Behaviour of Phosphorus-32 produced by the $^{35}Cl(n,\alpha)^{32}P$ Reaction in Crystals of Aluminium Trichloride

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Neutron-irradiated aluminium trichloride crystals have been analysed using a method involving solution in liquid sulphur dioxide in the presence of carrier phosphine and yellow phosphorus. The P^{-III} and P^0 fractions usually amount to *ca.* 80% of the total ^{32}P, the remainder appearing in an insoluble (liquid SO_2) fraction containing P^I, P^{III}, and P^V. Thermal annealing and short-term u.v. irradiation increase the proportion of phosphine precursors. But ionizing irradiation leads to increases in the proportion of oxidized forms at the expense of the phosphine and elemental phosphorus fractions.

We recently reported two methods of non-aqueous analysis for the determination of the distribution of ^{32}P produced by the (n,α) reaction on neutron irradiation of alkali-metal halides.[1,2] In both cases the results suggest that, like ^{35}S, the phosphorus is largely present as low-oxidation-state species. The alkali-metal chlorides, besides generally showing a low solubility in most non-aqueous solvents, have several disadvantages for these studies. They are very difficult to obtain in a state of high purity, it being particularly troublesome to remove trace amounts of hydroxide which Newton [3] and Cifka [4] and their co-workers have shown profoundly influence the fate of the ^{32}P.

Aluminium chloride seemed an interesting choice for

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[1] A. G. Maddock and A. J. Mahmood, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 509.

[2] A. G. Maddock and A. J. Mahmood, *Radiochem. Radioanalyt. Letters*, 1976, **25**, 293.

[3] J. L. Baptista, G. W. A. Newton, and V. J. Robinson, *Trans. Faraday Soc.*, 1968, **64**, 456.

[4] V. Bracokova and J. Cifka, *J. Inorg. Nuclear Chem.*, 1970, **32**, 365.

study. It is still fairly polar but is self-drying and is easily freed from all traces of oxide or hydroxide, and most other metal chlorides, by sublimation. In this way it can be easily obtained as large crystals. Turcanu[5] showed that neutron-irradiated $AlCl_3$ contains a reactive form of ^{32}P.

EXPERIMENTAL

Materials.—The aluminium chloride was prepared by chlorination of very high purity aluminium wire (99.999%). The product was distilled through a fine sintered-glass filter and sealed into silica ampoules for neutron irradiation. Generally, the $AlCl_3$ was melted in the tube and allowed to crystallize again before irradiation. Yellow phosphorus was distilled *in vacuo* before use. Sulphur dioxide obtained from a cylinder was dried and vacuum distilled before use. Other chemicals were of AnalaR grade.

Irradiations.—Some samples were irradiated in the Herald reactor at A.E.R.E. (these are distinguished by numbers) and some in the Universities reactor at Risley (these are identified by letters). Some irradiations in both reactors (identified by /N) were conducted at liquid-nitrogen temperature. Sample tubes were wrapped in aluminium foil and protected from light during and after irradiation, except where indicated.

Analysis.—Two procedures were explored: one involved solution in phosphorus trichloride, the other, chosen for extended application, solution in liquid SO_2. In each case the irradiated tubes were opened in a completely dry glove-box and portions of the crystals were loaded into two vessels attached to a vacuum line. One portion was then dissolved in a deaerated solution containing hypophosphite, phosphite, and phosphate carriers for a parallel aqueous analysis, using the method of Butterworth[6,7] as modified by Baptista *et al.*[3] The other portion was used for the non-aqueous analysis.

(*a*) *Phosphorus trichloride method*. Several years ago it was shown that the ^{32}P produced by neutron irradiation of alkali-metal chlorides could be extracted by PCl_3 at high temperature (800 °C).[8] More recently, Turcanu[5] found that some of the ^{32}P in irradiated $AlCl_3$ appeared to exchange with PCl_3 on solution in this solvent. This suggested a possible method of analysis.

The second portion of the irradiated $AlCl_3$ was dissolved *in vacuo* in a solution of phosphorus in PCl_3. The PCl_3 was then distilled off and the residue was treated with carbon disulphide *in vacuo*. The CS_2 and dissolved phosphorus were removed through a fine sintered-glass plate and the involatile carbon disulphide-insoluble residue was dissolved in an aqueous solution containing hypophosphite, phosphite, and phosphate carriers. After the usual separation of the aqueous components, all the fractions were oxidized to phosphate by bromine water and their activity was measured with an annular Geiger–Müller counter. Several experiments confirmed that only ^{32}P was being measured, by checking the decay over four half-lives of the phosphorus. The results are shown in Table 1.

The distribution obtained was not sensitive to the concentration of P^0 in the PCl_3. The specific activities of several samples from a fractional distillation of the PCl_3 were constant, suggesting that $^{32}P_2Cl_4$ was not present. Although the reproducibility of this method was acceptable, it did not give as much information as the sulphur dioxide method.

TABLE 1

Irradiation	Method	Fraction PCl_3	P^0	Residue	P^I	P^{III}	P^V
(1)	PCl_3	51.3	32.3	16.4			
	PCl_3	50.6	31.4	18.0			
	PCl_3	52.8	30.0	17.2			
	Aqueous				41.3	25.4	33.3
(2)	PCl_3	53.7	27.8	18.5	2.9	4.4	11.2

(*b*) *Sulphur dioxide method*. In this method the irradiated $AlCl_3$ was dissolved in liquid SO_2 at between −5 and −10 °C. Initial experiments were made in the presence of carrier yellow phosphorus, but subsequently both elemental phosphorus and phosphine were added as carriers. The SO_2 and phosphine carrier were distilled off into a trap containing an oxidizing aqueous bromine solution. This fraction is denoted by P^{-III}. The elemental phosphorus was extracted from the residue by dissolving in CS_2 and filtering the solution through a fine sintered filter. Subsequently the solvent was distilled off and the phosphorus was oxidized to phosphate with bromine and nitric acid; the activity of this fraction is designated as P^0. All these operations were conducted *in vacuo*. Finally, the involatile residue was washed out with an aqueous solution of hypophosphite, phosphite, and phosphate carriers. The manipulation involved demanded that all the samples were warmed to room temperature before dissolution. A standard interval of 35 min before dissolution was adopted.

The results of this procedure were not affected by changes in the proportions of phosphine and phosphorus carriers. No evidence was obtained of time-dependent exchange processes. The cold mixture of sulphur dioxide, phosphine, and phosphorus did not show any signs of chemical reaction, but on addition of the $AlCl_3$ a small amount of a yellow deposit always appeared. The amount apparently did not depend on the amounts of phosphine or phosphorus present. The activity carried by this deposit was shown to be unimportant.

TABLE 2

Irradiation	Method	Fraction P^{-III}	P^0	P^I	P^{III}	P^V
(3)	P^0 carrier only		73.2	6.4	7.2	12.2
	P^0 carrier only		73.4	6.1	6.8	13.7
	P^0 carrier only		74.2	6.2	8.3	11.3
	$P^0 + PH_3$ carriers	66.4	9.9	4.0	7.3	12.4
	$P^0 + PH_3$ carriers	67.7	8.1	3.1	7.0	13.1
	$P^0 + PH_3$ carriers	68.2	10.0	2.9	7.2	11.7
	Aqueous			48.9	17.8	33.8
(1)	P^0 carrier only		72.5	8.0	7.8	11.7
	$P + PH_3$ carriers	69.5	8.0	2.7	8.2	11.6
	Aqueous			43.3	23.4	33.3

Results using these methods of analysis are shown in Table 2. It will be observed that the use of the phosphine carrier distinguishes another ^{32}P component which otherwise is included in the P^0 fraction. Comparison of Tables 1 and 2 shows that the sum of the P^{-III} and P^0 fractions is rather smaller than that of the PCl_3 and P^0 fractions from the previous method, but much of the ^{32}P appearing in the P^0 fraction in the PCl_3 analysis appears as P^{-III} in the

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[5] C. N. Turcanu, *Radiochem. Radioanalyt. Letters*, 1970, **5**, 287.

[6] J. S. Butterworth, Thesis, Manchester University, 1964.

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sulphur dioxide method. The reproducibility of the sulphur dioxide method with PH_3 and P^0 carriers was acceptable although the method is very time consuming.

RESULTS

Since there were few previous data, attention was directed first to the distribution found for different types of aluminium trichloride sample and different conditions of irradiation. The results given in Table 3 suggest that even macrocrystalline $AlCl_3$ is sensitive to the presence of oxygen during the irradiation. The powdered material irradiated *in vacuo* behaved very like the macrocrystalline material irradiated in oxygen. Since the amount of oxygen even in the well evacuated system is large compared with the phosphorus generated, it is possible that the behaviour of the powder reflects its greater accessibility to the residual oxygen. Macrocrystalline material irradiated *in vacuo* seems to give reasonably reproducible distributions.

TABLE 3

Irradiation	Type of sample	Conditions	Method	Fraction				
				P^{-III}	P^0	P^I	P^{III}	P^V
(4)	*a*	*in vacuo*	SO_2	75.2	2.7	2.4	8.6	11.1
	a	*in vacuo*	Aqueous			45.5	19.3	35.2
	b	*in vacuo*	SO_2	73.9	4.3	2.9	7.2	12.7
	b	*in vacuo*	Aqueous			46.2	17.8	36.0
	a	in N_2	SO_2	74.6	3.7	3.2	5.1	13.4
	a	in N_2	Aqueous			44.8	18.8	36.4
	c	*in vacuo*	SO_2	54.0	11.6	4.2	12.0	18.2
	c	*in vacuo*	Aqueous			45.0	16.2	38.8
	a	in O_2	SO_2	51.9	9.4	4.8	14.2	19.7
	a	in O_2	Aqueous			36.5	18.5	45.0

[a] Vacuum-sublimed then melted. [b] Sublimed single crystal. [c] Vacuum-sublimed powder.

It was not possible for us to make a systematic study of the effects of radiation dose and temperature during neutron irradiation. However, for several irradiations at reactor temperature with doses of between 1×10^{17} and 2×10^{17} fast neutrons cm^{-2} and, it will be supposed, proportional doses of ionizing radiation, the proportion of the P^{-III} fraction tended to decrease and the P^0 fraction to increase with increasing dose. The total amount, and the distribution of ^{32}P, of the residual material hardly changed. Results for the irradiations at liquid-nitrogen temperature are given in Table 4. Under these conditions there was both an increase in P^0 and in the P^{III} and P^V fractions in the residual material on increasing the dose received by the sample in the reactor.

TABLE 4

Irradiation	Estimated dose fast neutrons cm^{-2}	Method	Fraction				
			P^{-III}	P^0	P^I	P^{III}	P^V
(A/N)	7.2×10^{14}	SO_2	85.8	0.8	0.2	5.2	8.0
	7.2×10^{14}	Aqueous			59.5	23.3	17.2
(5/N)	4.5×10^{16}	SO_2	70.0	3.4	2.4	9.0	15.2
	4.5×10^{16}	Aqueous			28.1	16.0	55.9
(6/N)	8.3×10^{16}	SO_2	64.6	6.6	2.7	10.4	15.7
	8.3×10^{16}	Aqueous			22.1	9.9	68.0

Storage of the irradiated material at room temperature led to a small reduction in P^{-III} and a corresponding increase in P^0, without appreciable change in the amount, or distribution, of the residual material (27 h at 25 °C transformed 2% of ^{32}P from P^{-III} to P^0).

Effects of Various Treatments of the Aluminium Chloride.—*Pre-irradiation with γ-rays.* Samples irradiated with ^{60}Co γ-radiation, inside the silica ampoules before neutron irradiation, with doses as high as 11 Mrad * gave substantially the same distributions of ^{32}P as untreated samples, both at reactor and liquid-nitrogen temperature.

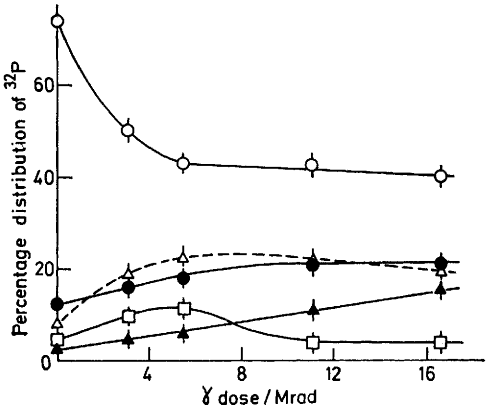

FIGURE 1 Effect of post-neutron γ-irradiation on ^{32}P: (○) P^{-III}; (●) P^V; (△) P^{III}; (▲) P^I; (□) P^0

Post-irradiation with γ-rays. Irradiation of the neutron-irradiated materials with ^{60}Co γ-radiation had a considerable effect on the ^{32}P distribution, in all cases leading to a higher average oxidation state for the phosphorus. The changes in the distribution with the dose absorbed are shown in Figure 1. These measurements were made on material irradiated at the reactor temperature [irradiation (4)]. Low-temperature neutron- and γ-irradiated material showed qualitatively similar changes. (The samples were effectively annealed for *ca.* 35 min at room temperature before analysis.) These samples were not protected from daylight after the neutron irradiation. Aqueous analyses showed much smaller changes in the distribution of the ^{32}P, the P^{III} decreasing and the P^V growing, with comparatively little change in P^I.

U.v. irradiation. Both daylight and u.v. irradiation, using light from a low-pressure mercury lamp, led to marked changes in the distribution. The data obtained with material from the reactor-temperature irradiation (4) are shown in Figure 2. With these and other samples the P^{-III} at first increased at the expense of P^V, but for long irradiations P^0, P^{III}, and P^V all increased at the expense of P^{-III}.

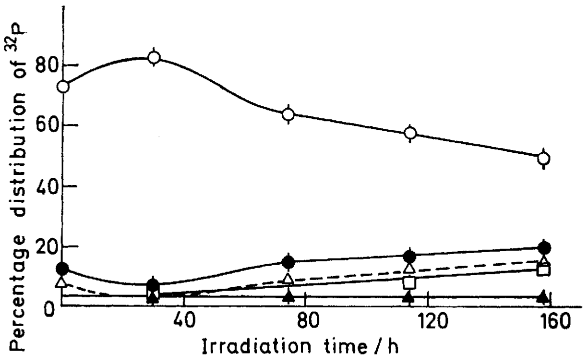

FIGURE 2 Effect of u.v. irradiation on ^{32}P. See Figure 1 for key

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* Throughout this paper: 1 rad = 10^{-2} J kg^{-1}; 1 mmHg ≈ 13.6 × 9.8 Pa.

Aqueous analyses showed that the P^{I} fraction increased at the expense of the P^{III}, but subsequently decreased as the P^{V} slowly increased.

Thermal annealing. The irradiated material was from irradiation (5/N) for the isochronal data and (6/N) for the isothermal measurements. All the samples were protected from daylight until dissolved for analysis. Heating took place in small sealed tubes with free volumes of only 2 or 3 cm^3. There was no evidence of melting or sublimation of the $AlCl_3$ during the annealing. The triple point of $AlCl_3$ is 192.6 °C and at 177 °C the vapour pressure is *ca.* 120 cmHg so that only a small proportion of the sample vaporizes. The isochronal data were obtained with a 4-h heating period and are shown in Figure 3. A change in the annealing processes was apparent at *ca.* 120 °C. Aqueous analyses only revealed smaller changes in distribution, but also indicated an anomaly at *ca.* 100 °C.

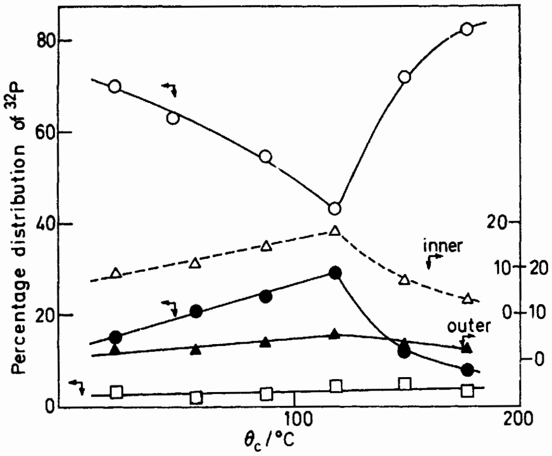

FIGURE 3 Isochronal annealing (for 4 h) of aluminium trichloride crystals. See Figure 1 for key

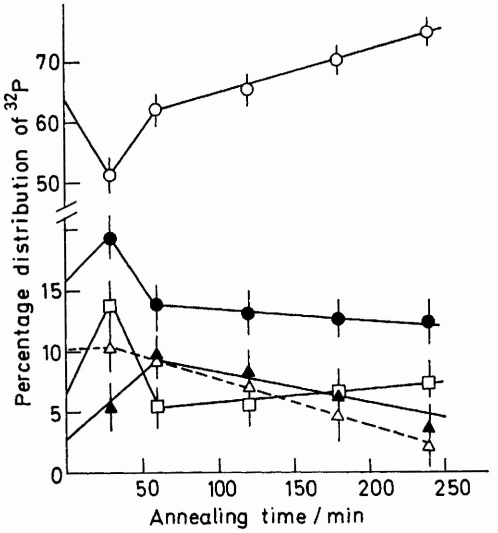

FIGURE 4 Isothermal annealing in aluminium trichloride single crystal

The isothermal annealing was conducted at 177 °C. The results are shown in Figure 4. The P^{-III} fraction passed through a minimum after annealing for *ca.* 30 min, the P^{V} and P^{0} showing maxima at about this time. The magnitude of both the maxima and minima were greater with material from a low-temperature irradiation. For long periods of heating the P^{-III} and, to a lesser extent, the P^{0} fractions increased at the expense of all the other fractions. The aqueous analysis showed a minimum in the P^{V} and maxima in the P^{I} and P^{III} fractions after annealing for *ca.* 50 min.

In another experiment the irradiated $AlCl_3$ was sublimed at 250 °C *in vacuo*. The sublimate contained 95% ^{32}P. The involatile residue contained 75% P^{I}, 10% P^{III}, and 15% P^{V}.

DISCUSSION

There appears to be no simple relation between the aqueous and non-aqueous analyses, although it is clear that a large proportion of the P^{III} and P^{0} fractions from the non-aqueous methods appears in the P^{I} fraction on aqueous analysis. The absence of such a relation can be explained in a number of ways. (*i*) In one or both analyses a given crystal precursor may give rise to more than one of the analytically measured species. (*ii*) Different reactions occur with the radiation-produced defects on dissolution. (*iii*) Different reactions take place with the solvent and/or dissolved air. Various investigators have shown that both (*ii*) and (*iii*) are concerned in the aqueous analysis of irradiated alkylmetal chlorides[2,10,11] and it is probable that all three factors are involved. Colour centres are produced during ionizing irradiation of $AlCl_3$ and it seems reasonable to suppose that, as with the alkali-metal chlorides, there should be equal amounts of electron-rich, reducing, possibly trapped-electron centres and electron-deficient oxidizing centres.

The identification of the crystal precursors of the species separated in the non-aqueous analyses still presents some difficulties. The sublimation experiments show that a large proportion of the ^{32}P can be volatilized at 250 °C in a good vacuum. Yellow phosphorus would sublime under these conditions. The involatile material might be due either to ionic species such as $[PCl_m]^{n+}$ remaining adsorbed on the silica tube, or, as we think more likely, to reaction of some of the elemental phosphorus with the silica tube. It has recently been shown in this laboratory that small amounts of elemental ^{35}S of very high specific activity cannot be volatilized in glass or silica vessels without some oxidation by reaction with the walls of the vessel; an involatile material is produced.[12]

Unlike previous investigators who examined a P^{-III} fraction,[13,14] our evidence does not suggest an exchange reaction with dependence of the P^{-III} yield on the carrier concentration. It is generally supposed that atomic

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phosphorus can undergo thermal exchange with PX_3 (X = H, F, Cl, or Br).[10,15-19] Halmann and Kugel[15] found moderators had little effect on the yield of $^{32}PH_3$ from neutron irradiation of phosphine. In all the mixtures, about half of the ^{32}P formed $^{32}PH_3$ and the remainder adhered to the walls of the container as an indeterminate, but water-soluble, form. They suggested that the $^{32}PH_3$ was formed by a relatively rapid thermal exchange of atomic $^{32}P^0$ with PH_3. However, the yields were little affected by a variety of potential scavengers of P^0, including oxygen. This would demand a rapid exchange of P^0 and PH_3, yet about half the ^{32}P still reached the walls of the container, presumably as $^{32}P^0$.

More recently, Stewart and Hower[18] and Gennaro and Tang[19] studied PH_3, PF_3, and their mixtures. The former workers found that the $^{32}PH_3$ yield from a mixture of 7% PH_3 in PF_3 decreased with increasing pressure of the neon moderator and they suggested that *ca.* 60% of the $^{32}PH_3$ arises from ' hot ' reaction. The latter workers found that buta-1,3-diene acted as an efficient scavenger on irradiation of PH_3 and reduced the PH_3 yield. Stewart and Hower[18] pointed out that the reaction $^{32}P^0 + PH_3 \longrightarrow {}^{32}PH + PH_2$ is likely to be slightly endothermic and might be expected to have an energy of activation of the order of magnitude of the P–H bond strength. It seems unlikely therefore that this can proceed as a thermal reaction. The corresponding process with the halide is still more unlikely as a thermal reaction. Similar arguments apply to other more direct exchange processes such as $^{32}P^0 + PH_3 \longrightarrow {}^{32}PH_3 + P^0$. However, once a PH or PH_2 species is produced, exchange may well proceed as a thermal reaction, this process being sensitive to scavengers. Indeed, there is evidence from studies on PCl_3, where high yields of $^{32}PCl_3$ are obtained in both gas and liquid phases,[16,17] that the formation of $^{32}PCl_3$ takes place through the intermediate $^{32}P_2Cl_4$, which can be separated in substantial yield when carrier material is present.[20,21] Similarly $^{32}P_2Br_4$ is formed from PBr_3.[22]

All these data are compatible with the suggestion that atomic phosphorus does not undergo thermal exchange with PH_3, or PX_3, but that the PH and PX species, surviving recoil or produced in ' hot ' reactions, readily form P_2H_4, P_2X_4, or even mixed species such as P_2X_3H. These species are not very stable and do not survive as such in the absence of carriers. They will attach more hydrogen or halogen, if available, giving phosphine or trihalide, or they will decompose on the walls of the container to yield phosphine or trihalide and an absorbed phosphorus species. Thus there will always be some production of relatively involatile ^{32}P species on the walls. It should also be pointed out that in the PH_3 system, where a very high retention is observed (78%), there must be a very high probability of formation of ^{32}PH fragments since, for purely dynamical reasons, rupture of all the P–H bonds by recoil is rather difficult.

Thus it seems reasonable to suppose that the atomic ^{32}P in irradiated $AlCl_3$ will all appear in the P^0 fraction. Although some polymerization of $^{32}P^0$ may occur before analysis, we think that it is likely to be small under the conditions of these experiments. However, if ^{32}PCl is formed by the irradiation this may well become distributed between the P^0 and P^{-III} fractions as described above. A comparison of Tables 1 and 2 shows that, although the samples from irradiation (1) were analyzed by both the PCl_3 and SO_2 methods and the $^{32}PCl_3 + {}^{32}P^0$ from the former method was approximately equal to the $P^{-III} + P^0$ fractions of the latter, the actual P^0 proportions are quite different. Some of the P^{-III} fraction may also arise from monatomic anionic ^{32}P in the irradiated material. It may be noted that Bogdanov and Murin[10] found evidence for two precursors forming $^{2}PH_3$ in irradiated alkali-metal halides.

The ' insoluble involatile ' residue is undoubtedly the species formed by the reaction of the ^{32}P with oxidizing defects produced by the irradiation. It seems probable that it will comprise charged species, such as $[PCl_2]^-$, *etc.* The sublimation experiments show that these species can be converted by heating mainly into volatile species.

The effects of post-neutron γ-irradiation and u.v. illumination are similar to those found for the alkali-metal chlorides using aqueous analysis. They show that the electronic processes involved are operating on comparatively simple ^{32}P species, principally the P^{-III} precursors. The photo effect, first observed by Süe and Caillat[23] and studied subsequently by many workers, now clearly resembles the more easily identified process with ^{35}S.[24] In this system both oxygen and OH impurity effects are thought to be minimal, but post-neutron ionizing irradiation still leads to increase in the average oxidation state of the ^{32}P, apparently by oxidation by electron-deficient defects and probably by P–Cl bond formation in the $AlCl_3$. The early stages of the thermal annealing also lead to oxidation, but at a moderate temperature there is a sharp reversal and both P^{III} and P^{V} start reforming P^{-III}.

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