ported[1] to occur only in perchloric acid solutions, also occurs in sulfuric acid solutions.

The following mechanism is proposed for the photoreduction of ceric ions in both perchloric and sulfuric acid solutions:

$$\mathrm{Ce^{++++}{\cdot}H_2O} + h\nu \longrightarrow \mathrm{Ce^{+++} + H^+ + OH} \quad (1)$$

$$\mathrm{OH + Ce^{+++} \longrightarrow Ce^{++++} + OH^-} \quad (2)$$

$$\mathrm{OH + OH \longrightarrow H_2O_2} \quad (3)$$

$$\mathrm{2Ce^{++++} + H_2O_2 \longrightarrow 2Ce^{+++} + 2H^+ + O_2} \quad (4)$$

Reactions (1) and (4) express over-all chemical processes. Experimental evidence has been recently obtained[2,3] for reaction (3) through a study of the effects of Br^- and Cl^- upon the formation of "molecular" H_2O_2 in the decomposition of water by cobalt gamma radiation.

Br^- and Cl^- enhance the rate of photoreduction of ceric ions. This is interpreted as experimental evidence for the intermediate formation of OH radical postulated by Weiss and Porret.[1] Br^- and Cl^-, which readily react[4] with OH radical in acid solutions, prevent the occurrence of reaction (2). The quantum yield for cerous ion formation then becomes equal to the primary quantum efficiency of reaction (1). Bromine and chlorine atoms are formed which combine to yield molecular bromine and chlorine since, as reported[5] for the thermal reaction of ceric ion with Br^-, no back reaction occurs.

HCOOH also enhances the rate of photoreduction by prevention of reaction (2) through reaction with OH radical as postulated by Hart[6]

$$\mathrm{OH + HCOOH \longrightarrow H_2O + HCOO} \quad (5)$$

The HCOO radical further enhances the rate of photoreduction by its behavior as a reducing agent according to reaction (6)

$$\mathrm{Ce^{++++} + HCOO \longrightarrow Ce^{+++} + H^+ + CO_2} \quad (6)$$

or through the sequence of reactions (7)[7] and (8).[8]

$$\mathrm{HCOO + O_2 \longrightarrow HO_2 + CO_2} \quad (7)$$

$$\mathrm{HO_2 + Ce^{++++} \longrightarrow Ce^{+++} + H^+ + O_2} \quad (8)$$

Hart[7] has concluded that HCOO is capable of reducing ferric ion which is a weaker oxidizing agent than ceric ion. The primary quantum efficiency for the formation of OH radicals, measured at 23°, is 0.10 in 0.8 *N* sulfuric acid solutions and 0.12 in 0.8 *N* perchloric acid solutions. These primary quantum efficiencies are equal to (a) the measured initial quantum yield (when Ce^{+++} concentration equals zero) for cerous ion formation in 0.8 *N* sulfuric acid when Br^- or Cl^- is present in 10^{-2} molar concentration and (b) one-half the measured initial quantum yields for cerous ion formation when HCOOH is present in 2×10^{-2} molar concentration both in 0.8 *N* sulfuric acid and in 0.8 *N* perchloric acid.

Since the primary quantum efficiency is about the same for sulfuric and perchloric acid solutions, the previous failure[1] to observe photoreduction in sulfuric acid solutions is attributed to the greater effectiveness of reaction (2) in sulfuric acid than in perchloric acid.

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE THOMAS J. SWORSKI

RECEIVED JANUARY 10, 1955

---

[2] T. J. Sworski, THIS JOURNAL, **76**, 4687 (1954).

[3] T. J. Sworski, *Radiation Research*, **2**, in press (1955).

[4] H. Taube and W. C. Bray, THIS JOURNAL, **62**, 3357 (1940).

[5] E. L. King and M. L. Pandow, *ibid.*, **75**, 3063 (1953).

[6] E. J. Hart, *ibid.*, **73**, 68 (1951).

[7] E. J. Hart, *ibid.*, **74**, 4174 (1952).

[8] T. J. Hardwick, *Can. J. Chem.*, **30**, 23 (1952).

A NEW TYPE OF SUBSTITUTED BOROHYDRIDE

Sir:

The authors have shown[1] that two moles of carbon dioxide when present in excess react with one mole of solid sodium borohydride in a sealed tube at 125° to form a white solid from which it is possible to recover, by hydrolysis, one half of the carbon as methanol and the remaining half as formic acid. These observations suggest the equation[2]

$$\mathrm{NaBH_4 + 2CO_2 \longrightarrow NaBO(O_2CH)(OCH_3)}$$

We wish to report the effect of reduced (room) temperatures and the use of liquid dimethyl ether as a solvent upon the course of the reaction. Under these conditions three, instead of two, moles of carbon dioxide are taken up per mole of sodium borohydride, and the product is a powdery white solid with a volume about 6 to 8 times as great as the sodium borohydride originally used. Treatment of this solid with hydrochloric acid produced 5.54 mmoles of hydrogen; when treated with dilute sulfuric acid, 5.94 mmoles of boric acid and 16.49 mmoles of formic acid were obtained (all values based on one gram of sample).

These data are consistent with a product formed according to the equation

$$\mathrm{NaBH_4 + 3CO_2 \longrightarrow NaBH(O_2CH)_3}$$

The product thus represents the first reported isolation of a formatoborohydride. Although this material is fairly stable, there is some evidence that, on standing, it slowly liberates methyl formate. This latter substance is, indeed, obtained in appreciable quantity when sodium triformatoborohydride is heated to the temperature at which it appears to melt (about 125°). It may be noted that the material obtained in the high temperature reaction is *not* the same as that obtained by heating the product of the low temperature reaction.

DEPARTMENT OF CHEMISTRY THOMAS WARTIK
PENNSYLVANIA STATE UNIVERSITY RICHARD K. PEARSON
COLLEGE OF CHEMISTRY AND PHYSICS
STATE COLLEGE, PENNSYLVANIA

RECEIVED JANUARY 7, 1955

---

[1] In a paper presented to the Division of Physical and Inorganic Chemistry of the American Chemical Society at the New York Meetings in the Fall of 1954. This material will shortly be submitted for publication.

[2] Although the product has tentatively been assigned the formula shown above, it is possible that it is a mixture of $NaBO_2$ and the hitherto unreported $NaB(OCH_3)_2(O_2CH)_2$. This possibility will be discussed in a forthcoming publication.