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## Some observations on the Labelling of $P_2S_5$ with carrier-free $^{32}P$ formed in elementary Sulphur by the Nuclear Reaction $^{32}S(n,p)^{32}P$

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$P_2S_5$  labelled with  $^{32}P$  can be obtained by synthesis or isotopic exchange. On the labelling of  $P_2S_5$  by isotopic exchange there are already some indications. Thus, J.E. Casida (<sup>1</sup>) obtained  $P_2S_5$  labelled with  $^{32}P$  by an isotopic exchange between  $HNa_2^{32}PO_4$  or  $H_3^{32}PO_4$  and  $P_2S_5$ . M. Dubini and G. P. Perucca (<sup>2</sup>) studied the labelling of  $P_2S_5$  with the carrier-free  $^{32}P$  present in the residu of distillation of the neutron irradiated elementary sulphur. The exchange yield after 3 hours at 300° C was 42%. If a mixture of red phosphorus and elementary sulphur (ratio 2 : 5) were reacted in the presence of the residual  $^{32}P$  the labelling yield of  $P_2S_5$  was 50-95% (<sup>2</sup>). From these paper (<sup>1, 2</sup>) we drew the conclusion that the labelling of  $P_2S_5$  by isotopic exchange can be carried out with  $^{32}P$  in various chemical forms. It is clear that the chemical form of the residual  $^{32}P$  (<sup>2</sup>) is not similar with  $HNa_2^{32}PO_4$  or  $H_3^{32}PO_4$  (<sup>1</sup>).

In our experiments we also studied the labelling of  $P_2S_5$  with the carrier-free  $^{32}P$  formed in elementary sulphur by the nuclear reaction  $^{32}S(n,p)^{32}P$ , but in different experimental conditions. The purpose of this paper was to obtain some information on the labelling mechanism of  $P_2S_5$ . This experiments were put in accordance with our earlier observations (<sup>3</sup>) on the chemical state of  $^{32}P$  atoms in the elementary sulphur. Thus, in the deaerated sulphur targets  $^{32}P$  atoms are stabilized in an elementary chemical state, but in the untreated sulphur targets in an oxydated chemical state. Also, we observed (<sup>4</sup>) that the carrier-free  $^{32}P$  formed in elementary sulphur can be adsorbed on the red phosphorus.

Taking into account these observations the labelling of  $P_2S_5$  with the carrier-free  $^{32}P$  in following experimental conditions was studied.

A — Synthesis of  $^{32}P_2S_5$  from red phosphorus and irradiated elementary sulphur. (ratio 2 : 5).

B — Synthesis of  $^{32}P_2S_5$  after the removal of sulphur target by the adsorbtion of  $^{32}P$  on the red phosphorus and then its reaction with the elementary sulphur (unirradiated sulphur)

C — Isotopic exchange between  $^{32}P$  atoms present in the sulphur targets and  $P_2S_5$ .

In all cases the experiments were carried out with untreated and deaerated sulphur targets.

The radioactivity induced in  $P_2S_5$  by two methods was determined :

$i$  = The transformation of  $^{32}P_2S_5$  in  $^{32}PSCl_3$  according to the chemical reaction :  
 $^{32}P_2S_5 + PCl_5 \rightarrow ^{32}PSCl_3$  and then the measuring of its radioactivity.

$i'$  = The measuring of radioactivity induced in  $PSCl_3$  by a catalysed isotopic exchange according to the chemical reaction  $^{32}P_2S_5 + PSCl_3 \rightleftharpoons ^{32}PSCl_3 + P_2S_5$ . This catalysed isotopic exchange was reported in an our earlier paper (5).

In this paper we used some notes which have the following significations :

Si.[ $^{32}Pox$ ] = untreated irradiated sulphur with  $^{32}P$  atoms stabilized in an oxydated chemical state.

Si.[ $^{32}P$ ] = deaerated irradiated sulphur with  $^{32}P$  atoms stabilized in an elementary chemical state.

Pr.[ $^{32}Pox$ ] = carrier-free  $^{32}P$  in an oxidated form adsorbed on red phosphorus.

Pr.[ $^{32}P$ ] = carrier-free  $^{32}P$  in an elementary form adsorbed on red phosphorus.

Analytical grade Z.W.K.S. (made in Poland) crystalline sulphur was irradiated in the core of the VVR-S reactor for 10-30 hours in a neutron flux of  $2 \times 10^{13}$  n/cm<sup>2</sup> sec and in a gamma flux of  $10^8$ R/hour. The amount of sulphur was 150 mg and the radioactivity of radiophosphorus 3-10 mCi/g sulphur. Red phosphorus used for synthesis of  $P_2S_5$  was Merck product.  $PCl_5$  used to transform  $P_2S_5$  in  $PSCl_3$  was B.D.H. product.  $P_2S_5$  used for isotopic exchange was obtained by synthesis from red phosphorus and elementary sulphur (6).  $PSCl_3$  used in the isotopic exchange reactions was obtained by synthesis from  $PCl_3$  and sulphur (7). The deaerated sulphur targets were obtained by a technique indicated elsewhere (8).

For the experiments A the irradiated sulphur targets were mixed with red phosphorus in the ratio 2 : 5. Then, the reaction mixture was melted on free flame in a glass ampoule and in a nitrogen current. After the end of reaction, the radioactivity of  $^{32}P_2S_5$  by two way was determined

$i$  =  $^{32}P_2S_5$  was reacted with  $PCl_5$ , then  $^{32}PSCl_3$  was distilled, hydrolysed into KOH solution and its radioactivity measured.

$i'$  =  $^{32}P_2S_5$  was treated with 10 ml of  $PSCl_3$  in the presence of  $AlCl_3$  (500 mg). After refluxing (one hour)  $PSCl_3$  was removed by distillation, hydrolysed and its radioactivity measured.

In the experiments B, to adsorb  $^{32}P$  atoms on the red phosphorus the irradiated sulphur targets were dissolved in 15 ml of  $CS_2$ , then the red phosphorus (200 mg) was added and the mixture was refluxed for 15-20 minutes. After refluxing  $CS_2$  is removed by decontation and the red phosphorus was washed with 6-7 portions of pure  $CS_2$  in order to remove all the sulphur. This red phosphorus was mixed with an amount of sulphur (ratio 2 : 5) and melted as above.

For the experiments C the irradiated sulphur targets was mixed with 1 gramme of  $P_2S_5$ , then the mixture was reacted at 150° C for one hour (experiments 1, 2 Table 2) and at 440° C for five minutes (experiments 3, 4 Table 2). Then,  $P_2S_5$  was reacted with  $PCl_5$  and  $^{32}PSCl_3$  formed was distilled, hydrolysed and its radioactivity measured. To determine the exchange yield the total radioactivity of  $^{32}P$  was measured for each experiment. The radioactivity was

measured with a standard G. M. thin Window end counter and for the  $^{35}S$  adsorbtion measurements a standard absorber of 32 mg Al/cm<sup>2</sup> was used.

In Table 1 the experimental results obtained in the synthesis of  $P_2S_5$  are presented. The results show that in all experiments the labelling yield is not affected by the chemical states of  $^{32}P$  atoms present in the irradiated sulphur targets ( $[^{32}Pox]$  or  $[^{32}P]$ ). These experiments confirm the results of J. E. Casida <sup>(1)</sup> and M. Dubini <sup>(2)</sup>.

The experiments (5-8) show that the labelling yield is not affected by the removal of sulphur targets and the adsorbtion of  $^{32}P$  atoms on the red phosphorus. On the other hand, this conclusion is very important for the obtaining of  $^{32}P_2S_5$  of a high activity (without  $^{35}S$ ) by this way.

TABLE 1. Determining of inducted radioactivity in  $^{32}P_2S_5$  obtained by its synthesis in the presence of the carrier-free  $^{32}P$  formed in elementary sulphur by nuclear reaction  $^{32}S(n, p)^{32}P$ .

No. crt.	System studied	Experimental conditions	Radioactivity of $^{32}P$	
			in residue	in $^{32}P_2S_5$
1 <sup>a</sup>	Si. $[^{32}Pox]$ + Pr	Synthesis of $P_2S_5$ in the presence of the sulphur targets (untreated sulphur)	10-38	62-90
2 <sup>b</sup>			16-30	70-84
3 <sup>a</sup>	Si. $[^{32}P]$ + Pr	Synthesis of $P_2S_5$ in the presence of the sulphur targets (deaerated sulphur)	20-25	75-80
4 <sup>b</sup>			5-27	73-95
5 <sup>a</sup>	Pr. $[^{32}Pox]$ + S	Synthesis of $P_2S_5$ after the adsorbtion of $[^{32}Pox]$ on the red phosphorus	9-38	62-91
6 <sup>b</sup>			10-27	73-90
7 <sup>a</sup>	Pr. $[^{32}P]$ + S	Synthesis of $P_2S_5$ after adsorbtion of $[^{32}P]$ on the red phosphorus	7-10	90-93
8 <sup>b</sup>			6-11	89-94

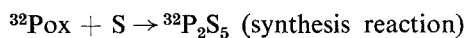
<sup>a</sup> Determination of inducted radioactivity in  $^{32}P_2S_5$  by the measuring of radioactivity of  $^{32}PSCl_3$  resulting by the following reaction :  $^{32}P_2S_5 + PCl_5 \rightarrow ^{32}PSCl_3$

<sup>b</sup> Determining of inducted radioactivity in  $^{32}P_2S_5$  by the measuring of radioactivity of  $^{32}PSCl_3$  labelled by the following isotopic exchange reaction :  $^{32}P_2S_5 + PSCl_3 \rightleftharpoons ^{32}PSCl_3 + P_2S_5$

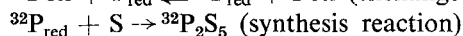
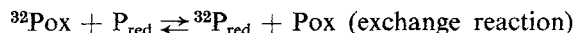
It is not possible only, by the interpretation of results presented in the table to explain the mechanism of labelling of  $P_2S_5$ .

In this discussion we thought that can be the following mechanisms. For example, we will take into consideration the case of  $[^{32}Pox]$  atoms (untreated sulphur targets).

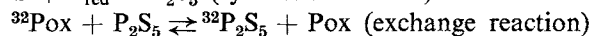
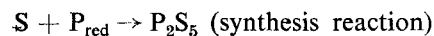
## I. The first mechanism



## II. The second mechanism



## III. The third mechanism



The first mechanism should explain the forming of  $^{32}\text{P}_2\text{S}_5$  by a direct reaction between the sulphur atoms and  $^{32}\text{P}$  atoms present in the irradiated sulphur targets.

But the existence of  $^{32}\text{P}_2\text{S}_5$  in the irradiated sulphur targets was discussed elsewhere <sup>(3, 5)</sup> and we arrived at the conclusion that the radiophosphorus atoms are not in the chemical form of  $^{32}\text{P}_2\text{S}_5$ . This conclusion results also from the following experiment. The irradiated sulphur targets were put in the same condition of temperature as a mixture of elementary sulphur and red radiophosphorus then  $^{32}\text{P}_2\text{S}_5$ , formed was investigated by the reaction with  $\text{PCl}_5$  and its transformation in  $^{32}\text{PSCl}_3$ . The existence of  $^{32}\text{PSCl}_3$  (respectively of  $^{32}\text{P}_2\text{S}_5$ ) was put into evidence only in the case of the mixture:  $^{32}\text{Pred} + \text{S}$ .

TABLE 2. Determining of inducted radioactivity in  $^{32}\text{P}_2\text{S}_5$  by the isotopic exchange reaction between the carrier-free  $^{32}\text{P}$  present in the irradiated sulphur targets and  $\text{P}_2\text{S}_5$ .

No. crt.	System studied	Experimental conditions	Radioactivity $^{32}\text{P}\%$	
			in residue	in $^{32}\text{P}_2\text{S}_5$
1	$\text{Si}.[^{32}\text{POx}] + \text{P}_2\text{S}_5 + \text{C}_2\text{H}_2\text{Cl}_4$	Refluxing at 150° C for one hour	94-98	2-6
2	$\text{Si}.[^{32}\text{POx}] + \text{P}_2\text{S}_5$	Melting at 150° C for one hour	89-95	5-11
3	$\text{Si}.[^{32}\text{POx}] + \text{P}_2\text{S}_5$	Melting at 440° C for five minutes	31-19	69-81
4	$\text{Si}.[^{32}\text{P}] + \text{P}_2\text{S}_5$	Melting at 440° C for five minutes	30-16	70-84

Other arguments in favour of an explanation that the carrier-free  $^{32}P$  formed in elementary sulphur is not in form of sulphide will be presented in a future paper.

The second mechanism should explain the forming of  $^{32}P_2S_5$  by an isotopic exchange reaction between  $^{32}P_{Ox}$  and the red phosphorus (Pred). But this mechanism is invalidated by our earlier experiments <sup>(8)</sup>. Thus, between  $^{32}P_{Ox}$  and Pred is not an isotopic exchange because in the reaction system:  $Pred[^{32}P_{Ox}] + PCl_5$  was not put into evidence the forming of  $^{32}PCl_3$ .

In Table 2 the experimental results obtained in the isotopic exchange reactions between the carrier-free  $^{32}P$  atoms and  $P_2S_5$  are presented. These results show that the labelling of  $P_2S_5$  is in accordance with the mechanism C. On the other hand, the results show that the labelling yield of  $P_2S_5$  is very much affected by the temperature.

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