COMMUNICATIONS TO THE EDITOR

THE TETRAVALENT AND PENTAVALENT STATES OF PROTACTINIUM

Sir:

It was presumed for some time that protactinium exists in the V state though it had been suggested that the III and IV states might be found.[1] Recently several workers have reported its existence in the IV state.[2,3,4] The analytical data and other evidence for the existence of these states are not unequivocal.

We have recently prepared on the microgram scale two anhydrous compounds of protactinium (IV) which demonstrate the stability of tetravalent protactinium and, in addition, one compound which is definitely in the V state.

The dioxide, PaO_2, a black solid, was prepared during an attempt to reduce the white volatile chloride ($PaCl_5$?) with zinc at 600°. Evidently enough water was present to hydrolyze the product to the oxide. The tetrachloride, $PaCl_4$, a yellow-green solid, volatile *in vacuo* at 400°, was prepared by action of hydrogen on the "$PaCl_5$" at 800°.

The formulas of both compounds were established by analysis of the X-ray diffraction patterns. The tetrachloride has the tetragonal UCl_4-type structure.[5] The unit cell dimensions for the set of isostructural compounds are

	a_1, Å.	a_3, Å.
$ThCl_4$	8.490 ± 0.001	7.483 ± 0.001
$PaCl_4$	8.377 ± .004	7.482 ± .004
UCl_4	8.303 ± .001	7.483 ± .001
$NpCl_4$	8.27 ± .01	7.48 ± .01

The dioxide has the fluorite structure and is thus isostructural with the dioxides of the other 5f-elements from thorium to americium. The unit cell constant is $a = 5.05 \pm 0.001$ Å.

The cubic form of Pa_2O_5, with a unit cell constant of 5.416 ± 0.001 Å., was obtained as a white solid by heating the dioxide to 1100° in oxygen. The oxide obtained by heating the hydrated oxide precipitated from solution is also cubic with a unit cell constant of 5.46 ± 0.01 Å. Its approximate composition is $PaO_{2.25}$ and *not* Pa_2O_5 as has been reported.[1] Other intermediate compositions were obtained by heating $PaO_{2.25}$ at elevated temperatures in pure oxygen or hydrogen. The cubic oxide phase extends over the entire range from PaO_2 to Pa_2O_5, the unit cell constant decreasing with increasing oxygen content.

(1) A. von Grosse, THIS JOURNAL, **52**, 1744 (1930); *Proc. Roy. Soc. (London)*, **A150**, 369 (1935); *J. Russ. Phys.-Chem. Soc.*, **60**, 844 (1928).

(2) W. H. Zachariasen, *Acta Cryst.*, **2**, 388 (1949).

(3) G. Bouissieres and M. Haissinsky, *J. Chem. Soc.*, Supplementary Issue No. 2, S-256 (1949).

(4) R. Elson, ANL-4252, p. 9, Oct.-Dec. 1948; paper presented before Detroit Meeting of Am. Chem. Soc., April, 1950.

(5) R. C. L. Mooney, *Acta Cryst.*, **2**, 189 (1949).

A second form of Pa_2O_5, orthorhombic and isostructural with U_2O_5, Ta_2O_5 and Nb_2O_5, was obtained as a white solid in the course of an attempt to prepare a fluoride by action of bromine pentafluoride on $PaO_{2.25}$ at 400°. This oxide represented material volatilized out of the original sample, suggesting the existence of a volatile fluoride or oxyfluoride.

Attempts to prepare the tetravalent bromide and iodide of protactinium by methods analogous to those used for the preparations of the corresponding compounds of the other heavy elements have yielded compounds whose X-ray diffraction patterns have not yet been interpreted.

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SYNTHESIS OF PHENYLALANINE AND TYROSINE IN YEAST

Sir:

Little evidence exists to indicate the biological origin of the benzenoid amino acids phenylalanine and tyrosine. In the present experiments yeast (*S. cerevisiae*) was grown in a medium containing glucose and small amounts of acetate. The labeled substrate was 1-C^{13}, 2-C^{14} acetate in one experiment and 1-C^{14} glucose[1] in another. The hydrolysates from the yeast proteins were separated on columns of Dowex 50.[2] It will be seen (Table I) that in a medium containing glucose

TABLE I

ISOTOPE CONCENTRATIONS IN YEAST CONSTITUENTS

Yeast grown in medium containing 0.555 mole *d*-glucose, 0.054 mole of acetic acid, 100 mg. *meso*-inositol.

	Labeled substrate		
	$C^{14}H_3C^{13}OOH$		1-C^{14} glucose 800 c.p.m. C^{14}
	c.p.m. C^{14}[a]	at % excess C^{13}	c.p.m. C^{14}[a]
Acetate added	23,000	10.4	0
Acetate recovered	1,300	0.70	800
Protein	2,000	0.91	690
Glutamic a.	3,700	1.83	...
Aspartic a.	730	0.25	...
Tyrosine	20	0.03	530
Phenylalanine	20	0.02	540
Leucine	3,300	1.27	...
Lysine	6,200	2.97	...

[a] All samples counted after conversion to $BaCO_3$ and correction to infinite thickness.

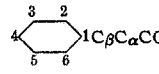
(1) D. E. Koshland and F. H. Westheimer, THIS JOURNAL, **72**, 3383 (1950).

(2) W. H. Stein and S. Moore, *Cold Spring Harbor Symp. Quant. Biol.*, **XIV**, 179 (1950).

and acetate, acetate carbon is extensively utilized in the synthesis of glutamic and aspartic acids, leucine and lysine, but not for the synthesis of phenylalanine and tyrosine. Hence neither acetate nor intermediates derived from acetate (α-ketoglutarate, oxaloacetate) could have been precursors for the benzenoid amino acids. On the other hand, carbon from 1-C^{14} glucose appears in the benzene rings and in the β positions of the side chains of the two amino acids (Table II). Carbon atoms 1, 3 and 5 of the ring obtained as bromopicrin after conversion of tyrosine to picric acid[3] contained no significant radioactivity. Carbons 2 and 6 of the ring, obtained as bromopicrin after conversion of phenylalanine to *p*-bromo, *o*-nitroacetanilide had a specific activity which accounted for about three-fourths of the total activity in the benzene ring.

TABLE II

DISTRIBUTION OF C^{14} IN PHENYLALANINE AND TYROSINE IN PROTEIN FROM YEAST GROWN ON 1-C^{14} GLUCOSE



	Tyrosine[c] c.p.m. C^{14}[d]	Phenylalanine[c] c.p.m. C^{14}[d]
Total	26 ± 3	22 ± 2
COOH[a]	3 ± 1	1 ± 1
β-Carbon[b]	77 ± 8	97 ± 10
Picric acid	23 ± 8	.....
2,4-Dinitroaniline	....	17 ± 2
$C_{1,3,5}$	2 ± 1	.....
$C_{2,6}$	....	37 ± 4
C_2 or C_6 calcd.	....	74 ± 7

[a] By tyrosine decarboxylase and ninhydrin respectively. [b] By decarboxylation of *p*-hydroxybenzoic acid and of benzoic acid respectively. [c] Degradations were performed after dilution of the isolated amino acids by non-isotopic phenylalanine and tyrosine. [d] All samples counted after conversion to $BaCO_3$ and corrected to infinite thickness.

If two isotopically equilibrated 3-carbon intermediates from 1-C^{14} glucose condensed, any resulting six-membered ring would contain C^{14} at adjacent carbon atoms or in para position. The observed isotope distribution rules out this possibility. If, on the other hand, benzene rings were formed by direct cyclization of 1-C^{14} glucose, C^{14} should be present in one position only. Our data indicate that at least three-fourths of the radioactivity in the benzene rings is present in positions 2 and 6. Since no reactions of glucose other than formation of two-carbon units are known which would lead to the appearance of C^{14} in meta positions, and since acetate is excluded as an intermediate it is likely that only C_2 or C_6 is labeled. The data are therefore best explained by assuming a cyclization of glucose to form the benzene rings of phenylalanine and tyrosine. This conclusion is in accord with data of Baddiley, Ehrensvärd, *et al.*,[3] on tyrosine synthesis in *Torulopsis utilis* grown on acetate as the sole substrate, assuming that under their conditions acetate was utilized by way of glucose.

It can be calculated from the data in the tables that the specific activity in the benzene rings was less than that of the glucose. The possibility that the inositol present in the nutrient medium is responsible for this isotope dilution is being investigated.

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(3) F. Baddiley, G. Ehrensvärd, E. Klein, L. Reio and E. Saluste, *J. Biol. Chem.*, **183**, 777 (1950).

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ADSORPTION OF IRON BY ANION EXCHANGE RESINS FROM HYDROCHLORIC ACID SOLUTIONS[1]

Sir:

As part of a more general study of the anion exchange behavior of metal ions in chloride and fluoride solutions it was found that iron(III) can be strongly adsorbed from relatively concentrated hydrochloric acid solutions.

The results of a series of elution experiments with tracer Fe^{59} and 0.023 cm.^{2} columns of Dowex-1 are shown in Table I. The elution constants $E = dA/V$ (where d = distance in cm. an adsorption band moves when V ml. of eluent pass through a column of cross sectional area A sq. cm.) were found to decrease rapidly with increasing hydrochloric acid concentrations above *ca.* 1 M and to reach the very small values of 2×10^{-4} in *ca.* 9 M HCl. In this respect Fe(III) is quite similar to Pa(V) which was previously discussed.[2] Adsorption is probably due to the formation of a strongly adsorbable negatively charged iron complex (or complexes) *e.g.*, $FeCl_4^-$ of probable negative charge minus one, the concentration of which increases with increasing hydrochloric acid concentration.

TABLE I

ADSORPTION OF Fe(III) BY DOWEX-1 FROM HYDROCHLORIC ACID SOLUTIONS

M HCl	E	D[a]	M HCl	E	D
0.5	1.74	0.16	4.0	0.0148	67
1.0	1.34	0.33	5.0	.0037	270
2.0	0.42	1.94	6.0	.00218	460
3.0	0.038	26	9.0	.00017	5900

[a] Calculated from equation $E = 1/(i + D)$ where i is the fractional interstitial space (*ca.* 0.42) and D is the volume distribution coefficient (amount per ml. of resin/amount per ml. of solution).

In view of this strong adsorbability of iron it can easily be separated from metal ions which do not form negatively charged complexes (*e.g.*, alkali metals, alkaline earths, etc.). In this con-

(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory. Part of this work was previously reported in report ONRL-286 (June, 1949).

(2) K. A. Kraus and G. E. Moore, THIS JOURNAL, **72**, 4293 (1950).