The Basic Hydrolysis of Hexakis(aryloxy)cyclotriphosphazenes

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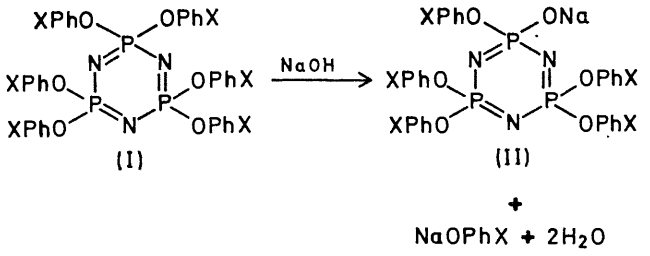
Summary Kinetic and product analysis studies of the alkaline hydrolysis of hexakis(aryloxy)cyclotriphosphazenes in 25 vol. % aqueous diglyme revealed an S_N2-type mechanism for cleavage of the first aryloxy-side-group from phosphorus: the hydrolysis rate was considerably enhanced by 2- or 4-nitro-groups and retarded by 4-methyl groups in the aryl ring.

RELATIVELY little work has been reported on the hydrolysis mechanisms of cyclic and polyorganophosphazenes (phosphonitriles) in basic media. Recently we showed that hexakis(trifluoroethoxy)cyclotriphosphazene, $[NP(OCH_2CF_3)_2]_3$, hydrolyses in alkaline aqueous methanol by a non-geminal pathway and that tris-(*o*-phenylenedioxy)-cyclotriphosphazene, $[NPO_2C_6H_4]_3$, hydrolyses rapidly in basic aqueous dioxan.[1] This latter result was ascribed to the destabilizing influence of the five-membered phenylenedioxyphosphorus ring. The alkaline cleavage of non-cyclized aryloxy-groups from cyclophosphazenes has not been described previously.

We now report the basic hydrolysis reactions in 25 vol. % aqueous diglyme of a series of hexakis(aryloxy)cyclotriphosphazenes (I), where X is 4-nitro, 2-nitro, 4-methyl, or hydrogen. In each case, the reaction studied involved cleavage of one side-group to give (II). The monohydroxyphosphazenes (or *N*-hydrophosphazanes) derived from (II) and the substituted phenols were isolated and characterised. The hydrolyses were found to obey the rate expression, rate $= k[OH^-][\text{phosphazene}]$. Reaction rates were examined under pseudo-first-order conditions with hydroxide ion being present in at least a 300-fold excess. U.v. spectroscopy was used to follow the kinetics. At 80°, with 1×10^{-2} N-sodium hydroxide, the following rate constants were obtained (k, sec^{-1}): X = 4-nitro ($5{\cdot}15 \times 10^{-3}$), 2-nitro ($2{\cdot}10 \times 10^{-4}$), hydrogen ($3{\cdot}54 \times 10^{-8}$), 4-methyl ($6{\cdot}93 \times 10^{-9}$). Activation energies for the 4-nitro- and 2-nitrophenoxy-derivatives were 10·25 and 18·20 kcal/mole respectively.



The ease of cleavage of an aryloxy-unit from phosphorus parallels the increase in acidity of the appropriate phenol, even in the case of the nitro-derivatives, thus demonstrating the importance of electronic rather than steric influences. It is also interesting to note the analogy between the results described here and those reported by Sowerby[2] for the S_N2 exchange of chlorine in hexachlorocyclotriphosphazene.

Attempts to follow accurately the cleavage of an additional aryloxy-group from (II) have so far proved unsuccessful, principally because of the slowness of this second step. For example, cleavage of the first aryloxy-group from hexakis-(4-nitrophenoxy)cyclotriphosphazene is 100% complete in 25 min at 80° with 1×10^{-2} N-sodium hydroxide, but removal of a second ligand was not observed during 48 hr of additional treatment.

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[1] H. R. Allcock and E. J. Walsh, *J. Amer. Chem. Soc.*, 1969, **91**, 3102.
[2] D. B. Sowerby, *J. Chem. Soc.*, 1965, 1396.