

SCIENTIFIC SECTION

BOARD OF REVIEW ON PAPERS.—*Chairman*, L. W. Rowe; John C. Krantz, Jr.; F. J. Bacon.

THE EFFECT OF VARIOUS COMPOUNDS UPON THE STABILITY OF HYDRIODIC ACID.*¹

BY WILLIAM J. HUSA² AND LOUIS MAGID.³

INTRODUCTION.

A study of the effect of various iodides upon the stability of hydriodic acid was carried out by Husa and Shattuck (1). The purpose of the present investigation was to make a further study of the effect of iodides and to determine the effect of various acids and salts upon the stability of hydriodic acid.

HISTORICAL REVIEW.

In 1877 G. Lemoine (2) reported that an aqueous solution of hydrogen iodide is not changed by the influence of light if air is absent, but that in presence of oxygen or air, slow decomposition takes place in the light as well as in the dark.

J. Pinnow (3), in 1901, found that the rate of oxidation of mixtures of sulphuric acid and potassium iodide increased proportionally with the concentration of the sulphuric acid in light, but not in darkness, provided the concentration of iodine did not exceed a Gm. per liter. The accelerating influence of light was most marked in dilute solutions. When sulphuric acid was replaced by hydrochloric acid, the reaction was twice as rapid, while phosphoric acid had only a slight accelerating influence on the rate of decomposition in light.

J. Plotnikoff (4) studied the oxidation of the hydriodic acid present in a mixture, charged with oxygen, of solutions of potassium iodide and hydrochloric acid. The oxidation proceeded at a measurable rate in darkness and was markedly accelerated by light of the spectral region around 4360 Angstrom units. It was concluded that the photochemical oxidation was proportional to the concentration of oxygen, to the two-thirds power of the concentration of potassium iodide and to the four-thirds power of the concentration of hydrochloric acid. The reaction in darkness was accelerated by a cupric salt or a mixture of ferric and cupric salts; manganese and lead salts exerted no appreciable catalytic action; the catalytic effect of nitrous acid was very marked even if the solution contained the equivalent of only 0.00000006 *N* nitrous acid. Additions of uranyl sulphite retarded the velocity of the reaction in light, as did starch, eosine and cupric sulphite; in the dark, the latter compound accelerated the reaction.

In 1908, Creighton and Mackenzie (5) found that under some conditions the decomposition of hydriodic acid was accelerated by the influence of radium but that at room temperature in absence of oxygen neither sunlight nor radium caused decomposition of dilute hydriodic acid solutions.

Kailan (6), in 1913, reported that slightly or strongly acid solutions of manganese, calcium, strontium and barium iodides are decomposed by X-rays. The decomposition increased with increased concentration. There was no connection between the molecular weight of the iodide and the rate of decomposition.

* Presented before the Scientific Section, A. PH. A., Toronto, Canada, 1932.

¹ This paper is based on a thesis presented to the Graduate Council of the University of Florida, by Louis Magid, in partial fulfilment of the requirements for the degree of Master of Science in Pharmacy.

² Head Professor of Pharmacy, University of Florida.

³ Winner of the Fairchild Scholarship, 1931.

Husa and Shattuck (1) found that the rate of decomposition of hydriodic acid was increased by the following factors: exposure to air, exposure to light, increase in temperature and increase in concentration. The effect of various iodides in 0.5 *M* concentration upon the rate of decomposition of 0.1 *N* hydriodic acid in the dark was as follows: marked acceleration, Fe⁺⁺ and Mn; appreciable acceleration, Na, Sr, NH₄; slight acceleration, Ca, K, Li; slight retardation, Mg, Cd, Zn; marked retardation, Ba. Only FeI₂ and MnI₂ had any effect on the rate of decomposition of 0.1 *N* HI when present in concentrations of 0.1 *M*, 0.01 *M* or 0.001 *M*; this effect was attributed to a specific catalytic effect of Fe⁺⁺ and Mn⁺⁺⁺ ions. The effect of iodides in general was explained on the basis of the increased concentration of HI molecules brought about by the common ion effect of the iodides. It was stated that on the basis of this hypothesis iodides which are only slightly ionized would have little effect and that the formation of double iodides such as 2 HI·CdI₂ or H₂CdI₄ would tend to withdraw some HI molecules and by thus lowering their concentration would lower the rate of decomposition; the experimental results were consistent with this explanation.

EXPERIMENTAL DATA.

Preparation of Hydriodic Acid.—The hydriodic acid was prepared by the action of hydrogen sulphide upon iodine in aqueous solution, the product being purified by distillation under reduced pressure. The details were as described by Husa and Shattuck (1) with the exception that the sulphur was removed by filtration through a layer of glass wool covered by a layer of short-fibre, acid-washed asbestos, instead of through glass wool alone. The choice of a filtering medium was based on tests of five methods as follows: (a) using glass wool alone, (b) using glass wool and asbestos, (c) using glass wool and asbestos with suction, (d) using

TABLE I.—EFFECT OF VARIOUS *N*/2 IODIDES ON RATE OF DECOMPOSITION OF *N*/10 HI.

	Black Bottles.		Colorless Bottles.	
	Control <i>N</i> /10 HI.	<i>N</i> /10 HI + <i>N</i> /2 iodide.	Control <i>N</i> /10 HI.	<i>N</i> /10 HI + <i>N</i> /2 iodide.
Ferrous Iodide.				
Dark (refrigerator)	0.40	72.25	0.56	74.28
Dark (room temp.)	1.43	74.28	1.35	78.36
Diffused light	1.19	89.55	1.03	80.39
Sunlight	1.07	87.51	15.26	76.32
Manganese Iodide.				
Dark (refrigerator)	0.24	3.24	0.24	2.79
Dark (room temp.)	1.43	6.29	1.43	6.29
Diffused light	1.59	6.29	1.59	7.24
Sunlight	1.19	9.23	15.36	57.31
Strontium Iodide.				
Dark (refrigerator)	0.24	1.51	0.28	1.67
Dark (room temp.)	0.44	1.77	0.48	1.77
Diffused light	0.46	1.77	0.48	5.27
Sunlight	0.54	2.27	14.59	54.44
Lithium Iodide.				
Dark (refrigerator)	0.40	0.80	0.48	0.88
Dark (room temp.)	1.43	3.66	1.47	6.65
Diffused light	1.35	3.82	1.35	6.73
Sunlight	1.83	4.46	14.76	65.13

TABLE I.—Continued.

Sodium Iodide.				
Dark (refrigerator)	0.45	0.89	0.46	0.87
Dark (room temp.)	0.85	2.63	0.94	2.99
Diffused light	0.85	2.63	1.00	6.45
Sunlight	2.85	7.37	15.12	61.47
Potassium Iodide.				
Dark (refrigerator)	0.09	0.16	0.09	0.16
Dark (room temp.)	0.48	1.39	0.50	1.48
Diffused light	0.50	1.35	0.55	4.81
Sunlight	0.62	1.87	16.67	59.65
Ammonium Iodide.				
Dark (refrigerator)	0.88	0.96	0.56	0.96
Dark (room temp.)	0.96	1.63	1.15	2.55
Diffused light	1.39	2.70	1.27	4.78
Sunlight	1.03	3.20	14.25	58.51
Calcium Iodide.				
Dark (refrigerator)	0.24	0.16	0.24	0.04
Dark (room temp.)	1.31	1.43	1.19	1.43
Diffused light	1.23	1.43	1.23	3.42
Sunlight	1.47	2.15	15.40	48.34
Magnesium Iodide.				
Dark (refrigerator)	0.32	0.48	0.40	0.72
Dark (room temp.)	0.96	1.83	1.00	1.83
Diffused light	1.00	1.71	1.03	2.47
Sunlight	1.03	1.99	10.98	22.61
Cadmium Iodide.				
Dark (refrigerator)	0.28	0.24	0.28	0.18
Dark (room temp.)	1.08	0.80	1.25	0.81
Diffused light	1.08	0.85	1.13	0.85
Sunlight	1.64	0.90	13.15	9.70
Zinc Iodide.				
Dark (refrigerator)	0.24	0.40	0.24	0.40
Dark (room temp.)	0.92	0.64	1.07	0.72
Diffused light	1.07	0.64	1.03	4.14
Sunlight	1.15	1.00	15.44	61.06
Mercuric Iodide.				
(Greater portion remained undissolved.)				
Dark (refrigerator)	0.24	0.04	0.24	0.04
Dark (room temp.)	0.72	0.24	0.72	0.28
Diffused light	0.72	0.20	0.76	3.20
Sunlight	0.92	0.51	14.25	8.65
Mercuric Iodide (Tenth-Normal.)				
Dark (refrigerator)	0.24	0.24	0.24	0.24
Dark (room temp.)	0.68	0.64	0.68	0.56
Diffused light	0.64	0.56	0.64	0.56
Sunlight	0.84	0.56	17.51	10.11
Barium Iodide.				
Dark (refrigerator)	0.07	0.00	0.09	0.00
Dark (room temp.)	0.38	0.00	0.48	0.00
Diffused light	0.36	0.00	0.40	0.00
Sunlight	0.84	0.00	17.51	54.37

an alundum filter with suction and (*e*) using a Gooch crucible and asbestos with suction. Method *b* was the only one which gave a perfectly clear, colorless filtrate. Methods *a*, *c* and *e* gave cloudy filtrates. The alundum filter had been used by Noyes and Freed (7) but under our conditions the filtration by this method was slow, and the filtrate was slightly colored due to decomposition, although it was very clear and free from particles.

Method of Conducting Experiments with Iodides.—The solutions were made by placing 50 cc. of $N/5$ HI in a 100-cc. volumetric flask and adding a weight of the iodide sufficient to make 100 cc. of a $N/2$ solution; water was then added up to the 100-cc. mark, making the solution $N/2$ with respect to the iodide and $N/10$ in respect to HI. Exactly 10-cc. portions of each solution were placed in black bottles and in colorless pyrex bottles of 125 cc. capacity and the bottles were placed under the following conditions: (*a*) dark (refrigerator), (*b*) dark (room temperature), (*c*) diffused light, (*d*) sunlight (on the roof). Controls of $N/10$ HI were placed in similar bottles under the same conditions at the same time. After three days, the amount of free iodine in the various solutions was determined by titration with 0.002 N $\text{Na}_2\text{S}_2\text{O}_3$ V. S. In the tables the amount of free iodine is expressed as percentage decomposition of the HI used.

The results in Table I indicate that the effect of various iodides was as follows: marked acceleration, Fe^{++} , Mn, Sr; appreciable acceleration, Li, Na, K; slight acceleration, NH_4 , Mg, Ca (under all conditions except in the refrigerator in the dark, where there was retardation); slight retardation, Cd, Hg^{++} ($N/10$), Zn (under all conditions except in the refrigerator in the dark and in colorless bottles in light, where there was acceleration); marked retardation, Hg^{++} , Ba (except in sunlight in colorless bottles, where there was acceleration).

Experiments with Acids.—The solutions were prepared by mixing equal portions of solutions of hydriodic acid and of the acid specified, both solutions being double the normality desired in the final mixture. The tests were conducted as in the case of the iodides.

As shown in Table II, the effect of acids on the rate of decomposition of $N/10$ HI was as follows: $N/1000$ HCl, slight acceleration except in sunlight in colorless bottles, where there was practically no effect; $N/100$ HCl, slight acceleration; $N/10$ HCl, slight acceleration; $N/2$ HCl, marked acceleration; $N/1000$ H_2SO_4 , practically no effect except in sunlight in colorless bottles, where there was a slight acceleration; $N/100$ H_2SO_4 , very slight acceleration; $N/10$ H_2SO_4 , slight acceleration; $N/2$ H_2SO_4 , appreciable acceleration.

Experiments with Salts.—In the experiments with various chlorides and sulphates, the solutions were prepared in the same manner as the solutions of iodides described above. The salts which showed an appreciable effect in $N/2$ concentration were tested further in concentrations of $N/10$, $N/100$ and $N/1000$.

As indicated in Table III, sodium chloride had practically no effect except in sunlight in colorless bottles, where there was a very slight retardation.

The results in Table IV show that the effect of various salts was as follows: marked acceleration, increasing with concentration, NiCl_2 , FeCl_2 , CoSO_4 ; practically no effect, NH_4Cl , NaCl , LiCl ; very slight retardation, MnSO_4 , MgCl_2 , SrCl_2 , BaCl_2 , ZnCl_2 , CaCl_2 , KCl ; marked retardation, increasing with concentration, $\text{Al}_2(\text{SO}_4)_3$, CdCl_2 .

TABLE II.—EFFECT OF VARIOUS ACIDS ON THE RATE OF DECOMPOSITION OF *N*/10 HI.*Percentage Decomposition after 3 Days.*

	Black Bottles.		Colorless Bottles.	
	Control <i>N</i> /10 HI.	<i>N</i> /10 HI + other acid.	Control <i>N</i> /10 HI.	<i>N</i> /10 HI + other acid.
<i>N</i> /1000 Hydrochloric Acid.				
Diffused light	0.39	0.46	0.40	0.50
Sunlight	0.50	0.65	17.19	17.06
<i>N</i> /100 Hydrochloric Acid.				
Diffused light	0.42	0.51	0.44	0.51
Sunlight	0.59	0.65	17.97	19.02
<i>N</i> /10 Hydrochloric Acid.				
Diffused light	0.47	0.91	0.50	1.13
Sunlight	0.55	1.08	16.15	23.97
<i>N</i> /2 Hydrochloric Acid.				
Diffused light	0.47	2.85	0.50	2.87
Sunlight	0.55	3.54	16.15	37.51
<i>N</i> /1000 Sulphuric Acid.				
Diffused light	0.58	0.57	0.62	0.59
Sunlight	0.44	0.44	14.59	17.19
<i>N</i> /100 Sulphuric Acid.				
Diffused light	0.58	0.69	0.62	0.69
Sunlight	0.44	0.46	14.59	18.19
<i>N</i> /10 Sulphuric Acid.				
Diffused light	0.58	0.85	0.62	0.85
Sunlight	0.44	0.51	14.59	22.14
<i>N</i> /2 Sulphuric Acid.				
Diffused light	0.58	1.73	0.62	1.77
Sunlight	0.44	1.04	14.59	31.26

TABLE III.—EFFECT OF SODIUM CHLORIDE ON THE RATE OF DECOMPOSITION OF *N*/10 HI.*Percentage Decomposition after 3 Days.*

	Black Bottles.		Colorless Bottles.	
	Control <i>N</i> /10 HI.	<i>N</i> /10 HI + NaCl.	Control <i>N</i> /10 HI.	<i>N</i> /10 HI + NaCl.
<i>N</i> /1000 Sodium Chloride.				
Diffused light	0.52	0.52	0.50	0.50
Sunlight	0.46	0.44	11.07	10.94
<i>N</i> /100 Sodium Chloride.				
Diffused light	0.52	0.51	0.50	0.50
Sunlight	0.46	0.46	11.07	10.42
<i>N</i> /10 Sodium Chloride.				
Diffused light	0.33	0.32	0.35	0.36
Sunlight	0.34	0.30	18.54	16.62
<i>N</i> /2 Sodium Chloride.				
Diffused light	0.33	0.37	0.35	0.39
Sunlight	0.34	0.22	18.54	15.89

TABLE IV.—PERCENTAGE DECOMPOSITION OF *N*/10 HYDRIODIC ACID ALONE AND IN PRESENCE OF VARIOUS SALTS IN BLACK BOTTLES IN THERMOSTAT AT 30° C.

Salt present	Percentage Decomposition after 3 Days of <i>N</i> /10 HI in Presence of Salts in Following Concentrations.				
	Expt. 1.	Expt. 2.	Expt. 3.	Expt. 4.	Expt. 5.
	<i>N</i> /2.	<i>N</i> /2.	<i>N</i> /10.	<i>N</i> /100.	<i>N</i> /1000.
Acid alone	0.69	0.79	0.79	0.79	0.79
Al ₂ (SO ₄) ₃	0.29	0.62	0.76	0.79
FeCl ₂	7.40	2.04	1.37	0.86
CoSO ₄	1.98	1.54	1.06	0.79
NiCl ₂	2.05	1.08	0.81	0.81
CdCl ₂	0.07	0.18	0.69	0.79
MnSO ₄	0.72
MgCl ₂	0.65
NH ₄ Cl	0.79
SrCl ₂	0.71
BaCl ₂	0.72
LiCl	0.80
ZnCl ₂	0.62
CaCl ₂	0.65
KCl	0.58
NaCl	0.65

Effect of Change of p_H on Solutions of Uniform Iodide Concentration.—Solutions containing NaI and HI in various proportions were tested for stability and the p_H was determined colorimetrically.

TABLE V.—THE EFFECT OF CHANGE OF p_H ON SOLUTIONS OF UNIFORM IODIDE CONCENTRATION.

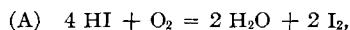
Normality of Solution		Percentage Decomposition after 3 Days in Black Bottles at 30° C.	p_H .
NaI.	HI.		
0.20	0.00	0.00	6.7
0.18	0.02	0.15	1.7
0.15	0.05	0.39	1.3
0.12	0.08	0.64	1.1
0.10	0.10	0.75	1.05
0.08	0.12	0.92	0.9
0.05	0.15	1.33	0.85
0.02	0.18	1.53	0.80
0.00	0.20	1.85	0.75

Table V indicates that with constant concentration of the iodide radical, the rate of decomposition increases with decrease of p_H .

*Determinations of p_H of Iodide and Other Salt and Acid Solutions Alone and in Presence of *N*/10 HI.*—The determinations of p_H were made colorimetrically.

DISCUSSION OF RESULTS.

Husa and Shattuck (1) explained their results on the basis of the hypothesis that the rate of decomposition is proportional to the concentration of HI molecules. However, the results may also be explained on the basis that the iodide ions are oxidized and that the decomposition is proportional to the concentration of the iodide ions. Thus, instead of representing the oxidation as:



it may be represented ionically as follows:

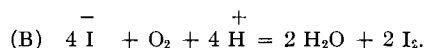


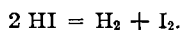
TABLE VI.

	p_H of Solution Alone.	p_H of Solution + $N/10$ HI.		p_H of Solution Alone.	p_H of Solution + $N/10$ HI.
$N/10$ HI	1.1	...	$N/2$ H_2SO_4	0.6-0.7	0.6
$N/2$ ZnI_2	3.3	1.1	$N/1000$ NaCl	5.6	1.1
$N/2$ NH_4I	5.5	1.0	$N/100$ NaCl	5.6	1.1
$N/2$ CdI_2	6.2	0.7	$N/10$ NaCl	5.6	1.1
$N/2$ MnI_2	6.3	0.9	$N/2$ NaCl	5.6	1.1
$N/2$ KI	6.5	0.7	$N/1000$ $Al_2(SO_4)_3$	4.3	1.1
$N/2$ NaI	6.8	1.1	$N/100$ $Al_2(SO_4)_3$	4.1	1.3
$N/2$ LiI	8.7	1.0	$N/10$ $Al_2(SO_4)_3$	3.7	1.5
$N/2$ BaI_2	8.7	1.1	$N/2$ $Al_2(SO_4)_3$...	1.7
$N/2$ MgI_2	8.8	0.9	$N/1000$ $FeCl_2$...	1.1
$N/2$ CaI_2	10.8	0.7	$N/100$ $FeCl_2$...	1.1
$N/2$ SrI_2	10.8	1.0	$N/10$ $FeCl_2$...	1.1
$N/10$ HgI_2	...	0.7	$N/2$ $FeCl_2$...	1.1
$N/1000$ HCl	3.0	1.1	$N/1000$ $CdCl_2$	5.5	1.1
$N/100$ HCl	2.0	0.9	$N/100$ $CdCl_2$	5.2	1.1
$N/10$ HCl	1.1	0.7	$N/10$ $CdCl_2$	4.9	1.1
$N/2$ HCl	0.4	0.3	$N/2$ $CdCl_2$	4.9	1.3
$N/1000$ H_2SO_4	3.1	1.1	$N/1000$ $NiCl_2$	5.5	1.1
$N/100$ H_2SO_4	2.1	1.1	$N/100$ $NiCl_2$	5.5	1.1
$N/10$ H_2SO_4	1.2	0.9	$N/10$ $NiCl_2$	5.3	1.1
$N/2$ $NiCl_2$	4.1	1.1	$N/2$ $SrCl_2$	5.1	1.1
$N/1000$ $CoSO_4$	4.3	1.1	$N/2$ $BaCl_2$	5.5	1.3
$N/100$ $CoSO_4$	3.5	1.1	$N/2$ LiCl	4.9	1.3
$N/10$ $CoSO_4$	3.0	1.3	$N/2$ $ZnCl_2$...	1.1
$N/2$ $CoSO_4$	2.1	1.3	$N/2$ $CaCl_2$	5.9	1.1
$N/2$ $MnSO_4$	4.9	1.5	$N/2$ KCl	5.5	1.1
$N/2$ $MgCl_2$	5.9	1.1	$N/2$ NaCl	5.5	1.1
$N/2$ NH_4Cl	5.0	1.1

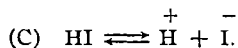
On the basis of equation (B), each iodide ion loses an electron and is converted into free iodine, while each oxygen atom gains two electrons and unites with two hydrogen ions to form water. From this equation it would follow that the rate of decomposition is dependent on the concentration of iodide ions, hydrogen ions and oxygen. The discharging potential of iodidion is given by Walker (8) as -0.80 and that of oxidion as -1.49 . These values indicate the reason for the readiness with which hydriodic acid decomposes in the presence of oxygen.

The results with sodium iodide (Tables I and VI) indicate that with constant p_H , an increase in iodide concentration causes an increase in the rate of decomposition. With constant iodide concentration, an increase in hydrogen-ion concentration increases the rate of decomposition (Table V). An increase in the concentration of hydriodic acid would increase the concentration of both hydrogen ions and iodide ions, as well as HI molecules, thus increasing the rate of decomposition, as was observed by Husa and Shattuck (1).

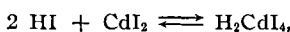
The decomposition of hydriodic acid that takes place in absence of oxygen is probably best represented as follows:



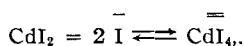
To summarize, the effect of various acids and salts on the rate of decomposition of hydriodic acid may be explained as follows: The effect of iodides that increase the rate of decomposition of hydriodic acid is due to the increased concentration of iodide ions and/or the increased concentration of HI molecules due to the common ion effect of the iodide ions in driving the following reaction to the left:



Iodides that are only slightly ionized have practically no effect, as the concentration of iodide ions is not appreciably affected. The retarding influence of certain iodides, such as cadmium iodide, may be correlated with the tendency toward formation of complex ions, thus reducing the concentration of iodide ions and HI molecules:



or represented ionically,



Hittorf (9) showed that complex formation in cadmium iodide solutions is considerable at higher concentrations, but decreases as the solution is made more dilute; in $N/100$ solution only simple ions appear to exist. It has been suggested by Noyes (10) that BaCl_3^- and BaCl_4^{--} ions probably exist in more concentrated solutions of barium chloride. Barium iodide also probably forms complex ions such as BaI_3^- and BaI_4^{--} . Mercuric, zinc and magnesium iodides likewise tend to form complex ions.

According to Glasstone (11), "since weak electrolytes probably have a definite heat of ionization in solution, an increase in temperature will cause a decrease in degree of ionization." It follows that a lowering of the temperature will increase the degree of ionization. Thus if a slightly ionized solution were placed in a refrigerator, the low temperature might cause a greater degree of ionization, and consequently a greater increase in rate of decomposition of hydriodic acid, unless at the lower temperature, there was a greater tendency toward formation of complex ions, which would decrease the rate of decomposition. The latter effect may explain why calcium iodide retards the decomposition in the refrigerator, but has a slight accelerating effect under the other conditions. On the other hand, zinc iodide has a slight retarding influence under all conditions except in the refrigerator and in colorless bottles in diffused light and sunlight, where the rate of decomposition is appreciably increased. Barium iodide has a marked retarding influence under all conditions except in colorless bottles in sunlight, where the rate of decomposition was appreciably increased. It thus seems that under the influence of light and higher temperatures, some of the iodides may have less tendency to form complex ions.

Iodides are frequently crystallized from slightly alkaline solutions to prevent decomposition; solutions of such iodides would show a higher p_{H} than the absolutely pure iodides. None of the iodides raised the p_{H} of $N/10$ HI, but some lowered it. The factors that might lower the p_{H} are: (a) hydrolysis of the iodide,

(b) the formation of double compounds, where the double compounds are appreciably ionized. H_2ZnI_4 is apparently a weaker acid than H_2CdI_4 .

The increased rate of decomposition of $N/10$ HI on addition of strong acids may be explained on the basis of the common ion effect of the hydrogen ion in driving reaction (C) to the left, and on the increased concentration of hydrogen ions on the basis of equation (B). In the higher concentrations of acid used, the increased rate of decomposition may be due to both of these factors. When the concentration of HCl or H_2SO_4 is $N/1000$ or $N/100$, the effect of increased hydrogen-ion concentration on the basis of equation (B) is probably the predominating factor, since the change in concentration of HI molecules according to equation (C) would be slight at those concentrations. The rate of decomposition of hydriodic acid is more sensitive to hydrogen-ion concentration than to iodide-ion concentration, as shown by the comparative effect of low concentrations of iodides, as observed by Husa and Shattuck (1) and low concentrations of acids, as observed in this investigation. As the concentration of the acids increased, the rate of decomposition of hydriodic acid increased. Decomposition was more rapid in colorless bottles than in black bottles, and more rapid in sunlight than in diffused light. The rate of decomposition of hydriodic acid is increased more by hydrochloric acid than by sulphuric acid. This may be explained on the basis of the greater degree of ionization of hydrochloric acid, which consequently supplies more hydrogen ions.

Hahn and Clos (12) in the course of an investigation on iodometric titrations of iron, observed that strong acids increased the rate of oxidation of hydriodic acid by atmospheric oxygen. This observation is in accord with the results of the present investigation. However, in the work of Hahn and Clos, the rate of oxidation of hydriodic acid would also be markedly increased by the Fe^{++} ions present in their solutions.

On the basis of the hypothetical explanations given above, it would be expected that the addition of a salt having no ion in common with hydriodic acid would have practically no effect. Experiments with $N/1000$, $N/100$, $N/10$ and $N/2$ sodium chloride indicate that this salt has practically no effect except in sunlight in colorless bottles, where the rate of decomposition is very slightly retarded. To the extent that the rate of decomposition of hydriodic acid is due to HI molecules, a very slight retarding effect of NaCl might be expected. On the basis of the Arrhenius theory of electrolytic dissociation, in a mixture of HI and NaCl, certain equilibrium concentrations of HCl and NaI molecules would be reached, and as this process would withdraw some of the hydrogen and iodide ions, there would be a further electrolytic dissociation of HI, thus decreasing the concentration of HI molecules. However, on the basis of the theory that strong electrolytes are completely or almost completely dissociated in aqueous solution, the concentration of all molecular species of the salts would be negligible and under these conditions sodium chloride should have no effect.

The salts that have no ion in common with hydriodic acid, but have a marked tendency to increase the rate of decomposition of HI, may be regarded as having a cation which has a catalytic effect on the oxidation of HI. Ni^{++} , Fe^{++} and Co^{++} may be regarded as having a specific catalytic effect.

The fact that MnSO_4 shows no accelerating influence on the rate of decompo-

sition of hydriodic acid is not in agreement with the previously reported statement (1) that Mn^{++} has a specific catalytic effect. The accelerating effect of MnI_2 may have been due entirely to the effect of increased iodide concentration and hydriodic acid concentration due to hydrolysis of MnI_2 .

The retarding influence shown by $Al_2(SO_4)_3$ is probably due to the formation of complex compounds in a manner similar to the formation of alums in concentrated solutions. It is to be noted that in $N/100$ solutions aluminum sulphate has practically no effect on the decomposition of hydriodic acid.

SUMMARY.

1. The effect of various iodides in $N/2$ concentration upon the rate of decomposition of $N/10$ hydriodic acid was as follows: marked acceleration, ferrous, manganese and strontium iodides; appreciable acceleration, sodium, potassium and lithium iodides; slight acceleration, magnesium, calcium and ammonium iodides; slight retardation, zinc and cadmium iodides; marked retardation, barium and mercuric iodides.

2. With constant p_H , an increase in iodide concentration increases the rate of decomposition of HI, and with constant iodide concentration an increase in hydrogen-ion concentration increases the rate of decomposition. The rate of decomposition is increased more by HCl than by H_2SO_4 .

3. The effect of various salts on the rate of decomposition of hydriodic acid was as follows: marked acceleration, $NiCl_2$, $FeCl_2$ and $CoSO_4$; no effect, NH_4Cl , $LiCl$ and $NaCl$; slight retardation, $MnSO_4$, $MgCl_2$, $SrCl_2$, $BaCl_2$, $ZnCl_2$, $CaCl_2$ and KCl ; marked retardation, $Al_2(SO_4)_3$ and $CdCl_2$.

4. The salts that have no ion in common with hydriodic acid, but have a marked tendency to increase the rate of decomposition of hydriodic acid, may be regarded as having a cation which has a specific catalytic effect on the oxidation of hydriodic acid. Ni^{++} , Fe^{++} and Co^{++} may be regarded as having a specific catalytic effect.

5. The retarding influence of certain salts may be correlated with the known tendency toward formation of complex ions, thus reducing the concentration of iodide ions and HI molecules.

REFERENCES.

- (1) William J. Husa and Paul Stanly Shattuck, *Jour. A. Ph. A.*, 21 (1932), 114-121.
- (2) G. Lemoine, *Ph. Centr. H.* (Nov. 22, 1877), page 396; through *Proc. A. Ph. A.*, 26 (1878), 356.
- (3) J. Pinnow, *Ber.*, 34 (1901), 2528-2543.
- (4) J. Plotnikoff, *Z. physik. Chem.*, 58 (1907), 214; 64 (1908), 215; cited by G. B. Kistiakowsky, "Photochemical Processes," pages 201-202.
- (5) H. Jermain, M. Creighton and A. Stanley Mackenzie, *Am. Chem. J.*, 39 (1908), 474.
- (6) Kailan, *Monatsh.*, 34 (1913), 1209-1210; through *J. Chem. Soc. Abstr.*, 103 (1913), 1030.
- (7) Arthur A. Noyes and E. Stanley Freed, *J. Am. Chem. Soc.*, 42 (1920), 478.
- (8) Walker, "Introduction to Physical Chemistry," 8th Edition, page 370.
- (9) Hittorf, *Ann. Physik*, 106 (1859), 337, 513; cited by Glasstone, "Electrochemistry of Solutions," pages 38-39.
- (10) Noyes, *Z. physik. Chem.*, 36 (1901), 63; cited by Glasstone, "Electrochemistry of Solutions," pages 38-39.

- (11) Glasstone, "Electrochemistry of Solutions," page 77.
(12) F. Hahn and H. Clos, *Z. anal. Chem.*, 79 (1929), 26-37.

COLLEGE OF PHARMACY,
UNIVERSITY OF FLORIDA,
GAINESVILLE, FLA.

A STUDY OF THE U. S. P. X METHOD AND A MODIFIED METHOD FOR THE ASSAY OF OLEORESIN OF ASPIDIUM.*

BY A. RICHARD BLISS, JR.,¹ M. L. PABST,² R. W. MORRISON³ AND E. O. PRATHER, JR.¹

INTRODUCTION.

In their investigations of the chemical and the biological methods for the standardization of Oleoresin of Aspidium, Pabst and Bliss (1) found certain factors which they believe may lead to varying results when the method of the U. S. Pharmacopœia X (2), the British Pharmacopœia method (3), the Swiss Pharmacopœia method (4), the Fluck modification of the Swiss procedure (5), and the Swiss method as modified by Lyons (6) are employed. They presented a modification of the U. S. Pharmacopœia X method which is more reliable, more accurate and more expeditious. The investigation herewith reported concerned itself with a comparative study of the U. S. Pharmacopœia method and the Pabst-Bliss modification of the U. S. Pharmacopœia X method.

MATERIALS USED.

Four samples of Oleoresin of Aspidium were purchased. Chemical and physical examinations proved the absence of adulterants.

THE PROCEDURES FOLLOWED.

Procedure I: The U. S. Pharmacopœia X Method (2).—"Warm the oleoresin on a water-bath and stir until it is thoroughly mixed. Transfer about 5 Gm., accurately weighed, to a 200-cc. flask, dissolve in 40 Gm. of ether and add 100 Gm. of aqueous solution of barium hydroxide (3 to 100), and shake vigorously for five minutes. Allow the liquids to separate and filter off 86 Gm. of the aqueous fluid. Transfer this to a separator, add sufficient hydrochloric acid to produce a distinctly acid reaction, and extract with three successive portions of 30 cc., 20 cc. and 15 cc. of ether. Draw off and combine the ethereal solutions, filter, wash the filter with ether, evaporate and dry the residue to a constant weight of 100° C. This residue weighs not less than 0.96 Gm., corresponding to not less than 24 per cent of crude filicin."

Procedure II: The Pabst-Bliss Modification of the U. S. P. Method (2).—"Warm the oleoresin on a water-bath and stir until it is thoroughly mixed. Transfer about 3 Gm., accurately weighed to a 250-cc. flask, dissolve in 40 cc. of ether, add 75 cc. of a three per cent aqueous solution of barium hydroxide, and shake vigorously for 5 minutes. Transfer this mixture to a separator. Allow the liquids to completely separate, draw off and filter the barium hydroxide layer. Rinse the 250-cc. flask with two 25-cc. portions of a 3 per cent aqueous barium hydroxide solution. After each rinsing, transfer the barium hydroxide solution to a separator, shake for one minute, allow the liquids to separate completely, draw off and filter the barium hydroxide layer. Transfer the combined filtered barium hydroxide solutions to a separator, make distinctly acid (to litmus) with concentrated hydrochloric acid, and extract with three successive portions of 30 cc., 20 cc.

* Scientific Section, A. P. H. A., Toronto meeting, 1932.

¹ University of Tennessee (Memphis).

² University of Buffalo.

³ University of South Carolina.