ELECTROPHORETIC SEPARATION OF PHOSPHORUS-32 SPECIES OBTAINED BY (n, gamma) ACTIVATION OF TRIPHENYL PHOSPHATE SOLUTION IN BENZENE*

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Chemical effects of the [31]P (n, gamma) ^{32}P nuclear reaction have been investigated predominantly in inorganic phosphorus compounds[1-8]. In all cases smaller or larger fractions of ^{32}P activity in the original chemical form (so-called retention, R) were observed and the influence of the irradiation conditions on the ^{32}P recoil yields was demonstrated.

In earlier work interest in ^{32}P recoil reactions in organic phosphorus compounds was focused mainly on the preparation of ^{32}P of high specific activity. Recently, studies of the ^{32}P recoil reaction in the aliphatic liquid tri-*n*-butyl phosphate[9,10] have shown that ^{32}P can be present in the initial form of tri-*n*-butyl phosphate, then di- and mono-*n*-butyl phosphate, as well as inorganic orthophosphate and phosphite. In various other organic systems organophosphorus compounds with C—P bonds were also identified[11-15].

Almost thirty years ago, ERBACHER AND PHILIPP[16] irradiated a benzene solution of triphenyl phosphate with the practical purpose of obtaining a high enrichment factor. They found that after the Ra—Be neutron irradiation of the benzene solution about 40 % of the total ^{32}P activity could be extracted into an aqueous phase. These authors were not, however, interested in the identification of the chemical forms of the ^{32}P present in the aqueous and organic phases or in the mechanism of their formation.

For this reason, and since up to now comparatively little attention has been paid to recoil reactions in aromatic phosphate systems and no comparison with the known facts concerning the behaviour of ^{32}P recoil in inorganic and aliphatic systems has been made, it seemed interesting to study in more detail the (n, gamma) activation of triphenyl phosphate in benzene.

EXPERIMENTAL

Materials

In addition to the target material—triphenyl phosphate $(C_6H_5O)_3PO$, (TPP), B.D.H. purissimum, in benzene (Merck p.a.)—about thirty other phosphorus compounds were used in this investigation, *viz.*

(a) Aromatic and aliphatic esters with the characteristic C—O—P chemical

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bond (e.g. diphenyl phosphate, monophenyl phosphate, triphenyl phosphite, diphenyl phosphite, monophenyl phosphite, dimethyl phosphate, monomethyl phosphate, diethyl phosphate, monoethyl phosphate, di-n-butyl phosphate, dimethyl phosphite, diethyl phosphite, di-n-propyl phosphite, di-n-butyl phosphite).

(b) Aromatic and aliphatic compounds with a C—P bond (e.g. monophenyl-phosphonic acid, monophenylphosphinic acid, diphenylphosphinic acid, triphenyl-phosphine, triphenylphosphine oxide, monomethylphosphonic acid, monomethyl-phosphinic acid, dimethylphosphinic acid).

(c) Inorganic compounds (e.g. sodium orthophosphate, sodium pyrophosphate, sodium hypophosphate, sodium isohypophosphate, sodium tripolyphosphate, sodium tetrapolyphosphate, sodium trimetaphosphate, sodium tetrametaphosphate, sodium orthophosphite, sodium pyrophosphite, sodium hypophosphite, sodium diphosphite).

Some phosphorus compounds such as: cyclic sodium trimetaphosphate, $Na_3P_3O_9$, sodium tetrametaphosphate, $Na_4P_4O_{12}$, and sodium pyrophosphite, $Na_2H_2P_2O_5$, were synthesized[17, 18], while the other compounds were of commercial origin, supplied by Merck, BDH, Albright (p.a.) and by many research workers.

All the compounds for identification were purified several times before use by repeated crystallization from alcohol and water or by distillation until their physical constants corresponded to the values cited in the literature.

All other chemicals used were obtained from Merck or BDH and were analytically pure.

Neutron irradiation

Samples of a triphenyl phosphate solution in benzene (0.5 ml, molar ratio 1:10 and 1:100) in sealed quartz ampoules were irradiated in the reactor for 2.5 min at a thermal neutron flux of $1.3 \cdot 10^{13}$ n/cm^{2}sec (gamma radiation and fast neutron dose of the order of 10^7 rad/h) or for 22 h at a flux of $2.8 \cdot 10^{10}$ n/cm^{2}sec (gamma radiation and fast neutron dose of the order of 10^5 rad/h).

For neutron activation analysis, made after inactive paper electrophoresis or chromatography, the paper strips were cut in 1 cm pieces and placed in Al-foils which were irradiated at a thermal neutron flux of $1.3 \cdot 10^{13}$ n/cm^{2}sec for 10 min. Before activity measurements the irradiated paper strips were cooled for a week so that ^{24}Na would decay.

Separation of ^{32}P species

To check for the possible appearance of ^{32}P recoil gaseous products, the quartz ampoules containing an irradiated solution of triphenyl phosphate in benzene were opened in a special apparatus in a nitrogen atmosphere and under a stream of inactive phosphine gas. Bromine water was used to oxidize the phosphine to phosphate, whose activity was subsequently checked.

An aliquot of 5–10 λ of the irradiated triphenyl phosphate solution was diluted with ethyl alcohol (1:1) and spotted on the cathode side of a Whatman 3 MM paper (2 × 100 cm) for the electrophoretic separation of chemical forms of ^{32}P.

The separation was performed by high-voltage electrophoresis[19–21] using a Virus type chamber (10,000V, 100 mA) with an agar–agar bridge, Pt-electrodes and a Cryomate Lauda 30D as the cooling system, under the following conditions: a mixture containing 96 % 0.1 M acetic acid and 4 % 0.2 M Na-acetate as the electrolyte (pH

3.7); gradient 80 V/cm, 3 mA per strip stream; temperature up to 10°. Under the above conditions the separation lasted about 100 min.

To check the results obtained by the above method a neutron irradiated TPP–benzene solution (0.5 ml) was diluted with inactive benzene to a volume of 10 ml and then extracted with water containing small amounts of anions (< 0.1 γ) of the above mentioned phosphorus oxyacids which acted as isotopic carriers.

A volume ratio aqueous/organic of one, an agitation time of 30 min and a phase separation time of 15 min were used during the extraction process. The extraction was repeated five times, and then a 10–20λ aliquot of aqueous extract containing a microgramme quantity (∼ 5 γ) of one of the above mentioned anions of phosphorus oxyacids was spotted on to Whatmann 3 MM paper and analysed by high-voltage electrophoresis.

The ^{32}P forms remaining in the organic phase after extraction were analyzed by ascending paper chromatography by the method of SVEDOV et al.[22]. For this, a 10 λ aliquot of the ethyl alcohol diluted benzene phase (1:1) was applied to acid-washed Whatman No. 1 paper strips (2 × 35 cm) and a mixture of butyl alcohol–ethyl alcohol–water (4:1:2) was used as a solvent; after 9–10 h the solvent front reached 21–22 cm at 21°.

Identification of the ^{32}P species

After electrophoretic or chromatographic separation of the ^{32}P chemical forms, the paper strips were sprayed with an acid ammonium molybdate solution and exposed to a stream of warm air and gaseous H_2S, thus obtaining characteristic blue-coloured spots of the reduced phosphomolybdate complex[23].

The identification was also performed by studying the behaviour of the ions towards oxidation and hydrolysis[24–27] (Tables I and II) and by using neutron activation analysis. This was done by electrophoresis or chromatography on paper strips of an active benzene solution of TPP parallel with a blank containing a chosen inactive phosphorus oxyacid anion which was subsequently irradiated in the reactor.

TABLE I

BEHAVIOUR OF PHOSPHORUS OXYANIONS IN OXIDATION IN NEUTRAL MEDIUM

Phosphorus oxyacid anion	I_2 in 0.1 N NaHCO$_3$, pH 7	Br$_2$ in 0.1 N NaHCO$_3$, pH 7
Orthophosphorous (HPO$_3$)$^{2-}$	In a few minutes quantitatively oxidized	Quantitatively oxidized immediately
Pyrophosphorous (H$_2$P$_2$O$_5$)$^{2-}$	o	Very slow reaction
Isohypophosphoric (HP$_2$O$_6$)$^{3-}$	o	Very slow reaction
Hypophosphoric (P$_2$O$_6$)$^{4-}$	o	In a few minutes quantitatively oxidized
Hypophosphorous (H$_2$PO$_2$)$^{1-}$	o	In one hour oxidized

Measurement of ^{32}P activity

The measurement of the activity of the bromine water (check of possible gaseous ^{32}P recoil products), the triphenyl phosphate solution after irradiation, and of the aqueous and organic phases after extraction was performed with a GM liquid

TABLE II

BEHAVIOUR OF PHOSPHORUS OXYANIONS ON HYDROLYSIS

Phosphorus oxyacid anion	After 0.1 N KOH, 30 min, T = 25°	After 1 N KOH, 60 min, T = 100°	After 1 N HCl, 120 min, T = 25°	After 4 N HCl, 60 min, T = 100°
Hypophosphorous $(H_2PO_2)^{1-}$	0	0	0	0
Pyrophosphorous $(H_2P_2O_5)^{2-}$	$\rightarrow 2\,(HPO_3)^{2-}$	$\rightarrow 2\,(HPO_3)^{2-}$	$\rightarrow 2\,(HPO_3)^{2-}$	$\rightarrow 2\,(HPO_3)^{2-}$
Isohypophosphoric $(HP_2O_6)^{3-}$	0	$\rightarrow (HPO_3)^{2-} + (PO_4)^{3-}$	$\rightarrow (HPO_3)^{2-} + (PO_4)^{3-}$	$\rightarrow (HPO_3)^{2-} + (PO_4)^{3-}$
Diphosphorous $(HP_2O_5)^{3-}$	0	0	$\rightarrow 2\,(HPO_3)^{2-}$	$\rightarrow 2\,(HPO_3)^{2-}$
Hypophosphoric $(P_2O_6)^{4-}$	0	0	0	$\rightarrow (HPO_3)^{2-} + (PO_4)^{3-}$

counter, or with a GM end-window counter after preliminary evaporation of the liquid to dryness.

The activity of the paper strips (2 × 1 cm) was measured with a well-type scintillation or a GM end-window counter. The usual corrections were made.

The radiochemical purity was checked by measuring the decrease in activity over nine half-lives. In addition, the beta energy was checked by the absorption method not only in the irradiated materials, but also at the activity peaks obtained on paper strips after electrophoresis. The activity was measured with an accuracy of ± 2 %.

RESULTS

The series of experiments made to check the possible appearance of gaseous ^{32}P recoil products have shown that in the system investigated no phosphine or any other gaseous product is formed in an amount which exceeds the sensitivity limit of our detection method (∼ 0.5 % of the total ^{32}P activity).

This finding is in accordance with the fact that triphenyl phosphate molecules are rich in oxygen so that in such a medium the reduction of phosphorus to —3 is hardly likely.

Figs. 1 and 2 represent histograms obtained by direct electrophoretic separation of ^{32}P recoil products, which show the activity (counts/min) of particular ^{32}P ionic species as a function of their path on the paper (cm).

From the complexity of the spectra obtained with fifteen activity peaks, it may be concluded that the identification was a difficult problem.

Therefore, all species were identified not only by the coincidence of the activity peaks with corresponding standards and by neutron activation analysis, but also by
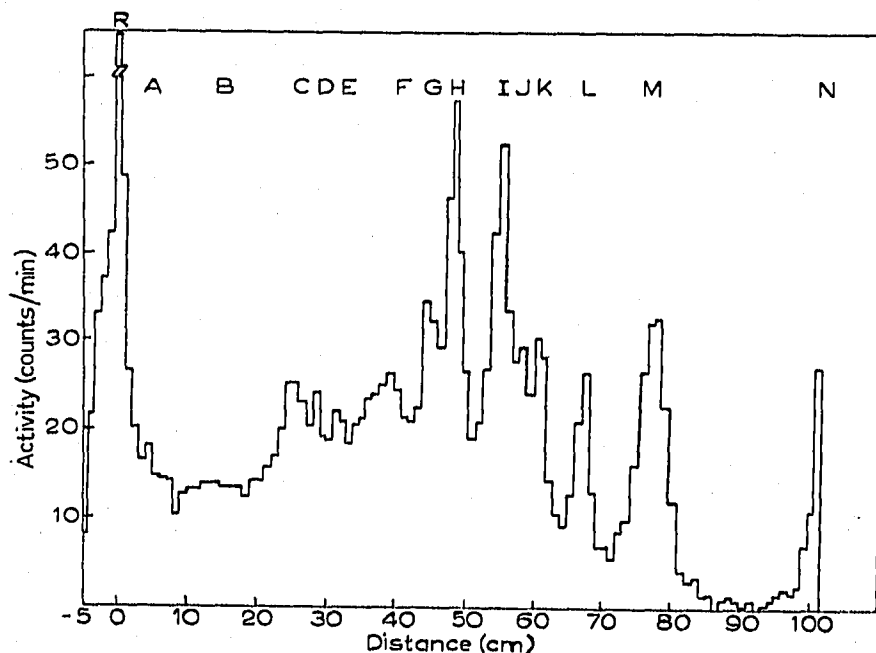

Fig. 1. Electrophoretic histogram of a benzene solution of triphenyl phosphate (molar ratio 1 : 10 irradiation condition 1.3 · 10[13] n/cm²sec, 2.5 min).
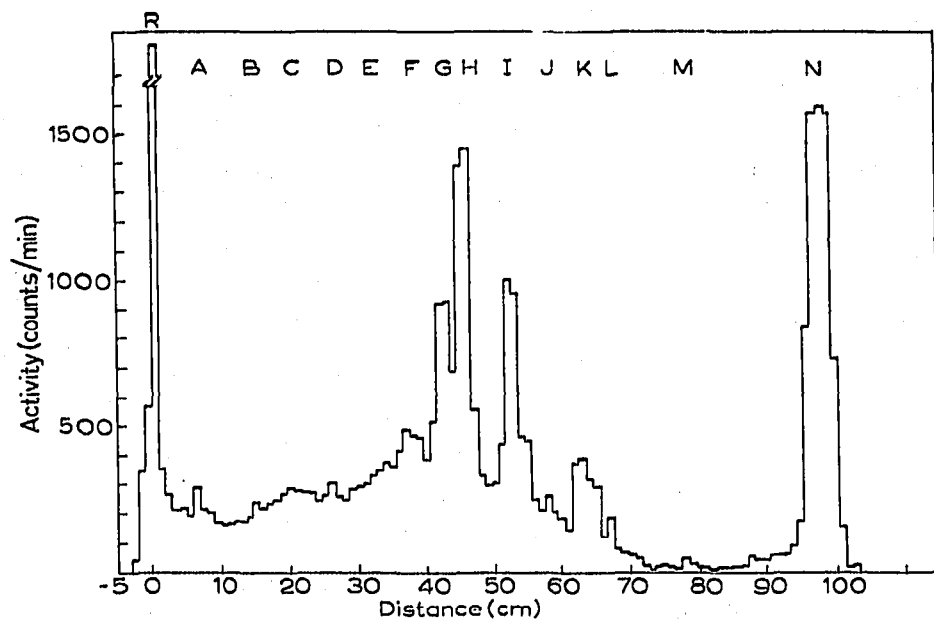
Fig. 2. Electrophoretic histogram of a benzene solution of triphenyl phosphate (molar ratio 1:10, irradiation condition 2.8·10^{10} n/cm^{2}sec, 22 h).

studying the chemical behaviour of the recoil reaction products towards oxidation and hydrolysis.

The results of all the above mentioned methods led to the identification of ^{32}P in the following forms:

R = triphenyl phosphate $(C_6H_5O)_3PO$
A = triphenyl phosphite $(C_6H_5O)_3P$
B = diphenyl phosphite $(C_6H_5O)_2HPO$
C = phenylphosphonic acid $(C_6H_5)P(O)(OH)_2$
D = diphenylphosphinic acid $(C_6H_5)_2P(O)(OH)$
E = dimethylphosphinic acid $(CH_3)_2P(O)(OH)$
F = diphenyl phosphate $(C_6H_5O)_2P(O)(OH)$
G = monomethyl phosphate $(CH_3O)P(O)(OH)_2$
H = monophenyl phosphate $(C_6H_5O)P(O)(OH)_2$
I = monophenyl phosphite $(C_6H_5O)HP(O)(OH)$
J = monophenylphosphinic acid $(C_6H_5)HP(O)(OH)$
K = orthophosphoric acid H_3PO_4
L = pyrophosphoric acid $H_4P_2O_7$
M = orthophosphorous acid $H_2(HPO_3)$
N = hypophosphorous acid $H(H_2PO_2)$.

As seen in Figs. 1 and 2 the activity peak R at the very beginning of the electrophoretic histogram was identified as the parent compound whose percentage represents the retention.

The activity peaks A, B, E and G were assigned to triphenyl and diphenyl phosphite, dimethylphosphinic acid and monomethyl phosphate, respectively. However, the identification of the first two activity peaks was less reliable owing to

the low migration rate and their comparatively low yield. In connection with the last two products, it is somewhat puzzling that ^{32}P-dimethyl phosphate, monomethyl-phosphinic acid and monomethylphosphonic acid could not be identified.

It is evident that significant changes in the retention (column R, Table III), in the total organic-bonded ^{32}P ("organic", Table III) and in the hypophosphite yield (column N, Table III) are mainly due to the irradiation conditions (see also Figs. 1 and 2).

From Table III it is also clear that the retention and the total organic ^{32}P yield tend to increase in more dilute solutions.

Table IV shows results obtained with TPP irradiated in a benzene solution containing small amounts of impurities such as dipicrylamine ($C_6H_2N_3O_6$-NH-$O_6N_3H_2C_6$), ethylenediamine (H_2N-CH_2-CH_2-NH_2) and bromine.

A comparison of the percentage distribution of the ^{32}P species in Tables III and IV shows a considerable decrease in the triphenyl phosphate R, phenylphosphonic acid C, monophenyl phosphite I, and monophenylphosphinic acid J yields if small amounts of dipicrylamine and ethylenediamine are present. Table IV also shows that the yield of R, C, I and J species is only slightly reduced if bromine is present.

The yields of all species were confirmed by the extraction method described earlier (see Separation of ^{32}P species).

The yields given in the tables are average values of at least 3–5 independent determinations. It should be stressed that owing to the difficulties encountered in analyses of these complex histograms, error estimation of the yields varies from compound to compound. It can be said that in the case of a well-separated activity peak the standard deviation of the yield is up to 10 %, while in the case of peaks not well separated, the error may be considerably greater.

Taking this fact into account, the possibility of the presence of unidentified species cannot be exluded completely, especially if they are present in low concentrations.

DISCUSSION

High-energy recoil atoms or ions lose their excess kinetic energy by collision with other atoms or recoil fragments ending their paths through matter as stable chemical species in which form they can be identified.

The importance of the present paper is primarily in showing a spectrum of the ^{32}P-labelled compounds obtained by the recoil reaction in the solution of triphenyl phosphate in benzene. So far aromatic phosphates have not been systematically studied.

The ^{32}P recoil reaction products in this system can be classified into four groups:

(a) Aromatic esters of phosphoric and phosphorous acids with characteristic C—O—P chemical bonds such as: triphenyl phosphate, diphenyl phosphate, monophenyl phosphate, triphenyl phosphite, diphenyl phosphite, and monophenyl phosphite.

(b) Aromatic organophosphorus compounds with C—P chemical bonds such as: phenylphosphonic acid, monophenylphosphinic and diphenylphosphinic acids.

(c) Simple inorganic products such as orthophosphate, pyrophosphate, ortho-phosphite, and hypophosphite.

TABLE III

³²P DISTRIBUTION IN A PURE TRIPHENYLPHOSPHATE–BENZENE SOLUTION

Irradiated system	Molar ratio	Irradiation conditions		Percentage of the total ^{32}P activity															Total ^{32}P yield in compounds	
		Thermal neutron flux (n/cm² sec)	Time	R	A	B	C	D	E	F	G	H	I	J	K	L	M	N	Organic	Inorganic
TPP–C₆H₆	1:10	1.3·10¹³	2.5 min	52.6	3.7	3.8	4.1	3.7	3.7	4.4	3.9	4.8	3.3	3.4	2.7	1.4	2.6	1.9	91.4	8.6
TPP–C₆H₆	1:10	2.8·10¹⁰	22 h	24.1	2.9	3.1	7.0	2.6	3.0	9.0	3.0	12.1	6.5	3.3	3.1	2.5	0.9	16.9	76.6	23.4
TPP–C₆H₆	1:100	1.3·10¹³	2.5 min	54.6	2.7	2.8	6.7	2.9	2.8	4.2	2.9	5.2	4.3	4.0	1.7	2.0	2.2	1.0	93.1	6.9
TPP–C₆H₆	1:100	2.8·10¹⁰	22 h	28.8	3.0	2.8	8.1	3.9	3.6	7.8	3.3	11.8	7.3	4.1	2.0	1.7	0.6	11.2	84.5	15.5

TABLE IV

³²P DISTRIBUTION IN A TRIPHENYLPHOSPHATE–BENZENE SOLUTION WITH SOME ADMIXTURES

Irradiated system	Molar ratio	Irradiation conditions		Percentage of the total ^{32}P activity															Total ^{32}P yield in compounds	
		Thermal neutron flux (n/cm² sec)	Time	R	A	B	C	D	E	F	G	H	I	J	K	L	M	N	Organic	Inorganic
TPP–C₆H₆ + dipicrylamine	1:100:1/100	1.3·10¹³	2.5 min	17.8	3.8	4.5	2.1	3.6	7.4	12.5	4.2	13.7	2.4	2.7	3.1	0.5	14.7	7.0	74.7	25.3
TPP–C₆H₆ + ethylenediamine	1:10:1/100	2.8·10¹⁰	22 h	14.5	3.4	4.6	3.7	3.5	4.5	10.1	4.0	13.1	—	11.5	—	23.8	3.3		61.4	38.6
TPP–C₆H₆ + bromine	1:10:1/100	1.3·10¹³	2.5 min	47.7	3.7	3.9	3.2	3.8	2.9	6.5	3.8	8.1	2.4	3.1	5.6	3.6	1.5	0.2	89.1	10.9

(d) Fragmentation products such as monomethyl phosphate, and dimethyl-phosphinic acid.

It is known that under certain conditions during (n, gamma) nuclear reactions, there is no breakage of the chemical bond between the newly formed atom and the parent molecule. This leads to the formation of a labelled parent compound—^{32}P-triphenyl phosphate R—in our case.

The formation of this species, according to WILLARD's[28] concept can also be due to the abundance of phenyl radicals and to the high probability of ^{32}P hot- and thermal-recombination reactions with recoil fragments. This explanation is supported by the fact that the total yield of organically bonded ^{32}P tends to increase with dilution.

The presence of diphenyl and monophenyl phosphate as well as other esters should be attributed to partial failure of bond rupture. In that case the formation of small amounts of phosphate might be also possible.

The formation of a ^{32}P-labelled pyrophosphate (P—O—P bond) recoil product could originate from a ^{32}P atom linked to the free oxygen ligand of a TPP molecule by sharing a free electron pair of this oxygen atom. This mechanism is also considered significant in the formation of pyrophosphate in inorganic systems. The collision compound formed is assumed to disintegrate yielding ^{32}P-pyrophosphate and phenyl radicals.

The formation of the aliphatic products—monomethyl phosphate and dimethyl-phosphinic acid—with a yield of about 7 % of the total ^{32}P activity does not seem to depend much on the conditions of irradiation and indicates that their presence is due to the ^{32}P recoil energy rather than to the gamma or fast neutron radiation. The presence of aliphatic species, in a similar yield, was also noticed after thermal neutron irradiation of some other aromatic systems[20,30].

The formation of the recoil products with a C—P bond can be explained as follows. During the process of deactivation, energetic ^{32}P atoms or ions in contact with the medium can produce: (a) hydrogen abstraction reactions followed probably by formation of hot radicals, (b) hydrogen displacement reactions by radioactive phosphorus whose valencies are later occupied by hydrogen or phenyl radicals, (c) insertion reactions of some radicals in the already formed C—C or C—H bond[14,31–34].

Similarly to the phenomena in inorganic phosphates and aliphatic liquid tri-n-butyl phosphate, the irradiation conditions have an effect which leads to a drop of retention from 52.6 % (for a thermal neutron flux of the order 10^{13} n/cm^{2}sec) to 24.1 % (for a thermal neutron flux of the order 10^{10} n/cm^2 sec). The influence of the irradiation conditions is also apparent in the total yield of the organic bonded ^{32}P and in the ^{32}P-hypophosphite yield.

In order to investigate the mechanism of the slowing-down process of the recoil atom according to WILLARD's concept, one should determine the degree of participation in hot and thermal reactions. Hot reactions are those produced before thermal equilibrium with the surrounding is reached.

It was shown[28] that small amounts of radical scavengers considerably affect the thermal, but not the hot reaction. It is then quite understandable that this factor should be used to distinguish between two reactions.

From the results shown in Tables III and IV it is clear that the percentage yields of parent compound R, phenylphosphonic acid C, monophenylphosphite I and

monophenylphosphinic acid J tend to decrease upon addition of radical scavengers in the form of dipicrylamine and ethylenediamine.

From the difference in the retention when dipicrylamine is present and absent, it was concluded that approximately 67 % of ^{32}P-labelled parent compound is formed in the course of diffusion—recombination processes in the ^{32}P thermal energy region, while about 33 % is due to the hot recombination reactions of the ^{32}P with recoil fragments.

The results obtained have shown also that the presence of phenylphosphonic acid, monophenylphosphinic acid and monophenyl phosphite should also be, at least to some extent, due to recombination processes of recoil ^{32}P, taking place in the region of thermal energies.

The role of amines as scavengers may, in general, be interpreted in terms of their chemical reaction with the excited molecules or the radicals formed[35-37].

The increase in the yield of mono- and diphenyl phosphate in the presence of scavengers can be explained by assuming that monoderivatives are the first step in the reaction between the recoil atom and the molecule of the medium, which in general takes place in the region which is close to the primary act. One can assume that the recoil atom bonded to the monophenyl radical can further react with a phenyl radical, or eventually it can be stabilised in the reaction with oxygen and hydrogen. The probability of bonding the second phenyl radical in the hot zone is smaller than that for the first one, where the probability for bonding the third one is lowest.

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SUMMARY

The ^{32}P activity distribution among the products of the (n,gamma) activation of triphenyl phosphate in benzene was investigated.

After thermal neutron irradiation in the reactor the solution of triphenyl phosphate in benzene was analysed by high-voltage paper electrophoresis and by a solvent extraction technique followed by paper electrophoresis and paper chromatography.

The following main groups of recoil products were found: (a) aromatic esters (C—O—P bonds) of phosphoric and phosphorous acids; (b) aromatic organophosphorus compounds (C—P bonds); (c) simple inorganic products; (d) aliphatic derivatives.

The influence of the irradiation conditions and the concentration of the solution on the yield of different ^{32}P species, particularly on the retention, the total ^{32}P organic and the ^{32}P-hypophosphite yields was noticed.

A scavenger technique has indicated that ^{32}P-triphenyl phosphate, ^{32}P-phenyl-

phosphonic acid, monophenylphosphinic acid as well as ^{32}P-monophenyl phosphite are formed at least to a certain extent by diffusion—recombination processes, taking place in the ^{32}P thermal energy region.

One can assume that in analogy to the mechanism of gradual bond breaking, the reformation of chemical bonds of ^{32}P atoms is also a stepwise process in the course of which higher substituted organic derivatives can be formed from the lower ones.

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