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Iodine Recovery from Brine Solutions

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Abstract

Iodine has been produced by the reaction of iodide with hydrogen peroxide in the presence of the catalyst ferrous sulfate. The presence of high concentrations of chloride or bromide in both natural and synthetic brines have no effect on the reaction specificity or kinetics. This approach is potentially a less caustic method for the recovery of iodine from brine as compared to the most commonly used chlorine displacement methods.

Introduction

Iodine, a product largely consumed in the U.S., is mostly produced in Chile and Japan. Although the U.S. consumes 30–35% of the world supply, it produces only 20% of that which it uses.

The iodine produced in the U.S. comes from brines usually containing in excess of 100 ppm iodide. In the most commonly used process, the brine is acidified with sulfuric acid and treated with a slight excess of chlorine to liberate the iodine in a denuding tower using a countercurrent stream of air. The iodine rich air passes into a second tower where it is absorbed into a solution of hydriodic and sulfuric acids and treated with sulfur dioxide to reduce the iodine to hydriodic acid. A portion of the acid is drawn off for iodine recovery, and the remainder recirculated to the absorption tower. The liquor in the reaction is retreated with chlorine and the iodine liberated [1].

The chlorine process, although very inexpensive at terms of chemicals required, it very costly in terms of equipment because of the highly corrosive nature of the chlorine. Highly corrosion resistant materials must be used such as high silicon iron Stellite 6, Hastelloy C, and several grades of stainless. In addition to these irons, other metals such as niobium, tantalum, and molybdenum are used.

The chlorine process for iodine extraction [1] is only one of several described in the literature [2–5]. Another process utilizes silver salts to precipitate silver iodide followed by chlorine recovery [6]. In recent years, the Japanese have introduced an ion exchange process which utilizes Amberlite IRA-400 (anion exchange) [7].

Our interest is the oxidation of iodide for the purpose of producing iodine economically from natural brines by utilizing H_2O_2 and $FeSO_4$ for the complete oxidation of iodide to iodine. There is a voluminous literature on the oxidation of I^- to I_2 by H_2O_2 and by iron salts, but most of these reported studies were mechanistic in nature. There are several mentions in the literature of the acceleration of the I^- oxidation by a mixture of H_2O_2 and $FeSO_4$ [8, 9] generally referred to as Schönbein's reaction [10]. These studies were directed mainly to the use of this reaction for analytical purposes. We are not aware of any reported studies in which Schönbein's reaction was tried in brine solutions for the purpose of obtaining iodine, even though this reaction has been known since prior to 1869 [1, 2, 11, 12].

This study deals with the kinetics of this reaction in both a saline model system and in natural brines, including recoveries of the iodine produced. The reaction is complex in detail, since several intermediate species are involved, and no attempt was made to elucidate detailed mechanisms. We believe that this simple, inexpensive and non-corrosive method for the oxidation of iodide to iodine may have potential as a replacement for the existing process.

Experimental

Kinetic Studies

Reaction curves for the formation of I_2 from I^- were measured spectrophotometrically. In Fig. 1 are given solution spectra of NaI only, NaI + H_2O_2 and $FeSO_4$ + H_2O_2. These spectra were recorded at least one hour after mixing the solutions. NaI only has no absorption bands in this spectral region while I_2 and Fe^{++} and/or Fe^{+++} show strong absorption bands near 340 nm. However, in the region above about 430 nm the only absorption measured is that due to I_2. All the reaction curves were obtained by measuring the OD changes at 460 nm.

Recovery Studies

The reaction solutions were extracted with $CHCl_3$ three times and the I_2 absorption was measured from

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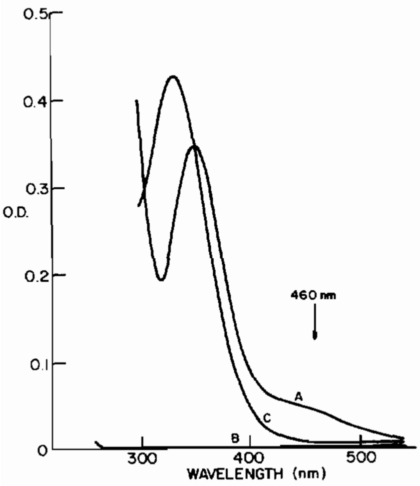

Fig. 1. Spectra of: (A) NaI solution reacted with H_2O_2, (B), NaI solution only, and (C) $FeSO_4$ solution with H_2O_2.

the band at 508 nm. A calibration curve was obtained by dissolving I_2 in $CHCl_3$. The whole band was scanned in order to correct for slight baseline variations. These measurements gave the quantity of I_2 formed in any given experiment.

Reagents

All added reagents were analytical grade. The natural brines, kindly supplied by Watkins Salt Co. (Watkins Glen, N.Y.) and Exxon Corp. (New York, N.Y.), were from two distinctly different sources. The Watkins Salt Co. brine was taken directly from a salt well and was high in total solids. The Exxon brine was from an oil well and had lower solids, but contained organic residues. Complete halide analyses were obtained for the brines and these are given in Table I.

Fresh stock solutions were prepared each day to a concentration such that 10 μl NaI solution dispensed into 10 ml of a brine solution gave 100 ppm (700 μM) NaI. Stock solutions for the iron salts and H_2O_2 were equimolar to the NaI stock solution.

The synthetic brine consisted of a 5% NaCl solution. All experiments were carried out at pH = 2.5 and ambient room temperature.

TABLE I. Brine Analyses.

	Chloride (ppm)	Bromide (ppm)	Iodide (ppm)	Total Solids (w/v)
Watkins Salt Co. Brine	190700	188	0.98	32.8%
Exxon Feezel Brine	65800	142	1.7	11.6%

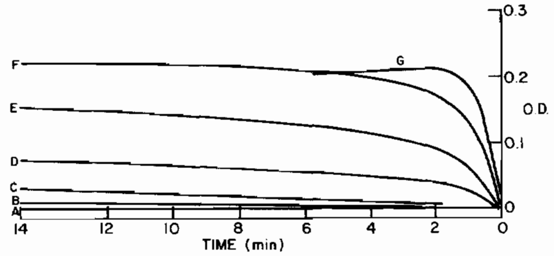

Fig. 2. Typical spectrophotometric reaction curves for iodine formation measured at 460 nm. (A) 700 μM $FeSO_4$, with 700 μM H_2O_2, (B) 700 μM NaI with 700 μM H_2O_2, (C) 700 μM NaI with 2800 μM H_2O_2, (D)–(G) 700 μM NaI and 1400 μM H_2O_2 with $FeSO_4$ varying from 140 μM to 1400 μM.

Results and Discussion

Some typical spectrophotometric reaction curves for I_2 formation are given in Fig. 2. Curve A, for $FeSO_4$ + H_2O_2 only, shows that these constituents do not interfere with the spectrophotometric measurements. Reaction curves B and C are for the uncatalyzed reaction between NaI and H_2O_2. Curves D, E, F and G are for this reaction in the presence of increasing concentrations of the Fe^{++} catalyst. Qualitatively it is clear that the Fe^{++} catalyst greatly accelerates the I_2 formation rate, and that with the appropriate choice of concentrations the reaction is essentially complete within 10 min.

In order to quantitatively measure the reaction rates from these reaction curves, an arbitrary linearizing function was used, with O.D. units. This function is given in Fig. 3 along with some of the linearized reaction curves. These plots are satisfactorily linear to >80% reaction, so that the reaction rates are proportional to the slopes.

In Table II are given the measured reaction rates for a series in which the Fe^{++} catalyst concentration

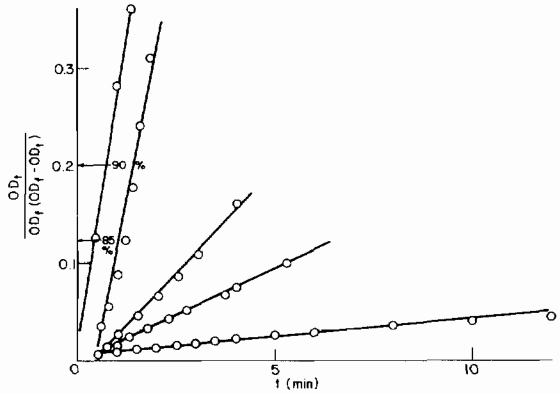

Fig. 3. Typical linearized reaction curves, using the O.D. function given on the ordinate *vs.* time. The slopes are proportional to the reaction rates.

TABLE II. Rate and Extent of Reaction as a Function of H_2O_2 Concentration.

[NaI][a] (μM)	[$FeSO_4$] (μM)	[H_2O_2] (μM)	End Point (O.D.)	Rate (OD. Units)
700	700	350	0.12	0.013
700	700	700	0.23	0.02, 0.03
700	700	1400	0.21	0.03
700	700	1400	0.22	0.044
700	700	2800	0.23	0.09
700	700	2800	0.22	0.085

[a] 700 μM NaI = 100 ppm.

was held constant and the H_2O_2 concentrations were varied. Also given are the end points of the curves measured after an extended period of time. The end point data show that the stoichiometry of the NaI + H_2O_2 reaction is 1:1. The reaction rates, as a function of the H_2O_2 concentration, are plotted in Fig. 4. It is seen that the reaction rates are directly proportional to the H_2O_2 concentrations.

To confirm that the reaction is first order in I^- and in H_2O_2, the kinetic data were also treated with a standard form of a second order integrated rate equation. Some plots are given in Fig. 5 for a series in which the Fe^{++} catalyst concentration was held constant and the NaI/H_2O_2 concentration ratio was varied from 0.25:1 to 10:1. The slopes of these plots, which are nicely linear, give the value of the absolute rate constant for the reaction. In view of the high sensitivity of the reaction rate to small varations in the catalyst concentration, the slopes are satisfactorily constant. The value obtained for the absolute rate constant is $k = 6.8 \pm 1.7$ lit/mol sec.

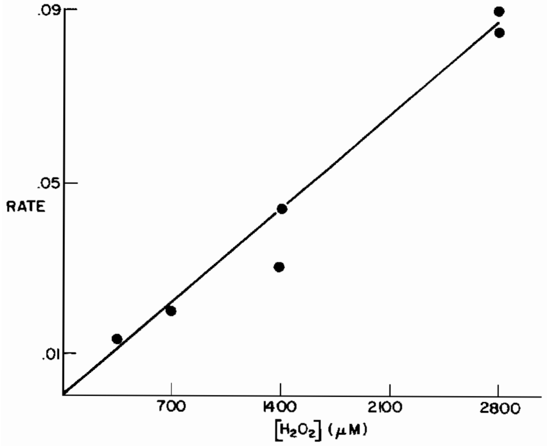

Fig. 4. Dependence of iodine production rate on H_2O_2 concentration. Solutions contained 700 μM NaI with 700 μM $FeSO_4$ and variable H_2O_2 concentration.

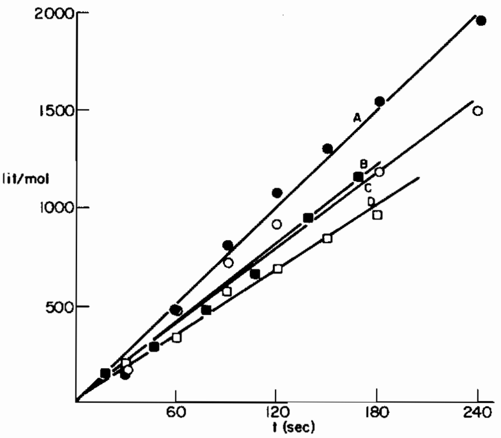

Fig. 5. Kinetic plot of second order integrated rate equation against time, using: (A) 700 μM NaI with 1400 μM H_2O_2, (B) 3500 μM NaI with 350 μM H_2O_2, (C) 700 μM NaI with 1400 μM H_2O_2, and (D) 700 μM NaI with 2800 μM H_2O_2. All solutions contained 700 μM $FeSO_4$. The slopes of the plots are equal to the absolute values of the rate constants.

TABLE III. Rate and Extent of Reaction as a Function of $FeSO_4$ Concentration.

[NaI] (μM)	[$FeSO_4$] (μM)	[H_2O_2] (μM)	End Point (O.D.)	Rate (O.D. Units)
700	0	2800	–	1.37×10^{-4}
700	140	1400	0.23	8×10^{-4}
700	350	1400	0.22	62×10^{-4}
700	700	1400	0.22	0.044
700	700	1400	0.21	0.02, 0.03
700	1400	1400	0.21	0.21
3500	1400	700	–	0.035[a]

[a] Initial rate only.

The Fe^{++} catalyzed decomposition of H_2O_2 has been widely studied. A proposed reaction scheme [13] involves the formation of OH^-, OH, HOO, HOO^- and Fe^{+++} in which the product Fe^{+++} reacts with HOO to regenerate the catalytically active Fe^{++}. The reported rate constant [13] for the Fe^{++} catalyzed decomposition of H_2O_2 is 56.0 lit/mol sec, which is about 8 X faster than the rate constant measured here for the catalyzed oxidation of I^-.

The data in Table III show that the end points attained after a long time period are essentially the same with various concentrations of $FeSO_4$, although the rates are widely different. These end point data show that the $FeSO_4$ effect is catalytic. The relative rates of the catalyzed reactions to the uncatalyzed reaction with respect to the $FeSO_4/H_2O_2$ ratio are plotted in Fig. 6. The rates vary as $[FeSO_4]^{2.5}$. Under the conditions used this gives a rate increase greater than a thousandfold for the catalyzed over the uncatalyzed reaction.

When the $FeSO_4$ is in molar excess to the H_2O_2 both the extent of reaction and the rate of reaction decrease. Presumably this is due to the concurrent rapid H_2O_2 decomposition.

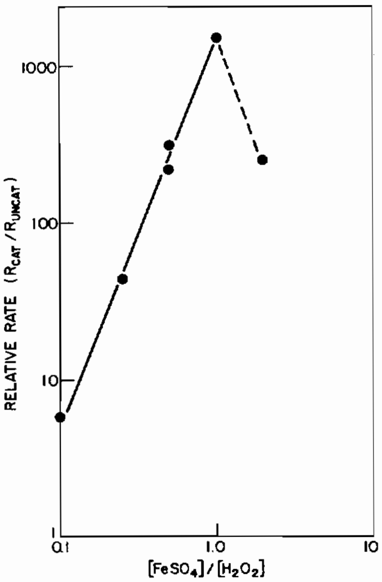

Fig. 6. Relative rates of the catalyzed reactions to the uncatalyzed reaction against the molar ratio of $FeSO_4$ to H_2O_2.

TABLE IV. Comparison of I^- Oxidation Rates with Various Fe^{++} and other Salts.

Salt	Rate (O.D. Units)[a]
$FeSO_4$	0.025
$FeCl_2$	0.028
$Fe(NH_4SO_4)_2$	0.027
None	1.4×10^{-4}
$Co(NO_3)_2$	*ca.* 1.4×10^{-4}
$NiCl_2$	*ca.* 1.4×10^{-4}

[a]Measured in 5% NaCl containing 100 ppm NaI with equimolar H_2O_2 and transition metal salt.

Since $FeSO_4$ is an ionic compound which dissociates completely in solution, the nature of the anion should be irrelevant. To confirm this, reaction curves were obtained using $FeSO_4$, $FeCl_2$ and $Fe(NH_4SO_4)_2$ as catalysts. The measured rates are essentially the same (*cf.* Table IV).

Reaction rates were also measured using $Co(NO_3)_2$ and $NiCl_2$ in place of the Fe^{++} catalysts. The rates obtained were the same as those obtained in the absence of any catalyst. Thus, Co^{++} and Ni^{++} are not catalytically active in this reaction.

When $FeCl_3$ is used in place of the Fe^{++} salt the reaction rate is considerably faster than in the uncatalyzed reaction, but slow in comparison to the rate obtained with Fe^{++} salts. Also, the reaction curve is slightly concave upwards. This suggests that as the uncatalyzed $H_2O_2 + I^-$ reaction takes place, one of the intermediates produced reacts with Fe^{+++} to produce Fe^{++}, thus increasing the Fe^{++} concentration as the reaction proceeds.

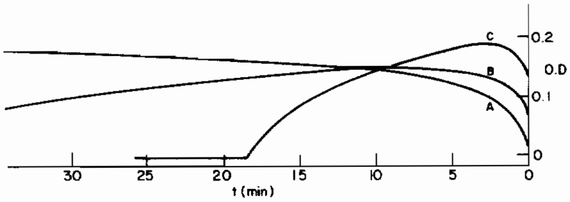

Fig. 7. Spectrophotometric reaction curves for iodine formation and disappearance in 700 μM NaI with 700 μM $FeSO_4$ for: (A) 700 μM H_2O_2, (B) 3500 μM H_2O_2, and (C) 6300 μM H_2O_2.

With a large excess of H_2O_2 oxidant present the product I_2 disappears over a period of time due to the further oxidation of the I_2 to IO_3^-. In Fig. 7 are given some reaction curves in which were used equimolar, fourfold and eightfold excess of H_2O_2. With equimolar H_2O_2, I_2 attains its maximum concentration and then remains constant; with excess H_2O_2 the I_2 formed reaches a certain value and then slowly decreases. The shapes of the curves are unusual in that they are concave downward and indicate a continually increasing rate. Since the oxidation of each I_2 molecule gives two IO_3^- it is reasonable to construct an autocatalytic model such that:

$$\frac{-d[I_2]}{dt} = k[H_2O_2][I_2][IO_3^-]^2$$

This differential rate equation can be integrated by the method of partial fractions and, in terms of the observed optical densities, gives the integrated rate equation shown on Fig. 8. The data from Fig. 7 are plotted in Fig. 8 using the integrated rate equation. The plots in Fig. 8 are satisfactorily linear over the

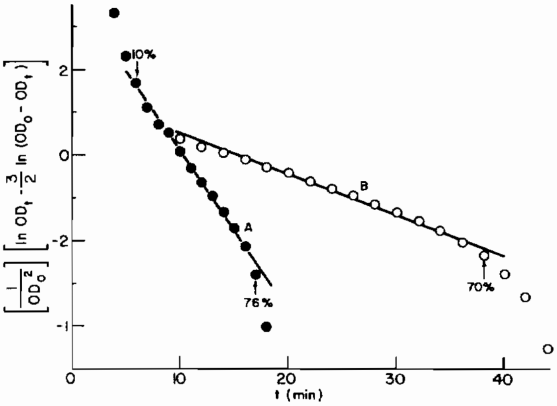

Fig. 8. Kinetic plots for iodine disappearance using autocatalytic rate equation given on ordinate. Data taken from Fig. 7.

TABLE V. Comparison of I^- Oxidation Rates in Various Brines Containing 100 ppm NaI with Equimolar H_2O_2 and $FeSO_4$.

Brine	Rate (O.D. Units)
5% NaCl	0.020
Exxon Brine	0.021
Watkins Brine	0.023

TABLE VI. Iodine Recovery from NaI + $FeSO_4$ + H_2O_2 System.

Brine[a]	$[H_2O_2]$ (μM)	I_2 Recovered (mg)[b]	
		t = 15 min.	t = 1 hr
Saline, 5%	700	0.60	0.91
Saline, 5%	1400	0.67	0.03
Saline, 5%	2800	0.29	0.03
Exxon Brine	700	0.48	
Exxon Brine	1050	0.71	
Exxon Brine	1750	0.79	
Exxon Brine	2800	0.71	
Watkins Brine	1750	0.68	

[a] Each brine contained 700 μM NaI with equimolar $FeSO_4$ at pH 2.5. [b] 700 μM (100 ppm) is equivalent to 0.85 mg I_2.

greater part of the I_2 comsumption reaction, suggesting that the proposed mechanism is correct. The ratio of the slopes is 3.9 for a twofold difference in excess of H_2O_2.

Iodine Recovery

Reaction curves were obtained for iodine formation in the model saline system and in the two natural brines. The rates obtained in the three systems were similar (*cf.* Table V). Large variations in rates due to the different ionic strengths of the media were not observed.

The iodide oxidation reaction was then carried out in the three systems and the product iodine was extracted for quantitative analysis. The results are given in Table VI. In the saline model system, equimolar H_2O_2 after one hour reaction time gives essentially 100% iodine recovery. In the brines, 15 minute reaction times only were used. By stopping the reaction after 15 min and using a 2.5 molar ratio of H_2O_2, iodine recovery of about 80–90% was obtained.

Conclusions

The current widely used chlorine process for iodine extraction is certainly low in direct material costs. It has the disadvantages, however, of being both polluting and corrosive to equipment. It is obvious from the data presented that iodine can indeed be processed semi-quantitatively in brines of extremely high salt content by this method. This Fe^{++} catalyzed reaction is simple, fast and non-corrosive.

Acknowledgement

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