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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 (1) 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 (2) studied the labelling of P_2S_5 with the carrier-free ^{32}P present in the residiu 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 residiual ^{32}P the labelling yield of P_2S_5 was 50-95% (2). From these paper (1, 2) 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 (2) is not similar with $HNa_2{}^{32}PO_4$ or $H_3{}^{32}PO_4$ (1).

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 (3) 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 (4) 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 inducted 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 inducted 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 2×10^{13} n/cm^2 sec and in a gamma flux of 10^8R/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^2 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 [1] and M. Dubini [2].

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 *a*	Si.[^{32}Pox] + Pr	Synthesis of P_2S_5 in the presence of the sulphur targets (untreated sulphur)	10-38	62-90
2 *b*			16-30	70-84
3 *a*	Si.[^{32}P] + Pr	Synthesis of P_2S_5 in the presence of the sulphur targets (deaerated sulphur)	20-25	75-80
4 *b*			5-27	73-95
5 *a*	Pr.[^{32}Pox] + S	Synthesis of P_2S_5 after the adsorbtion of [^{32}Pox] on the red phosphorus	9-38	62-91
6 *b*			10-27	73-90
7 *a*	Pr.[^{32}P] + S	Synthesis of P_2S_5 after adsorbtion of [^{32}P] on the red phosphorus	7-10	90-93
8 *b*			6-11	89-94

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

b 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

$^{32}Pox + S \rightarrow {}^{32}P_2S_5$ (synthesis reaction)

II. The second mechanism

$^{32}Pox + P_{red} \rightleftarrows {}^{32}P_{red} + Pox$ (exchange reaction)
$^{32}P_{red} + S \rightarrow {}^{32}P_2S_5$ (synthesis reaction)

III. The third mechanism

$S + P_{red} \rightarrow P_2S_5$ (synthesis reaction)
$^{32}Pox + P_2S_5 \rightleftarrows {}^{32}P_2S_5 + Pox$ (exchange reaction)

The first mechanism should explain the forming of $^{32}P_2S_5$ by a direct reaction between the sulphur atoms and ^{32}P atoms present in the irradiated sulphur targets.

But the existence of $^{32}P_2S_5$ in the irradiated sulphur targets was discussed elsewhere [3, 5] and we arrived at the conclusion that the radiophosphorus atoms are not in the chemical form of $^{32}P_2S_5$. 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 $^{32}P_2S_5$, formed was investigated by the reaction with PCl_5 and its transformation in $^{32}PSCl_3$. The existence of $^{32}PSCl_3$ (respectively of $^{32}P_2S_5$) was put into evidence only in the case of the mixture: $^{32}Pred + S$.

TABLE 2. Determining of inducted radioactivity in $^{32}P_2S_5$ by the isotopic exchange reaction between the carrier-free ^{32}P present in the irradiated sulphur targets and P_2S_5.

No. crt.	System studied	Experimental conditions	Radioactivity ^{32}P%	
			in residue	in $^{32}P_2S_5$
1	Si.[^{32}Pox] + P_2S_5 + $C_2H_2Cl_4$	Refluxing at 150° C for one hour	94-98	2-6
2	Si.[^{32}Pox] + P_2S_5	Melting at 150° C for one hour	89-95	5-11
3	Si.[^{32}Pox] + P_2S_5	Melting at 440° C for five minutes	31-19	69-81
4	Si.[^{32}P] + P_2S_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}Pox and the red phosphorus (Pred). But this mechanism is invalidated by our earlier experiments [8]. Thus, between ^{32}Pox and Pred is not an isotopic exchange because in the reaction system: Pred[^{32}Pox] + 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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