tion from the experimental data, excluding those marked (t) and (p) in Table I.

$3CaO \cdot B_2O_3$(c)

$H_T - H_{298.16} = 56.44T + 5.21 \times 10^{-3}T^2 + 13.02 \times 10^5 T^{-1} - 21,658$

(298–1760° K.; 0.4%)

$3CaO \cdot B_2O_3$(l)

$H_T - H_{298.16} = 94.00T - 35,400$

(1760–1900° K.; 0.1%)

$2CaO \cdot B_2O_3(\alpha)$

$H_T - H_{298.16} = 43.75T + 5.75 \times 10^{-3}T^2 + 10.69 \times 10^5 T^{-1} - 17,141$

(298–804° K.; 0.5%)

$2CaO \cdot B_2O_3(\beta)$

$H_T - H_{298.16} = 52.29T + 1.20 \times 10^{-3}T^2 - 18,633$

(804–1585° K.; 0.3%)

$2CaO \cdot B_2O_3$(l)

$H_T - H_{298.16} = 68.20T - 16,750$

(1585–1900° K.; 0.2%)

$CaO \cdot B_2O_3$(c)

$H_T - H_{298.16} = 31.02T + 4.88 \times 10^{-3}T^2 + 8.07 \times 10^5 T^{-1} - 12,389$

(298–1435° K.; 0.3%)

$CaO \cdot B_2O_3$(l)

$H_T - H_{298.16} = 61.70T - 28,130$

(1435–1700° K.; 0.1%)

$CaO \cdot 2B_2O_3$(c)

$H_T - H_{298.16} = 51.34T + 9.58 \times 10^{-3}T^2 + 17.16 \times 10^5 T^{-1} - 21,914$

(298–1260° K.; 0.4%)

$CaO \cdot 2B_2O_3$(l)

$H_T - H_{298.16} = 106.30T - 47,540$

(1260–1800° K.; 0.2%)

The corresponding molal heat capacity equations are:

$3CaO \cdot B_2O_3$(c): $C_p = 56.44 + 10.42 \times 10^{-3}T - 13.02 \times 10^5 T^{-2}$

$3CaO \cdot BaOO_3$(l): $C_p = 94.00$

$2CaO \cdot B_2O_3(\alpha)$: $C_p = 43.75 + 11.50 \times 10^{-3}T - 10.69 \times 10^5 T^{-2}$

$2CaO \cdot B_2O_3(\beta)$: $C_p = 52.29 + 2.40 \times 10^{-3}T$

$2CaO \cdot B_2O_3$(l): $C_p = 68.20$

$CaO \cdot B_2O_3$(c): $C_p = 31.02 + 9.76 \times 10^{-3}T - 8.07 \times 10^5 T^{-2}$

$CaO \cdot B_2O_3$(l): $C_p = 61.70$

$CaO \cdot 2B_2O_3$(c): $C_p = 51.34 + 19.16 \times 10^{-3}T - 17.16 \times 10^5 T^{-2}$

$CaO \cdot 2B_2O_3$(l): $C_p = 106.30$

Summary

High temperature heat contents of the calcium borates, $3CaO \cdot B_2O_3$, $2CaO \cdot B_2O_3$, $CaO \cdot B_2O_3$ and $CaO \cdot 2B_2O_3$, were measured from 298.16° K. to temperatures well above their melting points. Melting point temperatures and heats of fusion were determined and also the transition temperature and heat of transition in the case of $2CaO \cdot B_2O_3$.

Heat content and heat capacity equations, adequately representing the measured data, were derived for each borate in the crystalline and liquid states.

Entropy increments above 298.16° K. at 100° intervals and at phase-change points are tabulated, together with smooth values of the heat contents.

Electrophilic Attack on Halogen in a Homogeneous Medium: Reaction of Mercuric Nitrate with some Primary and Secondary Alkyl Bromides

BY O. THEODOR BENFEY*

Introduction

In the work of Dostrovsky and Hughes[1] on the series of bromides, methyl, ethyl, n-propyl, isobutyl, neopentyl, reactions expected to proceed by the nucleophilic substitution mechanism S_N2 gave the rate sequence

Me > Et > n-Pr > iso-Bu ≫ Neopentyl
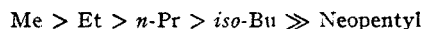
The sharp fall from isobutyl to neopentyl is attributed to a pronounced steric effect, the remaining rate sequence being explainable on the postulation of an inductive effect of methyl groups even on the β-carbon, opposing the approach of the nucleophilic reagent. Steric hindrance is a contributory factor except for methyl.

In order to bring out the alternative ionization mechanism S_N1, the behavior of the halides was studied by these workers both in the highly ionizing solvent formic acid, and in the presence of the electrophilic reagent silver nitrate, which acts by

virtue of its affinity for halogen. In these reactions the rate sequence was changed to

Me < Et > n-Pr > iso-Bu > Neopentyl
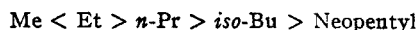
Steric hindrance was shown to be absent, and the last member reacted by a pure S_N1 mechanism. The fact that the Me–Et rate sequence is inverted speaks strongly for the idea that the ethyl halide reacts largely by the same mechanism, the inductive effect being operative in assisting the breaking of the carbon-halogen bond. This strongly suggests that the intermediate members also react by this mechanism in spite of the rate sequence Et > n-Pr > iso-Bu being opposite to that expected from the influence of the inductive effect. The authors' suggestion that the wrong sequence beyond ethyl is due to an appreciable incursion of mechanism S_N2 is therefore unlikely. An alternative explanation in the case of the silver ion catalyzed reaction is that the catalytic effect of solid silver halide produced during the reaction decreases along this series.

In the reaction of alkyl halides with mercuric

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(1) Dostrovsky and Hughes, J. Chem. Soc., 157 ff. (1946).

ion, the mercuric halide produced, though largely un-ionized, is appreciably soluble, and the catalytic effect of solid metal halide is thus eliminated. The reaction of mercuric nitrate with ethyl, n-propyl and isobutyl bromides was therefore studied. Roberts and Hammett[2] have presented strong evidence in the case of benzyl chloride that the reaction proceeds by way of a rate determining formation of a carbonium ion intermediate

$$Hg^{++} + RX \longrightarrow HgX^+ + R^+$$
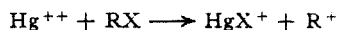
followed by fast reactions to form the alcohol or alkyl nitrate. The reaction rate of alkyl halides in ionizing solvents is normally accelerated by a factor of several hundred on addition of small concentrations of mercuric nitrate. The acceleration is no doubt due to the driving force derived from the energy of formation of a mercury–halogen bond. Mercuric ion and mercuric salts have a strong affinity for halogen, as shown by the small ionization of the mercuric halides,[3] and by their ability to form complex ions such as $HgCl_4^{--}$.[4] Mercuric nitrate converts neopentyl iodide, notoriously unreactive toward nucleophilic reagents,[1] into the rearranged t-amyl alcohol.[5]

Cyclohexyl chloride and bromide react in some reactions like typical secondary halides, while in others their rates are considerably slower.[6] Mercuric ion has a larger accelerating effect than silver ion on the reactions of alkyl halides and is consequently expected to favor even more the mechanism involving an ionic intermediate. A comparison was therefore made between the rates of reaction of cyclohexyl and isopropyl bromides with mercuric nitrate.

Experimental

Apparatus.—The thermostat at 12.50° was the one described previously.[7] That at 25.00° was of the conventional type. The temperatures were determined with thermometers calibrated by the U. S. Bureau of Standards. The thermostat temperatures were constant to ±0.02°.

Materials.—Technical 1,4-dioxane was purified in 2- to 3-liter quantities by a modification of the method of Beste and Hammett.[8] After treatment on the steam-bath with sodium hydroxide, the filtered product was boiled with 200 cc. of water and 25 cc. of concentrated hydrochloric acid for twelve hours, in a stream of air or nitrogen to carry away the aldehyde formed. The acid was neutralized and the aqueous portion removed with sodium hydroxide pellets. The dioxane was then refluxed over sodium wire for twelve hours and distilled through a 15-plate glass-helices packed column; b. p. 100.9–101.1° (760 mm).

n-Pentane and n-hexane used for extraction of alkyl halides in the fast kinetic runs were found to be free of halide and were used directly.

Eastman Kodak Co. ethyl bromide was distilled through

(2) Roberts and Hammett, This Journal, **59**, 1063 (1937).

(3) Sillén and Infeldt, Svensk Kem. Tid., **58**, 52, 61 (1946); Morse, Z. physik. Chem., **41**, 709 (1902).

(4) Nicolet and Stevens, This Journal, **50**, 135 (1928).

(5) Whitmore, Wittle and Popkin, ibid., **61**, 1586 (1939).

(6) (a) Tronow and Ladigina, Ber., **63**, 3060 (1930); (b) Conant and Hussey, This Journal, **47**, 476 (1925).

(7) Price and Hammett, ibid., **63**, 2387 (1941).

(8) Beste and Hammett, ibid., **62**, 2481 (1940).

a 15-plate column, b. p. 38.5–38.6°. Analysis for bromide gave 100.0%.

Eastman Kodak Co. **n-propyl bromide** and A. D. Mackay **isopropyl bromide** were washed with concentrated hydrochloric acid and dilute sodium hydroxide and dried over sodium sulfate. On fractional distillation n-propyl bromide boiled at 71.6–71.7° (761 mm.), isopropyl bromide at 59.1–59.5°.

Eastman Kodak Co. **isobutyl bromide** was shaken with water for one hour to hydrolyze any t-butyl bromide. It was washed with concentrated hydrochloric acid and a 10% sodium carbonate solution, dried over sodium sulfate and fractionated, b. p. 91.6–92.0° (762 mm.).

Eastman Kodak Co. **bromocyclohexane** (b. p. 61–62° (15 mm.)) was twice distilled at reduced pressure through a Vigreux column. It was colorless and free from acid.

Colorless C. p. J. T. Baker analyzed **nitric acid** was used in making up the reaction mixtures.

Primary standards for titration were Mallinckrodt ACS grade potassium acid phthalate, and ACS grade potassium chloride which was recrystallized, and dried at 130° in vacuo over phosphorus pentoxide.

Merck reagent grade mercuric nitrate and C. p. mercuric bromide were used directly.

Method.—The titration method for following the production of bromide is described in detail by Roberts.[9][2]

The same solvent, "70% dioxane by volume," was used throughout. It was made up by mixing seven parts of dioxane with three parts of water containing the amount of nitric acid required for an acidity of the solvent within the limits 0.281–0.286 N. Mercuric nitrate (0.025 N appr.) was added and its concentration as well as that of the nitric acid determined by titration. A known volume, usually 100 cc., was transferred into the reaction flask, and placed in the thermostat. For all runs except that of isopropyl bromide at 25°, the alkyl bromide (0.022 N appr.) was weighed out in a 1-cc. weighing bottle closed with a well-fitting ground glass stopper. The bottle was inserted in the reaction flask which was shaken rapidly till the bottle opened. The initial time was then taken. It was found that this method was accurate even for appreciably volatile compounds, while the alternative of taking infinity readings was invalidated, except for the very fast runs, by slow complicating reactions, probably between mercury salts and the solvent. In the case of isopropyl bromide the approximate quantity was transferred with a weight pipet, and reproducible infinity readings were obtained.

At measured intervals 10-cc. samples were pipetted out and the reaction stopped by delivering into 5 cc. of 0.1 N potassium chloride. The excess chloride ion was then determined. In the case of isobutyl bromide this simple sampling method could not be used because of the formation of a precipitate. The reaction was started as before, but when the reaction had proceeded for a few minutes, 10-cc. samples were transferred into a series of 25-cc. erlenmeyer flasks and were tightly closed with rubber stoppers. To stop the reaction 5 cc. of standard potassium chloride solution was added to the flask which was then allowed to stand so that the precipitate could react completely. On first addition the precipitate turns white and then slowly dissolves. The contents of the flask were washed into a larger erlenmeyer flask and titrated as before.

For the fast reactions of isopropyl and cyclohexyl bromides a pipet with an outflow time of eleven seconds was used. The pipet delivered accurately reproducible volumes. However, the reaction was not completely stopped by addition to potassium chloride solution, and the end-points were not sharp. Samples were therefore delivered into a mixture of 5 cc. of 0.1 N potassium chloride, 5 cc. of n-pentane (or n-hexane) and 5 cc. of water. The organic layer took up the bulk of unreacted alkyl halide, it was separated and washed several times with small amounts of water, the washings being added to the

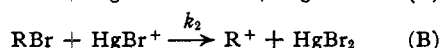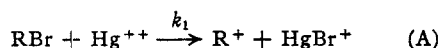(9) Roberts, Ind. Eng. Chem. Anal. Ed., **8**, 365 (1936).

aqueous layer. The aqueous portion was titrated as before, and gave very sharp end-points.

Roberts and Hammett[2] mention that an impurity in the dioxane slowly reacts with mercuric nitrate forming mercurous salt, but that the error introduced was found to be negligible under the conditions of their kinetics.

In the work here described a fine white precipitate was observed to form slowly in mercuric nitrate solutions in 70% dioxane, when the concentration of nitric acid was 0.015 N. Good kinetics were observed for the fast reactions, but considerable interference took place in the slower runs. On increasing the concentration of nitric acid to 0.3 N no precipitate appeared except after long ageing of the dioxane before use. This concentration was therefore used throughout.

Rate Calculations

A possible reaction scheme would be

$$\text{RBr} + \text{Hg}^{++} \xrightarrow{k_1} \text{R}^+ + \text{HgBr}^+ \qquad \text{(A)}$$

$$\text{RBr} + \text{HgBr}^+ \xrightarrow{k_2} \text{R}^+ + \text{HgBr}_2 \qquad \text{(B)}$$

with an equilibrium controlling the concentrations of the two mercuric ions.
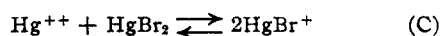
$$\text{Hg}^{++} + \text{HgBr}_2 \rightleftharpoons 2\text{HgBr}^+ \qquad \text{(C)}$$

$$K = \frac{[\text{HgBr}^+]^2}{[\text{Hg}^{++}][\text{HgBr}_2]} \qquad (1)$$

The following abbreviations are used

$x_0 = 2[\text{Hg}^{++}]_0 = $ initial concentration of mercuric ion in equivalents

$x = 2[\text{Hg}^{++}] + [\text{HgBr}^+] = $ concentration of total mercuric ion in equivalents

$y_0 = [\text{RBr}]_0 = $ initial concentration of alkyl halide.

$y = [\text{RBr}]$

Two methods are used for the approximate evaluation of initial rate constants[10]

Method I.—Assuming that $K = 0$, i. e., that an HgBr$^+$ ion when formed immediately disproportionates into $\frac{1}{2}\text{Hg}^{++} + \frac{1}{2}\text{HgBr}_2$, the second order rate equation becomes

$$k_a = \frac{2}{(x_0 - y_0) t} \ln \frac{y_0 x}{x_0 y} \qquad (2)$$

where t is the time in minutes. The factor 2 is required because one mole of mercuric ion reacts with two moles of alkyl halide. The values of k_a will rise or fall during the reaction depending on the actual values of k_2 and K, but will extrapolate at zero reaction to the correct value k_1.

Method II.—Assuming that k_2 is negligible and that an HgBr$^+$ ion when formed does not disproportionate, a value of k may be calculated, taking one mole Hg^{++} and one mole RBr as equivalent quantities. The rate equation then becomes

$$- dx/dt = k_b [\text{Hg}^{++}][\text{RBr}] \qquad (3)$$

$$k_b = \frac{1}{(\frac{1}{2}x_0 - y_0)} \ln \frac{y_0 (\frac{1}{2}x_0 - (y_0 - y))}{\frac{1}{2}x_0 y} \qquad (4)$$

If HgBr$^+$ disproportionates or reacts further, the titration of total mercuric ion will indicate greater reaction than expected, and the values of k_b will rise. In the case where $\frac{1}{2}x_0 < y_0$, the values of

(10) A similar method is described by Skrabal, "Homogenkinetik," Steinkopf, Dresden, 1941, p. 165.

k_b will approach infinity as $(y_0 - y)$ approaches $\frac{1}{2}x_0$. At zero reaction $k_b = k_1$.

For a full analysis of the observed data into k_1, k_2 and K, we have

$$x_0 = 2[\text{Hg}^{++}]_0 = 2[\text{Hg}^{++}] + 2[\text{HgBr}^+] + 2[\text{HgBr}_2] \qquad (5)$$

$$x_0 - x = [\text{HgBr}^+] + 2[\text{HgBr}_2] \qquad (6)$$

Substituting for [Hg^{++}] and [HgBr$_2$] in the equilibrium equation

$$K = \frac{[\text{HgBr}^+]^2}{[\text{Hg}^{++}][\text{HgBr}_2]} = \frac{4[\text{HgBr}^+]^2}{(x - [\text{HgBr}^+])(x_0 - x - [\text{HgBr}^+])} \qquad (7)$$

Solving for [HgBr$^+$] we obtain

$$[\text{HgBr}^+]/x = \frac{-x_0/x + \sqrt{(x_0/x)^2 + 4(x_0/x - 1)(4/K - 1)}}{2(4/K - 1)} \qquad (8)$$

$$\therefore [\text{Hg}^{++}]/x = \frac{1}{2} - \frac{-x_0/x + \sqrt{(x_0/x)^2 + 4(x_0/x - 1)(4/K - 1)}}{4(4/K - 1)} \qquad (9)$$

Now $-dx/dt = k_1[\text{RBr}][\text{Hg}^{++}] + k_2[\text{RBr}][\text{HgBr}^+]$ (10)

$\therefore -dx/[\text{RBr}]x dt = k_1[\text{Hg}^{++}]/x + k_2[\text{HgBr}^+]/x = N$ (11)

In the special case when $K = 4$

$$[\text{HgBr}^+]/x = 1 - x/x_0, [\text{Hg}^{++}]/x = \frac{1}{2}x/x_0 \qquad (12)$$

For any value of K, tables and graphs may be set up giving values of [Hg^{++}]/x and [HgBr$^+$]/x as a function of x/x_0.

Experimental Results and their Analysis

Initially all rate constants were calculated according to Method I, assuming $K = 0$. The resulting values of k_a invariably showed an appreciable decrease during the reaction, the final value of k_a being approximately 50% lower than the initial one for ethyl, n-propyl and cyclohexyl bromides, while that for isopropyl was even lower. The isobutyl case will be dealt with in the next section.

Values of k_b were calculated by method II, and were found to increase rapidly, approaching infinity as $(y_0 - y)$ approaches $\frac{1}{2}x_0$. On extrapolation of k_a and k_b to the point of zero reaction, a good estimate of the actual initial rate constant k_1 is obtained. The value, however, is very sensitive to small variations in the initial values of k_a and k_b and it is subject to the inherent uncertainties of non-linear extrapolation. It may therefore be in error by up to 5%. A plot of k_a and k_b against per cent. alkyl halide reacted is shown for n-propyl bromide in Fig. 1.

Isobutyl Bromide. Formation of an Olefin-Mercuric Complex.—In runs in the presence of this halide, an orange yellow precipitate appeared very soon after the beginning of the reaction.

The precipitate (I) was isolated on a large scale using 7 g. of isobutyl bromide in 200 cc. of $3N$ nitric acid. Approximately two equivalents of mercuric nitrate were required to react with the alkyl bromide. The precipitate was filtered,
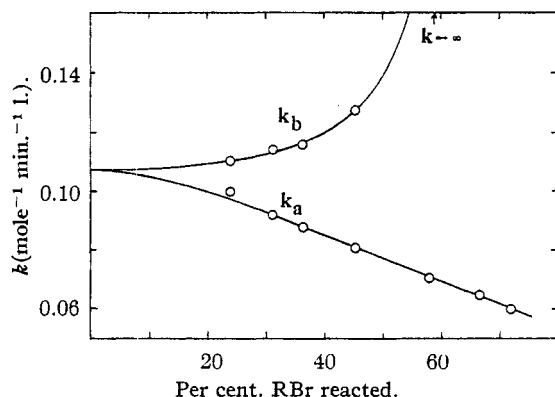
Fig. 1.—Approximate determination of k_1: $[n\text{-PrBr}]$ = 0.02185 N, $[\text{Hg(NO}_3)_2]$ = 0.02575 N, $[\text{HNO}_3]$ = 0.281 N, 70% dioxane, 25°.

washed with hot water and dried on a porous plate and in a desiccator. It is insoluble in hot and cold water, alcohol, ether and chloroform. Analysis showed the presence of mercuric ion and the complete absence of mercurous. The compound could not be prepared from isobutanol which is one of the reaction products, nor if mercuric nitrate is replaced by mercuric bromide. Now it is to be expected that an electrophilic attack on isobutyl bromide will produce isobutene as one of its major products. Many reactions of olefins with mercuric salts are reported in the literature,[11] the simplest being an addition compound of one mole olefin to one mole mercuric salt.

A compound of similar properties has been reported by Denigès[12] as being the product of the mercuric nitrate reaction with t-butanol or isobutene. The above procedure was repeated using tertiary butanol instead of isobutyl bromide, and an orange yellow solid (II) was quickly precipitated. Both compounds had the same properties toward solvents, both evolved a gas on treatment with concentrated hydrochloric acid. On heating slowly, their color changed to orange and red, on placing suddenly in an environment at 200° both decomposed, the t-butanol compound with detonation. Contrary to Denigès no mercurous mercury was detected in the t-butanol compound, nor did it decompose in sunlight.

Since Denigès has reported the formation of the precipitate from isobutene, this gas was tested for in the original precipitate I by treating it with concentrated hydrochloric acid and passing the gas evolved into a nitric acid solution of mercuric nitrate. A yellow precipitate III was formed of similar properties to those of I and II. That their physical properties are not identical is probably due to the presence of Hg–Br linkages in I, and to differences in the amount of washing and drying.

The common intermediate from the three start-

(11) (a) Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., Reinhold Publ. Corp., New York, N. Y., 1921, p. 106; (b) Lucas, Hepner and Winstein, This Journal, **61**, 3102 (1939).

(12) Denigès, Ann. chim. phys., [7] **18**, 387 (1899).

ing materials can only be isobutene. Rough titrations on the precipitates suggest the presence of one mercury atom to one isobutene molecule. This suggests the composition of the product from isobutyl bromide to be $C_4H_8 HgY_2$, and $C_4H_8\cdot HgBrY$ where Y is NO_3 or OH.

The formation of a compound $C_4H_8 Hg(NO_3)_2$ under similar conditions to ours is reported by Lucas, Winstein and co-workers.[13,11b] A similar compound with cyclohexene and one of isobutene with silver ion[14] have also been shown to exist.

N-Propyl and Ethyl Bromides. The Cause of the Decrease in Values of k_a—The fall in k_a during the n-propyl bromide reaction may be due to the removal of mercuric ion by olefin to form a soluble complex.

Instantaneous rate constants k'_a were calculated from the formula

$$k'_a = \frac{2}{(x_0 - y_0)(t_2 - t_1)} \ln \frac{y_1 x_2}{x_1 y_2}$$

where (x_1, y_1, t_1), (x_2, y_2, t_2), correspond to alternate reaction samples. Their values for the reaction of n-propyl bromide in the usual conditions are given in Table I, together with the corresponding mean concentration of alkyl halide. Detailed

TABLE I

Calculation of Instantaneous Rate Constants k'_a in the n-Propyl Bromide–Mercuric Nitrate Reaction in 70% Dioxane at 25°

$[\text{Hg(NO}_3)_2]$ = 0.02575 N, $[n\text{-PrBr}]$ = 0.02185 N, $[\text{HNO}_3]$ = 0.281 N

t_1, min.	t_2, min.	$x_1{}^a$	$x_2{}^a$	Mean [RBr] mol./l.	k'_a mol.$^{-1}$ min.$^{-1}$ l.
70.50	247.50	9.42	8.14	0.01821	0.0917
154.60	368.30	8.67	7.52	.01650	.0777
247.5	485.0	8.14	7.07	.01526	.0748
368.3	751.0	7.52	6.29	.01352	.0700
485.0	1384.0	7.07	5.21	.01158	.0618
751.0	2113.5	6.29	4.46	.00964	.0555
1384.0	2857.0	5.21	3.98	.00767	.0493

^{a} x_1, x_2, expressed in cc. of 0.02520 N Hg(NO$_3$)$_2$ per 9.99 cc. sample.

analysis of the rate constants gives an initial rate k_1 = 0.105 mole^{-1}min.$^{-1}$l. (next section). A second run was carried out, using half the usual concentrations of n-propyl bromide and mercuric nitrate, and adding 0.0125 N mercuric bromide. This duplicates the conditions of the run tabulated in Table I, at the point of half reaction. If the fall in rate constants is due to olefin formation in the first case, then its absence here should yield a rate constant of a value approximately 0.10. If the fall in rate is due to the equilibrium between mercuric ion and mercuric bromide, rate constants in this run should duplicate the previous ones for the same mean alkyl bromide ion concentration.

The values of k'_a for both runs are plotted against mean alkyl halide concentration in Fig. 2. The results leave no doubt that olefin complex for-

(13) Lucas and Eberz, This Journal, **56**, 460 (1934).

(14) Eberz, Welge, Yost and Lucas, ibid., **59**, 45 (1937).

TABLE II

n-PROPYL BROMIDE-MERCURIC NITRATE REACTION IN 70% DIOXANE AT 25°

[Hg(NO₃)₂] = 0.02575 N, [n-PrBr] = 0.02185 N, [HNO₃] = 0.281 N; N = −dx/[RBr]xdt, x expressed in cc. 0.02520 N
Hg(NO₃)₂ per 9.99 cc. sample; K = 4; [Hg⁺⁺]/x and [HgBr⁺]/x calculated by eqn. 12. By extrapolation methods
k₁ = 0.107 mol.⁻¹ min.⁻¹ l.

t_1, min.	0	247.5	368.3	485.0	751.0	1384.0	2113.5
t_2, min.	247.5	368.3	485.0	751.0	1384.0	2113.5	2857.0
x_1	10.21	8.14	7.52	7.07	6.29	5.21	4.46
x_2	8.14	7.52	7.07	6.29	5.21	4.46	3.98
[RBr](mol./l.)	0.01922	0.01584	0.01450	0.01294	0.01059	0.00827	0.00671
N	.0474	.0414	.0364	.0339	.0280	.0257	.0228
$N_{cor.}$	.0482	.0400	.0370	.0336	.0292	.0253	.0223
[Hg⁺⁺]/x	.450	.384	.358	.327	.282	.237	.207
[HgBr⁺]/x	.101	.233	.285	.346	.437	.527	.587
0.107 [Hg⁺⁺]/x	.0482	.0411	.0383	.0350	.0302	.0254	.0221
$k_1 = N_{cor.}/[Hg⁺⁺]/x$	.107	.104	.103	.103	.104	.107	.108

mation is not the cause of the fall in rate. It is likely therefore that the decrease in rate constant is due to an equilibrium between mercuric ion, mercuric monobromide ion, and mercuric dibromide.

In a run using mercuric bromide instead of mercuric nitrate, it was shown that catalysis of the reaction by mercuric bromide is negligible under the conditions of the kinetics. Mechanisms A and B alone should therefore account for the rate data.

The value of N was calculated for n-propyl bromide according to the left-hand side of equation 11, where dx/dt = $(x_2−x_1)/(t_2−t_1)$, with (x_1,t_1), (x_2,t_2), referring to consecutive points. The values of N were plotted against the mean x/x_0, and a smooth curve drawn through the points to give the corrected values of N. This procedure is necessary because of the small increments $(x_2−x_1)$. The calculated and corrected values of N for n-propyl bromide are shown in Table II.

Using the approximate value of the initial rate constant k_1, determined by extrapolation to zero reaction of k_a and k_b, the quantity k_1 [Hg⁺⁺]/x is calculated for differing values of K. The difference N − k_1[Hg⁺⁺]/x gives a measure of the rate of reaction B, i. e., k_2[HgBr⁺]/x. Hence k_2 may be obtained which must be constant during the reaction. The only constants that fitted the results were K = 4, k_2 = 0. For K < 4, k_2 is negative, for K > 4, k_2 increases during the reaction,

TABLE III

ETHYL BROMIDE-MERCURIC NITRATE REACTION IN 70% DIOXANE AT 25°

[Hg(NO₃)₂] = 0.02538 N, [EtBr] = 0.02201 N, [HNO₃] = 0.286 N; x_1, x_2 expressed in cc. 0.02518 N Hg(NO₃)₂ per 10.00 cc. sample; K = 4; k_1 = $N_{cor.}/[Hg⁺⁺]/x$ mol.⁻¹ min.⁻¹ l.

t_1, min.	t_2, min.	x_1	x_2	$N_{cor.}$	k_1, mole⁻¹ min.⁻¹ l.
0	45.8	10.08	9.14	0.1033	0.217
45.8	92.7	9.14	8.40	.0913	.210
92.7	153.9	8.40	7.73	.0824	.206
153.9	240.9	7.73	6.99	.0746	.204
240.9	510.3	6.99	5.59	.0646	.207
510.3	1354	5.59	3.88	.0510	.217

the increase being more pronounced the greater the value of K.
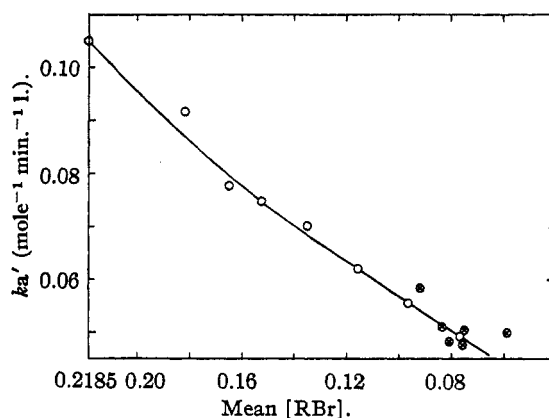

Fig. 2.—Runs to test the cause of the fall in rate: O, [n-PrBr] = 0.02185 N, [Hg(NO₃)₂] = 0.02575 N, [HNO₃] = 0.281 N, ⊗ [n-PrBr] = 0.00995 N, [Hg(NO₃)₂] = 0.01246 N, [HNO₃] = 0.284 N, [HgBr₂] = 0.0125 N; 70% dioxane, 25°.

If this analysis is correct, the ethyl bromide results should yield good rate constants if the same value of K is used. This was found to be the case k_2 again being zero. We may therefore calculate the rate constant k_1 for reaction A from the ratio

$$\frac{N}{[Hg⁺⁺]/x} = \frac{1}{[RBr][Hg⁺⁺]} \frac{dx}{dt} = k_1$$

Details of the calculation are given for n-propyl bromide in Table II. Results for ethyl bromide are shown in Table III.

Isobutyl Bromide.—Due to the formation of an olefin-mercuric salt complex, the rate coefficients k_a fell far more rapidly than in the case of other alkyl halides. An empirical equation of the form

$$k = \frac{2}{(x_0 − 3y_0)t} \ln \frac{y_0}{x_0} \frac{(x_0 − 3(y_0 − y))}{y}$$

gave constant values of k during a major part of the measured reaction. It derives from the expression −dx/dt = $ky(x_0 − 3(y_0 − y))$ and there-

fore coincides with k_1 when (y_0-y) is small. The rate constant obtained in this way had the value $k_1 = 0.0289$ mole^{-1}min.$^{-1}$l. (average deviation of mean ± 0.0002).

Now for ethyl and n-propyl bromide the equilibrium constant is given by $K = 4$, and the rate constant k_2 is negligible. The first condition must apply also for isobutyl bromide, since we have only changed the alkyl halide, while the second is highly probable.

Knowing K and an approximate k_1, as well as the experimentally determined dx/dt, we may calculate the value of x that is responsible for this rate of change of concentration. The difference between calculated and observed values of x gives the amount of total mercuric ion complexed for a given amount of alkyl bromide reacted. From this result the proportion of olefin in the product can be determined if we assume that the complex is a mixture of $C_4H_8\cdot HgY_2$ and $C_4H_8\cdot HgBrY$ (Y is NO_3 or OH) in the proportion in which Hg^{++} and $HgBr^+$ appear in solution, and that olefin when formed is immediately complexed. A very rough value of 63% olefin formation is obtained for the isobutyl reaction.

Knowing the proportion of olefin formed, we may calculate the amount of total mercuric ion in solution from the experimental titer by subtracting the amount removed by complex formation. This value is used in the rate equation. If the analysis is correct, calculation of the ratio $-dx/$[RBr][Hg^{++}] dt should yield constant values of k_1. The results are given in Table IV. Since the rate fell rapidly values of Δx are small, and liable to appreciable error. The values of N did not warrant the determination of corrected values N_{cor}. Rate constants were therefore calculated directly from N.

TABLE IV

Isobutyl Bromide–Mercuric Nitrate Reaction in 70% Dioxane at 25°

[Hg(NO$_3$)$_2$] $= 0.02567$ N, [iso-BuBr] $= 0.02218$ N, [HNO$_3$] $= 0.286$ N; x_1', x_2' = experimentally determined total concentration of mercuric ion; x = mean concentration of total mercuric ion not complexed with isobutene, assuming 63% olefin formation, and immediate complexing. x'_1, x'_2, x, expressed in cc. 0.02534 N Hg(NO$_3$)$_2$ per 10.00 cc. of sample. $x_0 - x = (1 + 2 \times 0.63)(x_0 - x') = 2.26(x_0 - x')$; $x_0 = 10.13$. $\Delta x/\Delta t$ determined for alternate reaction samples.

t_1, min.	t_2, min.	x_1'	x_2'	x	N	k_1, mole^{-1} min.$^{-1}$l.
163.3	352.0	9.47	9.07	8.19	0.01295	0.0283
254.2	471.0	9.29	8.84	7.73	.01375	.0308
352.0	591	9.07	8.65	7.26	.01275	.0291
471	777	8.84	8.40	6.72	.01165	.0274

A slight fast reaction was observed at the start of the reaction, probably due to a small amount of t-butyl bromide impurity. This was corrected for in the rough determination, of k_1, it does not affect the accurate determination, as instantaneous rate constants were calculated in this case.

Isopropyl Bromide.—Steady rate constants ($k_1 = 30.5$ mole^{-1}min.$^{-1}$l. ($K = 4$)) were obtained

in the reaction of this halide at 25°, up to 55% of alkyl halide reacted, followed by a decrease. It suggests slow formation of a soluble olefin–mercury complex due to a few per cent. olefin in the product. Small proportions of olefin (3–7%) are reported as products in the hydrolysis of the halide in formic acid[15] and in dry ethyl alcohol.[16]

An analogous run at 12.5° gave results that fitted the theoretical equations if the equilibrium is given by $K = 8$ and $k_1 = 8.81$ mole^{-1}min.$^{-1}$l. There was no decrease in the constants during the reaction, suggesting that the amount of olefin in the product is sharply reduced as the temperature falls. Hughes and Ingold[16] give evidence that in the S_N1 reactions of tertiary halides an analogous situation is observed. From the rate constants obtained at the two temperatures, an activation energy for the reaction of 16.8 kilocalories per mole is obtained.

Cyclohexyl Bromide.—Numerous reactions of this halide are cited in the literature in which the predominant product is cyclohexene.[17] Lucas, Hepner and Winstein[11b] have shown that unstable complexes are formed between cyclohexene and mercuric ion, followed by the precipitation of a solid which probably has the structure of a true addition compound. In an experiment using 8 g. of mercuric nitrate, 4 g. of cyclohexene, 25 cc. of 6 N nitric acid and 25 cc. of dioxane, a pale yellow precipitate was formed after one day. Since the reaction of the halide in our conditions is complete in a few hours, there may be little interference by reaction between cyclohexene and mercuric ion. This was actually found to be the case. Rate constants during the reaction in the usual conditions at 25° were $k_1 = 8.16$, 8.13, 8.16, 8.31, 8.72 mole^{-1}min.$^{-1}$l. The slight rise in rate as the reaction proceeds may be due to a slight incursion of attack by $HgBr^+$. The mean of the first three points gives $k_1 = 8.15$ mole^{-1}min.$^{-1}$l.

Discussion

General.—Sillén and Infeldt[3] have recently measured the equilibrium constant at 25° for the equilibrium $Hg^{++} + HgX_2 \rightleftarrows 2HgX^+$ (X = Br or Cl), in aqueous solution with excess perchlorate ion. The values obtained were $K = 5.8 \pm 0.5$ for X = Br, $K = 1.8 \pm 0.1$ for X = Cl, where K is defined by equation 1, and its analog for the mercuric chloride case. In the measurements here recorded a value of $K = 8$ at 12.5°, and of $K = 4$ at 25°, were obtained.

The rate data given in this paper can be analyzed into good second order rate constants derived according to the system

$$RBr + Hg^{++} \longrightarrow R^+ + HgBr^+$$
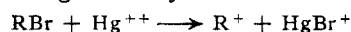
if the relative concentrations of the two mercuric ions are controlled by the above equilibrium.

Roberts and Hammett[2] calculated rate con-

(15) Bateman and Hughes, J. Chem. Soc., 945 (1940).

(16) Hughes and Ingold. Trans. Faraday Soc., 37, 657 (1941).

(17) Loevenich, Utsch, Moldrickx and Schaefer, Ber., 62, 3084 (1929).

stants k_a for the benzyl chloride reaction assuming $K = 0$ (Method I), and found these values to be constant or drifting upward in 60% dioxane while drifting downward in 75% and 95% dioxane. The fact that these drifts are far smaller than with alkyl bromides is explained by the far lower value of K when $X = Cl$. The upward drifts can only be explained if attack by $HgCl^+$ and probably by $HgCl_2$ contribute to the total reaction rate. This is possible since even the reaction of benzyl chloride in absence of mercuric nitrate is easily measurable at $50°$.[8]

The accelerations caused by nitrate and perchlorate ion in all three media can be explained by their salt effect on the equilibrium. The thermodynamic equilibrium constant K_0 is related to the experimentally determined constant K by the equation $K_0 = Kf_1^2/f_2$, where f_1, f_2 are the activity coefficients of $HgCl^+$ and Hg^{++}, respectively. According to the Debye–Hückel theory for dilute solutions the activity coefficient of an ion is independent of the nature of other ions present, being related only to the ionic strength of the solution according to the equation $-\log f = Az^2\sqrt{\mu}$ where z is the charge of the ion, μ the ionic strength and A a constant for all ions in the same conditions. It follows that $K = K_0 10^{-2A\sqrt{\mu}}$. An increase in ionic strength decreases K and therefore increases the concentration of doubly charged mercuric ion whose reaction is far faster than that of $HgCl^+$. In solvents of low dielectric constant, the Debye–Hückel theory breaks down even at quite low ionic strengths, and the specificity of ions soon becomes apparent. The differing accelerations caused by nitrate and perchlorate ions are probably due to this cause.

By the postulation of the equilibrium C, the effects of added nitrate ion and perchlorate ion become understandable without the assumption that complexes of the type $HgClO_4^+$, $HgNO_3^+$ react at differing rates. It may be that these complexes do exist, but the rate calculations suggest that the only factor influencing the rate of reaction of mercuric mercury is the number of halogens with which it is combined.

The Rate Sequence Ethyl, n-Propyl, Isobutyl. —The rate constants for the reaction of these halides were as follows: EtBr 0.210, n-PrBr 0.105, iso-BuBr 0.0289 $mole^{-1}min.^{-1}l$. These rate changes Et > n-Pr > iso-Bu are in the same order and of similar magnitude to those found in the reaction with silver nitrate. Heterogeneous catalysis by solid metal halide is therefore eliminated as a cause of the fall in rate along this series. Now the rate series Me < Et > n-Pr > iso-Bu can be explained if the determining factor in the stabilization of the transition state is the contribution of hyperconjugation due to the β-hydrogen atoms. Contribution in the transition state of resonance forms of the type

$$\text{H}^+ \ \text{C}\!\!=\!\!\text{C} \ \text{Br}^- \ldots \text{Hg}^{++}$$
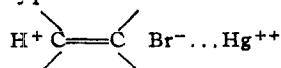
would greatly facilitate ionization on the attack of an electrophilic reagent on halogen. The effect would be far greater in the transition state than in the ground state, and it would be much more marked in a mechanism involving ionization than in one where electron transfer from a nucleophilic reagent compensates the electron demand created by the breaking of the carbon–halogen bond (S_N2).[18] Hyperconjugation effects increase with an increase in the number of available β-hydrogen atoms and therefore explain the rate sequence.

Hughes[19] objects to this explanation on the ground that in the tertiary halides, the rate of ionization increases along the series t-butyl, t-amyl, α,α-diethyl neopentyl, in spite of the progressive decrease in the number of β-hydrogen atoms. Crowding of methyl groups and hydrogen atoms however increases along this series and the decrease in these compression energies on attaining to the planar carbonium ion configuration may greatly influence the rate sequence.[20] Further progress in attributing rate changes unambiguously to specific electronic or steric influences can only be made when accurate energies and entropies of activation become available.

Cyclohexyl and Isopropyl Bromides.—The results (k_1(Cyclohexyl bromide) = 8.15, k_1(Iso-PrBr) = 30.5 $mole^{-1}min.^{-1}l.$) show that these halides have rates of the same order of magnitude in their reaction with mercuric nitrate. Evidence indicates that the rates of cyclohexyl chloride and bromide are far lower than those of the corresponding isopropyl halide toward iodide ion,[6b] pyridine and piperidine[6a] while the rates are normal toward sodium methoxide.[6a] An inspection of Fisher–Hirschfelder atomic models shows that there is considerable steric hindrance toward the approach of a nucleophilic reagent at the α-carbon atom if the bromine atom is in the radial position. A reagent whose reactivity toward carbon is much greater than that toward hydrogen (e. g., iodide ion) should therefore react at a very slow rate. Methoxide ion however has a strong affinity for hydrogen and can attack the β-hydrogen atom by the bimolecular elimination mechanism E2.[16] In agreement with this, the preponderant product is cyclohexene.[17] There should be no steric hindrance in the reaction of cyclohexyl bromide with mercuric ion, and its rate as well as that of attack by methoxide ion is found to be of similar magnitude to that of isopropyl bromide.

(18) Hughes, Ingold and Taher, *J. Chem. Soc.*, 949 (1940).

(19) Hughes, *Trans. Faraday Soc.*, **37**, 624 (1941).

(20) H. C. Brown, paper presented before the Organic Division of the American Chemical Society at its New York meeting, September, 1947.

Hammett for suggesting this work and for his continual interest, help and encouragement.

Summary

The reaction of mercuric nitrate with the primary alkyl bromides, ethyl, n-propyl, isobutyl and the secondary bromides isopropyl and cyclohexyl has been studied in aqueous dioxane. The reaction is shown to occur by the rate determining attack of doubly charged mercuric ion on halogen, with an equilibrium determining the relative concentrations of mercuric ion, mercuric monobromide ion and mercuric dibromide. Of the three mercuric species involved in the equilibrium only the first is shown to contribute perceptibly to the rate.

A precipitate of the probable composition $C_4H_8\cdot HgY_2$ and $C_4H_8\cdot HgBrY$ (Y = NO_3 or OH) forms during the reaction of isobutyl bromide. On making allowance for this secondary reaction the halide fits into the general reaction scheme.

The experimentally determined rate sequence ethyl > n-propyl > isobutyl is explained by a hyperconjugation effect. The approximate equality of rates between isopropyl and cyclohexyl bromides is expected because of the absence of steric hindrance in this reaction.

The work of Roberts and Hammett[2] on the analogous benzyl chloride reaction falls in line with the reaction scheme here outlined.


# Methyl Silicate from Silicon and Methanol

BY EUGENE G. ROCHOW[1a]

Knowing that hydrocarbon halides will react with elementary silicon in the presence of certain catalysts to yield the corresponding alkyl or aryl halosilanes,[1,2,3,4] it is of interest to inquire whether alcohols will react in similar fashion to form organosilanols or organosiloxanes

$$2ROH + Si \xrightarrow{\text{catalyst}} R_2Si(OH)_2 \xrightarrow{-H_2O} [R_2SiO]_x$$

It was found that of the several lower alcohols tried, only methanol reacted readily to form recognizable products. While the methanol responded to the action of the same copper catalyst used for the reaction of methyl chloride and silicon,[1] it followed an entirely different course of reaction and produced methyl silicate.

$$4CH_3OH + Si \xrightarrow[250°]{\cdot Cu} Si(OCH_3)_4 + 4H$$
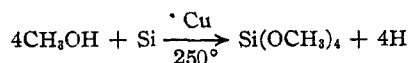
Some of the hydrogen resulting from the reaction appears in the effluent as molecular hydrogen, while the rest combines with the reactants to form silane linkages and reduction products of methanol:

$$H + Si \longrightarrow -\overset{|}{\underset{|}{Si}}-H$$

$$CH_3OH + 2H \longrightarrow CH_4 + H_2O$$
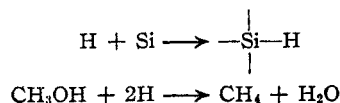
The reaction further is complicated by the action of the water on some of the methyl silicate to form condensed methoxysilanes, $2Si(OCH_3)_4 + H_2O \rightarrow (CH_3O)_3SiOSi(OCH_3)_3 + 2CH_3OH$, etc. A small fraction of the methyl groups later were shown to

be bonded directly to silicon $\left(CH_3-\overset{|}{\underset{|}{Si}}-\right)$ in the manner of the first equation given; no individual methylmethoxysilanes were isolated, however, and the effect was noticed only upon extensive analysis of the intermediate distillation fractions and the solid polymers produced.

Anhydrous *ethanol* was found to react sluggishly with silicon at 280 to 325° in the presence of copper as a catalyst to convert about 10% of the alcohol to condensed ethyl silicates. A search for a more effective catalyst was fruitless. A small amount of material containing C_2H_5–Si bonds was found after one run, but it does not seem likely at this time that ethyl silicate or ethylethoxysilanes can conveniently be prepared from ethanol and silicon in this way.

Experimental

A glass tube 2 cm. in diameter and 50 cm. long was packed with pellets of 90% silicon[5] and 10% copper prepared by pressing the mixed powders in a die and heating the pellets in hydrogen at 1050° for two hours. The tube was sealed to a water condenser leading to a receiver, and the uncondensed products were led through traps held at −80 and −196°. A dropping funnel was connected to the other end of the tube. The tube was heated to 280°[6] and 57.2 g. of anhydrous methanol was allowed to drip in slowly from the funnel. An exothermic reaction set in at once, and the furnace current had to be reduced. A combustible gas (hydrogen) issued from the −196° trap. Thirty-eight grams of liquid was recovered from the receiver, 8.4 g. from the −80° trap, and 2.0 g. from the −196° trap. The liquid in the receiver was found upon distillation to consist of methyl silicate (b. p. 120–122°, m. p. 2°), a little unchanged methanol, some water, and small amounts of materials boiling above and below methyl silicate. The −80° condensate melted at

(1a) Present address: Harvard University, Cambridge, Mass.

(1) Rochow, THIS JOURNAL, 67, 963 (1945).

(2) Rochow and Gilliam, *ibid.*, 67, 1772 (1945).

(3) Hurd, *ibid.*, 67, 1813 (1945).

(4) U. S. Patents 2,380,995 and 2,383,818.

(5) Commercial massive silicon, 98% Si, crushed to pass a 60 mesh sieve.

(6) As measured by a thermometer embedded in the silicon.