

THE PREPARATION OF HAFNIUM-FREE ZIRCONIUM

Sir:

We have recently performed a series of experiments which indicate that silica gel strongly and preferentially adsorbs hafnium compounds from a zirconium-hafnium compound mixture in certain organic solvents, and that this fact provides a new, simple, and effective means of preparing hafnium-free zirconium.

A solution of 455 g. of zirconium tetrachloride dissolved in 2275 ml. of anhydrous methanol was allowed to stand for three hours and filtered. The filtered solution contained 106 mg. total oxide per ml. A column 30" in length \times 27 mm. in diameter was packed with 290 g. of 28 to 120 mesh silica gel which had been purified by elution with 1:1 nitric acid and activated four hours at 300°. The column was prepared by sludging silica gel and methanol, and hence initially contained approximately 200 ml. of methanol; 1800 ml. of the above solution was then fed into the column, the flow being from bottom to top at a rate of 200 ml./hr. The effluent was collected in approximately 200-ml. batches and the total oxides in 5-ml. aliquots of each batch precipitated and analyzed spectrographically. The results were as shown (weights refer to ignited oxide, analyses to per cent. hafnium in sample).

TABLE I

COMPOSITION OF SUCCESSIVE BATCHES

No.	1	2	3	4	5	6	7	8	9
Wt. g.	7	18.2	21.5	22.5	22.9	25.0	24.7	18.5	22.1
% Hf	^a	0.00	0.03	0.15	0.38	0.66	0.80	0.93	1.10

^a Analysis uncertain due to large Fe and Ti content. The ZrCl₄ used contained approximately 0.13% FeCl₃ and 0.53% TiCl₄.

The column was then stripped with one liter of methanol made 1.2 M in anhydrous hydrochloric acid, the eluant being collected in four fractions. Analyses over 15% Hf are rough spectrographic estimates since the method has not yet been extended to this region.

TABLE II

COMPOSITION OF FRACTIONS OF ELUANT

No.	1	2	3	4
Wt. g.	9.0	2.5	0.68	0.48
% Hf	1.8	15	60	40

Similar, but not quite so striking results have been obtained using acetone instead of methanol as solvent; the degradation of acetone by zirconium tetrachloride tends to cause tars and clogging in the column which causes some inconvenience.

To summarize: Hafnium in zirconium may be reduced to less than 0.1% by passing a 1:5 solution of the chlorides in methanol through a silica gel column; 290 g. silica gel will furnish 60 g. purified oxide; the column can be stripped with 1

M anhydrous hydrochloric acid in methanol and re-used. By feeding in an oxide equivalent of approximately 65 g., in this case, the purified oxide yield would be about 90%.

Work on the mechanism of this and similar processes is being continued and will be reported at a later date.

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INSTITUTE FOR ATOMIC RESEARCH AND
DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE, AMES, IOWA

ROBERT S. HANSEN

WORK PERFORMED IN THE AMES LABORATORY
ATOMIC ENERGY COMMISSION

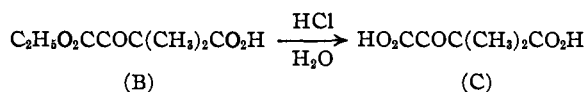
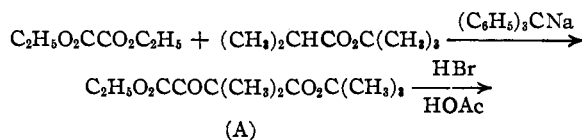
KEITH GUNNAR

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THE METAL ION CATALYZED DECARBOXYLATION OF DIMETHYLOXALOACETIC ACID

Sir:

Recent investigations¹ of the metal ion catalysis of the enzymatic and non-enzymatic decarboxylation of oxaloacetic acid have prompted us to make a detailed study of the mechanism of the decarboxylation of α, α -dimethylloxaloacetic acid and of its monoethyl ester. The synthesis of these compounds is outlined below.



The condensation was carried out by Hauser's method,² the cleavage of the *t*-butyl ester, A, by a method based on the work of Tronow,³ and the hydrolysis of the ethyl ester, B, by a method based on the work of Michael.⁴

Anal. Calcd. for diester, A, (b. p. 107–111° (7 mm.)): C, 59.0; H, 8.20. Found: C, 58.7; H, 8.21. Calcd. for monoester, B, (m. p. 38–39°): C, 51.0; H, 6.43. Found: C, 50.8; H, 6.44. Calcd. for diacid, C, (m. p. 105.5–106.5°): C, 45.0; H, 5.03. Found: C, 45.1; H, 5.18.

Both the monoester and the diacid decarboxylated smoothly at 25° in aqueous solutions of pH between 2 and 7 to form the expected products. (The 2,4-dinitrophenylhydrazone of α -keto- β -methylbutyric acid melted⁵ at 194–194.5°; the

(1) L. Krampitz and C. Werkman, *Biochem. J.*, **35**, 595 (1941); H. Krebs, *ibid.*, **36**, 303 (1942); A. Kornberg, S. Ochoa and A. Mehler, *J. Biol. Chem.*, **174**, 159 (1948); J. Speck, *ibid.*, **178**, 315 (1949); P. Nossal, *Australian J. Exptl. Biol. Med. Sci.*, **27**, 143 (1949).

(2) B. Hudson, Jr., and C. Hauser, *THIS JOURNAL*, **63**, 3156 (1941).

(3) B. Tronow and N. Ssibgatullin, *Ber.*, **62B**, 2850 (1929).

(4) A. Michael and J. Bucher, *ibid.*, **29**, 1792 (1896).

(5) G. Ramage and J. Simonsen, *J. Chem. Soc.*, 532 (1935).