hour, diluted with water and extracted with ether. The residue after evaporation of the ether was sublimed in high vacuum at 130°, then crystallized from 50% acetone. After three crystallizations a constant melting point of 136° was obtained. This product does not precipitate with digitonin and does not absorb bromine. Mixed with pregnanol-20-one-3 it gives a depression of 21° in melting point.

Anal. Calcd. for $C_{21}H_{34}O_2$: C, 79.2; H, 10.8. Found: C, 79.2; H, 10.7.

Acetate of *epi*-Pregnanolone.—A solution of 100 mg. of *epi*-pregnanolone in 5 cc. of acetic anhydride was refluxed for thirty minutes. The excess acetic anhydride was evaporated and the residue was crystallized from 70% acetone; m. p. 99°.

Anal. Calcd. for $C_{23}H_{36}O_3$: C, 76.8; H, 10.1. Found: C, 76.5; H, 10.2.

Pregnandione from *epi*-Pregnanolone.—To 100 mg. of *epi*-pregnanolone in 15 cc. of acetic acid at room temperature was added 50 mg. of chromic oxide in 25 cc. of acetic acid. It was let stand at 15° for twelve hours, then at room temperature for three hours. Water was added and the product was extracted with ether and the ether solution was washed with sodium carbonate solution. The residue after evaporation of the ether was sublimed under high vacuum at 100°. The product was then crystallized from dilute acetone; m. p. 120°. No depression in melting point was obtained upon mixture with an authentic sample of pregnandione from pregnandiol.

Anal. Calcd. for $C_{21}H_{32}O_2$: C, 79.7; H, 10.2. Found: C, 79.8; H, 10.5.

Reduction of *epi*-Pregnanolone.—To a solution of 100 mg. of *epi*-pregnanolone in 100 cc. of acetic acid was added 100 mg. of Adams platinum oxide catalyst. The solution was shaken with hydrogen at 45 pounds (3 atm.) pressure for three hours. The product was crystallized from alcohol and washed with ether, m. p. 230°. Mixed with pregnandiol of m. p. 242° it gave a depression in melting point to 215°. This differs from natural pregnandiol only in the configuration of the –OH group on C-20. It does not precipitate with digitonin, showing that the original –OH group was in the 3-position in the *epi*-form.

Anal. Calcd. for $C_{21}H_{36}O_2$: C, 78.8; H, 11.3. Found: C, 78.6; H, 11.3.

Summary

epi-Pregnanolone an isomer of *epi-allo*-pregnanolone has been isolated from human pregnancy urine, and its structure proved by oxidation to pregnandione and reduction to a pregnandiol. A monoacetate and a monosemicarbazone were formed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

Attempts to Prepare Cerous Amide[1]

BY F. W. BERGSTROM

Some years previously[2] it was found impossible to prepare aluminum amide by mixing liquid ammonia solutions of ammonium bromide and potassium ammonoaluminate. Since the substance so precipitated was of variable composition ($AlN + xNH_3$, an "ammonous nitride"), it became of interest to synthesize amides of other trivalent elements which might exhibit a similar behavior.

The addition of potassium amide to a solution of cerous iodide in liquid ammonia gives a fine white crystalline precipitate of an ammonobasic iodide, instead of the expected cerous amide. Dried in a vacuum at 20°, the compound corresponds to the formula, $CeI_3 \cdot Ce(NH_2)_3 \cdot 10NH_3$; heated in a vacuum at 150–180°, the composition becomes, $CeI_3 \cdot Ce(=NH)NH_2$. It has not yet proven possible to prepare pure cerous amide by the action of potassium amide on cerous thiocyanate in liquid ammonia.

Experimental

Cerous iodide, as prepared by the action of ammonium iodide on an excess of chemically pure metallic cerium in liquid ammonia, forms two colorless liquid phases.[3] At 0°, in a sufficiently large volume of ammonia, the two phases merge into one so that the ammonobasic salt is best precipitated at this temperature by the slow addition of somewhat less than the theoretical quantity of potassium amide. Prior to analysis, the crystals are washed several times with liquid ammonia and dried in a vacuum of 1–2 mm. at room temperatures, and at 150–180°.[4] The heated substance was a brick-red. It was hydrolyzed with water vapor, then dissolved in dilute sulfuric acid. Cerium was determined as the dioxide, after previous precipitation as hydroxide or oxalate. Iodine was weighed as silver iodide, and nitrogen was estimated by distillation of an aliquot portion with alkali into standard acid.

Mercuric cyanide reacts with an excess of cerium to form a sparingly soluble precipitate, probably of a cerous cyanide, which could not be freed from metallic cerium or mercury for analysis. Sulfur and selenium slowly dissolve

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[1] Original manuscript received June 11, 1935.

[2] Bergstrom, *J. Phys. Chem.*, **32**, 434 (1928).

[3] Bergstrom, *ibid.*, **29**, 162 (1925). The light pink solution previously reported was doubtless due to impurities in the cerium used.

[4] Franklin, "The Nitrogen System of Compounds," Reinhold Publishing Corporation, New York, N. Y., 1935, pp. 317–330.

TABLE OF ANALYSES

DRIED IN A VACUUM AT ROOM TEMPERATURES

	Calcd. for $Ce_2I_3N_{13}H_{36}$	1	2	3	4
Ce	31.87	32.5	31.9	30.8	32.7
N	20.70	20.5	20.3	21.3	19.4
I	43.30	42.9	43.0	43.0	43.1

HEATED IN A VACUUM AT 150–180°

	Calcd. for $Ce_2I_3N_2H_3$				
Ce	40.50	41.1	39.9	39.5	41.0
N	4.05	4.2	4.7	4.0	3.4
I	55.02	54.2	53.8	55.2	54.0

this precipitate to form cerous thiocyanate and selenocyanate,[5] respectively, neither of which could be crystallized, and so obtained in a pure condition, because of their high solubilities. When a solution of potassium amide in liquid ammonia is poured into one of cerous thiocyanate there results a flocculent yellow precipitate, which at first dissolves, becoming permanent only after further additions of amide. This indicates the formation of a soluble ammonobasic thiocyanate. The precipitate was not a pure cerous amide, imide or nitride. (Cerium content too low. Calcd. for $Ce(NH_2)_3$: Ce, 74.4. Found, 64–72.)

Summary

The ammonobasic iodide, $CeI_3 \cdot Ce(NH_2)_3 \cdot 10NH_3$ and its deammonation product, $CeI_3 \cdot Ce(NH)NH_2$, have been prepared.

STANFORD UNIVERSITY, CALIF. RECEIVED MAY 24, 1937

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(5) *Cf.* Bergstrom, THIS JOURNAL, **48**, 2319 (1926).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Rate of Dissolution of Benzoic Acid in Dilute Aqueous Alkali

BY CECIL V. KING AND S. S. BRODIE

If a crystal of barium hydroxide is dipped into a rapidly stirred solution of dilute acid containing phenolphthalein, a thin layer of solution at the surface of the crystal becomes pink. The thickness of the alkaline layer varies with the stirring speed, and, if the latter is very low, irregular streamers of alkaline solution may extend one or two centimeters out into the solution. With a very soluble base, as sodium hydroxide, even a high stirring speed cannot confine the alkaline solution to a thin, even layer.

The Nernst diffusion layer theory of dissolution rates predicts this behavior; it assumes that the base saturates a monomolecular film of liquid next its surface so rapidly that a layer is formed in which concentration gradients of both acid and base exist, due to their neutralization within the layer. This type of system was discussed briefly by Brunner[1] but no systematic study of such cases has been made.

If solid benzoic acid is immersed in an alkaline solution a similar gradient of acid and base concentrations should exist near the surface. It will be shown in this paper that the equations based on this assumption account satisfactorily for the dissolution rate of solid benzoic acid in dilute sodium and potassium hydroxide solutions. Benzoic acid was chosen for study because test cylinders with smooth, even surfaces can be prepared, the solubility in water is low and accurately known and the dissolution rate in water has been measured by several investigators.[2-4]

We shall assume, as an approximation, that the Nernst–Brunner treatment is essentially correct for this system. Let δ be the total thickness of the diffusion layer, $\delta - y$ the distance from the surface at which neutralization occurs. Then the rate of dissolution and neutralization will be given by Fick's law as

$$\frac{dx}{dt} = \frac{AD_A s}{\delta - y} = \frac{AD_B c}{y} \tag{1}$$

where x is the amount dissolved in time t, A is the surface area of the solid, D_A and D_B are the diffusion coefficients of acid and base, respectively, s is the solubility of the acid and c the concentration of the base, all in suitable units.

Actually, it is known that the effective thickness of the diffusion layer varies with the diffusion coefficient of the reagent.[5,6] The variation is not great over the range considered here and little error is introduced by neglecting this factor.

Many investigators believe that the outer surface of the diffusion layer is diffuse and ragged and that the average concentration gradient is not linear over a considerable fraction of the total layer thickness. The experiment described above with barium and sodium hydroxides indicates that

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(1) Brunner, *Z. physik. Chem.*, **47**, 56 (1904).

(2) Noyes and Whitney, *ibid.*, **23**, 689 (1897).

(3) Bruner and St. Tolloczko, *ibid.*, **35**, 283 (1900).

(4) Wildermann, *ibid.*, **66**, 445 (1909).

(5) King, THIS JOURNAL, **57**, 828 (1935).

(6) King and Howard, *Ind. Eng. Chem.*, **29**, 75 (1937).