Anal. Calcd. for $C_7H_6O_2N_2Cl_2$: Cl, 32.09. Found: Cl, 30.93.

4 - Methyl - 6 - oxypyrimidine - 5 - acetic Acid.—The above dichloro compound (11.8 g.) was reduced by the method of Gabriel and Colman.[9] The free acid, after liberation from its potassium salt with acetic acid, extraction with benzene and recrystallization from the latter, was obtained as snow-white crystals, melting at 147–149° and giving no Beilstein test; yield 3.5 g.

Anal. Calcd. for $C_7H_8O_3N_2$: N, 16.66. Found: N, 16.38.

4 - Methyluracil - 5 - carbethoxymethylamine.—The ethyl ester of 4-methyluracil-5-acetic acid (22 g.), m. p. 221–222°, was converted into the hydrazide in the usual way. From these white crystals that darkened slightly above 320° but did not melt by 375°, the azide was obtained easily and was converted into the urethan by heating with an excess of absolute alcohol. After the vigorous evolution of gas had ceased, the hot liquid was filtered from considerable insoluble white solid and concentrated. The urethan, which was soluble in water and in alcohol, was obtained as fine white crystals of m. p. 214–215° from absolute alcohol; yield, 12 g. of urethan from 20 g. of hydrazide.

Anal. Calcd. for $C_9H_{13}O_4N_3$: N, 18.50. Found: N, 18.48.

Our attempts to hydrolyze this urethan by heating with concentrated hydrochloric acid either at atmospheric pressure or in a sealed tube for a day at 130–140° failed to yield any of the desired 5-aminomethyl compound. The product was a white solid that did not melt or decompose by 320°, and which was insoluble in all organic solvents that we tried.

4-Methyluracil-5-methylamine.—In view of the unexpected difficulty encountered in the hydrolysis of the above urethan, we made use of Lindemann's method[7] for the conversion of an azide into an amine. By heating the azide with 50% acetic acid, the substance dissolved with evolution of gas. After a few minutes, white solid began to appear and was removed from time to time as the liquid was concentrated. This material was insoluble in water and did not melt below 310°. The filtrate was evaporated to dryness, the residue dissolved in water, filtered, and again concentrated. The white crystals obtained in this way, when dissolved in water, turned red litmus slowly, but distinctly, blue. With a drop of concentrated sulfuric acid the odor of acetic acid became easily perceptible, and the analysis also indicated that the product was the acetate of the amine. The yield from 12 g. of the azide was 2.8 g.

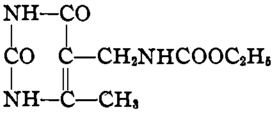
Anal. Calcd. for $C_6H_9O_2N_3 \cdot C_2H_4O_2$: N, 19.53. Found: N, 19.55.

The white salt turned to a very pale yellow material at 227–229°, but on further heating to 360° merely became progressively darker. On adding a solution of potassium hydroxide to a solution of the acetate there soon separated, upon scratching with glass, a finely crystalline white solid—fine needles under the microscope. After washing well with absolute alcohol, they were recrystallized from water in which they were easily soluble. The free base is a strong one, turning red litmus blue. On heating, it became brown by 335° but did not melt; yield 0.5 g.

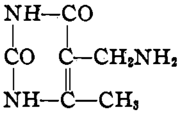
Anal. Calcd. for $C_6H_9O_2N_3$: C, 46.45; H, 5.85; N, 27.09. Found: C, 46.50; H, 6.50; N, 27.27.

Summary

Several new pyrimidines, whose preparation was stimulated by the work of Williams and others on vitamin B, are reported. Attention is called to the difficulty met in the attempt to hydrolyze the urethan



to the amine



PHILADELPHIA, PENNA. RECEIVED JULY 13, 1936

---

[9] Gabriel and Colman, *Ber.*, **32**, 1533–1534 (1899).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEW HAMPSHIRE]

A New Method for the Separation of Yttrium from the Yttrium Earths

BY H. C. FOGG AND LEWIS HESS

The use of urea as a precipitant for aluminum in the presence of calcium, barium, magnesium, manganese, zinc, cobalt, nickel, iron, cadmium and copper was the subject of an investigation by Willard and Tang,[1] and its use as a precipitant for gallium in the quantitative determination of that element was studied by Willard and Fogg.[2] Since the decomposition of urea[3] results in the formation of ammonia at a slow and uniform rate throughout the homogeneous solution, it may advantageously be applied to the fractionation of the yttrium earths.

Method of Separation

The mixed earths, in the form of their oxides, are dissolved in nitric acid, and the solution is nearly neutralized with ammonia and diluted. Ammonium sulfate is added in amount just insufficient to cause precipitation, followed by one- to two-tenths of an equivalent of urea. The solution is heated with stirring to 90–95°, and

---

[1] H. H. Willard and N. K. Tang, unpublished work.

[2] H. H. Willard and H. C. Fogg, unpublished work.

[3] E. A. Werner, *J. Chem. Soc.*, **113**, 84 (1918).

kept at this temperature for six to eight hours, during which time a precipitate gradually forms. This is filtered off, more urea is added, and the filtrate is again treated in the same manner, fractionation being continued until examination of the absorption spectrum indicates that the solution is nearly free of erbium.

Control of Fractionation

The materials subjected to fractionation were of two types, one a mixture of yttrium and erbium oxides containing very small amounts of the other yttrium earths, and the other a mixture of the hydroxides of the yttrium earths containing 2–3% of thorium. The separation was followed by means of the equivalent weight of the rare earth mixture, which was determined by conversion of oxide to sulfate.

Results of Fractionation

The results of two typical series of fractionations are given below.

TABLE I

FRACTIONATION OF YTTRIUM–ERBIUM MIXTURE

	At. wt.	% Er_2O_3	Weight, g.
Original material	134.6	58.0	100.6
Fraction 1	147.0	73.8	21.3
Fraction 3	141.3	66.5	11.3
Fraction 5	139.9	64.8	5.3
Fraction 7	135.9	59.7	8.2
Fraction 10[a]	107.8	24.0	18.7

[a] Represented the material remaining after the precipitation with urea, and was precipitated as oxalate.

TABLE II

FRACTIONATION OF MIXTURE CONTAINING THORIUM

	At. wt.	Equivalent % Er_2O_3,	Weight, g.
Original material	110.9	27.9	540.0
Fraction 2	131.9	54.6	18.3
Fraction 3	129.6	51.7	22.7
Fraction 5	120.1	39.6	49.7
Fraction 7	114.7	32.8	35.8
Fraction 9	107.2	23.2	31.7
Fraction 11[a]	98.2	11.8	211.3

[a] Represented the material remaining after the precipitation with urea, and was precipitated as oxalate.

The equivalent percentages in Tables II and III are computed upon the admittedly false assumption that the original material was a mixture of yttria and erbia only. The equivalent weight of fraction 1 of the series described in Table II was not determined as, due to its high thorium content, it was not soluble in hydrochloric acid. The thorium content of this fraction (as ThO_2) was found to be 36.4%. It was determined by the method of Carney and Campbell,[4] the solution of the sample being prepared by fusion with potassium pyrosulfate and extraction with water.

Several series of fractionations were carried out using a full equivalent of ammonium sulfate per equivalent of rare earth. This method was found to have no greater efficiency than the one recommended and to have a definite disadvantage, due to the limited solubility of yttrium sulfate. This made it necessary to use a dilute solution of the mixed nitrates with consequent increase in the volume and decrease in the quantity of material which could be handled conveniently. With the method described above, it was possible to use a relatively concentrated solution, say of the order of 5 to 6 per cent. Tables III and IV are representative of data obtained with the use of a full equivalent.

TABLE III

FRACTIONATION OF MATERIAL CONTAINING THORIUM

	At. wt.	Equivalent % Er	Weight, g.
Original material	112.8	30.3	101.1
Fraction 3	136.3	60.2	4.5
Fraction 5	125.4	46.3	5.8
Fraction 7	115.0	33.1	6.8
Fraction 9	108.5	24.9	6.7
Fraction 11	101.3	15.7	7.7
Fraction 13[a]	93.5	5.8	17.8

[a] Represented the material remaining after the precipitation with urea, and was precipitated as oxalate.

TABLE IV

FRACTIONATION OF YTTRIUM–ERBIUM MIXTURE

	At. wt.	% Er	Wt., g.
Original material	132.0	54.7	50.0
Fraction 1	144.7	70.9	3.9
Fraction 4	141.3	66.5	3.2
Fraction 7	136.8	60.8	2.9
Fraction 10	127.9	49.5	3.6
Fraction 14	110.9	27.9	1.2
Fraction 15[a]	101.7	16.2	3.8

[a] Represented the material remaining after the precipitation with urea, and was precipitated as oxalate.

Discussion

A comparison of the new method with those previously used may be of interest. The more important of the earlier methods include the fractional crystallization of the bromates,[5] the fractional decomposition of the nitrates by fusion,[6] and the fractional precipitation of the chromates,[7]

---

(4) R. J. Carney and E. D. Campbell, THIS JOURNAL, **36**, 1140 (1914).

(5) C. James, *ibid.*, **30**, 182 (1908).

(6) C. James, *ibid.*, **34**, 757 (1912).

(7) W. Muthmann and R. Böhm, *Ber.*, **33**, 42 (1900).

the basic nitrites,[8] the cobalticyanides[9] and the ferricyanides.[10] The bromate method is the standard one for the fractionation of the yttrium earths, but is not particularly effective for the preparation of pure yttrium. The new method compares favorably in efficiency with the nitrate fusion, chromate and basic nitrite methods. It appears to be superior to the ferricyanide and cobalticyanide methods. Grant and James[10] report a very high efficiency for the ferricyanide method, but no supporting data have been published.

Summary

A new method for the separation of yttrium from the yttrium earths has been proposed, and has been found to compare favorably in efficiency with the methods now in use.

DURHAM, NEW HAMPSHIRE RECEIVED MAY 1, 1936

---

[8] H. C. Holden and C. James, THIS JOURNAL, **36**, 1418 (1914).

[9] J. P. Bonardi and C. James, *ibid.*, **37**, 2642 (1915).

[10] A. J. Grant and C. James, *ibid.*, **39**, 933 (1917).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Activated Adsorption of Hydrogen and Carbon Monoxide on Zinc Oxide. The Effect of Water Vapor

BY ROBERT L. BURWELL, JR., AND HUGH S. TAYLOR

Poisons such as water vapor have been presumed to effect the retardation of catalytic processes by being adsorbed on the "active spots," thus blocking access of the reactants to such catalytically effective sections of the surface.[1] This access of reactants to catalytically effective sections of the surface consists according to Taylor[2] of an activated adsorption of the reactants on such regions of the surface. Reversible poisoning would accordingly result from an activated adsorption of the poison on the active sections of the surface, an adsorption possessed of energy relations such that the activation energy of desorption would be large compared with that of the other components of the system. In this fashion the activated adsorption of the reactants may be hindered.

Taylor and Sickman[3] and Taylor and Strother[4] investigated the activated adsorption of hydrogen on zinc oxide. The former investigators further reported that water vapor exerted an inhibitory influence on a catalytic action which they studied, the decomposition of propanol-2 on zinc oxide. It thus appeared of interest to study the effects of water vapor on the activated adsorption of hydrogen on zinc oxide.

Experimental

Rates of the activated adsorption of hydrogen on zinc oxide were determined by means of an apparatus and method similar to that described by Taylor and Strother.[4] The purified hydrogen could be saturated with water vapor at any desired temperature between 0° and room temperature by diverting it through a spiral bubbling column filled with distilled water and maintained at the desired temperature. Carbon monoxide was prepared by dropping formic acid on hot sulfuric acid. It was purified by passage over copper heated to 450°, soda lime, calcium chloride and phosphorus pentoxide. To supply water vapor to the adsorbent preliminary to rate runs, the apparatus was further provided with a buret of 410-cc. capacity. The zinc oxide was prepared from zinc oxalate as described by the above authors.

All gas volumes reported have been corrected to N. T. P. All the experiments described in this paper were performed on two samples of the same batch of zinc oxide. These samples were 3B, weight 16.5 g., and 3C, weight 22.7 g.

Before the start of these researches these adsorbents had been subjected to a series of determinations of the rates of activated adsorption, first of carbon monoxide and then of hydrogen. During the course of these adsorption measurements the activity of the surface had fallen slowly but steadily.

Results and Discussion

After a number of runs with hydrogen at 184 to 302°, it was observed that, at the completion of the adsorption, the preparations, notably 3B, had

---

[1] See, for example, Armstrong and Hilditch, *Proc. Roy. Soc.* (London), **A97**, 262 (1920); Dohse and Kälberer, *Z. physik. Chem.*, **5B**, 131 (1929).

[2] Taylor, THIS JOURNAL, **53**, 578 (1931).

[3] Taylor and Sickman, *ibid.*, **54**, 602 (1932).

[4] Taylor and Strother, *ibid.*, **56**, 586 (1934).