not stay on a high level. Chapin has determined *p*H colorimetrically after the decomposition of hypochlorite by sulfite or hyposulfite; Markuse used the buffer mixtures of known composition without any further controlling.[6]

Values of $K_{HOCl}$ of usual "static" methods of determination of dissociation constants are between $1 \times 10^{-8}$ and $4 \times 10^{-8}$.[7] Particularly the method of the glass electrode gives very consistent values $3 \times 10^{-8}$ to $4 \times 10^{-8}$ at room temperature.

Even if equation (1) is quite correct for hypochlorites, the "static" value can today hardly be checked by the kinetical method, since the limits of the experimental errors of the latter are too large.[7a]

The results of the kinetic and static methods applied to hypobromous acid differ among themselves, as remarked above, very much ($2.5 \times 10^{-8}$ and $2.06 \times 10^{-9}$). The discrepancy is hardly to be explained as due to the experimental errors of the two methods.[8]

The more plausible explanation of the divergence is the invalidity of the kinetic equation (1) in the application to hypobromous acid. Indeed equation (1) is only one of many possible equations of transformation of active bromine. As Skrabal indicated,[9] a change of the law of decomposition of hypobromous acid between $\Phi^2$ and $\Phi^3$ takes place $\Phi$ (being summary concentration of HOBr, $Br_2$ and $Br_3^-$), if *p*H and bromide concentration varies.[10] At these conditions the calculation of the dissociation constant of hypobromous acid from $(pH)_{max.}$ is very dubious.

On the contrary the determination of the dissociation constant of hypobromous acid enables one to calculate the composition of the reacting mixture at $(pH)_{max.}$. For the value found by Chapin, *i. e.*, $(pH)_{max.} = 7.3$, we calculate from the equation

$$[H^+][OBr^-]/[HOBr] = 2.06 \times 10^{-9}$$

that

$$[OBr^-] = 0.04\ [HOBr]$$

Thus only 4% neutralization of hypobromous acid present suffices to make the velocity of decomposition maximal. It may be regarded as a demonstration that equation (1) is not valid in the region of *p*H near to 7.

## Experimental

WITH J. N. GLADTCHIKOVA

The dissociation constant of hypobromous acid was determined by titration of free hypobromous acid with sodium hydroxide solution in presence of a glass electrode. The solutions of hypobromous acid were prepared by vacuum distillation of bromine water with silver phosphate. Contrary to the opinion of Pollak and Doktor,[11] shared by Liebhafsky and Makower,[12] who declared the preparation of pure hypobromous acid solution to be an insoluble problem, dilute solutions of hypobromous acid, containing practically no bromine and bromic acid, can be obtained easily by this method.

Sodium hydroxide solutions were prepared from metallic sodium and carbon dioxide-free water.

The apparatus, based on the use of an electrometer valve, was constructed by the scheme of Sokolov and Ptchelin.[13] The glass electrodes were calibrated by means of buffer solutions of which the *p*H had been determined with a hydrogen electrode.

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(6) The original article of Gallart is not available to me.

(7) From the solubility of carbon dioxide in sodium hypochlorite solutions: $3.7 \times 10^{-8}$ at 25° [Sand, *Z. physik. Chem.*, **48**, 614 (1904)] from the partition of hypochlorous acid between the aqeous solution and a vapor phase: $1 \times 10^{-8}$ at 25° [Soper, *J. Chem. Soc.*, **125**, 2227 (1924)]; from the electrical conductivity of hypochlorous acid solution: $\sim 10^{-8}$ at room temperature (Nernst, cited from Sand, *l. c.*); $1.9 \times 10^{-8}$ at 0° [Shilov and Kaniaev, *J. Phys. Chem.* (U. S. S. R.), **5**, 654 (1934)]; by titration with glass electrode: $4 \times 10^{-8}$ [Yorston, *Pulp Paper Mag. Can.*, **31**, 374 (1931)]; $3.7 \times 10^{-8}$ at 18–20° [Davidson, *J. Text. Inst.*, **24**, T185 (1933)]; $3.2 \times 10^{-8}$ at 15° [Britton and Dodd, *Trans. Faraday Soc.*, **29**, 537 (1933)]; $3.7 \times 10^{-8}$ at 18°; the "true" constant is calculated to be $2.95 \times 10^{-8}$ [Ingham and Morrison, *J. Chem. Soc.*, 1200 (1933)]; last value excepted, all others are the apparent dissociation constants. Two values fall out from this series: (1) that of Noyes and Wilson, $6.7 \times 10^{-10}$ [THIS JOURNAL, **44**, 1630 (1922)], the fallibility of which is demonstrated by Soper (*l. c.*), and (2) that of Ríus and Arnal, $1.46 \times 10^{-7}$ at 25° [*Anales soc. españ. fís. quím.*, **31**, 497 (1933); *C. A.*, **27**, 4989 (1933)] obtained by means of an unproved method (electrochemical titration with chlorine electrode).

(7a) During the printing of this article the writer obtained the knowledge of a paper of A. Skrabal and A. Berger [*Monatsh.* **70**, 168 (1937)], treating the determination of the dissociation constant of hypochlorous acid from kinetic data. The results of this thoughtful and thorough investigation are in accordance with the views evolved in this note. The mean kinetic value of $K_{HOCl}$, obtained by Skrabal and Berger, is $5.6 \times 10^{-8}$ at 25°.

(8) Our value of the dissociation constant of hypobromous acid is at present unique, but it may be confirmed to a certain degree by our determinations of the specific conductance of hypobromous acid. The observed specific conductance of 0.01 molal solution of hypobromous acid was $1.7–2.0 \times 10^{-6}$ rec. ohms at 0° (without any correction, *i. e.*, maximal). By calculating the specific conductance by means of the dilution law (under assumption that $\Lambda_\infty$ is 250) one finds for our value of $K_{HOBr}$ $\lambda = 1.1 \times 10^{-6}$, for Chapin's value $\lambda = 4.10^{-6}$.

(9) A. Skrabal, *Z. Elektrochem.*, **40**, 237 (1934).

(10) Certainly Prutton and Maron [THIS JOURNAL, **57**, 1653 (1933)] have found that ordinary reaction of decomposition of hypobromite at *p*H 6.4–7.8, *i. e.*, in the region of the maximal velocity, obeys equation (1). However, this conclusion rests on the dissociation constant of hypobromous acid calculated by Chapin by kinetical method based on equation (1). We have, therefore, a *circulus vitiosus* here.

(11) Pollak and Doktor, *Z. anorg. allgem. Chem.*, **196**, 89 (1931).

(12) Liebhafsky and Makower, *J. Phys. Chem.*, **37**, 1037 (1933); Makower and Liebhafsky, *Trans. Faraday Soc.*, **29**, 597 (1933).

(13) Sokolov and Ptchelin, *J. Applied Chem.* (U. S. S. R.), **7**, 1316 (1934).

The titrations were made at room temperature in a high beaker, provided with a stirrer, in carbon dioxide-free air.

The results were calculated by the Henderson–Hasselbalch formula

$$\log K = \log \frac{x}{A - x} - pH$$

where $A$ is the initial quantity of hypobromous acid and $x$ is the quantity of added alkali, both in moles.

The results of one experiment are reported in Table I. In this experiment 49.84 cc. of 0.0235 molal hypobromous acid was titrated by 0.0255 molal sodium hydroxide at 20°.

TABLE I

| NaOH, cc. | $x/(A-x)$ | Mv. | pH | $10^9 K$ |
|---|---|---|---|---|
| 00 | | 153.2 | 4.97 | |
| 1 | 0.0224 | 270.4 | 7.02 | (2.14) |
| 2 | .0458 | 288.6 | 7.36 | 2.00 |
| 4 | .096 | 306.9 | 7.67 | 2.05 |
| 6 | .1511 | 318.4 | 7.87 | 2.04 |
| 8 | .212 | 325.8 | 8.01 | 2.07 |
| 12 | .3546 | 338.1 | 8.22 | 2.14 |
| 16 | .5335 | 348.4 | 8.40 | 2.12 |
| 20 | .771 | 358.0 | 8.58 | 2.03 |
| 25 | 1.193 | 368.0 | 8.75 | 2.13 |
| 30 | 1.890 | 379.7 | 8.96 | 2.07 |
| 34 | 2.866 | 390.0 | 9.14 | 2.11 |
| 36 | 3.645 | 395.8 | 9.25 | 2.05 |
| | | | | 2.07 |

The mean value $K_{HOBr}$ in this experiment is $2.07 \times 10^{-9}$. The titration of 0.0437 molal hypobromous acid by 0.046 molal alkali has given mean value $K_{HOBr} = 2.04 \times 10^{-9}$.

The probable mean value of all (five) experiments is $K_{HOBr} = 2.06 \times 10^{-9}$ at 20°.

The procedure was controlled by determining the dissociation constant of hypochlorous acid. The value obtained, $K_{HOCl} = 3.16 \times 10^{-8}$ at 20°, is in agreement with the values of Britton and Dodd[7] and Ingham and Morrison.[7]

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## The Preparation of Benzotrifluoride

BY J. H. SIMONS AND C. J. LEWIS

Benzotrifluoride is made in yields approaching the theoretical and without the formation of tars or resins by the action of anhydrous hydrogen fluoride on benzotrichloride. Previous methods[1-3] have used antimony trifluoride, but the authors have found that the reaction in a copper vessel with hydrogen fluoride gives fewer side reactions than when antimony trifluoride is used either alone or with hydrogen fluoride.

The benzotrichloride is placed in a copper flask kept at 0° in an ice-bath. Gaseous hydrogen fluoride is admitted slowly and continuously through a copper tube that extends to the bottom of the flask, and the exit gases escape through another copper tube from the top of the flask. The reaction mixture is stirred or agitated during the course of the reaction.

The exit gases consist chiefly of hydrogen chloride with some hydrogen fluoride and small amounts of benzotrifluoride. As the reaction nears completion, the concentration of hydrogen fluoride and the desired product increase; and they should be trapped in a copper trap kept in a salt-ice bath. The exit gases can be analyzed qualitatively for hydrogen chloride and hydrogen fluoride and relative amounts estimated by the simple procedure of testing with beads of aqueous solutions of silver nitrate and calcium chloride held in nichrome wire loops. Although the reaction can be carried to 95% completion or further, the concentration of hydrogen fluoride in the exit gases rises at about 70% completion, and it is economical to stop the reaction at this point, separate the benzotrifluoride from the mixture by distillation, and return the residue (consisting chiefly of mono- and difluorides) with a new supply of benzotrichloride to the reaction flask for further conversion.

A charge of 500 g. of starting material required about seventy-two hours for the conversion. When the reaction is stopped, the temperature is allowed to rise to room temperature, and a small amount of sodium fluoride is added to remove any hydrogen fluoride present. After standing for a short time with occasional stirring, it is ready for distillation.

Yields of from 75 to 95% were obtained. Other than mechanical losses the chief cause for less than theoretical yield is the amount of the product escaping as vapor with the exit gases.

The benzotrifluoride made by this method was used to make trifluoroacetic acid by the method described by Swartz.[1] With careful technique a yield of about 50% of acid from the starting material, benzotrichloride, can be obtained.

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(1) Swartz, *Bull. acad. roy. sci. belg.*, **35**, 375 (1898).
(2) Aelony, THIS JOURNAL, **56**, 2063 (1934).
(3) Booth, Elsey and Burchfield, *ibid.*, **57**, 2066 (1935).