such a salt-formation seems improbable, for a displacement of chloride as an ion would remove most of the steric hindrance, permitting the electronegativity effect to establish a stability order opposite to that which is observed. This argument would fail only if the differences of lattice energy were sufficiently favorable to the stability of the adducts of the less chlorinated silanes—and the lattice energies in such systems can scarcely be large enough to permit such significant differences.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIFORNIA

Decomposition of Fused Sodium Hydroxide by Fast Electrons

BY C. HOCHANADEL

RECEIVED JANUARY 29, 1954

An experiment was carried out to determine the stability of fused sodium hydroxide under high energy radiation. Approximately six grams of reagent grade NaOH (Baker C.P., 98.9% NaOH) was first melted under vacuum in a cylindrical nickel crucible. After cooling, the crucible was rapidly transferred to a Pyrex irradiation cell of the type shown in Fig. 1, and the system immediately evacuated. By use of a vertical Van de Graaff generator, the sample was irradiated for 40 minutes with 1.3 Mv. electrons at a current of 20 microamperes. This energy was sufficient to maintain the NaOH at about 400° (m.p. 318°). Upon analysis by a micro method, the only gas found in the gas phase was 0.05 ml. (S.T.P.) of hydrogen. This corresponds to an extremely small net yield of 4×10^{-4} molecule per 100 e.v. energy absorbed. Upon dissolving the solid in degassed water, no additional gas was found, and the resulting solution showed negligible oxidizing power. On repeating the experiment by merely heating a degassed sample in the absence of radiation, approximately the same amount of hydrogen was produced. This indicates that the fused NaOH is extremely stable to radiation and that the small amount of hydrogen probably resulted from reaction with the nickel crucible. The corrosion was not visibly observable.

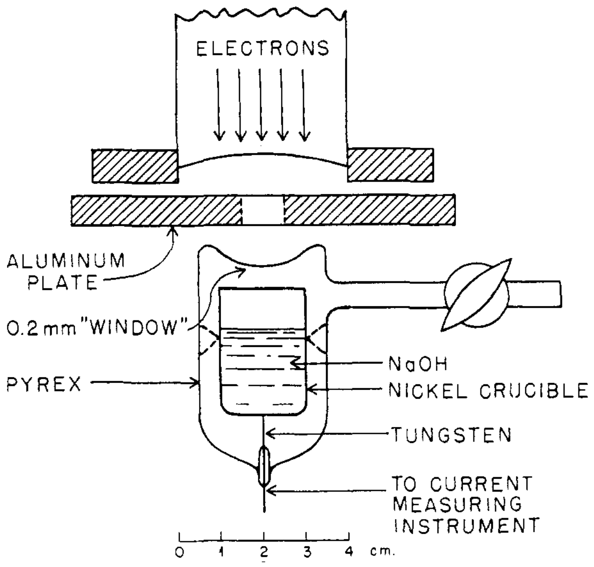

Fig. 1.—Apparatus for irradiating sodium hydroxide with electrons.

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

Electrophilic Displacement Reactions. IV. Kinetics of the Brominolysis of *m*-Chlorobenzeneboronic Acid in Aqueous Solution[1-3]

BY HENRY G. KUIVILA AND EDWARD J. SOBOCZENSKI

RECEIVED DECEMBER 28, 1953

The kinetics of the reaction of bromine with *m*-chlorobenzeneboronic acid have been investigated in the *p*H range 2.10–4.74. The dependence of the rate upon bromide ion concentration and *p*H indicates that molecular bromine and the boronate anion are involved in the transition state of the rate-determining step. Sodium fluoride and several chelating agents have been shown to function as specific catalysts for the reaction.

The areneboronic acids comprise a valuable group of compounds for the study of mechanisms of aromatic electrophilic displacement reactions. This is true because the boronic acid group undergoes replacement by several electrophilic reagents at measurable rates. In a previous communication[4] an investigation of the kinetics of the reaction between bromine and benzeneboronic acid, yielding bromobenzene, hydrogen bromide and boric acid, in aqueous acetic acid solution was described. The results indicated that molecular bromine reacts with a quadricovalent boronate anion in the rate-determining step.

Due to the limitations imposed by the use of an acidic solvent it was decided to extend this work using water as the solvent. The rate of reaction between bromine and benzeneboronic acid in water proceeds too rapidly for measurement by the conventional method involving assay of aliquots. Of the several acids which could be conveniently studied in water *m*-chlorobenzeneboronic acid was chosen because it is more soluble than the other

---

[1] For preceding publication in this series see H. G. Kuivila, THIS JOURNAL, **76**, 870 (1954).

[2] Taken in major part from the Master's thesis of E. J. Soboczenski, September, 1953.

[3] It is a pleasure to acknowledge substantial support of this work provided by the Office of Naval Research under Contract Nonr 806(01).

[4] H. G. Kuivila and E. K. Easterbrook, THIS JOURNAL, **73**, 4629 (1951).