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THE REACTION OF DIPHENYLPHOSPHINOUS CHLORIDE WITH SILVER PERCHLORATE

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Organophosphorus cations of the type R_2P^+ are unknown although they have been occasionally suggested as reaction intermediates in, for example, the aluminium chloride catalysed reactions of phosphorus (III) halides. The corresponding boron analogue has been reported.[1] It was felt that such species might be of considerable interest since the presence of a lone pair of electrons on the phosphorus atom might lead to the cation displaying some of the properties of a diradical.

Mixing equimolar solutions in dry benzene of diphenylphosphinous chloride and anhydrous silver perchlorate results in the evolution of heat and the rapid, quantitative precipitation of silver chloride. The orange-yellow filtrate was air and moisture sensitive and on aqueous work-up afforded diphenylphosphinic acid. When the reaction was run in nitrobenzene using an excess of the halide the filtrate had a low but appreciable conductivity. The electron spin resonance (e.s.r.) spectrum of the reaction carried out in benzene showed a clear. well resolved, four line spectrum, 54 gauss wide. This was identical with the spectrum of chlorine dioxide in benzene and the spin-active species could be transferred to fresh benzene by means of a stream of dry, purified nitrogen. Iodometric estimation of the chlorine dioxide indicated a yield of ca. 6 p.c. in a number of runs. No dioxide could be detected by e.s.r. in a blank experiment employing dry hydrogen chloride in place of the phosphorus halide, even when the solution was heated. Hence it does not arise from thermal decomposition of perchloric acid which could have been formed by traces of water in the reagents.

The signal is also observed when the reaction is carried out in toluene or acetonitrile but not in tetrahydrofuran. Benzene solutions of diphenylarsinous bromide and silver perchlorate gave results similar to those obtained with diphenylphosphinous chloride but the e.s.r. spectrum was much less intense. No signal was observed on mixing acetonitrile solutions of silver nitrate and diphenylphosphinous chloride, excluding the presence of NO and NO_2. However these solutions possessed approximately the same oxidising power as those prepared using silver perchlorate in benzene. Diphenylphosphinic chloride reacted much more slowly with silver perchlorate. No signal was detectable at any stage of the reaction nor did the filtered solution liberate iodine from acidified potassium iodide. Dialkyl-N-chloroamines do not react with benzene solutions of silver perchlorate in the cold.

It seems clear that the cation Ph_2P^+ is formed and reacts with perchlorate ion. A reasonable explanation would be the following :

$$Ph_2PCl + AgClO_4 \longrightarrow Ph_2P^+ClO_4^- + AgCl$$

$$Ph_2P^+ClO_4^- \rightleftharpoons Ph_2P\cdot + ClO_4\cdot$$

$$2Ph_2P\cdot \longrightarrow Ph_2PPPh_2$$

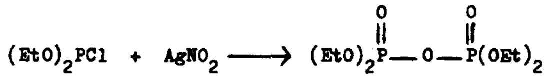
$$ClO_4\cdot \longrightarrow ClO_2 + O_2$$

There is some indirect evidence in support of this : (a) The presence of oxygen is indicated by the fact that the signal resolution was always enhanced by bubbling nitrogen through the reaction mixture even when the reagents had been thoroughly deoxygenated in this fashion beforehand; (b) Tetraphenyldiphosphine and tetraphenyldiphosphine dioxide could be detected by thin layer chromatography in the small neutral fraction obtained after hydrolysis of the reaction mixture, though attempts to isolate them by column chromatography were unsuccessful.

In an effort to detect the postulated $Ph_2P\cdot$ radical intermediate a low temperature study was carried out in benzene and toluene. The spectrum obtained by mixing 0.15M benzene solutions of diphenylphosphinous chloride and silver perchlorate at room temperature was compared with the spectra of chlorine dioxide in benzene and chlorine dioxide/0.15M silver perchlorate in benzene. Measurements were made at ca. 30° intervals between 0° and -160° using Varian low temperature equipment. In all cases solidification of solvent was accompanied by replacement of the four line spectrum by a single line which increased in width with decreasing temperature from about 5 to 20 gauss. At lower temperatures a fine line spectrum appears (Fig.) which, apart from line width, is identical in all three solutions. Saturation effects were most severe for chlorine dioxide in benzene which gave a weak and narrow (11 gauss) spectrum at -160°C compared with 55 gauss for $ClO_2/AgClO_4$ and 22 gauss for the reaction mixture. From this it is concluded that no spin-active species other than ClO_2 is present when the reaction is done at room temperature.

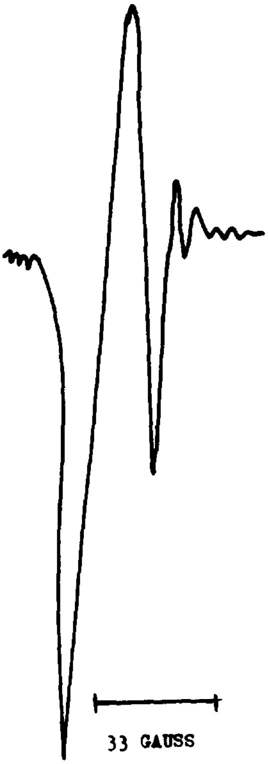
When the reagents are mixed in toluene solution at -80°C and a similar comparison made at liquid nitrogen temperature, essentially the same spectrum as in the Figure, but 7 gauss wide, is obtained indicating that any other spin active species formed is not stable at -80°C.

Very few reports of the action of silver salts on phosphorus halides have appeared. Burg has noted[2] the formation of the stable bistrifluoromethylphosphinous acetate and trifluoroacetate in this way and the following more closely related reactions have been observed[3,4] :



$$(EtO)_2PCl + AgNO_2 \longrightarrow (EtO)_2\overset{O}{\overset{\|}{P}}-O-\overset{O}{\overset{\|}{P}}(OEt)_2$$

$$(EtO)_2PCl + Ag_2N_2O_2 \longrightarrow (EtO)_2POP(OEt)_2$$



FIGURE

These reactions could also be explained in terms of radical intermediates. Dessy <u>et al.</u>[5] have reported the preparation of solutions of diphenylarsinous perchlorate in this fashion but no details were given. Sulphenyl halides and silver salts give deeply coloured solutions.[6]

The postulated intermediate, perchlorate radical, has been claimed[7] as a product of the γ-irradiation of frozen perchlorates but other claims to its existence[8] have been refuted on chemical grounds.[9] In support of the latter we find that solutions obtained by the action of iodine on silver perchlorate in ether or benzene are spin free.

Attempts to trap the Ph_2P^+ intermediate have not yet been successful. We are currently examining this together with other methods of generating members of what promises to be a very interesting class of compounds.

REFERENCES

1. J. M. Davidson and C. M. French, J. Chem. Soc., 1958, 114.
2. L. K. Peterson and A. B. Burg, J. Amer. Chem. Soc., 86, 2587 (1964).
3. D. Samuel and B. L. Silver, Chem. and Ind., 1962, 2063.
4. D. Samuel and B. L. Silver, J. Chem. Soc., 1963, 3582.
5. R. E. Dessy, T. Chivers, and W. Kitching, J. Amer. Chem. Soc., 88, 467 (1966).
6. G. K. Helmkamp, H. N. Cassey, B. A. Olsen and D. J. Pettit, J. Org. Chem., 30, 934, (1965).
7. T. Cole, J. Chem. Phys., 35, 1169 (1961).
8. M. Gomberg and H. R. Gamrath, Trans. Faraday Soc., 30, 24 (1934).
9. R. N. Hazeldine and A. G. Sharpe, J. Chem. Soc., 1952, 993.