

THE EFFECT OF VARIOUS IODIDES UPON THE STABILITY OF
HYDRIODIC ACID.***

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INTRODUCTION.

In a study of the stability of Solution of Arsenous and Mercuric Iodide, Husa and Enz (1), (2) found that in order to stabilize this solution it was necessary to prevent oxidation of the hydriodic acid formed by hydrolysis of the arsenous iodide. Several methods of improving the stability were found (1), (3), but the problem was complicated by the presence of the compounds of mercury and arsenic. It appeared, therefore, that it would be advantageous to make a study of solutions of pure hydriodic acid and that the results of such a study could later be applied to the Solution of Arsenous and Mercuric Iodide.

Since hydriodic acid as such is also used as a pharmaceutical, a further knowledge of its stability under various conditions would be of interest. In a report of the Committee on Actinic Values of Glass (4), Dr. W. L. Scoville suggested that a study be made of the effect of light upon Diluted Hydriodic Acid, U. S. P. X. Dr. Scoville also pointed out (5) that previous studies of hydriodic acid have been made chiefly on solutions protected by hypophosphorous acid, syrup or glycerin and that aside from this little or nothing is known about the effect of light and temperature. Likewise Kistiakowsky (6) has pointed out that little systematic investigation has been carried out on the influence of ions on the rate of oxidation of hydriodic acid.

The purpose of the present investigation was to make a study of some of the factors which might affect the stability of hydriodic and to determine the effect of various iodides on the rate of decomposition.

DECOMPOSITION OF HYDRIODIC ACID.

It is a well-known fact that solutions of hydrogen iodide turn brown after a time, due to liberation of free iodine. The hydriodic acid is oxidized by oxygen of the air in the following manner:



Solutions of hydriodic acid also appear to undergo decomposition into hydrogen and iodine as follows (7), (1):



PREPARATION OF THE HYDRIODIC ACID.

Among the methods which have been used for the preparation of hydriodic acid are the following: (a) direct union of hydrogen and iodine, (b) reaction of tartaric acid and potassium iodide, (c) hydrolysis of phosphorous tri-iodide, (d) action of iodine upon certain organic compounds such as copaiba, rosin, pinene, etc., and (e) action of hydrogen sulphide upon iodine.

In this investigation, the hydriodic acid was prepared by the action of hy-

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drogen sulphide upon iodine in aqueous solution. The product was purified by distillation under reduced pressure.

The hydrogen sulphide was prepared by the action of diluted sulphuric acid upon ferrous sulphide in a Kipp generator. The gas was passed through a solution of barium hydroxide to remove impurities (8).

Reaction of H_2S and I_2 (9).— H_2S was passed into a tall cylindrical bottle containing 3 Gm. of powdered iodine and 250 cc. of water. After this iodine was converted to HI, 20 Gm. more of iodine were added, a little at a time. Later 30 Gm. more of iodine were added and after this had been completely converted into HI the current of H_2S was stopped. The sulphur which had precipitated during the reaction was removed by filtration through glass wool and the dissolved H_2S was removed by bubbling hydrogen through the solution.

Distillation of the Hydriodic Acid.—The hydriodic acid was distilled at a pressure of about 8 mm. of mercury in an atmosphere of hydrogen. Since the acid was very prone to decomposition after removal of the H_2S , several precautions were taken, such as the use of ice water in the condenser, and uniform heating of the distilling flask by immersion in hot water. The product was collected in a Bogert receiver.

The acid made in this manner was water white and gave no color with starch T.S.; with $AgNO_3$ T.S. there were no indications of the presence of sulphides.

EXPERIMENTAL DATA.

The Effect of Various Conditions of Light and Temperature upon the Decomposition of $N/2$ Hydriodic Acid.—Ten cc. of $N/2$ HI were placed in each of sixteen glass-stoppered pyrex bottles of 150 cc. capacity, thus allowing for an ample supply of air. Four of the bottles were placed upon the roof in sunlight, four in the laboratory in diffused light, four in a dark locker, and four in a refrigerator in the dark. One bottle from each place was titrated with $N/500$ sodium thiosulphate solution at the end of one, two, four and seven days, using freshly prepared starch T.S. as indicator. The results were as follows:

TABLE I.

	Percentage Decomposition after			
	1 day.	2 days.	4 days.	7 days.
Sunlight	13.8	21.6	23.8	35.4
Diffused light	2.6	3.5	7.4	10.8
Dark (room temp.)	0.3	0.6	2.2	2.9
Dark (in refrigerator)	0.2	0.3	0.5	0.9

The rate of decomposition of hydriodic acid is thus accelerated by light and by increase in temperature.

Stability of Various Concentrations of HI in Diffused Light and Sunlight.—The results with 10-cc. portions of acid of various concentrations in 150-cc. bottles placed in diffused light at room temperature were as follows.

TABLE II.

Normality of HI.	Percentage Decomposition after			
	1 day.	2 days.	4 days.	7 days.
$N/2$	0.8	1.2	3.0	4.0
$N/10$	0.2	0.5	1.7	2.4
$N/100$	0.0	0.0	0.0	0.0
$N/1000$	0.0	0.0	0.0	0.0

This experiment shows that there is a relation between the concentration of the acid and the rate of decomposition. Solutions of a concentration of $N/100$ or less showed no free iodine after seven days, while more concentrated solutions showed appreciable decomposition.

A similar experiment was performed with bottles placed on the roof in sunlight.

TABLE III.

Normality of HI.	Percentage Decomposition after			
	1 day.	2 days.	4 days.	7 days.
$N/2$	18.1	20.5	34.3	47.0
$N/10$	4.8	6.0	19.6	28.1
$N/100$	0.5	0.6	2.1	17.0
$N/1000$	0.1	0.2	0.3	0.3

The decomposition of hydriodic acid in sunlight was more rapid as the concentration increased.

Choice of Concentration.—The acid used in experiments up to this point was of various concentrations ranging from $N/2$ to $N/1000$. The concentration that was finally selected for further experimental work was $N/10$, as this gave an appreciable amount of decomposition in a reasonable time and corresponded to the approximate concentration of U. S. P. X Diluted Hydriodic Acid.

Effect of Potassium Iodide.—The effect of various concentrations of potassium iodide on the rate of decomposition of $N/10$ hydriodic acid was determined. Ten-cc. portions in 150-cc. pyrex bottles were placed in diffused light. The results were as follows:

TABLE IV.

Iodide Present in Addition to $N/10$ HI.	Percentage Decomposition after			
	1 day.	2 days.	4 days.	7 days.
Blank (acid alone)	0.1	0.2	0.4	0.8
$M/1000$ KI	0.1	0.2	0.4	0.1
$M/100$ KI	0.1	0.2	0.5	0.8
$M/10$	0.2	0.2	0.5	0.8
$M/2$ KI	1.2	1.6	3.2	5.9

$M/2$ solutions of potassium iodide had an accelerating influence upon the decomposition of hydriodic acid, but lower concentrations apparently had no effect.

Effect of Iodides in Absence of Light.—In the experiments carried out in sunlight and diffused light at the temperature of the surrounding atmosphere it was found impossible to duplicate the exact numerical results. The variations were greatest in the experiments in sunlight where the variations in temperature and intensity of light were greatest. It seemed desirable to select conditions of light and temperature that could be duplicated at any time. Since natural light is always variable, it was decided to carry out the experiments in absence of light. This was accomplished by painting the outside of the pyrex bottles with a heavy coating of black asphalt paint. To avoid variations in temperature the bottles were placed in a Freas large size thermostat at 30° C.

A number of experiments were carried out to determine the effect of the iodides of potassium, cadmium, zinc, lithium, ammonium, manganese, strontium, sodium, calcium, barium, magnesium and ferrous iron upon the decomposition of hydriodic acid. The solutions were made tenth-normal in respect to hydriodic acid. The salts were present in concentrations of $M/2$, $M/10$, $M/100$ and $M/1000$.

One bottle of each concentration was titrated with $N/500$ sodium thiosulphate to determine the free iodine at the end of one day, two days, four days and seven days. The decomposition was calculated in per cent of free iodine as compared with the total iodine present as hydriodic acid. The results of an experiment with ferrous iodide were as follows:

TABLE V.

Iodide Present in Addition to $N/10$ HI.	Percentage Decomposition after			
	1 day.	2 days.	4 days.	7 days.
Blank (acid alone)	0.2	0.7	1.4	3.2
$M/1000$ FeI_2	0.3	0.7	1.5	2.7
$M/100$ FeI_2	1.3	1.5	3.2	5.7
$M/10$ FeI_2	6.1	8.0	10.5	18.1
$M/2$ FeI_2	18.4	21.4	31.9	56.3

Ferrous iodide has an accelerating influence upon the decomposition of hydriodic acid which increases with increasing concentration of the ferrous iodide. The results with the other iodides will be discussed below.

Another series of experiments was carried out under the same conditions upon solutions of the salts alone, to see how much the iodides themselves decomposed in absence of added hydriodic acid. The decomposition of solutions of ferrous iodide was as follows:

TABLE VI.

Concentration of Ferrous Iodide.	Percentage Decomposition as Shown by the Amount of Free Iodine after			
	1 day.	2 days.	4 days.	7 days.
$M/1000$	0.00	0.00	0.00	0.00
$M/100$	0.00	0.00	0.00	0.00
$M/10$	0.00	0.02	0.26	0.33
$M/2$	1.18	1.26	2.26	2.77

In concentrations of $M/1000$ and $M/100$, ferrous iodide showed no decomposition in seven days. In concentrations of $M/10$ and $M/2$ there was some decomposition, but this was small as compared with the amount of free iodine liberated from a mixture of ferrous iodide and hydriodic acid.

A similar test was made with manganese iodide solutions.

TABLE VII.

Concentration of Manganese Iodide.	Percentage Decomposition as Shown by the Amount of Free Iodine after			
	1 day.	2 days.	4 days.	7 days.
$M/1000$	0.00	0.00	0.00	0.00
$M/100$	0.00	0.00	0.00	0.00
$M/10$	0.00	0.00	0.00	0.00
$M/2$	0.06	0.18	0.69	0.96

Manganese iodide in $M/2$ solution showed some decomposition but in lower concentrations yielded no free iodine in seven days.

Each of the other iodides previously mentioned was tested in exactly the same manner as the ferrous iodide and manganese iodide. However, none of these other iodides showed any decomposition whatsoever in concentrations of $M/1000$, $M/100$, $M/10$ and $M/2$ within seven days.

Even with the careful control of light and temperature, there was still a variation in numerical data on repetition of the same experiments with hydriodic acid at different times. This appeared to be due to slight differences in the stability

of the hydriodic acid prepared at different times. Such a condition is frequently encountered in work on highly unstable substances. However, there was no difficulty in duplicating the general results.

Under these conditions, it was thought desirable to get an exact comparison of the effect of the various iodides by comparing them directly in the same experiment. Thus an experiment was conducted in which the effect of the whole series of iodides in $M/2$ concentration after three days was determined. Similarly the effect of $M/10$, $M/100$ and $M/1000$ concentrations of the series of iodides was studied. In the table below the separate experiments are designated as Exp. 1, 2, 3 and 4. It will be observed that there was a slight difference in the blank determinations made on the acid alone in the four experiments. Each column, giving the results with one certain concentration, must be considered separately, but all the figures in any one column are strictly comparable.

TABLE VIII.—PERCENTAGE DECOMPOSITION OF $N/10$ HYDRIODIC ACID ALONE AND IN PRESENCE OF VARIOUS IODIDES.

Iodide Present.	Per cent Decomposition of $N/10$ HI in Presence of Iodides in Following Concentrations:			
	Expt. 1, $M/2$.	Expt. 2, $M/10$.	Expt. 3, $M/100$.	Expt. 4, $M/1000$.
Blank (acid alone)	1.3	0.8	1.2	1.1
FeI_2	45.2	4.8	4.7	2.2
MnI_2	22.6	2.4	2.4	1.6
NaI	8.0	0.7	1.5	1.0
SrI_2	8.0	0.7	1.4	1.0
NH_4I	7.7	0.8	1.4	1.1
CaI_2	5.7	0.8	1.3	1.0
KI	4.4	0.8	1.4	1.1
LiI	3.4	1.0	1.4	1.0
MgI_2	1.0	0.8	1.3	1.1
CdI_2	0.8	0.8	1.4	1.0
ZnI_2	0.6	0.4	1.4	1.1
BaI_2	0.0	0.8	1.5	1.0

The foregoing table indicates that the $M/2$ solutions of the iodides divide themselves into four groups with relation to the magnitude of their effects on the decomposition of hydriodic acid. The iodides of the first group, composed of ferrous iodide and manganese iodide, have a marked accelerating influence upon the decomposition of hydriodic acid. Those of the second group, consisting of sodium, strontium and ammonium iodides, have a definite, though smaller, accelerating influence. The third group is made up of calcium, potassium and lithium iodides, which have a slight accelerating effect. In the fourth group are the iodides of magnesium, cadmium, zinc and barium, which have a retarding influence on the rate of decomposition of hydriodic acid. In the lower concentrations, the only iodides which had an appreciable effect were those of iron and manganese, which accelerated the decomposition.

DECOMPOSITION OF HYDRIODIC ACID IN ABSENCE OF OXYGEN.

In order to determine the effect of exclusion of oxygen upon the decomposition of hydriodic acid, $N/10$ HI was placed in ampules sealed with paraffin and exposed under various conditions. The results were as follows:

TABLE IX.

Conditions of Storage.	Percentage Decomposition after			
	1 day.	2 days.	4 days.	7 days.
Sunlight	1.0	1.1	1.1	2.6
Diffused light	0.2	0.3	0.8	1.0
Dark at room temperature	0.1	0.3	0.7	0.7
Dark in refrigerator	0.0	0.0	0.0	0.2

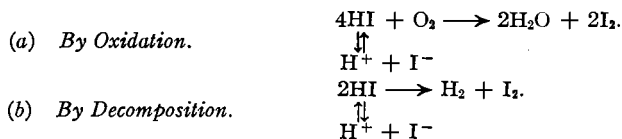
This experiment shows that decomposition takes place in the absence of oxygen. Since the access of air was prevented by the layer of paraffin, the only oxygen available for oxidation was that dissolved in the liquid. Assuming that the solubility of oxygen in the $N/10$ HI is the same as in water, there would be 0.08 cc. of oxygen dissolved in 10 cc. of the acid. The amount of oxygen necessary to cause 2.6% decomposition, such as shown after seven days, would be 0.29 cc. As only 0.08 cc. was available, it is apparent that the decomposition was greater than could be accounted for on the basis of oxidation by the available oxygen. This result substantiates the statement that part of the decomposition must be accounted for as follows: $2 \text{ HI} \rightarrow \text{H}_2 + \text{I}_2$.

Effect of Light of Different Wave-Lengths upon the Decomposition of Hydriodic Acid.—In order to determine the effect of different wave-lengths of light on the rate of decomposition of $N/10$ hydriodic acid, tests were made using light filters obtained from the Corning Glass Works. These light filters were in the form of plates of special glass about six inches square. Light-proof and water-proof wooden cabinets were used, in which the special glass plates served as windows. The cabinets were placed on the roof in direct sunlight, the hydriodic acid in pyrex bottles being placed within the cabinets. Eleven different light filters were used. From a study of the results obtained and the data on the light transmitted by the various filters, it was concluded that the part of the spectrum between 4600 and 6000 Å. has the greatest effect of increasing the rate of decomposition of $N/10$ hydriodic acid in pyrex bottles.

DISCUSSION OF RESULTS.

In the work outlined above there are two rather striking results: (1) the marked stability of hydriodic acid in concentrations of $M/100$ and $M/1000$, and (2) the markedly increased rate of decomposition of $N/10$ HI in the presence of $M/2$ concentrations of such iodides as NaI, SrI_2 , NH_4I , etc.

It appears that HI decomposes in two ways which may be represented as follows:



In both of the equations shown above, the free iodine is formed from molecules of HI, and not from iodide ions. Therefore the rate of deterioration would, to a great extent, be proportional to the concentration of molecules of HI. Any change of conditions which would increase the concentration of HI molecules would be expected to increase the rate of deterioration of HI, and conversely any change causing a decrease in concentration of HI molecules would be expected to decrease the rate of decomposition.

The unusual stability of hydriodic acid of low concentration finds ready explanation on the basis of the hypothesis outlined above. As the dilution of the hydriodic acid increased, there would be an increase in electrolytic dissociation of HI molecules into hydrogen ions and iodide ions. The decrease in HI molecules would decrease the rate of decomposition, as was actually observed in the experiments.

In carrying out the present investigation it was recognized that the various cations might have certain individual specific effects on the rate of decomposition of hydriodic acid. Since each cation must be accompanied by an anion, the cations were added in the form of iodides. Thus there was no new anion added, as the iodide ion was already present in the hydriodic acid solution. The effect of the iodides which had an appreciable accelerating influence (Na, Sr, NH_4) and of those which had a slight accelerating effect (Ca, K, Li) may be most readily explained on the basis of the effect of the iodide ions introduced. Thus sodium iodide in $M/2$ solution would be largely ionized as follows: $\text{NaI} \rightleftharpoons \text{Na}^+ + \text{I}^-$. The iodide ions from this source would cause the following reaction to proceed to the left: $\text{HI} \rightleftharpoons \text{H}^+ + \text{I}^-$. Thus the concentration of HI molecules would be increased and there would accordingly be an increase in the rate of decomposition. When the iodides were present in $M/2$ concentration in $N/10$ solution of hydriodic acid, the effect of the iodide ions of the iodide of the metal would be overwhelming. However, in $M/10$, $M/100$ and $M/1000$ concentrations, the iodides would not cause such an increase in concentration of the iodide ion and the effect would be less discernible. This reasoning is in accord with the experimental results, since in $M/10$, $M/100$ and $M/1000$ concentrations, the iodides had practically no effect on the rate of decomposition except in case of the iodides of iron and manganese.

Since ferrous iodide and manganese iodide had a pronounced accelerating effect on the decomposition which was distinct even in $M/1000$ concentration of the salt in a $N/10$ solution of hydriodic acid, it is apparent that Fe^{++} and Mn^{++} ions have a specific catalytic effect in addition to the common ion effect of the other iodides.

On the basis of the hypothesis as outlined above, the addition of an iodide which ionized to only a slight extent would not increase the rate of decomposition, since there would be no appreciable increase in concentration of iodide ion, with resulting increase in concentration of HI molecules. Very little is known regarding the degree of ionization of various salts. However, it is known that most of the soluble iodides are rather highly ionized, with some exceptions, such as cadmium iodide and zinc iodide, which ionize only to a slight extent. Cadmium iodide and zinc iodide were found to have a slight retarding influence on the rate of decomposition. The lack of an accelerating influence may thus be explained on the basis of the lack of the common ion effect. The formation of double iodides, such as $2\text{HI} \cdot \text{CdI}_2$ or H_2CdI_4 would tend to withdraw some HI molecules and by thus lowering their concentration, would increase the apparent stability. Such an effect may be responsible for the slight retarding influence actually observed.

SUMMARY.

1. The rate of decomposition of hydriodic acid is increased by the following factors: (a) exposure to air, (b) exposure to light, (c) increase in temperature and (d) increase in concentration.

2. The effect of various iodides in $M/2$ concentration upon the rate of decomposition of $N/10$ hydriodic acid was as follows: marked acceleration, Fe^{++} and Mn ; appreciable acceleration, Na , Sr , NH_4 ; slight acceleration, Ca , K , Li ; slight retardation, Mg , Cd , Zn ; marked retardation, Ba . Only FeI_2 and MnI_2 had any effect on the rate of decomposition of $N/10$ HI when present in concentrations of $M/10$, $M/100$ or $M/1000$.

3. Experiments were carried out to determine the rate of liberation of free iodine in solutions containing various iodides alone. The only iodides to yield any free iodine within seven days were ferrous and manganese iodides, and these only in the higher concentrations.

4. The results may be explained on the basis of the hypothesis that the rate of deterioration is proportional to the concentration of HI molecules. When the concentration of HI molecules is decreased, as by dilution or formation of double iodides or complex ions, the rate of decomposition is decreased. When the concentration of iodide ions is increased, as by the addition of sodium iodide, the following reaction proceeds to the left: $\text{HI} \rightleftharpoons \text{H}^+ + \text{I}^-$. This change increases the concentration of HI molecules and thus increases the rate of decomposition.

5. Since ferrous iodide and manganese iodide have a pronounced accelerating effect on the decomposition, which is distinct even in $M/1000$ concentration of the salt in a $N/10$ solution of hydriodic acid, it is apparent that Fe^{++} and Mn^{++} ions have a specific catalytic effect in addition to the common ion effect of iodides.

6. Iodides which are only slightly ionized, as CdI_2 and ZnI_2 , do not accelerate the decomposition of hydriodic acid.

7. Experiments with $N/10$ hydriodic acid in pyrex bottles, placed behind various light filters, indicate that the part of the spectrum between 4600 and 6000 Å. has the greatest accelerating effect on the rate of decomposition when the acid is in pyrex bottles.

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SYNTHETIC ALKALOIDS INVOLVED IN GERMANY.

The complete synthesis of hydroquinine and hydroquinidine has been announced in Hamburg as an accomplished fact. The scientist responsible for this development states that his experiments lead up to the synthesis of 14 additional alkaloids which have not been found in a natural state. (Consul Knowlton V. Hicks, Hamburg.)