amino)-6-methoxyquinoline (*cf.* ref. 11) by refluxing with hydrobromic acid.[12] The compound was used as the sulfate trihydrate, m.p. 118–120°.[10]

8-(4-Diethylamino-1-methylbutylamino)-6-quinolinol.[13]—Pamaquine base was demethylated with hydriodic acid and the product characterized[10] as the dihydriodide (m.p. 162–164°) and the methylene 1,1′-bis-(2-hydroxy-3-naphthoate) (m.p. > 250°).

The spectra were determined with a Cary recording spectrophotometer, using a dynode voltage of 4, a slit schedule of 20, and 1-cm. quartz cells. The concentrations of the solutions ranged from 0.01 to 0.200 g./l. and their spectral behavior conformed with Beer's law in all instances. The assistance of Mrs. M. Becker is gratefully acknowledged.

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[11] E. C. Kleiderer, J. B. Rice and V. Conquest, Office of Publication Board, Dept. of Commerce, Washington, D. C., 1945, Report 248, p. 32.

[12] W. Kikuth, U. S. Patent 2,291,235.

[13] Swiss Patent 129,425 (to I. G. Farbenindustrie).

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Observations on Curium Valence States; A Rapid Separation of Americium and Curium[1]

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A search for oxidation states higher than Cm(III) in aqueous solution has been made using macro amounts of curium (up to 238 μg. per experiment). Since Cm^{242} has a specific activity of *ca.* 7 × 10^9 α/min./microgram,[2] it was anticipated that production of hydrogen peroxide or other reducing materials might be a limiting factor in the oxidation. Consequently, americium, which does exhibit higher oxidation states (V)[3a] and (VI)[3b] in solution, was used as an internal check for oxidation. It was found that Am(III) was not oxidized to Am(VI) in the presence of curium concentrations of *ca.* 500 μg./ml. However, the oxidation of Am(III) to Am(VI) is complete at curium concentrations of *ca.* 160 μg./ml., or lower. The effect of curium α-radiation on the solution would presumably be the same for higher oxidation states of both curium and americium, and therefore could not be the limiting factor in the curium oxidation within the concentration ranges studied.

Experimental

The chemicals used were all reagent grade. The isotopes employed were Cm^{242} and Am^{241}, α-emitters of 162 day[2] and 475 year[4] half-lives, respectively.

Oxidation in Acid.—Experiments were performed with 0.1–0.3 *f* HNO_3 or $HClO_4$ solutions containing americium and curium in various weight ratios. These solutions were treated with solid ammonium peroxydisulfate and heated 1–2 hours in a water-bath at 85°. The oxidation of Am(III) to Am(VI) in the presence of curium was achieved best when the hydroxides were freshly precipitated with gaseous ammonia, dissolved in acid to give a solution of 0.1 *f* in hydrogen ion, and immediately oxidized with peroxydisulfate. Dilute acid solutions of americium and curium which had been left to stand for several hours or longer were not readily oxidized. Immediately following the oxidation, the solution was made 3–4 *f* in HF to precipitate CmF_3 and any americium still in the (III) state. (The 27 *f* HF used was pretreated with solid ammonium peroxydisulfate.) The fluoride precipitate was separated by centrifugation and washed with hot ammonium peroxydisulfate solution, 0.1 *f* in $HClO_4$ and 3 *f* in HF. The supernatant and wash were combined.

The fluoride precipitate was dissolved in 1 *f* HNO_3, saturated with H_3BO_3. Mixed $Cm(OH)_3$ and $Am(OH)_3$ were precipitated from the resulting solution with gaseous ammonia. The precipitate was dissolved in 0.2 *f* perchloric acid; Am(III) was determined in the Beckman DU spectrophotometer by observation of the 503 mμ peak (molecular extinction coefficient of 360 in 0.1 *f* $HClO_4$). Curium was determined by a total α-count after correction for the americium alphas present.

The fluoride supernatant was treated with hydrogen peroxide to reduce Am(VI) to Am(III) with consequent precipitation of AmF_3. The precipitate was dissolved as described above and americium(III) determined spectrophotometrically.

Experiments were performed with and without lanthanum as carrier for the curium. Typical results of this separation method are shown in Table I.

TABLE I

TYPICAL RESULTS FOR THE PEROXYDISULFATE SEPARATION METHOD (ONE CYCLE)

μg./ml.			Wt. fraction Cm:Am	
Cm	Am	La	Before oxidation	After oxidation (CmF_3)
3.7	1060	350	0.0035	0.11
82	210	800	0.39	10.0
85	28	215	3.0	19.0
160[a]	270	0	0.59	15.7
540	39[b]	0	14.0	15.8

[a] At this concentration, without lanthanum carrier, the solubility of CmF_3 limits the yield of curium in the precipitate to *ca.* 90%. [b] In the absence of curium, Am(III) is completely oxidized to Am(VI) at concentrations even as low as 11 μg./ml.

Curium was not oxidized to a fluoride-soluble state, since it was possible to precipitate CmF_3 and leave *ca.* 95% of the Am(VI) in solution. This eliminates the possibility that Cm(VI) was formed, but does not rule out the possibility of Cm(IV), which would also have an insoluble fluoride. Consequently, four experiments were performed using Zr(IV) phosphate; Cm(III) was treated with ammonium peroxydisulfate, both with and without silver catalyst, in 0.1–1 *f* acid and Zr(IV) phosphate precipitated. Since only 2–10% of the curium present was carried by zirconium phosphate, it seems evident that no Cm(IV) is formed under these conditions. (At these low acidities, the gelatinous precipitate would be expected to carry some Cm(III).)

Alkaline Oxidation.—Experiments were performed to attempt to form Cm(V) by peroxydisulfate oxidation in 2 *f*, 3 *f* and saturated K_2CO_3 solution, and to demonstrate its existence by co-precipitation with Am(V). The Am(V) precipitate contained only 0.5–2% of the curium. Concentrations ranged from 5 to 320 μg. of curium per ml. with 13 to 500 μg. of americium per ml. In this last experiment, only 2% of the curium was found in the Am(V) precipitate. It was concluded that curium is not oxidized to Cm(V) under conditions in which Am(III) is quantitatively oxidized to Am(V). Spectrophotometric examination of the carbonate supernatant was made to look for Cm(IV) or Cm(VI); only the absorption spectrum of Cm(III) was found.

The possibility of a slow step in the curium oxidation cannot be ruled out. However, the oxidation of very dilute americium solutions (4.5 × 10^{-5} *f*) is complete in less than an hour (Am(III) → Am(VI), 0.1 *f* H^+, peroxydisulfate). Inasmuch as Am(VI) and Am(V) undergo auto-reduction at the rate of a few per cent. an hour, due to the products of americium α-radiation,[5] and the specific activity of Cm^{242} is 1000 times that of Am^{241}, it seems likely that a sufficient concentration of reduction materials would be produced to prevent complete oxidation of americium when sufficient curium is present. However, the effect should not limit the

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[1] Work done under the auspices of the AEC.

[2] G. C. Hanna, B. G. Harvey and N. Moss, *Phys. Rev.*, **78**, 617 (1950).

[3] (a) L. B. Werner and I. Perlman, THIS JOURNAL, **73**, 495 (1951); (b) L. B. Asprey, S. E. Stephanou and R. A. Penneman, *ibid.*, **73**, 5715 (1951).

[4] B. B. Cunningham, S. G. Thompson and H. Lohr, unpublished work (1949).

[5] L. B. Asprey and S. E. Stephanou, AECU-924, November 10, 1950.

oxidation of curium only, while allowing *ca.* 100% oxidation of americium in the same solution.

No evidence for the existence of Cm(IV), -(V) or -(VI) was found in the oxidation of Cm(III)–Am(III) mixtures in either acid or alkaline media under conditions where Am(III) yielded Am(VI) or Am(V), quantitatively. Consequently, the potential of Cm(III) to Cm(IV), (V), or Cm(VI) is at least more negative than the corresponding americium couples. The Cm(III)–(VI) couple is probably more negative than −2 volts (the peroxydisulfate–argentic couple).

A rapid separation method based on the precipitation of CmF_3 from Am(VI) was developed. For macro amounts of curium, CmF_3 is precipitated without carrier, leaving Am(VI) in the supernatant; for amounts of curium where the solubility of CmF_3 is a limiting factor, lanthanum fluoride carrier is used. Where lanthanum is introduced as carrier for CmF_3, a later purification from this element must be performed. This is readily accomplished by means of a column elution using 13 *f* HCl.[6] Where no lanthanum carrier was used, the solubility of CmF_3 was found to be *ca.* 12 μg./ml.

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(6) K. Street, Jr., and G. T. Seaborg, THIS JOURNAL, **72**, 2790 (1950).

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Toluene-Soluble Copper and Silver Fluoborates. Decomposition of Diazonium Fluoborates[1]

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During the course of some investigations concerning copper hydrides, a variety of copper compounds was treated with lithium aluminum hydride under various conditions. Compounds of copper soluble in organic media (solvents stable toward lithium aluminum hydride) were sought, and phenylcopper seemed a promising material. Phenylcopper was prepared by Reich[2] *via* the action of Grignard reagents on copper(I) iodide at 0°, as a reactive and unstable substance. Gilman and Straley[3] also prepared phenylcopper and related compounds by Reich's method. Bolth, Whaley and Starkey,[4] and later Whaley and Starkey,[5] decomposed aromatic diazonium fluoborates in the presence of copper and boiling benzene or toluene, and observed that some of the copper was dissolved. They attributed this to the formation of arylcopper compounds, largely on the basis of examination of derivatives with pyridine and other materials. Thus they claimed the identification of the phenylcopper–pyridine derivative as $C_6H_5Cu \cdot 3C_5H_5N$, a blue, water-soluble compound.

Phenylcopper *via* Grignard and Diazonium Reagents.—The above preparative methods both were repeated, but gave products widely different, especially in stability and in behavior toward pyridine. Phenylcopper prepared by Reich's method decomposed in toluene solution slowly at 0°, more rapidly at room temperature, forming a copper mirror on the walls of the vessel; further it gave no blue coloration with pyridine. Neither Reich nor Gilman and Straley had noted coloration on dissolving phenylcopper in pyridine. On the other hand, toluene solutions prepared using benzenediazonium fluoborate and copper, according to Whaley, *et al.*, deposited no copper even on boiling, and with pyridine (and air) yielded blue crystals. Work was, therefore, undertaken to clarify this discrepancy, and possibly employ both types of copper compounds in the copper hydride studies.

The general techniques of Whaley, *et al.*, were followed in work with the diazonium compounds. The principal deviation from their procedure was the use of an all-glass apparatus designed to permit refluxing, stirring, filtration and introduction of pyridine in a strictly air-free system. Pyridine was distilled from aluminum chloride directly into the filtrate. Nitrogen, freed of oxygen by passage through activated cobalt(II) oxide[6] was employed to exclude air and to pressure the solutions through sintered glass disks. Benzene- and *p*-nitrobenzenediazonium fluoborates were prepared using fluoboric acid according to Roe,[7] and dried over sulfuric acid in vacuum desiccators. These compounds, especially the *p*-nitro derivative, were observed to decompose slowly, and preparations two or more weeks old gave some tarry products.

Toluene solutions of phenylcopper were prepared by Gilman and Straley's method; substitution of phenyllithium for phenylmagnesium iodide was found to be advantageous.

Treatment of the filtrate from the benzenediazonium fluoborate–copper reaction with pyridine under air-free conditions caused precipitation of a pale yellow material, and no blue color developed until the mixture was aerated. The yellow and blue substances thus appeared to be copper(I) and copper(II) compounds, respectively. Whaley, *et al.*, supposed the blue material to be formed without air oxidation, and to be $C_6H_5Cu \cdot 3C_5H_5N$.

Tetrapyridinecopper(II) Fluoborate.—The blue crystals (A) from benzenediazonium fluoborate were recrystallized from ethanol. *p*-Nitrobenzenediazonium fluoborate, when decomposed similarly in boiling toluene in the presence of copper, gave two reaction products with pyridine and air. Treatment with hot ethanol yielded blue crystals (B) from the soluble portion, and a green residue (C). Substance C was insoluble in the common solvents except glacial acetic acid, which on cooling deposited blue-green crystals (D). Qualitative analysis of A and B disclosed the presence of fluoborate ion, and analysis identified both as tetrapyridinecopper(II) fluoborate, $Cu(C_5H_5N)_4(BF_4)_2$, a substance previously prepared by Lange[8] and by Wilke-Dörfurt and Balz.[9]

The blue crystals were prepared in quantity by dissolving basic copper(II) carbonate in fluoboric acid and adding pyridine, and recrystallizing from ethanol. This preparation (E) was shown by analysis to have the same composition as A and B. Substance C was evidently impure copper(II) hydroxide, and D a partially hydrated copper(II) acetate.

Carbon, hydrogen and nitrogen analyses were made[10] using standard methods. Copper determinations were made iodometrically employing the blue crystals directly, or after successive digestions with alkali and nitric acid, both methods giving identical results. Fluoborate analyses were made gravimetrically by precipitating nitron fluoborate.[8,9,11]

Anal. Calcd. for $Cu(C_5H_5N)_4(BF_4)_2$: Cu, 11.48; C, 43.39; H, 3.64; N, 10.12; BF_4, 31.37. Found for A: Cu, 11.7; C, 43.5; H, 4.1; N, 9.71; BF_4, 31.1. For B: Cu, 11.5; C, 43.5; H, 4.5; N, 8.4; BF_4, 31.5. For E: Cu, 11.5; C, 43.4; H, 4.5; N, 9.0; BF_4, 31.8.

Anal. Calcd. for $Cu(OH)_2 \cdot 0.5H_2O$: Cu, 59.5; H, 2.8. Found for C: Cu, 60.0; C, 0.0; H, 3.5.

Anal. Calcd. for $Cu(C_2H_3O_2)_2 \cdot 0.63H_2O$: Cu, 32.9; C, 24.8; H, 3.8. Found for D: Cu, 32.9; C, 25.0; H, 4.5.

Hydrogen analyses of the fluoborates were high, probably on account of partial absorption of boron trifluoride in the weighing tubes. Nitrogen analyses were somewhat low and variable, probably owing to partial loss of pyridine during recrystallization and drying; a portion of A, freshly recrystallized from alcohol–pyridine mixtures, had a nitrogen content of 10.48%.

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(1) Presented at the XII International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951.

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(7) A. Roe, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 193 ff.

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