The Effect of Hydrogen-Ion Concentration on the Decomposition of Hypohalites

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It has long been known that hypochlorite and hypobromite are maximally stable in weakly alkaline solutions and—in absence of halide ion—in strongly acid solutions, while hypoiodite behaves differently. It is also known that the relative proportions of the products of decomposition, halites, halates and molecular oxygen, vary with hydrogen-ion concentration. It seemed desirable to determine the various maximal and minimal points more precisely, under conditions adapted to exclude, so far as possible, participation by molecular halogen, halide or halogen oxides in initial or subsequent reactions.

An essential feature of the plan was the maintenance of constant pH by the incorporation of appropriate buffers in the solutions to be studied. With mentioned exceptions, these comprised only hydroxyl, phosphate and sulfate anions with hydrogen and potassium cations. The decomposition of hypochlorite, at least over certain ranges of pH, was found to be notably accelerated by acetate, borate and carbonate. Inasmuch as even phosphate seemed to exert some effect, it was employed, unless otherwise noted, at not greater than 0.25 molar concentration. The initial concentration of hypohalite was chosen as low as practicable in order to preclude significant downward shifts of pH during decomposition. The desired proportion of a previously analyzed strong solution of hypohalite was mixed in appropriate order with the adequately cooled buffer solution in a flask—of Pyrex glass for strongly alkaline solutions—which was closed as circumstances dictated, either by a close-fitting glass stopper or by fusion. The flasks were then stored in darkened air chambers under automatic temperature control.

Analytical Methods

Under the conditions of the experiments only unimportant proportions of molecular halogen and of halogen monoxide were present. Neither halogen dioxide nor perhalate was detected. Consequently it was necessary to determine only hypohalite, halite and halate. A mixture of the members of a single series of oxy-halogen acids may be analyzed through methods based upon the differing oxidation potentials and oxidative capacities of the substances. Oxidative capacity is conveniently expressed in terms of "available oxygen," which here is

identical with oxygen content. Any observed loss in total available oxygen represents, in absence of perhalate, a corresponding formation of molecular oxygen. The methods used were sufficiently tested for accuracy with a single exception, the method for iodite. The validity of that must rest upon internal evidence and upon the probable close resemblance of iodite to bromite. The methods were derived from those described by Bray,[1] by Clarens,[2] by Foerster and Dolch,[3] by Peters and Deutschländer,[4] and by Pollak and Doktor,[5] with more or less modification to ensure quantitative results on unstable substances under conditions complicated by widely varying acidity or alkalinity. Strict attention to details is necessary.

Method A, the oxidation of arsenious oxide in neutral or alkaline solution, includes all three hypohalites, bromite and iodite. The sample was pipetted into a solution containing arsenious oxide in an excess equivalent to at least 2 cc. of 0.1 N and at least 4 g. of sodium bicarbonate. After five minutes a 10% solution of acetic acid was slowly poured in with constant agitation to the point of free effervescence, and the excess of arsenious oxide was titrated with iodine.

Method B, the oxidation of arsenious oxide as in Method A, after destruction of hypobromite or hypoiodite by phenol in alkaline solution, includes bromite and iodite. The sample was pipetted into a solution containing 1 cc. of a 5% solution of phenol, or more in case of high hypohalite content, and sufficient sodium or potassium hydroxide to provide for an excess of at least 0.1 N in case of bromite and of at least 0.5 N in case of iodite. In three to five minutes standard arsenious oxide was introduced in the necessary excess noted under Method A. After a further five minutes 4 g. of sodium bicarbonate was added, followed by acetic acid and standard iodine as in Method A. But here the final titration must immediately follow acidification in order to retain a high concentration of carbon dioxide in the solution. The end-point with starch, though sharp, will not be permanent, owing to slow action of phenol upon iodine. On the average, the titration will be too high by about 0.1 cc. of 0.04 N iodine. This method is new in that, although phenol has been used previously for the destruction of bromine in acid solution, its sharply selective power in alkaline solution appears to have escaped notice. Clarens[2] employed ammonia or urea in a similar manner, but these substances were here found to be attacked by bromite so readily that serious errors could appear in the results.

Method C, the liberation of iodine from iodide ion in acid solution, includes all hypohalites and halites, bromate and iodate. The sample was pipetted into a colorless solution of 2 g. of potassium iodide in sufficient dilute sul-

(1) William C. Bray, Z. physik. Chem., 54, 569 (1906).

(2) J. Clarens, Compt. rend., 157, 216 (1913).

(3) F. Foerster and P. Dolch, Z. Elektrochem., 23, 137 (1917).

(4) K. Peters and E. Deutschländer, Apoth. Ztg., 41, 594 (1926).

(5) F. Pollak and E. Doktor, Z. anorg. Chem., 196, 89 (1931).

furic acid to ensure a final concentration of at least 0.5 N. After precisely three minutes, with cooling if necessary, liberated iodine was titrated with thiosulfate. A little strong sulfuric acid finally was added to prove complete recovery.

Method D, the oxidation of arsenious oxide in strong hydrochloric acid solution, includes all three oxy-chlorine acids. The sample was pipetted into an Erlenmeyer flask containing an excess of arsenious oxide, about 0.5 g. of potassium bromide and sufficient hydrochloric acid to yield a final excess of about 15 cc. of concentrated hydrochloric acid per 100 cc. The contents of the flask were brought to full boiling, boiled gently for two minutes and allowed to cool spontaneously to about 90°. Excess of arsenious oxide was titrated with 0.05 N potassium bromate.
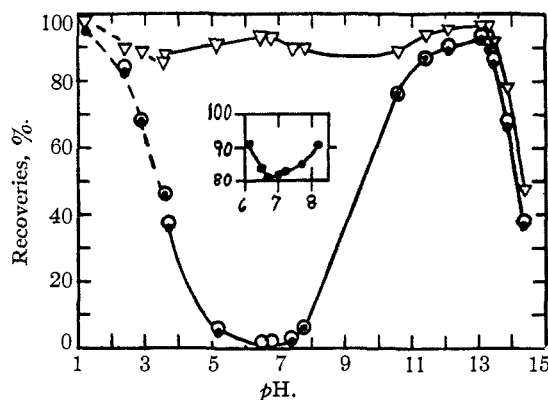

Fig. 1.—Recoveries of available oxygen in various forms from 0.02 molar hypochlorite after nine days at 80°; inset, after five days at 15°. ●, as ClO^-; O, as $ClO^- + ClO_2^-$; ▽, as $ClO^- + ClO_2^- + ClO_3^-$. ——, from chloride-containing hypochlorite; — —, from chloride-free hypochlorite.

Equipment for use of a glass electrode was lacking so that the final pH of the preparations had to be determined colorimetrically. Previous addition of a reducing agent was necessary to prevent bleaching of indicators. Sodium sulfite was employed above pH 9. Below pH 9 the calculated proportion of a normal solution of sodium thiosulfate was mixed rapidly[6] with the sample. Beyond the range of colorimetric methods, above pH 13.3 and below pH 0.5, phosphate and borate being absent, the samples were titrated with standard acid to the mid-point of phenolphthalein or with standard alkali and dimethylamido-azobenzene, and the corresponding pH was obtained by reference.[7]

Experimental Part

Hypochlorite.—A solution of potassium hypochlorite with chloride was prepared by leading pure gaseous chlorine into an ice-cooled normal solution of potassium hydroxide until the concentration of available oxygen approximated 0.5 normal. The solution was substantially free from chlorite and chlorate. Chloride-free hypochlorous acid was prepared by distilling under reduced

(6) Contact of the sample with insufficient thiosulfate would produce SO_4^{--} and H^+.

(7) Van Nostrand's "Chemical Annual," 6th issue, 1926, Tables 23 and 29.

pressure the solution obtained by leading gaseous chlorine into dilute sulfuric acid containing an excess of mercuric sulfate and receiving the distillate in ice-cooled dilute sulfuric acid. A solution of potassium chlorite was prepared essentially as described by Foerster and Dolch.[3] It contained only a trace of chloride while the chlorate content, for which correction was made, was equivalent to less than 3% of the total available oxygen.

In Fig. 1 is shown comprehensively the influence of pH upon the decomposition of hypochlorite. All the preparations were initially 0.04 normal with respect to available oxygen derived from hypochlorite. After storage the residual available oxygen in its various forms was determined by each of the three methods described and the results are given as corresponding percentage recoveries of the initial available oxygen.

The rate of decomposition near pH 6.7 and pH 10 was next determined in order to ascertain the order of reaction. For the preparations at pH 6.5, 100 cc. of the described hypochlorite–chloride stock solution was diluted with 290 cc. of 0.5 molar primary potassium phosphate in a flask provided with a well-fitting glass stopper. For the preparation at pH 10, 83 cc. of the hypochlorite–chloride stock solution was diluted with 233 cc. of 1.35% boric acid solution. The mixture was distributed among 50-cc. test-tubes with drawn-out necks which were then sealed off. The low buffer capacity of phosphate ion in this region precluded its use. The usual formulas were employed for calculating rates of decomposition, namely

$$\frac{2.3}{t} \log \frac{a}{a - x} = k_1$$

for the first order, and

$$\frac{1}{(n - 1)t} \left[\frac{1}{(a - x)^{n-1}} - \frac{1}{a^{n-1}} \right] = k_n$$

for higher orders. Each initial sample, at $t = 0$, was taken after constant temperature had been reached. No residue at the end of a run yielded more than an insignificant trace of molecular chlorine when extracted with carbon tetrachloride. No chlorine dioxide was detected, and only a trace of chlorite. Results are given in Table I.

It seemed desirable to study the progress of the equimolecular reaction between chlorite and hypochlorite over a considerable range of pH. The results are given in Table II.

Hypobromite.—An approximately 0.25 molar solution of potassium hypobromite with bromide was prepared by adding 2.5 cc. of bromine to 200 cc. of ice-cooled normal potassium hydroxide solution, with vigorous agitation. To prepare bromide-free hypobromous acid, bromine was added in successive portions to a mixture of 100 cc. of ice-cooled 0.5 normal sulfuric acid and 3.9 g. of silver sulfate in a glass-stoppered flask until the orange color of excess bromine persisted after continued shaking. After brief settling the liquid was decanted into a separatory funnel and freed from molecular bromine by successive extractions, near 0°, with carbon tetrachloride, which also, in the interface, removed all particles of silver bromide. The solution was analyzed immediately for hypobromite and bromate and was used at once for the desired preparations. Bromite was never present.

Bromite was prepared by Clarens' method modified for increased yield. In 495 cc. of normal sodium hydroxide

TABLE I

RATES OF DECOMPOSITION OF HYPOCHLORITE

Conditions	t, hours	$a - x$, mole per liter	k_1	k_2	k_3
pH 6.5;	0	0.0638			
temp., 37.5°	17.5	.0212		1.8	56
	44	.0128		1.4	66
	90	.0079		1.2	87
	162	.0052		1.1	112
pH 6.5;	0	.0633			
temp., 0°	25	.0599		0.036	0.58
	68	.0553		.034	.57
	162	.0481		.031	.56
	332	.0403		.023	.55
	475	.0359		.025	.55
	687	.0312		.024	.57
	1070	.0261		.021	.57
pH 10;	0	.0659			
temp., 80°	18	.0578	0.0074	.12	
	49	.0474	.0069	.12	
	120	.0313	.0062	.14	
	234	.0155	.0062	.21	

TABLE II

RECOVERIES OF CONSTITUENTS FROM MIXTURES OF 0.015 M HYPOCHLORITE AND 0.015 M CHLORITE AFTER FIVE DAYS AT 37.5°

Final pH	ClO⁻, %	ClO₂⁻, %	Total avail. Cl, %
KOH, 4.2 N	74.3	76.2	99.9
pH 14.1	94.4	97.2	
13.6	98.5	99.7	
12.9	97.9	98.0	
10.5	30.3	31.3	98.9
9.4	10.4	10.5	99.7
6.8	0.9	0.1	98.8

were successively dissolved 10 cc. of bromine and 7 g. of boric acid. The flask was immersed in a water-bath at 40 to 50°. In one to three hours the bromite content approached a maximum equivalent to about 36% of the total available oxygen, after which it would diminish. The flask was then at once placed in cold water and 10 cc. of 18-normal sodium hydroxide was added. After thorough cooling 2 cc. of 5% mercuric chloride was introduced to serve as indicator and an approximately normal solution of ammonium hydroxide was slowly added with thorough mixing until a precipitate of mercuri-ammonium halide persisted after vigorous shaking. The preparation was repeatedly passed through a fluted paper until about 50 cc. of perfectly clear filtrate was obtained which was treated with one drop of the mercuric chloride solution. If a precipitate appeared, the whole preparation was treated with 2 cc. of mercuric chloride solution and repassed through the filter. Finally a clear, light-yellow filtrate was obtained free from hypobromite and ammonium ion and containing only an apparently harmless trace of mercuric ion.

Figure 2 shows the influence of pH upon the decomposition of 0.02 molar hypobromite.

Rates of decomposition of hypobromite are given in Table III, together with the molar ratios found between bromite and hypobromite. The preparations above

pH 9 were made by direct admixture of bromine with potassium hydroxide solution or by dilution of such a solution
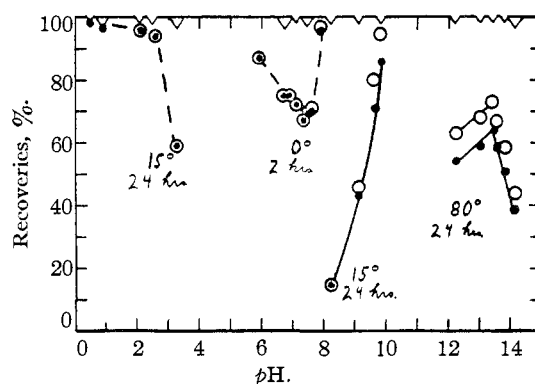

Fig. 2.—Recoveries of available oxygen in various forms from 0.02 molar hypobromite after storage. ●, as BrO⁻; ○, as BrO⁻ + BrO₂⁻; ▽, as BrO⁻ + BrO₂⁻ + BrO₃⁻. ——, from bromide-containing hypobromite; — —, from bromide-free hypobromite.

with boric acid solution. Below pH 9 the presence of bromide ion led to interference by molecular bromine;

TABLE III

RATES OF DECOMPOSITION OF HYPOBROMITE

Conditions	t, hours	Mole ratio, BrO₂⁻/ BrO⁻	$a - x$, mole per liter	k_2	k_3
HNO₃, 0.44 N;	0	0.003	0.0599		
Excess Ag⁺;	1.75	.001	.0511	1.64	29.6
temp., 37.5°	3.33		.0454	1.59	30.8
	5.33		.0400	1.56	32.5
	23		.0207	1.37	44.9
	71		.0096	1.24	75.2
pH 9.1;	0	.12	.0327		
temp., 37.5°	0.62	.12	.0207	28.7	1135
	1.4	.11	.0154	24.5	1170
	2.7	.10	.0113	21.3	1265
	4.2	.09	.0089	19.4	1375
	5.7	.08	.0075	18.0	1485
pH 9.4;	0	.11	.0565		
temp., 0°	17.3	.10	.0279	1.05	28.2
	23.8	.09	.0243	0.99	28.9
	42	.08	.0190	.83	29.2
	68	.07	.0141	.79	34.8
	114.0	.06	.0105	.68	38.4
pH 11.1;	0	.25	.0622		
temp., 37.5°	24.3	.34	.0395	.38	7.9
	73.5	.40	.0231	.37	10.9
	145	.42	.0150	.35	14.5
	362	.44	.0075	.32	24.1
pH 14.1;	0	.045	.1078		
temp., 37.5°	23	.049	.0974	.043	
	69	.052	.0822	.042	
	119	.052	.0691	.044	
	189	.056	.0564	.045	
	311	.055	.0437	.044	
	573	.053	.0292	.043	
	960	.057	.0199	.043	

TABLE III (Concluded)

Conditions	t, hours	Mole ratio, BrO$_2^-$/BrO$^-$	a − x, mole per liter	k$_2$	k$_3$
KOH, 5 N;	0	0.021	0.2044		
temp., 37.5°	3	.022	.1883	0.143	
	20	.024	.1285	.145	
	27	.022	.1138	.145	
	44	.022	.0888	.145	
	68	.022	.0680	.144	
	116	.023	.0463	.144	
	190	.023	.0310	.144	

TABLE IV

RECOVERIES OF CONSTITUENTS FROM MIXTURES OF 0.015 M HYPOBROMITE AND 0.015 M BROMITE AFTER FORTY-FIVE HOURS AT 37.5°

Final pH	Recoveries BrO$^-$, %	Recoveries BrO$_2^-$, %
KOH, 4.2 N	51.8	59.0
KOH, 2.3 N	78.5	83.0
KOH, 0.75 M	90.0	93.7
pH 13.4	95.4	94.0
13.2	94.4	94.6
13.0	93.7	94.6
12.4	92.8	94.4
11.4	60.9	75.1
9.5	1.4	0.1

consequently a preparation was made from 2 cc. of bromine and 15 g. of silver nitrate dissolved in 400 cc. of 0.3 normal nitric acid with thorough shaking and subsequent decantation, though, by analogy with hypochlorite, the presence of excess silver ion[8] might be expected to promote first-order decomposition. Each initial sample at t = 0 was taken after the concentration of bromide had reached its maximum.

Data on the equimolecular reaction between bromite and hypobromite are given in Table IV.

Hypoiodite.—The percentage recoveries of available oxygen in various forms from initially 0.02 molar hypoiodite are shown in Fig. 3. For the preparations stored one hour, 10 cc. of a 0.5 normal iodine solution in 0.5 molar potassium iodide was added to 115 cc. of potassium hydroxide solution. For the preparations stored five minutes, upon 10 cc. of the same iodine solution in a flask was poured, in succession and as rapidly as possible, with thorough mixing, 62.5 cc. of 0.5 normal sodium hydroxide and 52.5 cc. of primary potassium phosphate solution.

Fig. 3.—Recoveries of available oxygen in various forms from 0.02 molar hypoiodite stored at 0°. ●, as IO$^-$; ○, as IO$^-$ + IO$_2^-$; ∇, as IO$^-$ + IO$_2^-$ + IO$_3^-$.

Determinations of the rate of decomposition are given in Table V. The preparations were made by direct solution of elementary iodine in potassium hydroxide solution and the initial sample at t = 0 was taken after appropriate delay.

TABLE V

RATES OF DECOMPOSITION OF HYPOIODITE

Conditions	t, min.	Mole ratio, IO$_2^-$/IO$^-$	a − x, mole per liter	k$_2$
KOH, 4.9 N;	0	0.014	0.0471	
temp., 0°	12	.016	.0363	0.53
	33	.016	.0256	.54
	79	.016	.0157	.54
	161	.015	.0085	.59
	293	.013	.0053	.57
KOH, 1.0 N;	0	.088	.0170	
temp., 0°	6.5	.083	.0096	7.0
	17.5	.087	.0055	7.0
	35.5	.100	.0032	7.1

Discussion

The experimental work was completed in ignorance of two recent pertinent papers. Gallart[9] determined the velocity of decomposition of hypochlorite in solutions of crystallized sodium hypochlorite and sulfuric acid between pH 5.7 and pH 8. The decomposition was found to be a reaction of the third order, and the rate-determining step was inferred to be

$$2HClO + ClO^- \longrightarrow 2HCl + ClO_3^- \qquad (1)^{10}$$
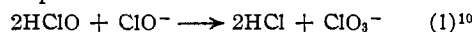
Therefore pH 6.68, at which the velocity of decomposition was maximal (k = 32.9 per hour at 25°), was assumed to be the pH at which hypochlorite was one-third dissociated, and accordingly the dissociation constant of hypochlorous acid was calculated to be K = 1.05 × 10^{-7} at 25.[11] Gallart developed a formula whereby the results of all his rate determinations were combined to afford the most consistent value for K. The writer (Fig. 1) found the velocity of decomposition at 15° to be maximal at pH 6.7, while the rates given in Table I are consistent with Gallart's intermediate rate at an intermediate temperature.

In the second paper referred to, Liebhafsky and Makower[12] conclude the rate law

$$-d\Sigma(X_2)/dt = k\ (HXO)^2\ (XO^-)$$

with a rate-determining step similar to Equation 1, to be of general importance in the formation of

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(8) In presence of silver ion the analytical methods A and B must be modified in that sufficient bromide ion to precipitate all silver ion is present with the respective initial reagents before introduction of the sample.

(9) J. M. Gallart, Anales soc. españ. fis. quim., 31, 422 (1933).

(10) First indicated for hypochlorite by Foerster and Jorre, J. prakt. Chem., 59, 53 (1899), later doubted by Foerster and Dolch²; indicated for hypobromite by Kretzschmar, Z. Elektrochem., 10, 789 (1904), and for hypoiodite by Skrabal, Monatsh., 32, 815 (1911).

(11) Values reported by users of the glass electrode range from about 4 × 10^{-8} to 3 × 10^{-8} at 15 to 20°.

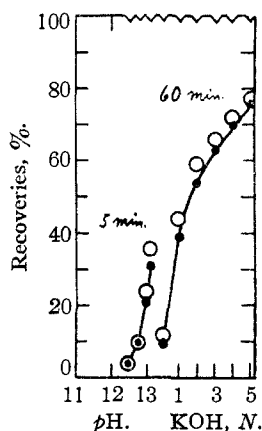(12) H. A. Liebhafsky and B. Makower. J. Phys. Chem., 37, 1037 (1933).

all three halates. Their experimental work, however, was confined to derivatives of bromine. They determined rates of decomposition of hypobromite at 25° in solutions containing silver ion and buffered with phosphate at various points over a range of hydroxyl-ion concentration 0.67×10^{-8} to 52×10^{-8}. The maximum observed velocity was found at $(OH^-) = 19.6 \times 10^{-8}$, equivalent to pH 7.3, which is identical with the optimal pH observed by the writer at 0° (Fig. 2). They did not derive from these results a value for the dissociation constant of hypobromous acid. Their data, taken as a whole, did not appear amenable to treatment by Gallart's formula, but a one-third dissociation at pH 7.3 would indicate $pK = 7.6$ and $K = 2.5 \times 10^{-8}$. The data here presented (Table III) confirm a decomposition of higher than the second order at and below pH 9.4.

Clarens[2] found both the formation of bromite from hypobromite in alkaline solution and its subsequent conversion to bromate to be reactions of the second order. Foerster and Dolch[3] later demonstrated similar reactions of chlorine derivatives. Weiss[13] inferred the rate law to be

$$-d\ (ClO)/dt = k\ (ClO^-)^2$$

Liebhafsky and Makower[12] inferred a similar rate law for hypobromite[14] also. However correct that rate law may be in solutions as alkaline as pH 13.5, it appears that at somewhat lower alkalinity the possibility of the rate law

$$-d\ (XO)/dt = k\ (HXO)\ (XO^-)$$

deserves investigation. For (Table III) the rate of decomposition of hypobromite at pH 11.1 was about eight times the rate at pH 14.1, and that of hypoiodite (Table V) was about twelve times as great in normal as in 4.9 normal potassium hydroxide, although the order of the decomposition in neither case rose much above the second order.

The subsequent reaction between halite and hypohalite (Tables II and IV) appeared to be, except for a certain degree of independent decom-

position of hypohalite, equimolecular throughout the range of pH investigated. Each mixture was maximally stable at the same pH at which the individual hypohalite itself was most stable. Neither halite, in absence of hypohalite, was appreciably decomposed by four-normal potassium hydroxide.

Foerster and Dolch[3] observed that the decomposition of hypochlorite approached a reaction of the first order when the alkalinity of the solution was sufficiently increased above 0. /normal, and attributed the result to catalysis. Borate ion (Table I) appeared to exercise a similar effect upon hypochlorite at pH 10. In contrast, no evidence of a first-order decomposition and no important formation of molecular oxygen was here observed in the case of either hypobromite or hypoiodite.

In contrast with hypochlorite and hypobromite, the stability of hypoiodite appeared to increase steadily with alkalinity and no region of comparative stability in strongly acid solution could be demonstrated. However, the data on hypoiodite are presented chiefly as illustrative of the application of a particular technique, without present reference to existing work.

Summary

Aside from notable stability in strongly acid solutions, the stability of dilute hypochlorite was found greatest at pH 13.1 and least at pH 6.7; of hypobromite greatest at pH 13.4 and least at pH 7.3. The stability of hypoiodite increased with increasing hydroxyl-ion concentration between pH 12.5 and five-normal potassium hydroxide.

Halite was found in alkaline solutions. Improved methods for the preparation and determination of bromite ion are described.

The third-order formation of chlorate and bromate in acid solutions, and the second-order formation of all three halites and subsequent conversion to halates in alkaline solution were confirmed.

(13) J. J. Weiss, *Z. anorg. allgem. Chem.*, **192**, 97 (1930).

(14) It must be remarked that the utilized data of Kretzschmar[10] are dubious to the extent that his analytical method for hypobromite also included bromite, without distinction.