6H_5CNBr$ | 44.80 | 4.19 | 5.98 | 13.08 | 44.26 | 4.51 | 5.74 | 12.70 |
| $[(C_2H_5)_2N]_3PCNI$ | 39.13 | 7.39 | 14.61 | 8.03 | 39.00 | 7.50 | 14.00 | 7.75 |
| $[(C_2H_5)_2N]_3PCNBr$ | 44.05 | 8.86 | 15.98 | 9.01 | 44.19 | 8.50 | 15.86 | 8.78 |
| $CH_3P(C_6H_5)_2P(CN)_2$ | 70.99 | 5.21 | 11.49 | 12.43 | 71.43 | 5.16 | 11.11 | 12.31 |
| $(CH_3)_2PC_6H_5(CN)_2$ | 63.83 | 6.01 | 14.39 | 15.98 | 63.16 | 5.78 | 14.73 | 16.14 |
| $[(C_2H_5)_2N]_3P(CN)_2$ | 56.81 | 10.11 | 23.08 | 10.59 | 56.19 | 10.03 | 23.41 | 10.37 |



Fig. 1—Conductometric titration graphs

Table 2—Molar conductance values calculated at 1:1 and 2:1 breaks (Fig.1)

| Curve | (ohm$^{-1}$ $\Lambda_m$ cm$^2$ mol$^{-1}$) | $C_m$(mol.1$^{-1}$) |
|---|---|---|
| | 1:1 breaks | |
| 1 | 92.12 | 0.0315 |
| 2 | 99.31 | 0.0365 |
| 3 | 104.06 | 0.0372 |
| 4 | 115.39 | 0.0416 |
| 5 | 119.82 | 0.0430 |
| 6 | 127.73 | 0.0441 |
| | 2:1 breaks | |
| 1 | 38.0762 | 0.0326 |
| 2 | 49.1306 | 0.0420 |
| 3 | 57.7284 | 0.0462 |

$\Lambda_m = \dfrac{10^3 K}{C}$, $K$ = Specific conductance in ohm$^{-1}$ cm$^{-1}$

$C_m$ = Concentration in mol.1$^{-1}$
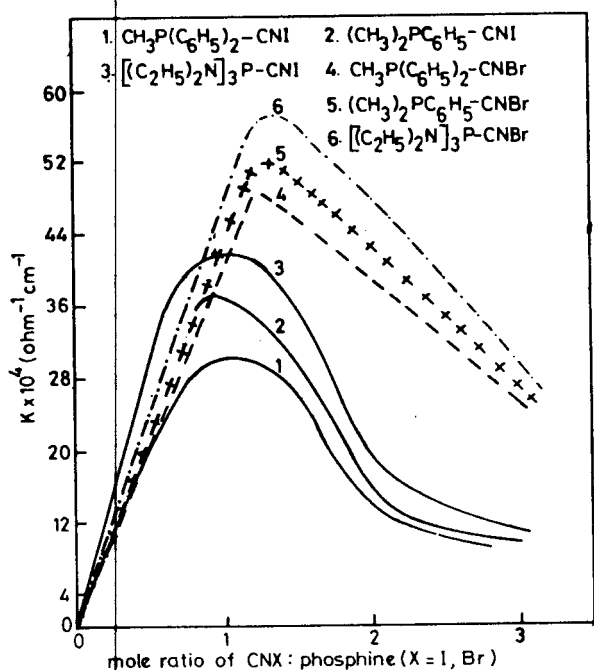
## Results and Discussion

The interaction of $CH_3P(C_6H_5)_2$, $(CH_3)_2PC_6H_5$ and $[(C_2H_5)_2N]_3P$ with CNX, X = Br and I, in methyl cyanide was investigated by conductometric titration technique. The conductance graphs obtained are shown in Fig.1. Curves show two inflections around 1:1 and 2:1 mole ratios of CNI:phosphines, and one break only close to 1:1 mole ratio of CNBr:phosphines.

These breaks clearly indicate that the two systems behave differently after the 1:1 mole ratio in methyl cyanide solution.

The molar conductance measured at the observed breaks in the conductometric titration graphs are given in Table 2. Thus it is evident that both adducts (of CNI and CNBr) formed in solution at 1:1 mole
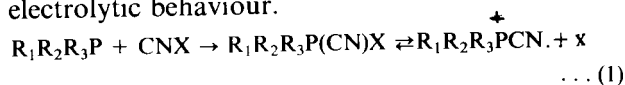
ratio are strong electrolytes. Hence, Eq.(1) might explain the formation of such adducts, and their electrolytic behaviour.

$$R_1R_2R_3P + CNX \rightarrow R_1R_2R_3P(CN)X \rightleftharpoons R_1R_2R_3PCN.+ x$$

... (1)

The above mode of ionization is supported by electrolysis experiment[2] where the halogen was generated at the anode compartment giving pale yellow coloration in case of cyanogen bromide adduct and orange coloration in case of cyanogen iodide adduct. UV spectral studies for solutions of phosphines and cyanogen halide in methyl cyanide in rather similar mole ratios to those used in conductometric titration studies gave no indication for the presence of any trihalide ions.

Furthermore, adduct preparation at mole ratios similar to the breaks indicated by conductometric graphs, resulted in the isolation of two compounds $R_1R_2R_3P(CN)X$ (X = Br and I) by using equimolar
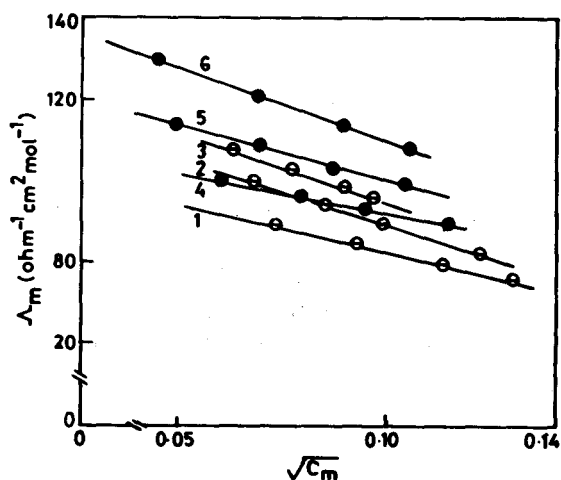
Fig. 2—Electrolytic conductance of cyanogen halide adduct

Table 3—Molar conductance at 0.1$M$ (Fig.2)

| Compound | Molar conductance $(\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1})$ |
|---|---|
| $CH_3P(C_6H_5)_2CNI$ | 81.5 |
| $(CH_3)_2PC_6H_5CNI$ | 88.0 |
| $[(C_2H_5)_2N]_3PCNI$ | 93.0 |
| $CH_3P(C_6H_5)_2CNBr$ | 92.5 |
| $(CH_3)_2PC_6H_5CNBr$ | 100.5 |
| $[(C_2H_5)_2N]_3PCNBr$ | 110.5 |

amounts of reactants. Their molar conductances at different concentrations, at 25°C (Fig.2) and at 0.1 $M$ concentration (Table 3) indicate that these adducts are strong electrolytes and hence support the previously suggested mode of ionization.

These isolated 1:1 adducts were confirmed by elemental analysis as well as infrared spectral studies. The observed sharp strong absorption band at ca. 2174 $cm^{-1}$ was assigned to the CN stretching frequency in $R_1R_2R_3P(CN)I^{12,13}$.

However, after the 1:1 mole ratio the system in which CNBr was used behaved differently from the CNI system. The latter system gave further break close to the 2:1 mole ratio of CNI:phosphine whereas the former did not show any indication for such break.

From the conductance value (Table 2) calculated at 2:1 mole ratio of CNI:phosphine and that of the isolated adduct (Table 4) it is obvious that this adduct is non-electrolyte. The isolated adduct showed an absorption band (very sharp) at ca. 2165 $cm^{-1}$ in its infrared spectrum which was attributed to the stretching mode of the CN group[12,13]. From this and elemental analysis, the above isolated adduct was

Table 4—Values for molar conductance of 2:1 adducts

| Compound | $(\text{ohm}^{-1}\,\Lambda_m$ $\text{cm}^2\,\text{mol}^{-1})$ | $C_m$ (mol $1^{-1}$) |
|---|---|---|
| $CH_3P(C_6H_5)_2(CN)_2$ | 2.13 | 0.0061 |
| $(CH_3)_2PC_6H_5(CN)_2$ | 2.37 | 0.0058 |
| $[(C_2H_5)_2N]_3P(CN)_2$ | 2.71 | 0.0053 |

suggested to have the constitution of $R_3P(CN)_2$. Its UV spectrum in methyl cyanide solution exhibited an absorption band of $\lambda_{max}$ 460. This is due to the presence of free iodine in solution. Therefore reaction (2) may well represent its formation in solution.

$$R_3P(CN)I + CNI \rightarrow R_3P(CN)_2 + I_2 \qquad \ldots (2)$$
(1:1 mole ratio)
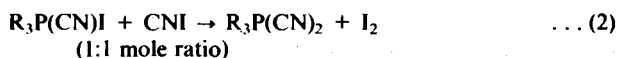
The higher value of conductance found for such adduct when formed during the conductometric titration graph (Fig.1, graphs 1,2 and 3) could be due to the formation of the 1:1 adduct of strong electrolyte behaviour prior to the 2:1 adduct.

In view of results obtained from molar conductance measurements (Table 3) it is clear that there is a steady increase in the electrolytic behaviour of the cyanogen iodide and bromide adducts on the exchange of organic groups of phosphines by others of stronger electron donating nature due to the change in the basicity of the phosphine which is effected by inductive and resonance effects as well as steric effects. Also, the cyanogen bromide adduct was found to be a stronger electrolyte than cyanogen iodide one (Table 3).

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