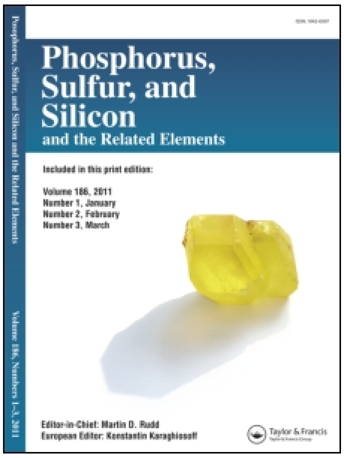

Phosphorus, Sulfur, and Silicon and the Related Elements

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M. Murray[a]; C. J. Penkett[a]; I. M. Rillie[a]; G. Singh[a]
[a] School of Chemistry, University of Bristol, England

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HYDROLYSIS AND PHENOLYSIS REACTIONS OF PHOSPHONITRILIC CHLORIDE TRIMER

M.MURRAY, C.J.PENKETT, I.M.RILLIE, and G.SINGH

School of Chemistry, University of Bristol, BS8 1TS, England

At IRIS VI, in Berlin in 1991, we presented[1] some preliminary results from our ^{31}P NMR studies of the hydrolysis of hexachlorotriphosphazene, $P_3N_3Cl_6$. These studies were carried out in $CDCl_3$ solution, with added triethylamine to absorb the HCl released. While those studies were in progress, a report by Gabler and Haw[2] appeared of the hydrolysis in THF solution, without added base. Their results were to some extent at variance with ours, and both they and we reported NMR evidence for species which could not be identified on the basis of a simple hydrolysis mechanism. Both they and we suggested the formation of P-O-P bridged species, but their spectra, unlike ours, showed no evidence of the P-P coupling across the bridge which would be expected. (Symmetrical species show second order spectra from which the coupling can often be extracted). We have therefore repeated the measurements of Gabler and Haw, and extended our own studies to include the use of other bases than triethylamine.

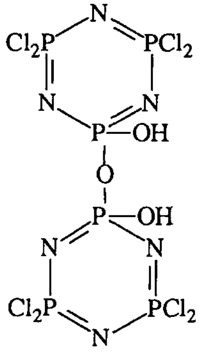
The initial product formed should be $P_3N_3Cl_5(OH)$ (I), for which three tautomeric forms can be proposed, or the corresponding anion $P_3N_3Cl_5O^-$. Comparison of our NMR data (Table 1) with that obtained by van de Grampel et al.[3] for the anion indicated that our species was deprotonated, as expected in the presence of triethylamine. In more acidic conditions however both a shift of the PClO (triplet) resonance and an increase of the coupling constant J_{PP} were observed. The spectra (AB_2 spin system) indicated two-fold symmetry of the species formed, suggesting that the NH-P(=O) tautomer, if present, was undergoing rapid exchange of the proton. At low temperatures (-50°C) the spectra were unchanged, except that the broadening caused by the quadrupolar ^{14}N nuclei was much reduced. Substitution of a second chlorine by OH to give $P_3N_3Cl_4(OH)_2$ (**II**) was shown to proceed in a totally geminal fashion (also an AB_2 spin system, same variable temperature behaviour) in the presence of base, where no evidence was obtained for products beyond disubstitution. Again, the NMR parameters of (**II**) were dependent on the acidity of the solution, but here the neutral solutions, presumably containing the mono-anion, gave the same parameters (high J_{PP}, positive PO_2 shift) as the acidic solutions, excess base being required to shift to the low J_{PP}, negative PO_2 shift situation, where the NMR parameters suggest the presence of the free dianion. At intermediate base concentrations broad signals were observed for (**II**), indicating a slow exchange process between mono- and di-anion.

Table 1 ^{31}P NMR data for (I) and (II).

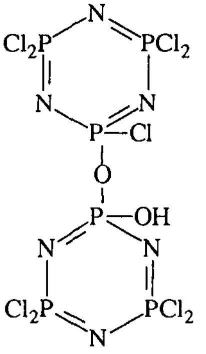
	$P_3N_3Cl_5OH$ (I)			$P_3N_3Cl_4(OH)_2$ (II)			
	δ_{PCl_2}	δ_{PClO}	J_{PP}	δ_{PCl_2}	δ_{PO_2}	J_{PP}	Reference
XS Et_3N	20.9	-0.7	44	10.5	-10.2	36	This work
"Neutral"	20.2	-2.5	45	19.6	-0.5	67	This work
XS HCl	21.3	7.3	60	21.1	2.7	65	This work
XS HCl	21.5	7.3	61	19.9	1.4	67	2

The high values of both the PClO shift and J_{PP} for (I) in acidic conditions approach those observed for alkoxyphosphazenes (e.g. $P_3N_3Cl_5OCH_3$, δ_P 22.5 (d), 16.7 (tr), J_{PP} 63.3 [4]), and suggest that the protonated species is more correctly formulated as the OH tautomer. Indeed the basicity constants derived by Shaw et al.[5] suggest this site for protonation too. Abstraction of a proton by base to yield the anion reduces J_{PP}, suggesting more single bond character in the ring (cf. values for J_{PP} in phosphazenes and phosphazanes in refs. [1,5]) and consistent with resonance structures in which the negative charge is located on the ring nitrogens rather than the exocyclic oxygen. The high value for J_{PP} in (II) even in neutral solution suggests that the mono-anion is best described as a $P(OH)(O^-)$ structure.

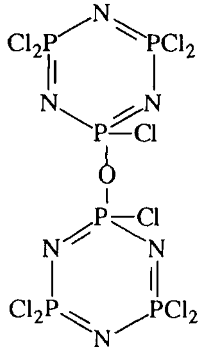
While (I) and (II) are the principal species formed in basic solution, additional species were observed, one monomeric (III) (δ_P 20.3(d), 2.8(t), J_{PP} 43.5) and similar to (I) and (II), and two dimeric species, one symmetrical (IV) and one asymmetrical (V).



(IV)



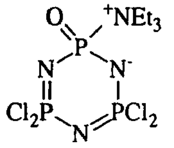
(V)



(VI)

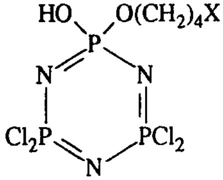
The structures of both dimers were deduced from the ^{31}P chemical shifts by comparison with (I) and (II), and the results of van de Grampel et al.[6], who reported the isolation of the dimer (VI) from the reaction of $P_3N_3Cl_6$ with the sodium salt of uracil, the bridging oxygen coming from traces of water. The second-order ^{31}P NMR spectrum they reported, which differed from that we had obtained for (IV), was only consistent with a dimeric structure, which was confirmed by an X-Ray structure determination.

The structure of (III) was initially left open[1] , but was subsequently revealed by a proton-coupled ^{31}P NMR spectrum. The triplet phosphorus was coupled to six protons, which were located by a ^{31}P-^{1}H correlation experiment as a quintet (doublet of quartets) signal at δ_H 3.26. This proves that an $^{+}NEt_3$ group is attached to the triplet phosphorus, and the structure is



The location of the negative charge on the ring nitrogens is indicated by the low PP coupling constant.

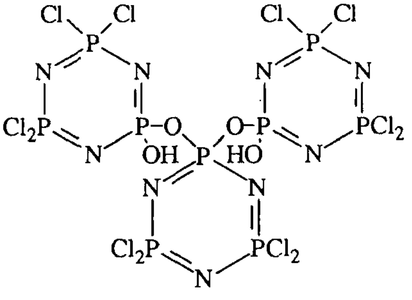
In Gabler and Haw's results there was a similar unexplained AB_2 spin system (δ_P 21.7(d), 3.2(t), J_{PP} 65.5), though it obviously could not be (III) since they did not use NEt_3. They assigned to it the structure (IV) and ascribed the proton coupling they observed (triplet, 8 Hz, on the unique phosphorus) to the two OH protons, although there is no precedent for phosphorus coupling to OH protons in such systems. We showed by a selective decoupling experiment that the coupling arises from a doublet of triplets proton signal at δ_H 3.93. A HOHAHA difference experiment was then carried out on this signal, which revealed that it was part of a spin system which included two complex signals at δ_H 1.5-1.6 and a triplet at δ_H 3.18. This is evidence that this product (VII) has an -O-CH_2-CH_2-CH_2-CH_2-X group attached to phosphorus, which has obviously come from reaction with the solvent THF.



(VII)

This is unsurprising since (VII) only appears after considerable acidity has built up in the reaction medium. The identity of X is difficult to determine; it is most likely OH, but it could be Cl or another -O-CH_2-CH_2-CH_2-CH_2-X group.

The absence of any dimeric products in Gabler and Haw's reactions under acidic conditions, the small amounts produced in the reactions with triethylamine, and the formation of (III) led us to try stronger, less nucleophilic bases such as DBU (diazabicycloundecane) and Hünig's base (di-isopropylethylamine). As expected, no equivalent structure to (III) was formed in these experiments, but DBU in particular was no better than triethylamine in forming bridged species. With Hünig's base increased amounts of the dimer (IV) were formed, while the symmetrical dimer (V) seemed to have been converted to two new bridged species, (VIII) and (IX), though both of these were only formed in very small amounts.



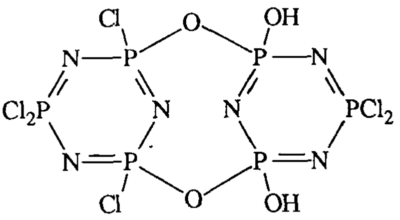
(VIII)

δ_P 21.3(d) J_{PNP} 80 (PCl_2)

δ_P 18.5(d) J_{PNP} 59 (PCl_2)

δ_P -20.8(tt) J_{PNP} 80, J_{POP} 20 ($P(OP)_2$)

δ_P -16.8(td) J_{PNP} 59, J_{POP} 20 (POP)



(IX)

δ_P 23.5 (t) J_{PNP} 76, (PCl_2)

δ_P 20.6 (t) J_{PNP} 69, (PCl_2)

δ_P -3.9 J_{PNP} 76,~70, J_{POP} 21 (POH)

δ_P 10.3 J_{PNP} 69,~60, J_{POP} 21 (PCl)

This molecule has an AA'BB'XM spin system.

The formation of (VIII) can be explained by the Hünig's base increasing the nucleophilic character of the $P(OH)_2$ groups in (II) thus promoting reaction with (V), while (IX) is clearly a product of vicinal substitution in (IV) or (V). Vicinal substitution is otherwise uncommon in basic conditions, though competitive with geminal substitution in acidic conditions.

Fedorov et al.[7] had reported P-O-P bridged dimers from reactions of phenols and fluoroalcohols with $P_3N_3Cl_6$ in the presence of wet pyridine at elevated temperatures. We repeated the reaction with phenol, but were unable to unequivocally identify any dimeric products. The structures proposed by Fedorov et al., with phenoxy groups substituted on the phosphazene rings, would probably exist in a number of regio- and stereoisomers. A number of monomeric products resulting from substitution of chlorine by OH and/or phenoxy groups were identified, particularly after the reaction was repeated at lower temperatures.

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