

The author is greatly indebted to Professor F. O. Rice of the Johns Hopkins University, who suggested this investigation.

Summary

1. A technique has been developed for measuring the relative rates of certain ionic reactions, namely, the oxidation of some inorganic reducing agents by bromine in aqueous solution. This consists in making these reactions compete with certain irreversible organic substitution reactions.
2. The ratios between the rates of the inorganic and the organic reactions are practically independent of temperature and of concentration.
3. By changing the solvent it is shown that the reactivity of a solute is increased by a decrease in solubility and, like thermodynamic activity, is at a maximum in saturated solution.
4. Ten inorganic compounds have been studied, and shown to have definite velocity constants for oxidation by bromine in aqueous solution, varying in magnitude from 10^4 to 10^8 .
5. A new and convenient method for the volumetric analysis of arsenic acid has been found.
6. Sodium thiosulfate reacts more quickly with iodine than does sodium bisulfite.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, UNIVERSITY OF BUFFALO MEDICAL SCHOOL, AND THE DEPARTMENT OF LABORATORIES, BUFFALO GENERAL HOSPITAL]

A COLORIMETRIC METHOD FOR THE ESTIMATION OF HYDROXYLAMINE

BY GEORGE W. PUCHER AND HAROLD A. DAY

RECEIVED NOVEMBER 27, 1925

PUBLISHED MARCH 5, 1926

The procedure reported in this paper is based on the reaction of hydroxylamine with benzoyl chloride and ferric chloride described by Bamberger¹ in 1895. This reaction, as indicated by the literature available from 1907-1925, although used qualitatively, has not been applied to the quantitative analysis of hydroxylamine.

Experimental Part

Standard Solutions and Reagents.—The hydroxylamine hydrochloride used in this work was prepared according to the procedure of Semon.² The crude salt so obtained is recrystallized from one-half of its weight of hot water and dehydrated by thoroughly drying in a desic-

¹ Bamberger, *Ber.*, **32**, 1805 (1895).

² Semon, *THIS JOURNAL*, **45**, 188 (1923).

cator over calcium chloride. For preservation the salt should be kept over unslaked lime.³

Stock Solution of Standard.—Exactly 5 g. of the purified hydroxylamine hydrochloride is diluted to 500 cc. with distilled water; 25 cc. of this solution is equivalent to 250 mg. of hydroxylamine hydrochloride. The stock solution is stable for a period of at least ten months.

Hydroxylamine Standard.—Twenty-five cc. of the stock solution is diluted to 500 cc. with distilled water. Two cc. of this solution is equivalent to 1 mg. of hydroxylamine hydrochloride or 0.475 mg. of hydroxylamine. The dilute standard is stable for two to three months.

Benzoyl Chloride.—The c. p. compound was used. If it is dark, it is distilled at atmospheric pressure and the constant-boiling fraction used.

Alcohol.—Ordinary 95% ethyl alcohol is used. This reagent is added as a solvent for the benzoyl chloride. Previous to the use of this substance, the results were entirely unsatisfactory.

Sodium Acetate.—Two g. of sodium acetate trihydrate is dissolved and made up to 100 cc. with distilled water; the solution is preserved with chloroform.

Acid Ferric Chloride.—Five-tenths g. of ferric chloride hexahydrate and 2 cc. of concd. hydrochloric acid are dissolved and made up to 100 cc. with distilled water.

Method of Analysis

To a solution (in a 200 × 25mm. test-tube graduated at 25 and 50 cc.) containing from 0.8 mg. to 3.5 mg. of hydroxylamine hydrochloride in 4 cc., add 2 drops of benzoyl chloride, 4 cc. of ethyl alcohol and 2 cc. of the sodium acetate solution. Shake for 20–30 seconds and then allow to stand for two to three minutes. Now add 2 cc. of the ferric chloride solution and dilute to 25 or 50 cc. as desired. Allow to stand for several minutes for the undissolved benzoyl chloride to settle, and read in the colorimeter. Most of the unreacted benzoyl chloride will have settled to the bottoms of the test-tubes when the colorimeter readings are to be taken. However, if there should be some present on the surface, gentle shaking will, as a rule, settle most of the excess. The presence of a small amount of benzoyl chloride in the colorimeter cup does not interfere with the reading.

The unknown solution before the development of the color should be neutral or very slightly acid in reaction. If this is not the case, neutralize with dil. hydrochloric acid or sodium hydroxide solution as the case requires, using phenolphthalein as an indicator. Care should be taken to avoid heat or an excess of alkali in the process of neutralization as a partial decomposition of the hydroxylamine may occur.

A Study of the Variables in the Method

Range of Color.—An intensity of color suitable for colorimetric work should approximate that given by 0.8 to 3.5 mg. of hydroxylamine hydrochloride or 0.4 to 1.7 mg. of hydroxylamine in a final dilution of 25 cc. When using amounts within this range, results come within the ordinary

³ Holleman, "Inorganic Chemistry," John Wiley and Sons, 1921, 6th ed., p. 181.

experimental error for colorimetric work as is shown by the data in Table I. It will be observed from this table that with a 1mg. standard, amounts of hydroxylamine hydrochloride from 0.5 mg. to 2.0 mg. can be satisfactorily determined, while with a 2mg. standard the amount estimable may be increased to 4.0 mg.

TABLE I

ANALYSIS OF KNOWN QUANTITIES OF HYDROXYLAMINE HYDROCHLORIDE							
NH ₂ OH.HCl present, mg.	Standard, mg.	Colorimetric reading, mm. ^a		NH ₂ OH.HCl recovered, mg.	Error, %		
		Calcd.	Found				
0.500	1.0	20.0	20.2	0.495	-1.0		
		20.0	20.9	.478	-4.5		
		20.0	20.8	.480	-4.0		
		20.0	20.8	.480	-4.0		
.750	1.0	13.3	14.3	.697	-7.0		
		.800	1.0	12.5	12.2	.819	+2.4
.800	1.0	12.5	12.8	.781	-2.4		
		12.5	12.6	.794	-0.8		
		12.5	12.8	.781	-2.4		
		12.5	12.7	.786	-1.7		
		12.5	12.8	.781	-2.4		
		1.00	1.0	15.0	14.7	1.02	+2.0
		15.0	14.8	1.013	+1.3		
10.0	9.9	1.01	+1.0				
10.0	9.8	1.02	+2.0				
1.25	1.0	8.0	7.8	1.28	+2.5		
2.00	1.0	10.0	9.5	2.10	+5.0		
		10.0	9.9	2.02	+1.0		
		10.0	9.9	2.02	+1.0		
		10.0	10.0	2.00	0.0		
		10.0	9.9	2.02	+1.0		
2.80	2.0	7.1	7.1	2.80	0.0		
3.00	2.0	6.7	7.1	2.82	-6.0		
		6.7	7.3	2.73	-9.0		
3.20	2.0	6.3	6.5	3.10	-3.2		
3.40	2.0	6.0	6.3	3.23	-5.0		
3.60	2.0	5.5	6.0	3.31	-8.3		
		5.7	6.1	3.37	-6.6		

^a Each reading here recorded represents a separate determination which is the average of at least five colorimetric readings.

Effect of Time on the Stability of the Color.—That the full color develops almost instantaneously upon the addition of the acid ferric chloride is borne out by the fact that solutions allowed to stand for one-half to two hours before reading check with those read immediately after the addition of the iron solution.

Effect of Temperature.—When the solution before the addition of the iron solution is warmed for five minutes at 40°, 60° and 80°, it assumes a milky appearance that prevents colorimetric reading. After the color

is developed, temperatures up to 60° have no effect. Above 60°, the intensity of the color is rapidly diminished.

Effect of Light.—Sunlight and electric light have no appreciable effect on the stability of the color. The solutions have been kept in daylight for several weeks without any detectable change in color.

Effect of Chemicals.—Compounds that react with hydroxylamine in the cold should be absent. Substances that give color with iron should also be absent. Excess of alkalis interferes and the adding of sodium carbonate to the hydroxylamine hydrochloride solution in order to set free the base does not increase the color.

Effect of Neutralization.—The neutralization of an hydroxylamine solution either with an acid or base using phenolphthalein as an indicator has no effect on the results when care is taken to avoid an excess of alkali and an increase of temperature incident to neutralization.

Effect of Dilution.—Dilution to any desired volume after the color has been developed is permissible. Milkyness on dilution may occur when an excess of the benzoyl chloride is brought into solution by the alcohol. No trouble, however, is encountered when the benzoyl chloride is added apart from the alcohol and not in excess of the prescribed amounts.

Effect of the Presence of an Excess of Glucose.—These experiments were undertaken to ascertain the effect of an excess of glucose on the estimation of hydroxylamine. Table II shows that large excesses of glucose (1:20) have no effect on the determination of hydroxylamine when the reaction is carried out at room temperature.

TABLE II

EFFECT OF GLUCOSE ON THE ESTIMATION OF HYDROXYLAMINE

Room temperature, 20–25°. Time of reaction, 10–15 minutes. 1.0 mg. of hydroxylamine hydrochloride present. Calcd. colorimeter reading = 15.0.

Glucose, mg.	Colorimetric reading	
	Found ^a	Error, %
10.0	15.1	– 0.67
	14.9	– .57
	15.0	.00
	15.5	– .87
20.0	16.1	– 7.3
	15.3	– 0.87
	16.5	– 10.0
	15.8	– 5.3

^a Each reading here recorded represents a separate determination which is the average of at least five colorimetric readings.

Summary

1. A colorimetric method is described for the estimation of hydroxylamine based on the reaction of this substance with benzoyl chloride and ferric chloride.

2. Hydroxylamine may be determined in the presence of glucose if the ratio, hydroxylamine : glucose, is not greater than 1:20.

BUFFALO, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE DETERMINATION OF CALCIUM BY THE CONVERSION OF THE OXALATE TO THE CARBONATE

BY H. W. FOOTE AND W. M. BRADLEY

RECEIVED DECEMBER 2, 1925

PUBLISHED MARCH 5, 1926

The usual method of determining calcium by precipitating the oxalate and igniting to the oxide has the disadvantages that it requires, in ordinary practice, ignition in platinum to a very high temperature, making it impracticable to use a porcelain Gooch crucible for filtering; and the oxide must be weighed promptly to prevent its taking up moisture and carbon dioxide. The decomposition of the oxalate to the carbonate by heating at a lower temperature, either with or without the addition of ammonium carbonate, has sometimes been recommended but it gives inaccurate results for the reason that at a temperature where the oxalate decomposes rapidly, the dissociation of the carbonate becomes appreciable. It is evident, however, that if the latter dissociation could be entirely prevented the quantitative conversion to the carbonate could be accomplished and the method would have some advantage over the determination as oxide.

The dissociation pressures of calcium carbonate determined by Johnston,¹ are as follows.

<i>T</i> , °C.	500	600	700	800	850	900	950	1000
<i>p</i> , mm.	0.11	2.35	25.3	168	373	773	1490	2710

It is evident from these data that calcium carbonate should be entirely stable and suffer no decomposition when heated in an atmosphere of carbon dioxide at any temperature not exceeding 890°. When heated in air, however, decomposition will begin at a much lower temperature since the partial pressure of carbon dioxide in the air is negligible.

We have found that by heating the oxalate at a temperature ranging between 675° and 800° in a current of dry carbon dioxide, the oxalate is decomposed rapidly and completely, yielding the carbonate, and this furnishes a very satisfactory method of determination which, so far as we are aware, has not previously been used.

Experimental Part

Transparent cleavage crystals of Iceland spar served as a source of calcium. The sample contained a trace of ferrous carbonate equivalent to 0.04% of ferric oxide. The material was powdered and dried at 100° before use.

¹ Johnston, *THIS JOURNAL*, **32**, 938 (1910).