zoins. The acidic fraction contained the stilbene-α,α'-bis-thioglycolic acid.

The mixtures of chlorodesoxybenzoins were analyzed as follows. The original chlorodesoxybenzoin mixture (isolated in 55% yield in each case) was recrystallized from ligroin (b. p. 70–90°). The mixture was shown to give the correct carbon and hydrogen analysis. The melting point was determined and also the melting point of the unknown mixture to which had been added a small amount of pure 4- or 4'-chlorodesoxybenzoin. The composition of the mixture was then read from the melting point diagram, the preparation of which is described below. It was shown that crystallization from ligroin did not effect a change in the composition of a known mixture of the two chlorodesoxybenzoins.

The mixture of dimethylaminodesoxybenzoins was separated by a procedure of Jenkins, Bigelow and Buck[11] involving fractional crystallization from ethanolic hydrochloric acid.

Melting Point Diagram for the System 4-Chlorodesoxybenzoin and 4'-Chlorodesoxybenzoin (Fig. 2).—A procedure similar to that described by Rheinboldt[12] was used. 4-Chloro- and 4'-chlorobenzoin were prepared by the method of Jenkins[13] and purified by recrystallization from ligroin (b. p. 70–90°). Mixtures totalling 0.500 ± 0.0002 g. were weighed out, brought to complete fusion and cooled slowly while stirring. This fusion was repeated three to five times to ensure adequate mixing. A small portion of each was powdered with an agate mortar and pestle. Samples were introduced into capillary tubes 0.5–1 mm. in diameter and were 4–5 mm. in height. The melting points were determined in an aluminum block which had a lens of high magnifying power so that the samples could be seen clearly. The rate of heating of the block was controlled by a variable voltage transformer. A 360° thermometer, calibrated in degrees, was used. All readings were corrected. The temperature of the block was brought rapidly to within 5° of the melting range, and then allowed to rise at the rate of one degree per ten minutes. The melting point range was recorded as the point where the first liquid appeared (lower curve) and the point where the last crystal disappeared (upper curve). Several samples from the same mixture were taken to determine whether adequate mixing had occurred, and samples were subjected to remelting to prove that no decomposition had occurred during fusion. The m. p. ranges were reproducible to within 1° which corresponded to an error of ±4% in composition of the mixture.

Treatment of Mandelic Acid with Thioglycolic Acid.—The procedure described for the benzoins was followed except that the reaction mixture was neutralized to congo red paper (acid to litmus) and a sample, withdrawn by pipet and diluted, was titrated with a solution of iodine in ethanol. Titration showed that 92% of the initial thioglycolic acid remained.

Reaction of Benzoin Methyl Ether with Thioglycolic Acid.—Benzoin methyl ether was prepared by the method of Fischer.[14] When it was treated in the manner described above for benzoin an 88% yield of desoxybenzoin was obtained, as well as 12% of the stilbene-α,β-bis-thioglycolic acid. When a stream of hydrogen chloride was passed into a solution of benzoin methyl ether in acetic acid for thirty minutes at 100° the ether could be recovered quantitatively.

Ultraviolet Absorption Curves (Fig. 1).—The instrument used was a Beckman quartz spectrophotometer model DU. The solvent was 95% ethanol and the concentration ranged from 2.5–3.5 $\times$ 10^{-5} mole per liter. The average deviation in ϵ was 0.1, and this corresponded to an error of 1.5% in the region of the maximum.

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[11] Jenkins, Bigelow and Buck, THIS JOURNAL, **52**, 4495 (1930).

[12] Rheinboldt, *J. prakt. Chem.*, [2] **111**, 242 (1925).

[13] Jenkins, THIS JOURNAL, **56**, 682 (1934).

[14] Fischer, *Ber.*, **26**, 2412 (1893).

High-Silica Fluosilicic Acids

BY S. MILTON THOMSEN

Current chemical literature teaches that the end-product of the reaction of aqueous hydrofluoric acid on silica, with silica in excess, is fluosilicic acid, having the composition represented by the formula H_2SiF_6.

Tannanaev,[1] reported in 1936 that more silica may be present in fluosilicic acids (giving them a higher Si/F ratio) than the formula indicates. In agreement with that report, it has been found here that the reaction end-product (silica-saturated fluosilicic acid) has a composition very nearly approaching that represented by the formula $H_2SiF_6 \cdot SiF_4$ (fluodisilicic acid). Little more than 5 moles of HF suffices to "dissolve" one mole of silica, the product being almost 20% higher in silica than the formula H_2SiF_6 indicates.

Two consequences of the presence of "extra" silica are readily demonstrated: (1) Much heat is evolved when silica-saturated fluosilicic acid is mixed with hydrofluoric acid. The temperature rise is roughly proportional to the amount of extra silica in a less-than-saturated acid. (2) Mixing sodium chloride solution (in excess) with fluosilicic acid produces a granular precipitate of sodium fluosilicate which settles rapidly, followed by a slow precipitation of the extra silica.

Most commercially available fluosilicic acids have compositions approximating that of H_2SiF_6 (30% by weight) and will dissolve approximately 30 g. of silica per liter.

[1] Ivan Tannanaev, *J. Gen. Chem. U. S. S. R.*, **6**, 1430 (1936).

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Chemical Properties of Berkelium

BY S. G. THOMPSON, B. B. CUNNINGHAM AND G. T. SEABORG

The recent production by Thompson, Ghiorso and Seaborg[1] of a radioactive isotope of berkelium (atomic number 97) makes it possible to investigate the chemical properties of this transuranium element by means of the tracer technique. This isotope has been prepared through the bombardment of Am^{241} with about 35 Mev. helium ions in the 60-inch cyclotron of the Crocker Laboratory and is believed to have the mass number 243, or possibly 244. This Bk^{243} has a half-life of 4.6 hours and decays by electron capture with about 0.1% branching decay by alpha-particle emission.

In the present tracer chemical experiments, the radiations accompanying the electron capture process were used as a means of detection and were counted in two ways. Where the sample deposits on the platinum plates were essentially weightless, as was the case following the evapora-

[1] S. G. Thompson, A. Ghiorso and G. T. Seaborg, *Phys. Rev.*, **77**, 838 (1950).

tion and ignition of the elutriant solutions in the column adsorption experiments, a high efficiency was obtained by using a windowless proportional counter to count the Auger electrons. The thicker samples from the precipitation experiments in which carrier materials were used were counted close to the thin window (3 mg./sq. cm. mica) of a bell type Geiger counter filled with 10 cm. of xenon to enhance the efficiency for counting the X-rays. An aluminum absorber of thickness about 20 mg./sq. cm. was used between the sample and counter window to reduce errors due to variable absorption of soft components caused by small differences in sample thickness.

The tracer Bk^{243} was isolated by a combination of chemical procedures including the use of a cation exchange resin (Dowex 50). Following the bombardment, most of the americium was separated from the curium (largely Cm^{242}, formed in the bombardment), berkelium, and the rare earth fission products by oxidizing the americium to the VI, fluoride soluble, oxidation state.[2] Following this, the precipitation of insoluble fluoride using some carrier such as lanthanum separated a fraction containing unoxidized radioactive curium, berkelium, the unoxidized fraction of the americium, yttrium, and the rare earth fission products from the remainder of the fission products. The three heavy elements, americium, curium and berkelium, were then separated from the others by adsorbing the dissolved mixture on the resin and selectively eluting them with 13 *M* hydrochloric acid which forms complex ions[3] with the actinide elements but not with the lanthanide elements.

The berkelium, curium and americium were separated from each other through the use of the Dowex 50 ion-exchange resin under the following conditions. The mixture was adsorbed on a small amount of the resin and placed on top of a column 2 mm. in diameter and 20 cm. long, packed with the ammonium salt of the resin in fine spherical form. The eluting agent was ammonium citrate[4] (buffered with citric acid to *p*H 3.5—total citrate concentration 0.25 *M*). In order to decrease the time of separation, the elution was carried out at an elevated temperature of about 87°. The flow rate of the eluting agent was held at one drop ($\sim$0.030 cc.) about every two minutes.

Figure 1 shows the plot of the elution peaks of berkelium, curium, and americium. Similar data are also included for yttrium and the rare earths promethium, samarium, europium, gadolinium and terbium for purposes of comparison.[5] As it was more convenient for our purposes first to separate the actinide elements from lighter elements, Fig. 1 showing the citrate elution curves is a composite of several separate experiments carried out under as nearly identical conditions as possible. The radioactive isotopes of these elements were present at tracer concentrations without added inactive isotopes. The ordinate is given as counts per minute per drop, where the counting was done with a Geiger counter, for all except americium and curium whose alpha-particles were counted. The data are given in this direct manner since in tracer experiments of this type the relative amounts are unimportant and no purpose is served by calculating the number of atoms on an absolute basis through the use of the half-lives and counting efficiencies of the isotopes concerned.

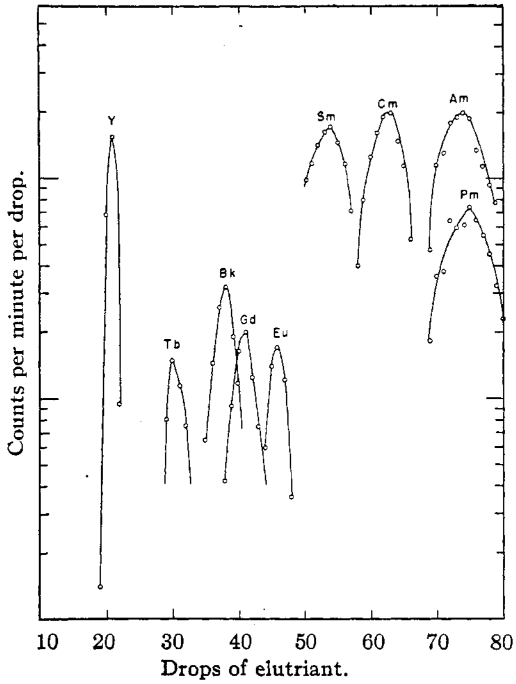

Fig. 1.—Elution of Bk, Cm, Am, Y, Tb, Gd, Eu, Sm and Pm from Dowex-50 with ammonium citrate at 87°.

Since a more careful comparison of the two groups, berkelium–curium–americium and terbium–gadolinium–europium, is of primary interest, the data for these elements are plotted in Fig. 2 in a manner which facilitates this comparison. Here the ordinates are normalized for convenience to show equal amounts and the data for terbium–gadolinium–europium are from another experiment performed under as nearly identical conditions as possible. A remarkable analogy between these two groups of elements is apparent indicating the same kind of break in ionic radius at the point of half-filling of the 5f electron shell (curium for the actinide elements) as has been known to exist for the analogous point of half-filling of the 4f electron shell[6] (gadolinium for the lanthanide elements). It may be seen also that the difference in rates of elution is greater between neighboring actinides than it is for the corresponding lanthanides.

In view of the anticipated similarity of berkelium to its rare earth homolog terbium, attempts were made to oxidize the predominantly tripositive berkelium in aqueous solution to the IV oxidation state. It is known that terbium, the first ele-

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[2] L. B. Asprey, S. E. Stephanou and R. A. Penneman, THIS JOURNAL, **72**, 1425 (1950).

[3] K. Street, Jr., and G. T. Seaborg, *ibid.*, to be published.

[4] B. B. Cunningham, E. R. Tompkins and L. B. Asprey (unpublished, April, 1947) first demonstrated the usefulness of the cation exchange column method for separating americium and curium, using Dowex 50 and room temperature elution with 0.25 *M* ammonium citrate plus citric acid at *p*H 3.05.

[5] K. Street, Jr., and G. H. Higgins, THIS JOURNAL, to be published.

[6] See, *e. g.*, H. Bommer, *Z. anorg. allgem. Chem.*, **241**, 273 (1939).

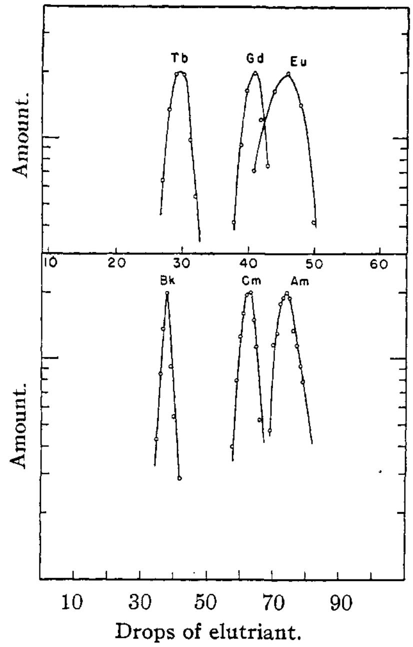

Fig. 2.—Comparison of elution of Bk, Cm and Am with their homologs Tb, Gd and Eu.

ment beyond the middle of the lanthanide group, can be oxidized to the IV state as solid TbO_2, but that this oxidation is not possible in aqueous solution. It was predicted[7] that element 97 should have a IV as well as a III oxidation state and this should be easier to reach than is the case for terbium. In fact it seemed quite likely that it should be possible to effect this oxidation in aqueous solution, and this has proved to be the case.

Table I shows the results of a series of carrying experiments in which solutions containing Bk^{243} tracer were treated with oxidizing agents of various strengths. Carrying with zirconium phosphate or cerium(IV) iodate was used as the test for oxidation, it being assumed that Bk(IV) would be carried and Bk(III) not carried by these precipitates. After the separation of the precipitate, a precipitation of lanthanum fluoride was made from the supernatant in order to check the amount remaining there. It has been shown in many experiments that lanthanum fluoride carries Bk(III) fluoride quantitatively and, in fact, all indications point to similar behavior of Bk(III) in other chemical properties to that of the tripositive actinide and lanthanide elements. In the zirconium phosphate or cerium(IV) iodate experiments, carrying of some 90% of the berkelium is considered to represent essentially complete oxidation to the IV state, while carrying of some 5% is considered to represent no oxidation on the basis of analogy with the behavior of other actinide elements in tracer experiments.

TABLE I

CARRYING OF TRACER BERKELIUM FROM SOLUTIONS OF VARIOUS OXIDIZING AND REDUCING STRENGTHS

Conditions for oxidation	% Carried by zirconium phosphate[a]
3 M HCl, reduced with Zn amalgam, 25°	5
3 M HCl, satd. Br_2, 75°, 15 min.	5
3 M HCl, satd. Cl_2, 75°, 15 min.	5
3 M HNO_3, 75°, 15 min.	5
3 M HNO_3, 0.1 M $NaBrO_3$, 0.2 M H_3PO_4, 75°, 5 min.	85
7 M HNO_3, 0.1 M $NaBrO_3$, 25°, 15 min.	88
5 M HNO_3, 0.1 M $Na_2Cr_2O_7$, 75°, 15 min., heated 15 min. at 75° after pptn.	89
0.015 M Ce(IV), 0.015 M Ce(III), 8 M HNO_3, 75°, 5 min.	56[b]
0.015 M Ce(IV), 0.006 M Ce(III), 8 M HNO_3, 75°, 5 min.	69
0.015 M Ce(IV), 8 M HNO_3, 75°, 5 min.	80

[a] Zirconium phosphate precipitations made under following conditions: 3 M HNO_3 or 3 M HCl, ~0.5 M H_3PO_4, 0.2 mg./ml. Zr(IV), solution heated a few minutes to allow complete precipitation. [b] Cerium(IV) iodate used as carrier here and following experiments.

It is, of course, difficult to determine a thermodynamic "standard" oxidation potential from tracer experiments. Moreover, the activity coefficients of the aqueous actinide ions are not known. However, with the benefit of the wide experience extant for tracer experiments with the actinide elements, together with the fact that their formal oxidation potentials are known through experiments with macroscopic quantities, it is known that estimates of the formal potentials, based on tracer experiments of this sort, may be reasonably reliable. It can be seen from Table I that, in 8 M nitric acid the oxidation potential corresponding to the Bk(III) → Bk(IV) change is very nearly the same as that for the corresponding change in cerium. This conclusion is not inconsistent with the observed oxidation by dichromate ion and bromate ion, since in both cases the berkelium was heated with the oxidizing agent in the presence of phosphoric acid. It has been shown by Howland, Hindman and Kraus[8] that the formal potential of the Pu(III)–Pu(IV) couple in 1 M hydrochloric acid is rendered less negative by about 0.15 volt by the addition of 0.1 M phosphoric acid. Because of the smaller ionic radius of the Bk(IV) ion, the effect of phosphoric acid on the Bk(III)–Bk(IV) couple would presumably be somewhat greater. It seems likely that berkelium is subject to the same type of complex ion formation as cerium and hence, like cerium, its oxidation potential must always be regarded with this in mind. The data, therefore, indicate a formal oxidation potential of about -1.6 volts for the Bk(III)–Bk(IV) couple.

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(7) G. T. Seaborg, *Nucleonics*, **5**, No. 5, 16 (1949).

(8) J. J. Howland, J. C. Hindman and K. A. Kraus, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 3.3 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).

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Coördination Compounds of Uranyl Nitrate

BY GEORGE W. WATT AND ALBERT R. MACHEL

A recent paper by Katzin[1] on the formation of mixed solvates of uranyl nitrate with water and a number of organic addenda prompts us to report some of our work relating to similar compounds.[2]

Experimental

Uranyl Nitrate and Methyl Isobutyl Ketone.—In an effort to prepare and isolate anhydrous uranyl nitrate, samples of uranyl nitrate 2-hydrate were dissolved in anhydrous methyl isobutyl ketone ("hexone") and about two-thirds of the solvent was removed by distillation. Water in excess of its solubility in hexone was observed in the distillate and upon dilution of the dark brown still residue with Skellysolve A, a viscous amber oil separated. Since preliminary examination of this product[3] indicated that it was a monohexone solvate of uranyl nitrate, the reaction was studied in more detail.

The nearly quantitative removal of water from the 2-hydrate during the course of the distillation was demonstrated as follows. Uranyl nitrate 2-hydrate (7.014 g.) was dissolved in 70 ml. of hexone and 50 ml. of the solvent was removed by distillation at atmospheric pressure. Samples of the distillate were analyzed for water by a modification of Bryant, Mitchell and Smith's procedure[4] for the determination of water in the presence of carbonyl compounds by means of Karl Fischer reagent.[5] Water found in the distillate amounted to 0.557 g. as compared with 0.586 g. of water present in the weight of 2-hydrate used. In similar experiments, distillates were found to contain 0.277 and 0.511 g. of water as compared with calculated values of 0.291 and 0.586, respectively. The average of these data corresponds to the removal of 1.84 of the 2.00 moles of water present per mole of nitrate.

The dark brown still residue was diluted with 700 ml. of Skellysolve A (boiling range, 28–30°), whereupon a viscous amber oil separated. After the two phases had remained in contact at room temperature for several hours, the pale yellow supernatant solution was removed, concentrated and analyzed for uranium. The oil was transferred to a weighing bottle and dried in a vacuum oven at 58° and a pressure of 3 mm. Data relative to this and other typical experiments are given in Table I; these data amply demonstrate the reproducibility of the solvate having the formula $UO_2(NO_3)_2 \cdot C_6H_{12}O$. Katzin[1] reported a mixed solvate having the composition $UO_2(NO_3)_2 \cdot 2.71H_2O \cdot 0.28C_6H_{12}O$, but this was formed under conditions quite different from those employed in the present work.

During drying, or upon prolonged standing at room temperature, the viscous oil sets to a brittle resinous solid. This product is soluble in hexone, from which the oil is reprecipitated upon dilution with Skellysolve A. The compound is hydrolyzed slowly by water at room temperature, and qualitative tests show that the nitrate ion remains intact. All efforts to crystallize this compound were ineffective.

TABLE I

DATA ON REACTIONS BETWEEN URANYL NITRATE 2-HYDRATE AND HEXONE[a]

$UO_2(NO_3)_2 \cdot 2H_2O$, g.	Diluent, ml.	Anal. of insol. prod.[b] U, %	C,[c] %	U pptd. as $UO_2(NO_3)_2 \cdot C_6H_{12}O$, %	U retained in organic solvent, %
3.498	700[d]	49.5	14.4	77.0	17.7
7.069	350	49.8	16.2	76.5	21.4
6.989	700	49.2	15.4	70.9	29.1
7.014	1400	49.8	14.8	63.4	34.6
14.025	700[d]	46.8	16.7	32.5	63.0

[a] All experiments employed 70 ml. of anhydrous hexone, 50 ml. of which was removed by distillation prior to addition of diluent. [b] Calcd. for $UO_2(NO_3)_2 \cdot C_6H_{12}O$: U, 48.2; C, 14.6. [c] Determined by the method of Lindenbaum, Schubert and Armstrong, *Anal. Chem.*, **20**, 1120 (1948). [d] Reaction mixture maintained at 0° for 6 hr. following addition of diluent.

Other Coördination Compounds of Uranyl Nitrate.—Using essentially the procedure of Lloyd and Cleere,[2] treatment of 2.46 g. of uranyl nitrate 2-hydrate in 100 ml. of 95% ethanol at room temperature with 7.60 g. of hexamethylenetetramine in 80 ml. of the same solvent gave a pale yellow precipitate which was washed with ethanol and dried at 105°.

Anal. Calcd. for $UO_2(NO_3)_2 \cdot (CH_2)_6N_4$: U, 44.6; N, 10.5. Found: U, 43.8; N, 11.0.

A similar reaction with excess ethylenediamine yielded a gelatinous yellow precipitate which was dried *in vacuo* over concentrated sulfuric acid.

Anal. Calcd. for $UO_2(NO_3)_2 \cdot [(CH_2NH_2)_2]$: U, 52.5; N, 6.2. Found: U, 50.4; N, 6.1.

When this same reaction was carried out in the presence of phosphate ion at concentrations insufficient to precipitate uranyl hydrogen phosphate, the product consisted of the monoethylenediamine solvate of uranyl hydrogen phosphate. This compound is probably more properly represented as the ethylenediamine analog of ammonium uranyl phosphate, *i. e.*, $[(CH_2NH_3)_2](UO_2PO_4)_2$.

Anal. Calcd. for $UO_2HPO_4 \cdot [(CH_2NH_2)_2]$: N, 3.5; P, 7.8. Found: N, 3.9; P, 7.4.

Efforts were made to prepare coördination compounds of uranyl nitrate with other organic addenda such as urea, thiourea, guanidine, nitrilotriacetic acid and ethylenediamine tetraacetic acid. No evidence of compound formation was observed at room temperature, following refluxing in ethanol, or following dilution with organic solvents including Skellysolve A, diethyl ether, etc.

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(1) Katzin, AECD-2213, Aug. 17, 1948.

(2) *Cf.* Lloyd and Cleere, *Science*, **108**, 565 (1948).

(3) These experiments were carried out by Mr. G. L. Sutherland.

(4) Bryant, Mitchell and Smith, THIS JOURNAL, **62**, 3504 (1940).

(5) The authors are indebted to Dr. C. M. Slansky, through whose coöperation these analyses were obtained.

Preparation of Indole

BY FLOYD T. TYSON

In the previously reported[1] preparation of indole by the condensation of *o*-formotoluide, potassium amide of alkoxides were used as condensing agents. The maximum yield reported was 0.40 mole of indole per mole of *o*-formotoluide. It has now been found that potassium *o*-toluide is a more effective condensing agent

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(1) Tyson, THIS JOURNAL, **63**, 2024 (1941); Marion and Ashford, *Can. J. Research*, **23B**, 26 (1945); Galat and Friedman, THIS JOURNAL, **70**, 1280 (1948).