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Abstract

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ISOMER Pd^{111*}

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In a previous work (^{1}) it was established that, upon irradiation of cadmium with 14 MeV neutrons, three palladium activities are formed, with half-lives of 22 min, 5.5 hr, and 14 hr. As a result of a radiochemical investigation it was proved that the half-lives $T = 22$ min and 14 hr belong to the known palladium isotopes Pd^{111} and Pd^{109}, formed by the reactions Cd$^{114}(n,\alpha)$Pd^{111} and Cd$^{112}(n,\alpha)$Pd^{109}. The assignment of the 5.5-hour period to a definite isotope or isomer of palladium was not proved.

In the literature there is only one brief report (^{2}) stating that this period was obtained upon irradiation of palladium with deuterons and was identified as the isomer Pd^{111*}, decaying according to the scheme

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                    75%
(5.5 hr) Pd^111*          $\rightarrow$  Pd^111 (22 min)

         $\beta$-                         $\beta$-
         25%
        ↓                           ↓
             Ag^111 (7.5 days)

                      $\beta$-
                    ↓
             Cd^111 (stable)
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On the basis of this report, Pd^{111*} appears in Seaborg’ s isotope tables for 1953 (^{3}) with the reliability rating “B.” In the later tables of A. N. Nesmeyanov (1954) (^{4}), however, it is not listed.

We therefore considered it advisable to prove unambiguously the assignment of the 5.5-hour palladium activity to a definite isotope or isomer of palladium. For this purpose experiments were carried out on the radiochemical separation of isomers in a mixture of radioactive palladium isotopes formed by the reactions Cd(n,α) and Pd(n,γ).

The method of chemical separation of nuclear isomers is based, as is known, on the Szilard-Chalmers effect. In an isomeric transition, if it is fully or partially converted, the atoms of the isomer in the ground state prove to be multiply ionized, i.e., they change their valence and consequently their chemical properties, and under certain conditions they can be separated from the atoms of the parent isomer by ordinary chemical methods. The most favorable conditions for successful separation are the following: the isomer in the higher excited state is present as part of an organic compound soluble in organic solvents and insoluble in water. In this case the inorganic ions of the daughter isomer, expelled from the organic molecule during the isomeric transition, are simply washed out with water and then precipitated with a carrier from the aqueous solution by a specific precipitant.

In developing a method for separating palladium isomers, we tested a series of organic reagents that form water-insoluble compounds with palladium: dimethylglyoxime, acetoxime, salicylaldoxime

and α-nitroso-β-naphthol. The most convenient reagent proved to be salicylaldoxime, which selectively precipitates palladium from strongly acidic aqueous solutions in the form $Pd(C_7H_6O_2N)_2$. The precipitate, dried at 110°, has a constant composition (28.17% Pd).

Table 1

No. of experiment	Volume of saturated $Pd(C_7H_6O_2N)_2$ in benzene, ml	Weight of $Pd(C_7H_6O_2N)_2$, isolated from the solution, mg	Solubility, mg/100 ml
1	10	7.3	73
2	10	7.0	70
3	10	7.9	79

Table 1 presents data on the solubility of palladium salicylaldoximate in benzene, found by the gravimetric method, and Table 2 gives data on the distribution coefficient of palladium salicylaldoximate between benzene and water, obtained with the use of the radioactive indicator Pd^{109}.

From Tables 1 and 2 it follows that salicylaldoximate is convenient for the separation of nuclear isomers of palladium: it is satisfactorily soluble in benzene (70 mg/100 ml) and about four orders of magnitude less soluble in water.

Separation of the isomers Pd^{111*} and Pd^{111} formed in the reaction $Cd^{114}(n, \alpha)Pd^{111}$. 400 g of cadmium nitrate were irradiated for 4 hours in a flux of 14-MeV neutrons of ~10^7 neutrons/$cm^2 \cdot$ sec. The irradiated salt was dissolved in water, and from the solution, with carrier (100 mg), palladium salicylaldoximate was precipitated. The solution above the precipitate was decanted, and the precipitate was washed several times with a 1% nitric-acid solution until the unbound salicylaldoxime had completely disappeared from the wash waters. The washed precipitate was dissolved in 200 ml of hot benzene, the solution was diluted with 2 l of cold benzene and washed several times with water and with an acidic (pH ~ 1) solution of $Pd(NO_3)_2$ (until a clear lemon-yellow solution was obtained, rapidly and cleanly separating from water).

Table 2

No. of experiment	Activity of Pd^{109} extracted from 1 ml of benzene, p-p-a, imp/min	Activity of Pd^{109} in water (100 ml) after shaking with 50 ml of benzene, p-p-a, imp/min	Distribution coefficient water/benzene
1	35100	430	$1.2 \cdot 10^{-4}$
2	32500	560	$1.7 \cdot 10^{-4}$
3	36800	550	$1.5 \cdot 10^{-4}$

10 hours after the end of irradiation the benzene solution was shaken vigorously in a separatory funnel with 150 ml of an acidic (pH ~ 1) aqueous solution of $Pd(NO_3)_2$ (50 mg). The aqueous layer was separated, and the palladium in it was precipitated with dimethylglyoxime. The precipitate was quickly dried and its activity measured with a Geiger counter. The activity decreased with a period $T = 21.5$ min., in good agreement with the value of the half-life of Pd^{111} reported in the literature.

Thus it was shown that in the mixture of radioactive isotopes of palladium formed by the reactions Cd(n, α)Pd, there is present the isomer Pd^{111*}, genetically related to Pd^{111} ($T = 22$ min.).

Fig. 1. Decay curves of the activity of Pd^{111}, washed out from a benzene solution of the salicylaldoximate of a mixture of radioactive palladium isotopes formed by the reaction (n, γ). The activity was measured:
a –through 310 mg/cm^2 Al; b –through 440 mg/cm^2 Al

Identification of Pd^{111*} ($T = 5.5$ h) in a mixture of radioactive palladium isotopes formed in the reactions Pd(n, γ). 50 mg of metallic palladium were irradiated for 1 hour in a neutron flux of ~$5 \cdot 10^{11}$ $neutrons/cm^2 \cdot sec$. The irradiated metal was dissolved in aqua regia, and palladium was precipitated from the solution with salicylaldoxime. The precipitate was wash-

was washed and dissolved in benzene as described above. The solution was divided into two equal parts. By shaking with carrier solutions, Pd^{111} was separated from one part every 2 hours over the course of a day, and Ag^{111} from the other. The palladium was then precipitated from the aqueous solution with dimethylglyoxime, and the silver with hydrochloric acid.

In Fig. 1 are shown typical decay curves of the activity of palladium precipitates. The activity of the precipitates was measured through aluminum filters

Fig. 2

Figure 1: Fig. 2

Fig. 3

Figure 2: Fig. 3

of 310 mg/cm^2 (a) and 440 mg/cm^2 (b). In measurements without an absorber, the 22-minute period of Pd^{111} is appreciably distorted by the 14-hour period of Pd^{109}, whose yield in the (n, γ) reaction is several orders of magnitude higher than the yield of Pd^{111*}. Figure 2 presents a typical decay curve of the activity of radioactive silver precipitates. Figures 3 and 4 illustrate the kinetics of the change in the initial activities of Pd^{111} and Ag^{111} as a function of the time of separation. Both activities decrease with a period $T \approx 5.5$ hours, in good agreement with the value of the half-life of Pd^{111*} given in the literature.

Fig. 2. Decay curves of the activity of Ag^{111}, washed out from a benzene solution of the salicylaldoximate of a mixture of radioactive palladium isotopes formed in the (n, γ) reaction.

Thus, the formation of Pd^{111*} with $T = 5.5$ h in the reaction $Pd(n, \gamma)$ was established, and its genetic connection with Pd^{111} with $T = 22$ min and Ag^{111} with $T = 7.5$ days was demonstrated.

The data of this experiment were used to estimate the conversion coefficient of the isomeric transition $Pd^{111*} \to Pd^{111}$. Since separation of the isomers should be expected only in the case of a converted transition, the lower limit of the coefficient of internal conversion can be determined as the ratio of the number of Pd^{111*} atoms (a) that decayed during a given time interval with expulsion from the organic molecule to the total number of Pd^{111*} atoms (b) that decayed during this time.

Fig. 3. Decay curves of Pd^{111*}, obtained by repeated separations at equal time intervals of the daughter Pd^{111} (22 min.) (a and b, see Fig. 1).

The quantity a was found from the relation $a = \Delta I_{Pd^{111}}/k_1$, where $\Delta I_{Pd^{111}}$ is the decrease in the activity of Pd^{111} in a definite 2-hour interval (the difference of ordinates in Fig. 3), and k_1 is the coefficient of absorption of the radiation of Pd^{111} in the aluminum filter and the counter wall. The quantity b was found from the activity of Ag^{111} accumulated over the same time period (the corresponding ordinate in Fig. 4) from the relation $b = I_{Ag^{111}}/k_2$ (k_2 is the coefficient of absorption of the activity of Ag^{111} in the counter wall).

Fig. 4

Figure 3: Fig. 4

Fig. 4. Decay curve of Pd^{111*}, obtained by repeated separations of daughter Ag^{111} (7.3 days).

The internal conversion coefficient calculated in this way was found to be $\alpha = a/b \geq 0.185$. Taking into account the given decay scheme $Pd^{111} \rightarrow Pd^{111}$, $\alpha \geq 0.185 : 0.75 = 0.25$.

Determination of the relative yield of Pd^{111} and Pd^{111*} in the (n, γ) reaction.

As a result of irradiation with thermal neutrons of a natural mixture of iso-

palladium isotopes, the isomer Pd^{111*} is formed in a mixture with other radioactive isotopes of palladium. The activity of the latter, mainly Pd^{109} with $T = 14$ h, completely masks the weak activity of Pd^{111*}. Therefore determination of the yield of Pd^{111*} from its activity is impossible in this case. In the present work the relative yield of Pd^{111*} and Pd^{111} was determined as a result of studying the kinetics of accumulation of radioactive silver in samples of irradiated palladium.

0.5 g of metallic palladium was irradiated for 15 min with fission neutrons. The irradiated metal was dissolved in aqua regia and the solution divided into three parts. In each of the parts silver was precipitated (by repeated addition of carrier) at 5.5, 15, 27, and 80 h after the end of irradiation. The AgCl precipitates were reprecipitated from ammonia, dried, and their activity was measured with a Geiger counter. The results of the measurements are presented in Table 3.

Table 3

Time after the end of irradiation, h	Activity of precipitates	Activity of precipitates	Activity of precipitates	Activity of precipitates
	1	2	3	Mean
5.5	$3.78 \cdot 10^6$	$3.82 \cdot 10^6$	$3.78 \cdot 10^6$	$(3.79 \pm 0.02) \cdot 10^6$
15	$5.95 \cdot 10^4$	$6.70 \cdot 10^4$	$5.75 \cdot 10^4$	$(6.13 \pm 0.38) \cdot 10^4$
27	$1.91 \cdot 10^4$	$1.89 \cdot 10^4$	$2.20 \cdot 10^4$	$(2.00 \pm 0.13) \cdot 10^4$
80	$7.00 \cdot 10^3$	$5.80 \cdot 10^3$	$5.70 \cdot 10^3$	$(6.10 \pm 0.53) \cdot 10^3$

The calculation of the relative yields of Pd^{111} and Pd^{111*} was carried out from these data as follows: the activity of the silver separated after 5.5 h ($I_{5.5\ \mathrm{h}}$) is due to the decay of all Pd^{111} (22 min) and half of Pd^{111*} (5.5 h); the sum of the activities of Ag^{111} separated after 15, 27, and 80 h (ΣI) is due to the decay of the remaining half of Pd^{111*} (according to Table 3 it is easy to see that the activities separated after 15, 27, and 80 h are genetically related only to the 5.5-hour precursor). Hence

$$\sigma_{\mathrm{Pd}^{111}}/\sigma_{\mathrm{Pd}^{111*}} = (I_{5.5\ \mathrm{h}} - \Sigma I) : 2\Sigma I = (3.79 \cdot 10^6 - 8.73 \cdot 10^4) : 2 \cdot 8.73 = 22.$$

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CITED LITERATURE

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