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(54) Title: HIGH PURITY CHLORIC ACID

(57) Abstract

A process for producing chloric acid which comprises converting an aqueous solution of hypochlorous acid containing at least 20 percent by weight of HOCl at a temperature in the range of from about 10 to about 120 °C to a reaction mixture comprising a dilute aqueous solution of chloric acid and gaseous by-products while continuously removing the gaseous by-products to produce a chloric acid solution containing about 10 percent or greater by weight of $HClO_3$. Using the novel process it has been found that chloric acid can be produced efficiently at substantially reduced production costs using a process which can be operated commercially. In addition, the chloric acid solutions are produced in high concentrations and high purity being substantially free of impurities such as alkali metal ions, chloride ions and sulfate ions.

* See back of page

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High Purity Chloric Acid

Cross Reference to Related Application

This application is a continuation-in-part of application U.S. Serial No. 403,279, filed September 5, 1989.

Background of the Invention

Field of the Invention

This invention relates to the production of chloric acid, $HClO_3$. Chloric acid can be used in the formation of chlorine dioxide, a commercial bleaching and sanitizing agent.

Description of the Prior Art

Chloric acid is a known compound which has been made in laboratory preparations by the reaction of barium chlorate with sulfuric acid to precipitate barium sulfate and produce a dilute aqueous solution of chloric acid which was concentrated by evaporation of water under partial vacuum. In another method sodium chlorate is reacted with an acid such as hydrochloric acid or sulfuric acid to produce an aqueous solution of chloric acid containing sulfate or chloride ions as impurities. In addition, commercial processes for producing chlorine dioxide form chloric acid as an intermediate.

U.S. Patent 3,810,969 issued May 14, 1974 to A.A. Schlumberger teaches a process for producing chloric acid of high purity by passing an aqueous solution containing from 0.2 gram mole to 11 gram moles per liter of an alkali metal chlorate such as sodium chlorate through a selected cationic exchange resin at a temperature from 5° to 40° C. The process produces an aqueous solution containing from 0.2 gram mole to about 4.0 gram moles of $HClO_3$.

Kirk-Othmer: "Encyclopedia of Chemical Technology" 3rd edition, vol. 5, page 587 teach that the decomposition of dilute hypochlorous acid solutions (1 M) can occur in two ways:

$$2\,HOCl \rightarrow 2\,HCl + O_2 \xrightleftharpoons{2\,HOCl} 2\,Cl_2 + O_2 + 2\,H_2O \qquad (I)$$

$$\left\{\begin{array}{ll} 2\,HOCl \rightarrow [HClO_2] + HCl & (IIa) \\ 2\,HOCl + [HClO_2] \rightarrow HClO_3 + HCl \xrightleftharpoons{HOCl} HClO_3 + Cl_2 + H_2O & (IIb) \end{array}\right.$$

in the second mechanism, chlorous acid $[HClO_2]$ is stated to be an intermediate in the formation. Decomposition of HOCl by both mechanisms is said to increase with concentration, temperature and exposure to light and are pH dependent. The first reaction mechanism is said to be accelerated by catalysts and the second mechanism favored by the pressure of electrolytes such as the chloride ion. The reference, however, has no teachings regarding the decomposition of concentrated hypochlorous acid solutions.

Chloric acid, however, up to the present time, has not been commercially produced or available commercially because of the high manufacturing costs and/or the undesired impurities present in the solutions of $HClO_3$ made by these reactions.

Summary of the Invention

Now it has been found that chloric acid can be produced efficiently at substantially reduced production costs using a process which can be operated commercially. In addition, the chloric acid solutions produced are of high purity and are stable at ambient conditions.

In accordance with this invention, there is provided a process for producing chloric acid which comprises converting an aqueous solution of hypochlorous acid containing at least 20 percent by weight of HOCl at a temperature in the range of from about 10° to about 120 °C. to a reaction mixture comprising a dilute aqueous solution of chloric acid and gaseous by-products and continuously removing the gaseous by-products to produce a chloric acid solution containing about 10 percent or greater by weight of $HClO_3$.

Detailed Description of the Invention

The novel process of the present invention employs as the starting material a concentrated solution of high purity hypochlorous acid, HOCl. One method of producing high purity concentrated HOCl solutions is that in which gaseous mixtures, having high concentrations of hypochlorous acid vapors and chlorine monoxide gas and controlled amounts of water vapor are produced, for example, by the process described by J. P. Brennan et al in U.S. Patent No. 4,147,761, which is incorporated in its entirety by reference. The gaseous mixture is then converted to a concentrated hypochlorous acid solution as described in WO 90/05111 published May 17, 1990 by J. K. Melton, et. al. which is incorporated in its entirety by reference.

The concentrated hypochlorous acid solution employed as a reactant contains at least 20 percent by weight of HOCl. Preferred solutions are those having concentrations in the range of from about 30 to about 60, and more preferably from about 40 to about 55 percent by weight of HOCl. The solution is substantially free of ionic impurities such as chloride ions and alkali metal ions and has low concentrations of dissolved chlorine. For example, concentrations of the chloride ion are preferably less than about 50 parts per million and the alkali metal ion concentration is preferably less than about 50 parts per million. The dissolved chlorine concentration in the hypochlorous acid solution is normally less than about 2 percent, and preferably less than about 1 percent by weight.

The concentrated hypochlorous acid is converted to chloric acid in any suitable manner and because the hypochlorous acid reagent is of high purity, the conversion is believed to produce chloric acid according to the following reactions:

$$3HOCl \longrightarrow HClO_3 + 2HCl \qquad (1)$$

$$2HOCl + 2HCl \longrightarrow 2Cl_2 + 2H_2O \qquad (2)$$

$$5HOCl \longrightarrow HClO_3 + 2Cl_2 + 2H_2O \qquad (3)$$

In one embodiment of the process of the invention conversion of the concentrated hypochlorous acid to chloric acid takes place in an open vessel. Under these conditions the gaseous by-products are released as formed, for example, to a scrubbing apparatus containing an alkaline solution. Suitable temperatures are those, for example, in the range of from about 10 to about 120° at autogenous pressures. The conversion times are directly related to the temperature, however, as the conversion temperature increases, the yield of chloric acid is reduced. Therefore the hypochlorous acid conversion, where the by-product gases are released or continuously removed, is preferably at from about 25 to about 70°C. A dilute aqueous solution of chloric acid is produced which is may be further concentrated.

In a preferred embodiment, the chloric acid is produced by heating the hypochlorous acid solution at elevated temperatures while maintaining the gaseous by-products formed in contact with the reaction mixture during the reaction period. This can be accomplished, for example, by carrying out the process in a sealed reactor at the autogenous pressures attained wherein a substantial increase in the yield of chloric acid results. For example, the concentrated hypochlorous acid solution may be heated at temperatures in the range of from about 40 to about 120, preferably in the range of from about 50 to about 110 °C., and more preferably in the range of from about 60 to about 100°C.

Where the chloric acid solution produced by the process of the invention is dilute, i.e. less than about 10 percent by weight of $HClO_3$, the chloric acid solution is further concentrated by removing a portion of the water by evaporation. During evaporation any residual hypochlorous acid is converted to chloric acid product. Concentration is suitably accomplished by heating the chloric acid solution at temperatures above about 40°C., for example at temperatures in the range of from about 40 to about 120 °C, preferably at from about 70 to about 120 °C. and more preferably at from about 95 to about 120 °C.

The chloric acid solutions may also be concentrated by vacuum distillation. Any suitable vacuum pressures may be used such as those in the range of from about 0.01 to about 100 mm Hg.pressure

The highly pure chloric acid solutions which are produced by the novel process of the present invention contain at least about 10 percent, for example 12 percent or greater, by weight of $HClO_3$. Concentrated solutions up to about 45% by weight of $HClO_3$ may be produced. Preferred chloric acid solutions are those having from about 15% to about 40%, and more preferably 18% to about 35% by weight of $HClO_3$. The highly pure concentrated solutions produced i.e. those above about 30% by weight of $HClO_3$, are surprisingly stable and can be stored safely without significant decomposition for extended periods of time.

The novel process of the present invention is further illustrated by the following examples with no intention of being limited thereby. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

A solution of hypochlorous acid containing 30% by weight of HOCl was added to a large open vessel at ambient temperature and pressure. The solution was analyzed periodically and when the reaction had produced a solution containing 6.0% of $HClO_3$, 5.3% of HOCl and 0.1% HCl by weight, the solution was heated at 30°C and a solution containing 7.8% $HClO_3$, 0.6% HOCl and 0.1% HCl by weight produced. This chloric acid solution was further concentrated by vacuum distillation at 20-24°C and about 0.1 mm Hg to a solution containing 20.03% $HClO_3$ and less than 0.1% by weight of either HOCl or HCl.

EXAMPLE 2

A concentrated solution of hypochlorous acid containing 41% by weight of HOCl was placed in the large open vessel employed in Example 1, and allowed to remain at room temperature for 24 hours. The solution was then concentrated by vacuum evaporation at 25°C to produce a chloric acid solution containing 23.5% by weight of $HClO_3$. The analyses are as follows:

TABLE I

	Initial	After 24 hrs. Weight %	After Concentration
$HClO_3$		14.31	23.51
HOCl	41	0.80	0.12
HCl		BDL*	BDL*

*Below detectable limits

EXAMPLE 3

A concentrated hypochlorous acid solution (600g.) containing 40.54% by wt. of HOCl was poured into a sealed reactor and heated at 55°C.. The gases produced were fed to a caustic scrubber. Following the reaction a solution (454.8 g) containing 11.91% $HClO_3$, 4.92% HOCl and 0.1% HCl was produced. The yield of $HClO_3$ based on HOCl was 71%. The analyses of the reaction solution and the scrubber solution (1124.7 g.) are as follows:

TABLE II

	Initial Solution	After HOCl Conversion	Caustic Scrubber
		Weight %	
HOCl	40.54	4.92	
$HClO_3$	0.29	11.91	
HCl	0.12	0.1	
NaOCl			10.93
$NaClO_3$			0.69
NaCl			10.07

EXAMPLE 4

A concentrated hypochlorous acid solution containing 40.54% by wt. of HOCl (600g.) was heated in the sealed reactor used in Example 3 at a temperature of 95°C. The yield of $HClO_3$ (445.5 g) based on HOCl was 81%. The analyses are given in Table III below.

TABLE III

	Initial Solution	After HOCl Conversion
	Weight %	
HOCl	40.89	2.45
$HClO_3$	1.04	13.74
HCl	0.54	0.22

EXAMPLE 5

A solution containing 22.8% by weight of $HClO_3$ produced by the process of the invention was further concentrated by heating at 95°C in an open vessel. The chloric acid product recovered contained 43.34% by weight of $HClO_3$.

EXAMPLE 6

A solution containing 15% by weight of $HClO_3$ was concentrated to 28% by weight by boiling under atmospheric pressure at 102-4°C. Recovery of the chloric acid value was 97.2%. The total time required for the concentration was 45 minutes, of which 13 minutes was required to heat the initial solution to boiling. No evidence of chlorine or chlorine dioxide emission was observed.

EXAMPLES 7-8

Chloric acid solutions containing 30% and 37.87% by weight of $HClO_3$ were produced in the process of the invention.

An aliquot (1000 ml.) of each solution was placed in an open vessel and stored at 30°C. and 40°C. During the storage period, the solution was periodically analyzed by titrimetry for the concentration of $HClO_3$. The results are given in Table IV below.

TABLE IV

STABILITY OF $HClO_3$ SOLUTIONS AT 30 AND 40 DEG C

	30 DEG. C. Wt% HClO3	Days	40 DEG. C. Wt% HClO3
Example 7			
	30.01	0	30.01
	29.79	3	29.78
	29.99	6	29.87
	30.01	14	30.03
	30.68	26	30.45
	30.37	44	30.42
	30.34	64	30.07
	30.54	81	30.46
Example 8			
	37.87	0	37.87
	37.78	3	37.87
	37.84	6	38.01
	38.13	14	38.40
	38.58	26	38.51
	38.27	44	38.70
	37.89	64	38.73
	38.30	81	40.12
	39.27	121	40.93

EXAMPLE 9

Hypochlorous acid (44%, 600 g.) was heated in an open vessel at 95° for 1 hour. The product solution contained 6.3% HOCl and 5.5% $HClO_3$ (yield 29%). The product solution may be further concentrated by evaporation of water, for example, by the method of Example 1.

WHAT IS CLAIMED IS:

1. A process for producing an aqueous chloric acid solution which is characterized by converting an aqueous solution of hypochlorous acid containing at least 20 percent by weight of HOCl at a temperature in the range of from about 10° to about 120 °C. to a reaction mixture comprising an aqueous solution of chloric acid and gaseous by-products while continuously removing the gaseous by-products to produce an aqueous chloric acid solution containing about 10 percent or greater by weight of $HClO_3$.

2. The process of claim 1 characterized in that the aqueous solution of hypochlorous acid contains from about 20 to about 60 percent by weight of HOCl.

3. The process of claim 1 characterized in that the aqueous solution of chloric acid is concentrated at a temperature in the range of from about 40° to about 120°.

4. The process of claim 1 characterized in that the dilute aqueous solution of chloric acid is concentrated by vacuum distillation.

5. The process of claim 4 characterized in that the conversion temperature is in the range of from about 25° to about 70°.

6. A process for the production of an aqueous chloric acid solution characterized by heating an aqueous solution of hypochlorous acid containing at least 20 percent by weight of HOCl at above ambient temperature to form a reaction mixture comprised of an aqueous chloric acid solution and gaseous by-products, retaining the gaseous by-products in contact with the chloric acid solution, and producing an aqueous chloric acid solution containing about 10 percent or greater by weight of $HClO_3$.

7. The process of claim 6 characterized in that the solution of hypochlorous acid is heated at a temperature in the range of from about 40° to about 120 °C.

8. The process of claim 6 characterized in that the solution of hypochlorous acid contains from about 20 to about 60 percent by weight of HOCl.

.9. The process of claim 8 characterized in that the solution of hypochlorous acid is heated at a temperature in the range of from about 50° to about 110°C.

10. The process of claim 6 characterized in that the solution of hypochlorous acid contains from about 30 to about 55 percent by weight of HOCl.

11. The process of claim 10 characterized in that the solution of hypochlorous acid is heated at a temperature in the range of from about 60° to about 100°C.

12. The process of claim 6 characterized in that the aqueous chloric acid solution is further concentrated by evaporation.

13. The process of claim 12 characterized in that the aqueous chloric acid solution is evaporated at a temperature of from about 70° to about 120°C.

14. The process of claim 12 characterized in that the aqueous chloric acid solution is concentrated by vacuum distillation.

15. The process of claim 14 characterized in that the aqueous chloric acid solution is evaporated at a temperature of from about 95° to about 120°C.

16. The process of claim 1 characterized in that the chloric acid solution contains about 12 percent or greater by weight of $HClO_3$.

17. The process of claim 3 characterized in that the aqueous chloric acid solution produced contains from about 15 to about 40 percent by weight of $HClO_3$.

18. The process of claim 6 characterized in that the chloric acid solution contains about 12 percent or greater by weight of $HClO_3$.

19. The process of claim 10 characterized in that the aqueous chloric acid solution produced contains from about 15 to about 40 percent by weight of $HClO_3$.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US90/05008

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

US CL.: 423/473
IPC(5): C01B 11/12

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	423/472, 473, 477

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	Kirk-Othmer, "Encyclopedia of Chemical Technology, 3rd Ed., Vol. 5, published 1979 by John Wiley & Sons (New York) see pages 587-588.	1-19
A	Masschelein, "Chlorine Dioxide, Chemical and Environmental Impact of Oxychlorine Compounds" Published 1979 by Ann Arbor Science (Michigan) see pages 9-11.	1-19
A	Gerhartz, Ed., "Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A6, published 1986, see page 501.	1-19
A	Stecher, Ed., "The Merck Index" 8th Edition, published 1968 by Merck & Co., Inc. (New Jersey), see page 236.	1-19
A	"Supplement to Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry" Supplement II, published 1956 by Longmans, Green and Co. (London) see pages 546-549.	1-19
A	GB, A, 984,378 (COULTER ET AL) 24 February 1965, See the entire document	1-19
A	US, A, 2,347,151 (CRAWFORD ET AL) 18 April 1944, See the entire document	1-19

* Special categories of cited documents: [15]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 22 OCTOBER 1990	Date of Mailing of this International Search Report [2] 07 DEC 1990
International Searching Authority [1] ISA/US	Signature of Authorized Officer [20] for Andre Robinson GARY P. STRAUB