Identification of Complex Phosphates in Neutron Irradiated
Phosphorus Oxy-Anion Salts

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Summary

An attempt was made to identify the complex phosphates previously identified as being formed in thermal neutron irradiated orthophosphates, orthophosphites and hypophosphites. Gradient elution anion exchange chromatography, under different conditions, was the analytical method used. It is concluded that the species are high molecular weight and contain more than 14 or 15 phosphorus atoms.

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Anselmo (1) has reported on the presence of complex compounds in thermal neutron irradiated phosphorus oxy-anion salts. The presence of these was detected by electrophoresis (2) and gradient elution anion exchange chromatography. In the latter case they are eluted only with 6M hydrochloric acid. An attempt was made to identify these activities because such an identification is important to a finer understanding of the recoil process as the following argument shows.

Complex polyphosphates, viz. of the metaphosphate composition (MPO_3) where M is a monovalent cation, may be formed in a thermal reaction by dehydrating the proper salt to give the required $\text{M}_2\text{O}/\text{P}_2\text{O}_5$ ratio (=1, in this case). For example, heating Na_2HPO_4 at $\sim 500^\circ\text{C}$ for 4 hours gives a salt of the Graham's salt type (3) after suitable quenching. In the case of the hot-atom reactions in a solid orthophosphate, when a P^{32} atom recoils it liberates a large number of atomic fragments, the number and kind depending on the particular salt irradiated. The high density of the matrix plus the energy of the primary fragment, meaning many secondary fragments, give rise to the presence of complex polyphosphates in irradiated phosphorus oxy-anion salts. The fact that they are eluted with 6M hydrochloric acid in a sense indicates their complexity since phosphates are eluted from an anion exchange column in order of increasing weight, as has been shown (4, 5). The exact nature of the species formed is going to depend, to some extent, on the O/P ratio in the irradiated salt. However, if the ratio is too low, it does not preclude the formation of such complex species because they do not have to be stabilized in the solid, but rather thermodynamic stabilization is completed on reaction with the solvent. Another major difference between the thermal reaction and the hot-atom reaction is that the latter is not a true dehydration reaction so that reduced states may be formed. This is not unusual since species with a skeleton as P-P-O-P (6) have already been reported.

Jameson (4) reported the separation of a "strong" phosphoric acid and found that an acid with 14 phosphorus atoms was separated at about 0.6 g ion/l of chloride ion in a gradient elution procedure while a fraction remained that could only be removed with 6M hydrochloric acid. Similarly, Rothbart, and coworkers (5), in a report on the separation of a mixture of "oligophosphates" on a column similar to the one used here, was able to elute up to a species containing 13 phosphorus atoms. Again, the remainder was eluted with strong acid solution.

these activities may be collected and re-separated followed by analysis of the new activities with the possibility of then deducing the nature of the original material.

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TABLE I

Percent P^{32} Found as Activities Eluted with 6N HCl in Various Neutron Irradiated Salts

Salt	Conditions	Percent P^{32}
$Na_2O_3PHN_2 \cdot 6H_2O$	Liquid N_2 temperature (a)	29
$(NH_4)_2HPO_4 \cdot H_2O$	Liquid N_2 temperature (a)	21
	Annealed at $86^\circ C$ for 8 hours	30
$Ca(H_2PO_2)_2$	Liquid N_2 temperature (a)	13
	Annealed at $86^\circ C$ for 16 hours	10
$(NH_4)H_2PO_2$	Liquid N_2 temperature(a)	23
	Annealed at $86^\circ C$ for 16 hours	7
	Annealed at $120^\circ C$ for 16 hours	4
$NaH_2PO_2 \cdot H_2O$	Ambient temperature	5 (b)
$Na_3PO_4 \cdot 12H_2O$	Ambient temperature	4
$Na_2HPO_4 \cdot 2H_2O$	Ambient temperature	43
$NaH_2PO_4 \cdot H_2O$	Ambient temperature	30
KH_2PO_3	Ambient temperature	12

(a) Ambient temperature irradiation followed by storage in liquid nitrogen.

(b) This value and all the following from Radiochim. Acta, 4, 203 (1965).

Bibliography

1. Anselmo, V. C., *Radiochim. Acta*, 4, 203 (1965).
2. Anselmo, V. C., Ph.D. Thesis, Kansas University, 1961.
3. Klement, R., in *Handbook of Preparative Inorganic Chemistry*, Edited by G. Brauer, Academic Press, 1963, Vol. 1, Second Edition, pp. 550-1.
4. Jameson, R. F., *J. Chem. Soc.*, 1959, 752.
5. Rothbart, H. L., H. W., Weymouth, and W. Rieman, *Talanta*, 11, 33 (1964).
6. Van Wazer, J. R., *Phosphorus and its Compounds*, Interscience, N. Y., 1958, Vol. 1, pp. 411-13.
7. Anselmo, V. C., AEC Report COO-1618-1.