tion of per acid was checked by titration[9] of aliquots at timed intervals. At the end of 111.7 hours at room temperature the adduct had consumed exactly one molar equivalent of per acid, and would take up no more.

Per acid titration of a 0.246-g. sample of B was carried out in the same manner. During the course of the reaction, the product crystallized from solution. Exactly one molar equivalent of per acid had been consumed when the reaction stopped, 125.9 hours after mixing. The crystalline product was filtered, washed, and purified by sublimation under high vacuum. The product sintered above 300°.

Anal. Calcd. for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 61.68; H, 4.28.

Hydrogenation of the Adducts.—To 0.10 g. of Adams catalyst prereduced in 10 ml. of ethanol was added 0.400 g. of adduct A dissolved in 40 ml. of alcohol. Hydrogenation at atmospheric pressure and room temperature progressed to the absorption of one molar equivalent of hydrogen (45 ml.) in the course of five and one-half hours, and stopped. After removal of catalyst and solvent, the crude dihydro product melted at 240–245° as reported by Reppe.

A similar hydrogenation of 0.30 g. of B in methanol likewise progressed to the extent of exactly one mole up take (37 ml.) of hydrogen in one hour and stopped.

Acknowledgment.—We gratefully acknowledge receipt of several samples of purified cycloöctatetraene from General Aniline and Film Corp., Easton, Pa.

[9] See ref. 7, p. 434.

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The Anion-exchange Separation of Zirconium and Hafnium[1]

BY E. H. HUFFMAN AND R. C. LILLY

An effective separation of zirconium and hafnium as negative fluo-ions has been obtained by using one of the strongly basic anion exchange resins recently developed, although earlier attempts using the weakly basic resins first available were unsuccessful.

Twenty milligrams of zirconium and 10 mg. of hafnium, as oxides, were added to zirconium and hafnium tracers in a small amount of hydrofluoric and nitric acids, warmed until dissolved, and fumed with 0.5 ml. of sulfuric acid. The residue was dissolved in water and the hydroxides precipitated with ammonium hydroxide. The precipitate was centrifuged, washed with water, dissolved in 5 ml. of 0.64 *M* hydrofluoric acid and diluted to 10 ml. with water. Six hundred milligrams of 200–325 mesh Amberlite IRA-400 resin, in its original chloride form, was added to the sample and the mixture shaken for three hours. The resin was separated from the solution and washed well with 10 ml. of water. Tracer count of the solution and washings indicated that 96% adsorption had taken place. This portion of resin was slurried onto the top of a column of the same resin 30 cm. in length and 0.78 sq. cm. in cross section. Elution with a solution of 0.2 *M* hydrochloric acid and 0.01 *M* hydrofluoric acid at the rate of 6 ml. per hour gave the results shown in Fig. 1. The solid parts of the curve were obtained by counting Zr^{95} and Hf^{181} tracers and the dotted parts by spectrographic analysis. The order of elution of the two elements is the reverse of that obtained by cation-exchange.[2]

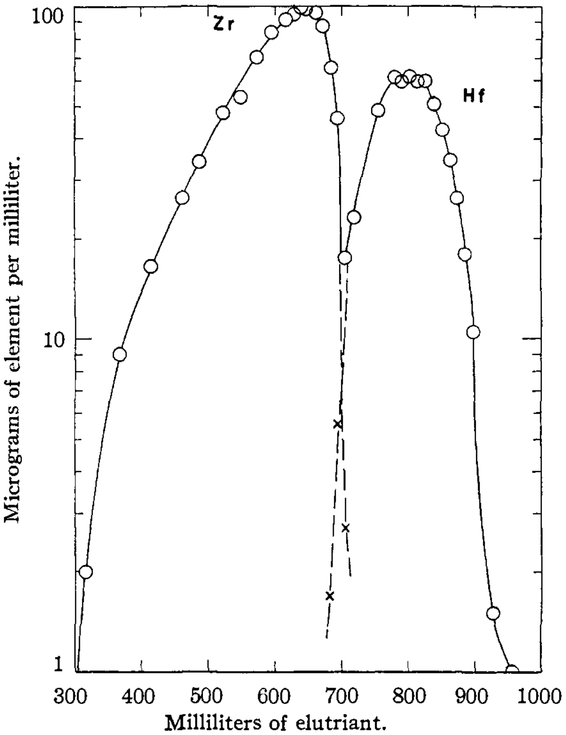

Fig. 1.—Elution of fluozirconate and fluohafniate with 0.2 *M* hydrochloric acid and 0.01 *M* hydrofluoric acid.

Combined fractions of elutriant from 300 ml. to 653 ml., containing 13.8 mg. of zirconium or 69% of the starting material, were found to contain no hafnium detectable by spectrographic analysis. The portion from 300 ml. to 686 ml., containing 17.0 mg. of zirconium or 85% of the starting material, was found to contain 0.04% hafnium. Spectrographic analysis of the 752–1020-ml. portion showed 0.02% zirconium in the 6.9 mg. of hafnium (69% of the starting material). Similarly, 0.03% zirconium was found in the 704–1020-ml. portion containing 8.3 mg. of hafnium (83% of the starting material). The amounts of the major constituents in these portions were determined from the curves.

This work was done under the auspices of the Atomic Energy Commission.

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[1] While official declassification of this paper was being awaited, a communication on a similar separation appeared by Kraus and Moore, THIS JOURNAL, **71**, 3263 (1949). The separation reported here uses a different resin, a much shorter column, a more dilute eluting solution and macro quantities of zirconium and hafnium instead of micro quantities.

[2] Kenneth Street, Jr., and G. T. Seaborg, THIS JOURNAL, **70**, 4268 (1948).

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Derivatives of 5,6-Dihydrophenanthridine

BY CHARLES P. HUTTRER[1]

In the course of studies concerned with antihistaminic substances a number of derivatives of 5,6-dihydrophenanthridine[2] have been prepared in which the hydrogen in position 5 is

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[1] Present address: National Research Council, Washington, D. C.

[2] Nomenclature according to: "Naming and Indexing of Chemical Compounds," *C. A.*, **39**, 5867 (1945).