with more than 5 kernel charges on the octet joining the ring plus its attached hydrogens, are indicated as favoring Pattern *o. p.* (in toluene and chlorobenzene), and those with 5 or less charges, as favoring Pattern *m.* (in nitrobenzene and benzaldehyde).

8. Substitution is considered as possible only when the hydrogens are lightly held ("open" positions of the adjacent aromatic electrons). The influence of these electrons is to "open" or "close" positions according to their attractive action on the hydrogen kernels.

9. Relative ease of substitution into the various substituted benzenes is treated as a result of polarity considerations, which are developed as an essential consequence of the octet theory, and an addition to the above aromatic structural considerations. Preference for substitution in *ortho* vs. *para* positions is treated in like manner.

10. Pyridine, thiophene, furane and pyrrol are treated similarly and afford striking confirmations of the postulated structure in their behavior.

11. *Addition* of any kind is shown to be inconsistent with the retention of aromatic structure in the remainder of the ring.

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THE IONIZATION CONSTANT OF HYPOCHLOROUS ACID. EVIDENCE FOR AMPHOTERIC IONIZATION

By WILLIAM A. NOYES AND THOMAS A. WILSON

In a very careful and extended experimental study published in 1899, Jakowkin[1] demonstrated conclusively that chlorine is hydrolyzed by water to hydrochloric and hypochlorous acids. He determined the partition coefficient of chlorine between carbon tetrachloride and pure water and also between carbon tetrachloride and solutions of strong and weak acids, chlorides, and hypochlorous acid. He also determined the conductivity of pure hypochlorous acid solutions and of solutions of chlorine in water, and observed that the conductivity of the latter is almost wholly due to the hydrochloric acid formed by the hydrolysis, and that the hypochlorous acid is ionized scarcely at all under these conditions. Finally, he showed that hypochlorous acid volatilized more rapidly than hydrochloric acid

[1] Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

from a dilute solution of chlorine in water, and that this difference in rate reaches a maximum at $90°$. The simplest explanation of Jakowkin's result is that in the hydrolysis, chlorine separates into positive and negative ions, and that these combine with the ions of water: $Cl^- Cl^+ + H^+ OH^- = H^+ Cl^- + Cl^+ OH^-$.

This conclusion was not mentioned by Jakowkin, but was very clearly stated, two years later, by Stieglitz[2] in commenting on a paper by one of us[3] in which the opinion was expressed that the chlorine of nitrogen trichloride is positive in character.

If the point of view expressed by Stieglitz is true, hypochlorous acid should have two ionization constants : one, k_a, for the acid; $H^+ ClO^-$; and the other, k_b, for the base; $Cl^+ OH^-$. Washburn[4] has developed a method of obtaining these constants, k_a and k_b, from conductivity measurements. According to this method, an a normal solution of a base will have a certain specific conductivity, L_1. If another solution is now prepared of an a normal base and an a normal amphoteric electrolyte, its specific conductivity will be L_2, and L_1 is greater than L_2 because of the partial progress of the reaction, $B(OH) + HA = H_2O + BA$; as a result of this some of the very mobile hydroxyl ions are removed from solution and some more slowly moving acid ions take their place. For a solution of hypochlorous acid in sodium hydroxide, Washburn's equation takes the form

$$k = \frac{\dfrac{1000(L_1 - L_2)}{\Lambda_{OH} - \Lambda_{ClO}} \left[\dfrac{K_w}{\dfrac{1000 \; L_1}{\Lambda_{Na} + \Lambda_{OH}}} - \dfrac{1000(L_1 - L_2)}{\Lambda_{OH} - \Lambda_{ClO}} \right]}{C_a - \dfrac{1000(L_1 - L_2)}{\Lambda_{OH} - \Lambda_{ClO}}}$$

where $K_w = (H^+)(OH^-)$, and C_a is the total concentration of the hypochlorous acid, in equivalents per liter. It is evident that an equation of precisely similar form would apply to the calculation of k_b, provided that L_1 was the specific conductivity of a b normal solution of some strong acid, and L_2 that of a solution b normal with respect to the same strong acid and b normal with respect to hypochlorous acid.

Jakowkin[1] has shown that the only satisfactory way to prepare hypochlorous acid for conductivity experiments is to distil the acid from a solution of chlorine treated with freshly prepared yellow mercuric oxide. In this work, the acid used was distilled from this mixture under a pressure of 4 mm. of mercury after the substances had been left in contact overnight. The distillate collected came off at a temperature below $32.4°$. The vapors were passed through a Vigreaux tube of 84 cm. length, through

[2] Stieglitz, This Journal, 23, 797 (1901).
[3] Noyes and Lyon, ibid., 23, 460 (1901).
[4] Washburn, "Principles of Physical Chemistry," McGraw-Hill Book Co., 1921, p. 375.

a 25cm. reflux condenser, and were collected in a receiver cooled in ice. All parts of the apparatus were of Pyrex glass. The distillation and all subsequent operations involving hypochlorous acid had to be carried out in a dark room illuminated by dull red light, or small 30-watt carbon incandescent bulbs placed at a considerable distance from the acid. After the still had been kept running for 3 days, a product was obtained of negligible conductivity, which could be preserved satisfactorily for a day if it was kept on ice and in the dark. Its usual concentration was about $0.08 N$ as determined by iodometry.

The sodium hydroxide solution used was prepared by suspending a platinum crucible containing a piece of thoroughly scraped sodium over a beaker of water in a desiccator fitted with a Bunsen valve for the escape of hydrogen. The water distilled into the crucible under its own vapor pressure. At the end of a week or so, a concentrated alkali solution remained in the crucible. This was diluted with conductivity water to the desired concentration and kept under crushed sodium hydroxide.

Calcium hydroxide for conductivity measurements was prepared by three successive precipitations from a conc. calcium chloride solution by means of sodium hydroxide. The product so obtained was heated for 2 hours in a platinum crucible with the full heat of the Meker burner, then was dissolved in water to the desired concentration, and kept under crushed calcium hydroxide.

Nitric acid solution was prepared by distillation of a commercial c. p. nitric acid into conductivity water. This solution was again distilled, and the product diluted to the desired concentration.

Standard potassium chloride for cell constant determinations was prepared from the c. p. salt which had been subjected to three precipitations from solution by addition of hydrochloric acid and drying in filtered air. Three concentrations of this solution, 0.1, 0.05, and $0.01 N$, were used in determining the cell constant. The value actually used was the mean of 15 determinations.

Kohlrausch's standard method for measuring the conductivity of electrolytes was the one chosen, after over a year had been spent in attempts to use the method described by Newbery.[5] Sand[6] reports that Nernst tried preliminary experiments by the method we have used and obtained values of the order of 10^{-8}, but that accurate values could not be secured because of the decomposition at the electrodes. Sand determined the constant by determining the amount of carbon dioxide absorbed by a solution of sodium hypochlorite, and found $k_a = 3.7 \times 10^{-8}$ at $17°$. This was substantially the same result which we obtained by the Newbery method and also by the Kohlrausch method when the conductivity was

[5] Newbery, *J. Chem. Soc.*, **113**, 701 (1918).
[6] Sand, *Z. physik. Chem.*, **48**, 610 (1904).

determined in the usual way with a sample of the electrolyte. It was impossible to obtain definite results by these methods of procedure, owing to the large differences existing between successive readings. These differences in general indicated a marked increase in conductivity during the passage of the current.

Kohlrausch's method, however, was satisfactory when a stream of electrolyte was kept flowing around the electrodes so that the conductivity measurement was always made on a fresh sample. A high frequency machine of foreign make supplied an alternating current of 1000 alternations; all other equipment except the cell was standard Leeds and Northrup apparatus. The cell was a flow type arrangement, so designed that the electrolyte flowed through a long glass tube in the thermostat water before entering .the cell, from which it discharged through a side tube. With this apparatus, in the dark, using freshly prepared hypochlorous acid in all cases, no trouble was experienced in securing a series of constant conductivity measurements on any sample desired.

Tables I and II below show the results obtained in measurements for the determination of k_b. Each column represents a new solution. Readings were made at 5-minute intervals during the time of flow of the electrolyte. The temperature of the thermostat was kept at $25° \pm 0.01°$. Table I shows the result of measurements made on $0.001\ N$ solutions;

TABLE I

$L_1 \times 10^4$ for $0.001\ N$ HNO$_3$			$L_2 \times 10^4$ for $0.001\ N$ HNO$_3$ and $0.001\ N$ HOCl	
		Solutions		
1	2		3	4
3.55	3.54		3.54	3.55
3.55	3.54		3.55	3.55
3.55	3.54		3.54	3.55
3.55	3.54		3.54	3.55
3.55	..		3.55	..

TABLE II

$L_1 \times 10^5$ for $0.0001\ N$ HNO$_3$				$L \times 10^5$ for $0.0001\ N$ HNO$_3$ and $0.0001\ N$ HOCl		
			Solutions			
1	2	3		4	5	6
3.58	3.62	3.59		3.67	3.59	3.54
3.59	3.59	3.59		3.70	3.61	3.50
3.59	3.57	3.64		3.54	3.62	3.62
3.60	3.58	3.62		3.57	3.62	3.57
3.60	3.58	3.57		3.61	3.60	3.58

Table II those made on $0.0001\ N$ solutions; dilutions of this order were chosen partly because of the impracticability of preparing hypochlorous acid of stronger concentration in sufficient quantity for conductivity work, partly because it was desirable to change the mobility of the ions involved as little as possible from the values at infinite dilutions.

Inspection of Tables I and II shows that within the limits of experimental error, $L_1 = L_2$, although the greater obscurity of the end-point in the case of $0.0001\ N$ solutions makes this less apparent; k_b is too small to be determined by this method.

TABLE III

$L_1 \times 10^4$ for 0.001 N Ca(OH)$_2$			Solutions	$L_2 \times 10^4$ for 0.001 N Ca(OH)$_2$ and 0.001 N HOCl		
1	2	3		4	5	6
2.31	2.32	2.31		1.28	1.27	1.30
2.31	2.32	2.32		1.29	1.29	1.26
2.31	2.32	2.32		1.28	1.28	1.27
2.32	2.32	2.32		1.26	1.28	1.28
2.32	2.32	2.31		1.27	1.29	1.28

Average $L_1 = 2.315 \times 10^{-4}$ Average $L_2 = 1.278 \times 10^{-4}$
$L_1 - L_2 = 1.037 \times 10^{-4}$ $k_a = 6.79 \times 10^{-10}$

Table III shows the results of measurements made on calcium hydroxide solutions. The results shown above were called in question owing to the lack of knowledge regarding the manner of ionization of di-univalent electrolytes. Runs made with sodium hydroxide gave the results below.

TABLE IV

$L_1 \times 10^4$ for 0.001 N NaOH			Solutions	$L_2 \times 10^4$ for 0.001 N NaOH and 0.001 N HOCl		
1	2	3		4	5	6
2.16	2.16	2.15		1.15	1.15	1.16
2.16	2.16	2.15		1.15	1.15	1.15
2.16	2.16	2.15		1.14	1.15	1.15
2.16	2.16	2.15		1.13	1.15	1.15
2.16	2.15	2.15		1.12	1.15	1.15

Average $L_1 = 2.157 \times 10^{-4}$ Average $L_2 = 1.147 \times 10^{-4}$
$L_1 - L_2 = 1.010 \times 10^{-4}$ $k_a = 6.60 \times 10^{-11}$

The value of K_w used in the calculations is 1×10^{-14} at $25°$.[7]

In a paper which seems to have been overlooked by all recent authors, Pelouze[8] showed that a concentrated solution of hypochlorous acid gives on treatment with calcium nitrate, chlorine monoxide, Cl_2O, which he called "hypochlorous acid" in accordance with the nomenclature of the day. Jakowkin[1] has shown that hypochlorous acid has a normal molecular weight corresponding to the formula HClO in aqueous solutions. He and several others have shown that hypochlorous acid volatilizes readily from its solutions. We have demonstrated that the vapor phase contains chlorine monoxide and not hypochlorous acid, by the following experiments.

[7] Ref. 4, p. 365.
[8] Pelouze, *Ann. chim. phys.*, [3] **7**, 126 (1843).

One hundred g. of freshly prepared mercuric oxide was placed in a solution of chlorine in a 2-liter flask. A steady stream of chlorine gas was conducted through the flask for 6 hours, so that the passage of the gas kept the oxide constantly in suspension. At the close of this period, the flask was allowed to stand overnight with frequent shaking. The product gave a fine, dark straw-colored suspension when a little of it was shaken with mercury, and showed a normality of 0.2715.

A slow current of air which had been passed through potassium hydroxide to remove carbon dioxide, and through water in a serpentine tube to secure saturation with water vapor was passed through a bottle containing a liter of the solution of hypochlorous acid prepared as described. The air was then passed through a weighed tube containing anhydrous calcium nitrate to absorb the water vapor, and through weighed bulbs containing sodium hydroxide to absorb the chlorine monoxide. At the end of 4 or 5 hours, the volume of air passed was determined, also the gain in weight of the drying tube and of the sodium hydroxide bulbs. (See Table V.)

TABLE V

	I	II	III
Volume of air passed, measured over water, cc.	3572.	2715.	3442.
Barometer, mm	736.2	739.3	750.2
Temperature, °C	21.5	22.1	21.2
"Moles" of air passed	0.1395	0.1061	0.1371
Temperature of thermostat, °C	25.1	25.1	25.1
Normality of solution (volume)	0.271	0.173	0.224
(1) Weight of water carried over (actual), g	0.0878	0.0630	0.0790
(2) Weight of water carried over (theoretical), g	0.0897	0.0641	0.0800
Weight of gas collected by sodium hydroxide bulbs, g	0.9929	0.1300	0.2201
Moles of gas collected, assuming it Cl_2O	0.01140	0.001495	0.00253
Volume of 0.1513 N $Na_2S_2O_3$ required for titer, cc	....	20.32	33.81
Volume of same required theoretically, cc	....	19.90	33.50
(3) Total weight of water if HOCl vaporizes as such, g	....	0.0910	0.1270

The table shows that the weight of water collected by the drying tube corresponded almost exactly with the theoretical amount for saturated air under the conditions of the experiment, and did not correspond at all with the amount which would be collected if the hypochlorous acid were volatile as such, and had lost its water in the drying tube. That the gas collected in the sodium hydroxide was chlorine monoxide and not hypochlorous acid is demonstrated also by the titrations. This confirms the observations of Pelouze.

That the acid volatilizes as Cl_2O as shown is not a contradiction of Clark

and Iseley,[9] who report the monomolecular reaction, $2\,HOCl = 2\,HCl + O_2$, as taking place in the sunlight.

Discussion

The simplest explanation of the results we have obtained is to suppose that hypochlorous acid undergoes an amphoteric ionization, and that while the hydrogen and hypochlorite ions preponderate, enough positive chlorine ious are present so that these combine with the hypochlorite ions to form chlorine monoxide, $Cl^+ + ClO^- = Cl^+\,O^=Cl^+$.

According to the Lewis-Langmuir hypothesis as usually interpreted, the union between oxygen and chlorine in hypochlorous acid is "non-polar." In terms of that hypothesis, only such positive ions as hydrogen, lithium, glucinum, and the carbon of the positive ion of triphenylmethyl, have less than 8 electrons in their outer shell. These experiments seem to demonstrate the existence of positive chlorine ions having only 6 electrons in the outer shell. In a similar manner, nitration and sulfonation are most simply explained by assuming the positive groups NO_2^+ and SO_3H^+ to be present in conc. nitric and sulfuric acids.[10]

Summary

1. New determinations of the conductivity of hypochlorous acid and of sodium hypochlorite give the value $k_a = 6.70 \times 10^{-10}$.

2. The value of k_b for hypochlorous acid is too small to be determined by the change in conductivity of $0.0001\,N$ nitric acid when hypochlorous acid is added to it.

3. Chlorine monoxide and not hypochlorous acid, as such, escapes from a solution of the acid when a current of air is passed through it.

[9] Clark and Iseley, *J. Ind. Eng. Chem.*, **12**, 1116 (1920).

[10] A member of the Board of Editors of the JOURNAL has suggested that "The simplest explanation is the dehydration reaction: $2HClO = Cl_2O + H_2O$."

Such a statement seems to overlook the fact that the dehydration reaction still requires explanation. About the only explanation possible in accordance with the Lewis-Langmuir theory is indicated by the diagram:

$$H\,\vert\,\colon \overset{\cdot\cdot}{O} \colon \overset{\cdot\cdot}{Cl} \colon$$
$$H \colon \overset{\cdot\cdot}{O} \colon\vert\, \overset{\cdot\cdot}{Cl} \colon$$
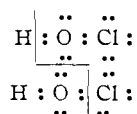
This means that the water must be formed from a positive hydrogen ion from one mol of hypochlorous acid and a negative hydroxyl ion from the other. Unless we assume that pairs of electrons are divided in the reaction, the 2 electrons between the oxygen and the chlorine must go with the oxygen of the negative hydroxyl, leaving only 6 electrons with the chlorine atom. The latter would, therefore, be positive. There is very little difference between such an explanation and that of actual ionization giving a very few positive chlorine ions.

This indicates the presence of positive chlorine ions in such a solution and the amphoteric ionization of the acid.

4.   If the Lewis-Langmuir hypothesis is accepted, it requires an interpretation consistent with these facts.

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THE CATALYTIC FORMATION OF WATER VAPOR FROM HYDROGEN AND OXYGEN IN THE PRESENCE OF COPPER AND COPPER OXIDE

By Robert N. Pease and Hugh S. Taylor

In an earlier paper,[1] dealing with the reduction of copper oxide by hydrogen, it was shown that the presence of small concentrations of oxygen in the hydrogen markedly diminished the rate of reduction of copper oxide. It was demonstrated, moreover, that this reduction *occurred only at an interface between copper metal and copper oxide*, when moderate reduction temperatures (100–200°) were employed. The free oxygen in the hydrogen manifestly affects, therefore, the reactivity of oxygen attached to copper at a copper-copper oxide interface. These observations are of undoubted importance in the problem of hydrogen-oxygen catalysis in the presence of copper or copper oxide or both. It is natural to infer that a catalytic action of this type, conducted in presence of a metal which is readily oxidized and whose oxide is easily reduced, should occur by a series of alternate oxidations and reductions. Bone and Wheeler,[2] however, contend that this is not true in the case of copper oxide. They suggest that the explanation of the catalytic process,........"in the case of copper oxide, would appear to involve the condensation of a film of 'active' oxygen on the surface and that this film actually protects the catalyzing oxide from the attacks of the hydrogen, which would otherwise energetically reduce it. At low pressure (that is after the reaction has proceeded for some time), the film becomes too attenuated to ensure complete protection and, in consequence, the formation of steam is accelerated by reason of hydrogen penetrating through on to the oxide and reducing it. In conformity with this idea,[3] the rate of steam formation when the gases are not present in combining ratios was found to be proportional to the partial pressure of the oxygen." In regard to the combination of hydrogen and oxygen in the presence of

[1] Pease and Taylor, This Journal, **43**, 2179 (1921).

[2] Bone and Wheeler, *Phil. Trans.*, **206A**, 1 (1906).

[3] Presumably the idea of reaction being between hydrogen and a surface film of "active" oxygen. (Pease and Taylor.)