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.

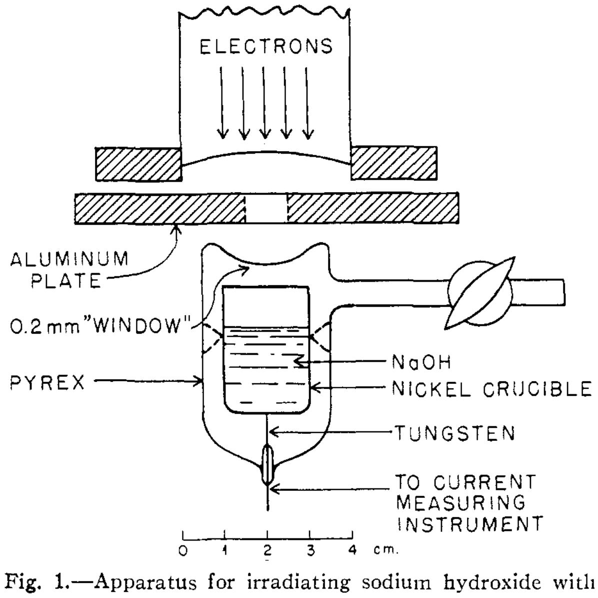


Fig. 1.—Apparatus for irradiating sodium hydroxide with electrons.

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).

readily accessible *meta* and *para* halogeno derivatives.

We have studied the kinetics over most of the range *p*H 2 to 5 and have found a significant difference between the nature of the base catalysis in water and that in "50%" aqueous acetic acid. It has been possible to determine quantitatively the catalytic efficiencies of sodium fluoride and several hydroxy acids.

Experimental

Reagents.—*m*-Chlorobenzeneboronic acid was prepared by the method of Bean and Johnson.[5] It was recrystallized from water, dried for two hours at 110° and recrystallized from benzene. After repetition of this process the pure anhydride was obtained; m.p. 181.5–183° uncor. (lit. 178–179°)[6]; neut. equiv.[7] calcd. 138.4, found 138.0.

Chloroacetic acid was recrystallized from benzene and the sodium salt was made by adding the acid (slight excess) in methanol to sodium methoxide in methanol at 0°. The salt was filtered, washed twice with methanol and dried, ultimately at 110° for three hours. To minimize the danger of solvolysis to glycolic acid (a good catalyst for the reaction) the chloroacetate buffer solutions were prepared on the day they were used. α-Hydroxyisobutyric acid was obtained by saponification of the commercially available ethyl ester. The ether extract of the acidified saponification product yielded upon evaporation the crude hydroxy acid which was recrystallized from benzene; m.p. 79.0–80.0° uncor. (lit. 79.0°).[8] *cis*-Cyclohexane-1,2-diol was prepared by permanganate oxidation of cyclohexene.[9] Sodium perchlorate which was used to adjust ionic strengths was dried to constant weight at 110° and stored in a desiccator. All other reagents were the purest available commercially and were used as obtained. A Beckman model H_2 *p*H meter was used for *p*H measurements.

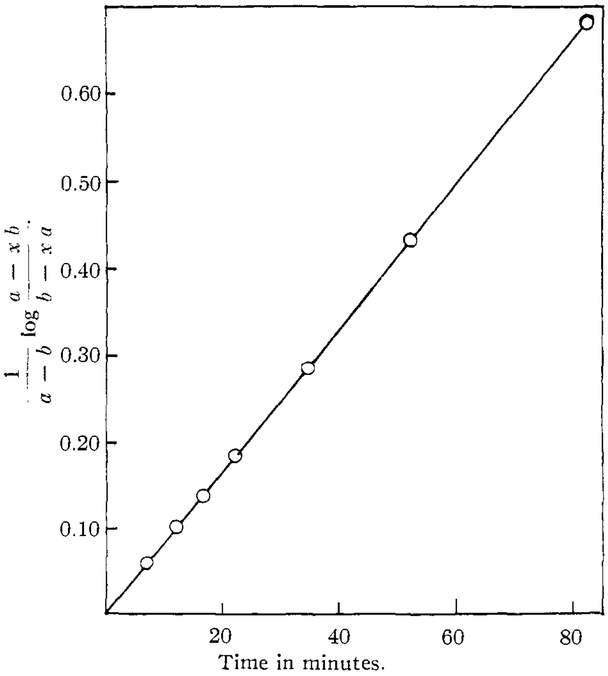


Fig. 1.—Kinetic plot for brominolysis of *m*-chlorobenzeneboronic acid in aqueous solution at 25.0°; $[Br_2]_0$, 0.0100 *M*; $[RB(OH)_2]_0$, 0.00507 *M*; *p*H, 4.20; [NaOAc], 0.45 *M*; [HOAc], 1.05 *M*; μ, 0.70.

Kinetic Procedure.—The kinetic runs were carried out at 25.0 ± 0.03° in the same way as before[4] with the exception that the boronic acid was weighed into a small beaker 10 mm. × 15 mm. which was dropped into a solution containing desired amounts of water and buffer and sodium perchlorate solutions. Then, after the boronic acid had dissolved the reaction vessel was placed in the bath at 25.0 ± 0.03°.

The run was started at least 15 minutes later by the addition of bromide–bromine solution.

It was ascertained experimentally that none of the chelating agents used reacted significantly with bromine under the conditions of the kinetic experiments.

Product Isolation.—A reaction mixture (500 ml.) at *p*H 4.8, 0.30 *M* in acetic acid, 0.45 *M* in sodium acetate, 0.25 *M* in sodium bromide, 0.030 *M* in bromine and in boronic acid was kept at 25.0° until the reaction was more than 90% complete. The excess bromine was reduced with thiosulfate and the product was extracted with ether. After evaporation of the ether *m*-chlorobromobenzene, 2.1 g. (66%), boiling at 196–200° was distilled. This product was allowed to react with 0.23 g. of magnesium in 20 ml. of dry ether and the reaction product poured onto a suspension of Dry Ice in ether. The *m*-chlorobenzoic acid isolated after hydrolysis was recrystallized from water; m.p. 151–152°, undepressed upon admixture with an authentic sample of m.p. 152–153°.

Results and Discussion

Kinetic Order.—The data from all rate experiments were used in evaluating the second-order rate constant, $k_{\text{obsd.}}$, by the conventional integrated rate equation

$$\frac{1}{a-b}\ln\frac{a-x}{b-x}\times\frac{b}{a}=k_{\text{obsd.}}t \qquad (1)$$

where a and b represent stoichiometric initial concentrations of bromine and boronic acid and x represents the concentration of products. All reactions were carried out at high bromide ion concentrations to minimize volatility losses and simplify computations. Since the reaction rate depends on *p*H, all solutions were buffered.

A typical rate plot (for the run marked with an asterisk in Table I) is shown in Fig. 1. The constancy of $k_{\text{obsd.}}$ as initial concentrations of reactants were varied is shown in Table I. It can be seen that the maximum difference in rate constants is about 7.5%. The values in the two parts of Table I differ by about 15% because of the difference in buffer concentrations which is discussed below.

TABLE I

VARIATION OF INITIAL BROMINE AND BORONIC ACID CONCENTRATIONS

Bromine, moles l. × 10^3	Boronic acid, moles l. × 10^3	100 × $k_{\text{obsd.}}$, l. mole^{-1} sec.$^{-1}$	Bromine, moles l. × 10^3	Boronic acid, moles l. × 10^3	100 × $k_{\text{obsd.}}$, l. mole^{-1} sec.$^{-1}$
2.50	5.09	6.86	4.00	1.95	7.55
2.50	5.11	6.77	4.00	5.11	7.66
4.00	5.02	6.66	4.00	7.47	7.83
6.00	5.01	6.56	4.00	7.81	7.60
8.00	5.01	6.45	20.00	9.92	7.37
8.00	5.07	6.50	10.00	1.95	7.64
10.00	5.01	6.46*	6.00	5.11	7.28
20.00	5.09	6.38	10.00	7.47	7.26
20.00	5.07	6.48			

First three columns of table: *p*H, 4.20 ± 0.02; acetate, 0.45 *M*; acetic acid, 1.05 *M*; bromide, 0.25 *M*, μ, 0.70. Last three columns of table: *p*H, 4.17 ± 0.03; acetate, 0.30 *M*; acetic acid, 0.70 *M*; bromide 0.25 *M*, μ, 0.70.

In order to identify the effective brominating species runs with different concentrations of so-

---

[5] F. R. Bean and J. R. Johnson, This Journal, **73**, 5068 (1951).

[6] H. G. Kuivila and A. R. Hendrickson, *ibid.*, **74**, 5068 (1952).

[7] G. E. K. Branch, D. L. Yabroff and B. Bettman, *ibid.*, **56**, 1865 (1934).

[8] E. P. Wightman and H. C. Jones, *Am. Chem. J.*, **40**, 80 (1911).

[9] W. Markownikoff, *Ann.*, **302**, 22 (1898).

TABLE II

EFFECT OF BUFFER CONCENTRATION ON OBSERVED RATE

Ionic strength, 0.70 and sodium bromide, 0.25 *M* in all runs.

NaOAc, moles/l.	*p*H, 4.74; *R*,[b] 0.667		*p*H, 4.41; *R*,[b] 1.22		*p*H, 4.15; *R*,[b] 2.33		*p*H, 3.71; *R*,[b] 5.67	
	$k_{obsd.}$[a]	$k_{calcd.}$[a]	$k_{obsd.}$[a]	$k_{calcd.}$[a]	$k_{obsd.}$[a]	$k_{calcd.}$[a]	$k_{obsd.}$[a]	$k_{calcd.}$[a]
0	0.355	(0.355)[c]	0.177	(0.177)[c]	0.0955	(0.0955)[c]	0.0370	(0.0370)[c]
0.12	...	...	...	...	.0876	.0886	....	....
.15	.360	.344	.160	.163	....	....	.0275	.0293
.225	.363	.337	.160	.158	....	....	.0262	.0254
.30	.339	.331	.159	.154	.0767	.0780	.0220	.0216
.375	.339	.325	.153	.151	....	....	.0192	.0177
.45	.320	.319	.150	.149	.0666	.0692	.0147	.0138

[a] Units, l. mole^{-1} sec.$^{-1}$. [b] R = ratio of concentration of acetic acid to concentration of sodium acetate. [c] This value used as k_0 in evaluating other constants in this column.

dium bromide (0.10 to 0.40 *M*) were carried out. For each concentration the fraction of the stoichiometric bromine which was present as molecular bromine at the beginning of the run was calculated. The value for the equilibrium constant of formation of tribromide ion was estimated from the data of Griffith, McKeown and Winn.[10] Their data include values of the constant as a function of ionic strength at 16.5 and 21.5°. We have used a value (16.2) obtained by linear extrapolation from their value at 21.5°. A plot of k_{obsd} *vs.* fraction of free bromine is shown in Fig. 2. From the fact that the plot is linear it is evident that the effective brominating species is molecular bromine. Furthermore, since the intercept is at the origin it may be concluded that, as might have been anticipated, tribromide ion is essentially ineffective as a brominating agent.

Effect of *p*H and Buffer Concentration.—It was shown that in "50%" acetic acid various bases have specific catalytic effects which are not correlated by the Brönsted catalysis law.[4] On the basis of this fact it was anticipated that the rate in water would increase with buffer concentration. With acetate buffers the opposite effect was observed as can be seen from the values of k_{obsd} in Table II. Scrutiny of this effect reveals that it cannot be attributed to either acetate or acetic acid alone. However, it can be regarded as being due to a combined effect of these two species. This has been done by assuming the expression (2)

$$k_{obsd} = k_0\,\{1 - \alpha[\mathrm{HOAc}] - \beta[\mathrm{AcO^-}]\} \qquad (2)$$

where k_0 is the value of k_{obsd} obtained by extrapolating a plot of k_{obsd} *vs.* buffer concentration to zero and α and β are empirical constants assumed to be independent of *p*H. These constants were evaluated by the method of averages.[11] Examination of the data shows a maximum deviation of about 7% between k_{calcd} and k_{obsd} when values of 0.233 for α and 0.070 for β were used.

The decrease due to acetic acid is undoubtedly a reflection of the change in the equilibrium constant for tribromide ion formation brought about by a change in solvent composition. In water at 15° the value of the constant is 16.7 but in 25% acetic acid it has increased to 41.6.[12] Our highest acid concentration, 2.55 *M*, corresponds to about 15% acetic acid. A quantitative comparison of the change in equilibrium constant with α cannot be made because values for the former are not available at acetic acid concentrations below 25%. A linear change cannot be assumed because in 50% acetic acid the value of the constant has changed to only 50.

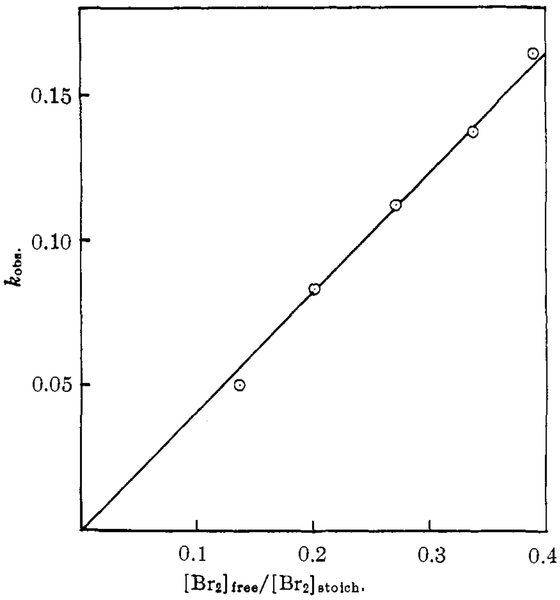


Fig. 2.—Dependence of observed rate constant on fraction of stoichiometric bromine present as Br_2.

The specific nature of the rather small effect of acetate is uncertain. It may merely be due to the change in medium as sodium acetate replaces sodium perchlorate. At high concentrations it would be fortuitous if each had exactly the same effect on the activities of the reacting species and the transition state complex.[13]

Runs at different buffer concentrations were also carried out in the chloroacetate buffers at *p*H 2.1 2.6 and 3.2. No significant trend in the rate constants which could not be accounted for by the slight variation in *p*H (0.02 to 0.06 unit) was observed.

Figure 3 is a plot of log k_0 *vs.* *p*H from the data just discussed. The line as drawn has slope 0.975, in good agreement with the theoretical value of 1.00 for specific lyate ion catalysis.

---

(10) R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 101 (1932).

(11) T. B. Crumpler and J. H. Yoe, "Chemical Computations and Errors," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 215.

(12) W. J. Jones, *J. Chem. Soc.*, **99**, 392 (1911).

(13) As pointed out by a referee some interaction between boronic acid and buffer constituents as the cause of the rate decrease cannot be definitely excluded.

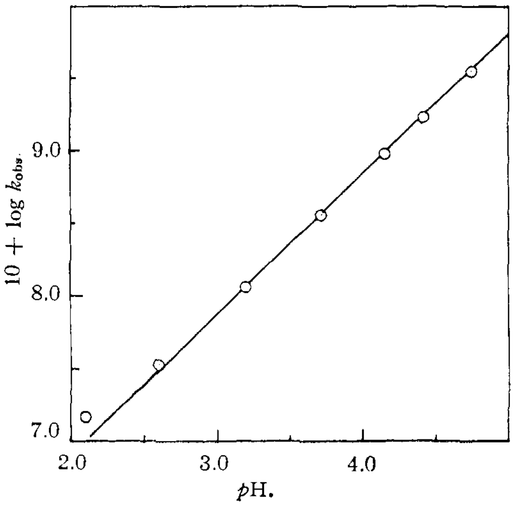


Fig. 3.—Effect of pH on the rate of brominolysis of *m*-chlorobenzeneboronic acid.

Since the brominating agent has been shown to be molecular bromine, whose concentration in the region investigated is essentially independent of pH, it must be the substrate whose concentration increases with pH. It is, therefore, a boronate anion.

Specific Catalysts.—In the previous work[14] it was indicated that sodium fluoride functions as a powerful specific catalyst for the reaction in "50%" acetic acid. We have now obtained quantitative measures of catalytic effects for this salt and five chelating agents.

Table III lists values of k_c defined by equation

$$k_{obsd.} = k_0 + k_c[\text{catalyst}] \qquad (3)$$

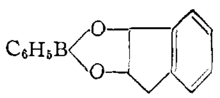
where k_0 is the rate constant observed in the absence of catalyst and k_{obsd} that observed when catalyst is present. It is apparent that the value of k_c for fluoride is about 6000 times k_0 which indicates a rather powerful catalytic activity. With regard to the chelating agents two points are of particular interest. α-Hydroxyisobutyric acid is about ten times as effective as glycolic acid and about as effective as tartaric acid. Further, *cis*-cyclohexane-1,2-diol is essentially ineffective. It was not possible to test *cis*-indane-1,2-diol which forms a very stable ester, I, with benzeneboronic acid[15] because the addition of even 0.001 M diol led to the immediate formation of a precipitate presumed to be the corresponding ester of *m*-chlorobenzeneboronic acid.

TABLE III

EFFECT OF CATALYSTS ON OBSERVED RATE CONSTANTS

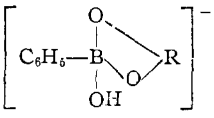
NaBr, 0.25 M; sodium chloroacetate 0.45 M; chloroacetic acid, 0.45 M; pH, 2.62, μ, 0.70.

Catalyst	$10^3 \times$ concn., moles l.	$10^3 \times$ $k_{obsd.}$, l. mole^{-1} sec.$^{-1}$	k_c, l.^{2} mole^{-2} sec.$^{-1}$
None	..	3.79	...
Glycolic acid	1.00	5.21	1.42
	2.00	7.72	1.97
	4.00	10.80	1.78
α-Hydroxyisobutyric acid	1.00	20.5	16.7
	2.00	37.2	16.2
d-Tartaric acid	1.00	20.3	16.5
	2.00	36.6	16.4
Citric acid	2.00	9.33	2.77
	4.00	14.70	2.73
Sodium fluoride	1.00	25.8	22.0
	2.00	46.8	21.5
cis-Cyclohexane-1,2-diol	1.00	3.57	...
	2.00	3.12	...
	3.00	4.11	0.1

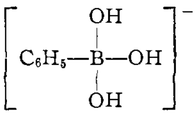


I

Reaction Mechanism.—For the reaction in water or aqueous acetic acid it can be stated confidently that molecular bromine and a benzeneboronate anion are involved in the rate-determining step. Furthermore the simplest picture consistent with all of the facts involves a quadricovalent rather than tricovalent boron in the anion. The following pertinent facts are easily accommodated in this picture: (a) catalysis by sodium fluoride, (b) specific catalysis by bases in acetic acid and (c) catalysis by chelating agents. In the latter case formation of a chelate complex analogous to structure I could provide a driving force for the formation of a quadricovalent anion II. This follows if the O–B–O bond angle in I is near the 108° of a regular pentagon, for then the fourth covalency of the boron with tetrahedral angles would be filled more easily than when the O–B–O angle is 120° as in normal tricovalent boron compounds. It would be difficult to predict the relative reactivities toward bromine of III and of II with various R groups. Since each of the hydroxy acids used had a positive catalytic effect it may be concluded that each of the corresponding anions II is more reactive than III. The fact that *cis*-cyclohexane-1,2-diol is not a catalyst may be due to the fact that it does not form a water-stable ester with benzeneboronic acid.[14] Addition of two methyl groups in going from glycolic acid to α-hydroxyisobutyric acid promotes chelation due to increased nucleophilic character in the oxygen atoms. This effect can also be transmitted through the boron atom to the ring carbon to some extent, thus facilitating attack by the bromine molecule.



II



$\left[C_6H_5\text{—}\overset{\text{OH}}{\underset{\text{OH}}{\text{B}}}\text{—OH}\right]^-$

III

It is interesting that in "50%" acetic acid the availability of hydroxyl ions for the "fourth" coordination on boron becomes small enough that other anions are able to compete favorably in this role. The fact that fluoride ion is effective even in water is not surprising in view of the stability of fluoborates.

DURHAM, NEW HAMPSHIRE

---

(14) Reference 4, footnote 12.

(15) H. G. Kuivila, A. H. Keough and E. J. Soboczenski, *J. Org. Chem.*, in press.