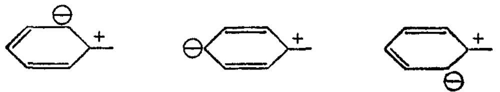
formation. These would vary in the degree of overlap which they would give in the bond, and therefore in the concentration of the negative cloud charge which they would give between the nuclei. At large internuclear distances, the orbitals giving greatest overlap would be least favored because they would require the removal of the negative centroid somewhat from each nucleus. If, however, either or both the atoms have high electronegativities, the high axial concentration resulting from these orbitals would increase stability, because the positive nuclei would be better shielded from each other, *i. e.*, the nuclei would be better "cemented" together, so they could approach more closely, the electrostatic potential energy of the system would be reduced, and accordingly, the total energy would also be lowered. There might, in fact, be opposing tendencies: on the one hand, for the electrons to remain held in the configurations which are best in the fields of the separate nuclei, and on the other hand, for them to move from these into others that are most favorable in the joint, binuclear field. We think it possible that in the C–F link a considerable degree of such redistribution might occur, with the results indicated, *viz.*, a shortening and strengthening of the C–F bond and a reduction in its dipole moment. Furthermore, if the bond shortens, the density of electronic charge on the carbon atom might actually increase, with the result that electronic distributions in the neighborhood might be repelled; *i. e.*, driven into the nucleus. If this field effect occurs by resonance with polar structures (IV) (as has previously been postulated[62]) the appearance of *o,p*-direction in fluorobenzene might be expected.


IV

## Summary

The valence angles (C–X–C) in diphenyl ether, sulfide, sulfone, ketone, amine and in triphenylamine have been determined from the dipole moments in benzene solution of the unsubstituted and the *p*-fluoro-substituted compounds. They are, in the same order: 116 ± 4°, 106 ± 4°, 102 ± 4°, 130 ± 4°, 113 ± 3° and 114 ± 3°. The relation of these to other reported values, and their significance, have been discussed.

The moments of phenoxthine and phenthiazine have also been measured. They are 0.92 and 2.13 *D*, respectively. These agree with angles of 155 ± 5° and 145 ± 5° between the planes of the benzene rings, the molecules being folded along the OS and NS lines.

The moments resulting from the interaction between fluorine atoms substituted on benzene, with other groups *para* to them, show that fluorine has unique power to suppress mesomeric effects which conflict with its own.

The origin of the mesomeric effect in fluorobenzene has been discussed.

[62] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939, p. 141.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

# Search for Elements 94 and 93 in Nature. Presence of $94^{239}$ in Pitchblende[1]

BY GLENN T. SEABORG AND MORRIS L. PERLMAN[1a]

The discovery[2] of a rather easily prepared form of radioactive element 94 and the subsequent determination of the chemical properties[3] of 94 with the help of this isotope as tracer make it possible to conduct a search for 94 in natural minerals. It is convenient to search for 93, whose chemical properties[3,4] are also known, at the same time. The hope would be to discover a very long-lived 94 or 93 and that this be present in an amount large enough so that useful quantities chould be extracted from the minerals. Alpha and beta radioactivity is to be tested for in the final very thin sample which, in view of the chemical procedure, would contain the 94 or 93. In case the 94 or 93 is not alpha or beta active, a test for fissions with neutrons should be made since it appears likely that any isotopes of these elements will undergo fission either with slow or with fast neutrons. The presence of an amount of the order of one microgram can be established by the neutron tests; therefore, starting with about 1 lb. of the pitchblende, the sensitivity for the detection of these elements can be about 1 part in $10^8$ or $10^9$.

This report describes a careful search for elements 94 and 93 in a sample of pitchblende concentrate obtained from the Great Bear Lakes region of Canada. Since this pitchblende, which is

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[1] This article was mailed, as a secret report, from Berkeley, California, to the "Uranium Committee" in Washington, D. C., on April 13, 1942. The experimental work was done during 1941 and the early part of 1942. The report is unchanged from its original form except for slight editing to make it conform to JOURNAL standards.

[2] G. T. Seaborg, E. M. McMillan, J. W. Kennedy and A. C. Wahl, *Phys. Rev.*, **69**, 366 (1946) (submitted January 28, 1941); G. T. Seaborg, A. C. Wahl and J. W. Kennedy, *Phys. Rev.*, **69**, 367 (1946) (submitted March 7, 1941).

[3] G. T. Seaborg and A. C. Wahl, THIS JOURNAL, **70**, 1128 (1948).

[4] E. M. McMillan and P. H. Abelson, *Phys. Rev.*, **57**, 1185 (1940).

said to contain some 40 different elements, seems to offer more hope to contain 94 and 93 than does any other mineral, it was decided to make an extremely careful search in this mineral. Great care was taken to be sure that all the material was dissolved, even down to the last few milligrams, and the most sensitive means of detection for 94 and 93 in the final fraction, including tests for alpha and beta radioactivity and neutron induced fissions, were employed.

Another reason that seemed to make it definitely worth while to extend the sensitivity of the method to the limit was the possibility of establishing the presence of the 30,000-year $94^{239}$ [5] in this material. From the spontaneous fission rate of uranium, one can calculate the amount of $94^{239}$ which might be formed as a result of the absorption by $U^{238}$ of the neutrons emitted in the spontaneous fission process. In an amount of pitchblende of the order of one pound, there might be expected to be present an amount of $94^{239}$, formed from spontaneous fission neutrons, corresponding to an alpha counting rate of several thousand counts per hour, provided an appreciable fraction of these neutrons were absorbed by $U^{238}$ ultimately forming $94^{239}$. Even if only a small percentage of the neutrons leads to the formation of $94^{239}$ from $U^{238}$ in this manner, it still should be possible to detect the $94^{239}$, since alpha counting rates of the order of a few counts per hour are readily determinable. Our experiments indicate that we have discovered the presence of $94^{239}$ in pitchblende.

## Experimental

Four hundred grams of the pitchblende concentrate was treated successively with a number of reagents, and after each treatment the solution which was obtained was set aside and the residue was subjected to the action of the next reagent. The reagents, in the order in which they were used, were (1) boiling concentrated hydrochloric acid followed by boiling aqua regia, (2) hot 6 *N* sodium hydroxide, (3) hot aqua regia, (4) boiling 6 *N* hydrochloric acid, (5) boiling 27 *N* hydrofluoric acid followed by nitric acid extraction, (6) fuming hot sulfuric acid followed by water extraction, (7) sodium hydroxide fusion followed by dilute sodium hydroxide extraction, (8) boiling 6 *N* hydrochloric acid, and (9) hydrofluoric acid solution followed by sulfuric acid, sodium carbonate and nitric acid solutions. After this series of treatments the final undissolved matter was entirely negligible, perhaps of the order of a few milligrams in weight.

The acidity of each of these solutions was adjusted to the range from 1 to 6 *N*, sulfur dioxide was added, and hydrofluoric acid was added to each in order to remove a fluoride precipitate. When necessary, lanthanum and cerium carrier material was added before the addition of the hydrofluoric acid.

The various fluoride precipitates were all combined and dissolved in concentrated sulfuric acid, and after dilution with water and the addition of dilute nitric acid (to oxidize any uranous uranium to the uranyl form) the rare earth fluorides were again precipitated by the addition of hydrofluoric acid. This rare earth and thorium fluoride precipitate, which amounted to about 20 g. and which would contain, in their reduced forms, any 94 or 93 which might have been present in the original pitchblende, was dissolved in sulfuric acid and reprecipitated as the fluoride. It was now necessary to go through a chemical procedure designed to isolate any such 94 or 93 into a very thin layer (0.3 mg./sq. cm.) of rare earth carrier material, special care being taken to eliminate all the elements in the uranium, thorium and actinium radioactive series which would interfere with the detection of the 94 or 93 in the final sample.

This rare earth and thorium fluoride precipitate was dissolved in sulfuric acid and after the addition of a few grams of potassium peroxydisulfate, $K_2S_2O_8$, and a few tenths of a gram of silver nitrate, hydrofluoric acid was again added to precipitate the rare earth and thorium fluoride. In this procedure, the 94 and 93 remain in solution, present in their higher oxidation states. This solution, after the removal of the fluoride preicpitate by centrifugation, was boiled in order to remove the hydrofluoric acid and decompose the peroxydisulfate and it was then treated with sulfur dioxide to reduce the 94 and 93 to their lower (fluoride-insoluble) oxidation states. About 120 mg. of lanthanum and cerium carrier was then added and the fluoride precipitated by the addition of hydrofluoric acid.

This 120 mg. fluoride precipitate was then dissolved in sulfuric acid and taken through another identical cycle in which the amount of rare earth was reduced to about 5 mg. The 5 mg. of rare earth, which would contain the 94 or 93, was then dissolved in sulfuric acid and, after the addition of peroxydisulfate and silver ion, the rare earths were removed from solution by precipitation as the fluoride. The hydrofluoric acid was removed by boiling the solution until the white fumes of sulfur trioxide appeared and after dilution another 0.2 mg. of rare earth carrier was added. After treatment with peroxydisulfate and silver ion, this 0.2 mg. of rare earth was precipitated as fluoride. The purpose of this last precipitation, which was made just before the final isolation of the material which would contain the 94 and 93 was to establish that there was a negligible amount of isotopes of thorium ($UX_1$, Io) present in the solution at this stage. This 0.2 mg. of precipitate showed no detectable beta activity, above the background of the Geiger–Müller counter, and an alpha counting rate of about 45 per hour when placed on one electrode of an ionization chamber in which the calibrated counting efficiency amounted to about 45 per cent.

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(5) J. W. Kennedy, G. T. Seaborg, E. Segrè and A. C. Wahl, *Phys. Rev.*, 70, 555 (1946) (submitted May 29, 1941).

The hydrofluoric acid was removed from the solution by boiling until the dense white fumes of sulfur trioxide appeared, and after dilution and reduction with sulfur dioxide, another 0.2 mg. of rare earth was added. This was precipitated as fluoride by the addition of hydrofluoric acid, and centrifuged onto a platinum disk for final measurements. This sample would contain any 94 or 93 which was present in the original pitchblende. (Calibration experiments, starting with 20 g. of rare earth and ending with 0.2 mg. of rare earth fluoride in an identical chemical procedure, in which the 50-year alpha-emitting 94 was added as tracer to the original 20 g., proved that the yield of 94 in this rather lengthy chemical procedure amounted to about 80 per cent.) Previous careful counting experiments had proved that the rare earth carrier material and the platinum, upon which the final sample was mounted, were free from alpha-emitting contamination.

## Results

This final sample showed no detectable beta-activity, above the background of the Geiger–Müller counter. It showed an alpha counting rate of about 90 per hour when placed on one electrode of an ionization chamber in which the calibrated counting efficiency was about 45 per cent. Since it is likely that any isotopes of 94 or 93 would undergo fission with slow or fast neutrons, a test for fissions with neutrons was made by placing the final sample on one electrode of an ionization chamber connected to a linear amplifier and recording system adjusted to record the impulses due to fissions. When slow neutrons were used, from a 300-mg. radium-beryllium source with paraffin between the chamber and neutron source and around the chamber and neutron source, there was recorded zero fissions in seven hours of counting. When the sample was replaced by a "standard" 200-microgram uranium sample, containing therefore 1.4 microgram of $U^{235}$, the fission counting rate due to slow neutrons amounted to about 15 counts per hour. Therefore, assuming that the slow neutron fission cross section of the 94 or 93 would be of the same order of magnitude as that of $U^{235}$, there was present in the final sample no more than a small fraction of a microgram of any isotope of 94 or 93 capable of undergoing fission with slow neutrons. So far as fast neutrons are concerned our experiments place an upper limit of the order of a microgram on the amount of any isotope of 94 or 93 which was present and capable of undergoing fission with fast neutrons; therefore, we can say that there was not present in this pitchblende as much as one part in $10^8$ or $10^9$ of 94 or 93.

On the other hand, the alpha counting rate might very well be due to the presence of $94^{239}$ in view of the expectation that some of this isotope would be present as the end-product formed as the result of absorption of spontaneous fission neutrons by $U^{238}$. The chemical procedure is very stringent and specific for the isolation of 94 (and 93). A counting rate of about 90 per hour, amounting to some $10^{-6}$ microcuries, would correspond to the order of $10^{-5}$ microgram of 30,000-year $94^{239}$. This would correspond to something like one part in $10^{14}$ of $94^{239}$ in the original pitchblende concentrate. This amounts to only a few per cent. of the amount to be expected if a large proportion of the spontaneous fission neutrons were absorbed by the $U^{238}$, but this is not surprising in view of the number of other neutron absorbing materials which might be present in the pitchblende.

## Summary[6]

A chemical method for separating and concentrating elements 94 and 93 from uranium and thorium has been applied to a sample of pitchblende concentrate from the Great Bear Lakes region of Canada. A final fraction of 94 and 93 precipitated with rare earth carrier has been counted for fissions with slow and with fast neutrons, and an upper limit of 1 part in $10^8$ to $10^9$ has been set for the amount of these elements in the sample. Based on the number of alpha-particle counts in the sample, 1 part in $10^{14}$ is estimated as the amount of 30,000-year $94^{239}$ in the original pitchblende concentrate.

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(6) Summary was written at time of publication, since the original report contained no summary.