

for an unsubstituted cyclopentenone. Wolff-Kishner reduction of VI followed by chromic acid oxidation of the product in a current of steam⁸ gave acetic acid and 1-methylcyclopentanecarboxylic acid.⁹

The appropriate blank experiments showed that only the chromophore of ring A of I was involved in photochemical change. As expected⁴ III was stable to hot aqueous acetic acid and is *not* the precursor of II. It is possibly analogous to the "compound A4" obtained recently¹⁰ by irradiation of 1-dehydrotestosterone acetate.

(8) F. Pregl, "Quantitative Organic Microanalysis," Ed. J. Grant, J. and A. Churchill, London, 5th edition, 1951, p. 206.

(9) H. Meerwein, *Ann.*, **417**, 255 (1918).

(10) H. Dutler, H. Bosshard and O. Jeger, *Helv. Chim. Acta*, **40**, 494 (1957).

(11) Arthur D. Little, Visiting Professor, Massachusetts Institute of Technology, Cambridge, Mass., 1958.

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COPPER SALT CATALYSIS OF THE AIR OXIDATION OF REDUCED URANIUM COMPOUNDS IN CARBONATE-BICARBONATE SOLUTIONS¹

Sir:

Recent increasing interest in the carbonate leaching of uranium ores² prompts us to report the following data.

We have found that copper salts, especially in the presence of ammonia, catalyze the air oxidation and dissolution of reduced uranium compounds in carbonate-bicarbonate solutions.

The rate of U_3O_8 dissolution in air-blown 0.5 M Na_2CO_3 -0.5 M $NaHCO_3$ was increased by a factor of approximately seven in the presence of 25 mg. copper/l. (added as copper sulfate) and by a factor of 14 when 0.1 M NH_4OH was also present. When the copper sulfate was added to the 0.5 M Na_2CO_3 -0.5 M $NaHCO_3$ solution, no precipitate formed, but the solution acquired a blue color more intense than can be accounted for on the basis of a simple cupric species. This suggests the formation of a cupric carbonate complex.³ The addition of ammonia intensified the color further indicating a change in the cupric species present. The rate of UO_2 dissolution was increased only slightly by the presence of copper salts alone but was increased by a factor of over two in the presence of copper salts and ammonia. The U_3O_8 for these experiments was prepared by decomposition at 1100° of UO_3 obtained from the S. W. Shattuck Co. The UO_2 was obtained from them as such.

A brief study was made to determine the factors involved in the rate of the copper-catalyzed U_3O_8 dissolution. Since dissolution at 90° is over three times faster than at 70° all of the following results were determined at 90°. The initial rate is directly proportional to the surface area of the U_3O_8 added. Neither ionic strength nor total CO_2 , at constant pH, has any effect. The use of oxygen instead of

air has no effect beyond that due to the increase in the rate of uncatalyzed air oxidation. The use of nitrogen instead of air decreases the rate by a factor of over 2.5. (Sufficient copper salt was used so that the decrease in cupric copper concentration was not significant.) This indicates that in the air blown system an oxidizing species other than cupric copper is formed in the catalytic process. The most likely compound is hydrogen peroxide from the reduction of oxygen during the air oxidation of the reduced copper substance. Part of the U_3O_8 is presumably oxidized by this hydrogen peroxide.

The dependence on copper concentration is approximately first power under nitrogen, but very low (less than 0.3 power) under air (see Fig. 1).

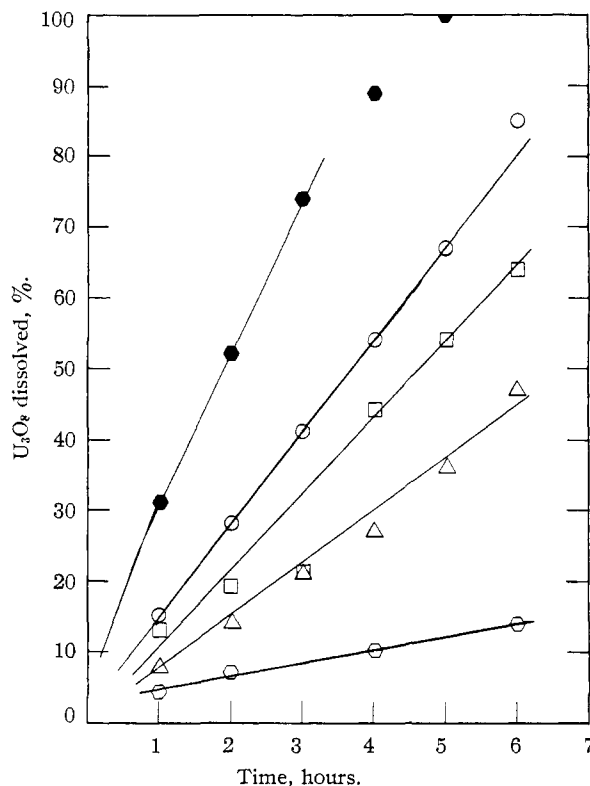


Fig. 1.—Dissolution of 1 g./l. U_3O_8 in air-blown 0.5 M Na_2CO_3 at 90°: ●, 25 mg./l. Cu, 0.1 M NH_4OH ; ○, 25 mg./l. Cu; □, 2.5 mg./l. Cu; △, 0.25 mg./l. Cu; ◇, no Cu.

The effects of the variables on the rate of U_3O_8 dissolution in the presence of copper and ammonia are qualitatively similar to those with copper alone.

Cobalt, manganese, thallium and vanadate salts have also been shown to act as catalysts, but they are not as effective as copper salts.

WESTERN DIVISION
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A NEW SYNTHESIS OF TROPOLONE

Sir:

A new synthesis of tropolone starting from tetrafluoroethylene and cyclopentadiene has been discovered. The key to this synthesis is the thermal

(1) This work was carried out for the Atomic Energy Commission under Contract AT(49-6)-923.

(2) R. G. Beverly, A. W. Griffith and W. A. Millsap, *Mining Engineering*, **9**, 988 (1957).

(3) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, London, England, 1950, p. 168.