## Summary

The rates of oxidation of benzaldehyde, enanthaldehyde and solutions of sodium sulfite have been studied both in monochromatic light and in the dark. In every case the photochemical reaction is a chain reaction, the maximum yields obtained amounting to about 10,000, 15,000 and 50,000 molecules per quantum, respectively.

The photochemical reactions show negative catalysis as well as the thermal reactions, and there is a marked parallelism between them as regards the action of different inhibitors.

It is concluded that the mechanism of the thermal reactions is similar to that of the photochemical reactions and, consequently, that these reactions are examples of thermal chain reactions, in accordance with Christiansen's theory of negative catalysis.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

# THE DETERMINATION OF FERROUS IRON IN SILICATES

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## Introduction

An excellent discussion of the determination of ferrous iron in silicates is given by Hillebrand in his "Analysis of Silicate and Carbonate Rocks,"[1] including a comparison of the merits of the sealed-tube and hydrofluoric acid methods of decomposition, the effects of fine grinding, sulfides and other factors, as well as the proper conditions for the titration. In addition to this, Barnebey[2] has given a thorough review of the literature up to his time, so it need not be repeated here.

The consensus of opinion has been that the hydrofluoric acid method of decomposition leaves nothing to be desired in the way of accuracy, and when carried out according to Pratt[3] with coarse powders, an analysis can be completed in a very short time. Until 1915 the end-point with permanganate was fleeting and unsatisfactory, and the results were high when much ferrous iron was present; however, in that year Barnebey[2] proposed the use of boric acid to secure a good and permanent end-point, the effect being to tie up the hydrofluoric acid as $HBF_4$, and thus prevent the oxidation of the bivalent manganese by the permanganate, and ferrous iron by the air during the titration. In a later paper Barnebey[4] suggested the use of potassium dichromate for standard solution, with boric acid

[1] Hillebrand, *U. S. Geol. Survey Bull.* No. **700**, 189 (1919).

[2] Barnebey, THIS JOURNAL, **37**, 1481 (1915).

[3] Pratt, *Am. J. Sci.*, [3] **48**, 149 (1894).

[4] Barnebey, THIS JOURNAL, **37**, 1829 (1915).

to stabilize the ferrous iron against the action of the air during the somewhat slow titration with the outside indicator, potassium ferricyanide, and also to avoid a large displacement of the observed end-point in the presence of hydrofluoric acid. Dichromate is preferable to permanganate for standard solutions for several reasons: (1) it is more stable; (2) it can be easily purified, so standard solutions can be made up by weight, if desired; (3) it acts much less readily on organic matter, so that there is less likelihood of interference from this source. The chief objection has been the necessity of an outside indicator, with a slow titration and danger of oxidation of the iron by the air.

Recently, however, Knop[5] has worked out details for the use of diphenylamine as internal indicator for this reaction, so it seemed that if it were possible to use it in the presence of hydrofluoric acid, all objections to the use of potassium dichromate for the determination of ferrous iron in silicates had been removed.

## Experimental Part

As the result of two years' experience with this indicator in the hands of several hundred students, it is felt that it does not possess quite all the unalloyed virtues claimed by its discoverer, so that one testing it for the first time may easily give it up in disgust; yet it is capable of giving good results if properly employed. Both the shade and intensity of the color have been found to vary greatly for no apparent reason, so one who expects the intense violet-blue described in the original article may greatly overstep the end-point and permanently oxidize some of the indicator. Overstepping often does no harm, but occasionally a muddy precipitate is obtained which somewhat obscures subsequent color changes; in such cases an abnormal amount of the dichromate is required. The color produced when the end-point is first reached is frequently very faint indeed, but still unmistakable to the experienced eye, the green of the reduced chromium being obscured in 10 to 15 seconds. Several drops of dichromate may then be added without markedly increasing the intensity of color; however, if a drop of ferrous solution be added to such an overstepped titration mixture, the intense color is obtained, and the final end-point can be determined with great accuracy. One drop of 0.01 *N* dichromate solution gave a distinct coloration to a titration volume of 50 cc., and a 0.04 *N* solution gave good results in a volume of 100 cc. The important points to remember are: (1) keep the titration volume small; (2) add only a few drops of dichromate solution after the first trace of violet has been observed; (3) make the final adjustment of volumes quite deliberately. The change from blue to green seems to be faster than the reverse change.

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[5] Knop, This Journal, **46**, 263 (1924).

The production of the blue color has been explained by Kehrmann and Micewicz[6] as being caused by the oxidizing action of chromic acid on diphenylbenzidine, which is formed from diphenylamine in the presence of ferric salts. If this be true, it might be more satisfactory to use this compound directly as an indicator in the first place, instead of depending upon forming it in the solution. The search for a better internal indicator for this titration is being continued in this Laboratory.

The presence of hydrofluoric acid seemed to brighten the colors somewhat, and did not affect the accuracy of the titrations. Barnebey[4] found that hydrofluoric acid very seriously interfered with potassium ferricyanide indicator, causing large quantities of ferrous iron to escape detection, but that the determination was accurate in the presence of boric acid. Table I shows that with diphenylamine as indicator the only effect of hydrofluoric acid is to render the iron very sensitive to oxidation, and that it does no harm when its mixture with dichromate is being titrated with ferrous solution (Expts. 1–12). However, when the dichromate is being added to the mixture of iron and hydrofluoric acid (Expts. 13–20), the error is greater with longer time of exposure and greater concentration of the hydrofluoric acid. On the other hand, when the titration solutions

TABLE I

EFFECT OF HYDROFLUORIC ACID UPON THE IRON-DICHROMATE TITRATION

0.0300 g. of FeO present in each determination

| Detn. No. | $H_2F_2$, $N$ | Time of contact, min. | FeO found, g. | Detn. No. | $H_2F_2$, $N$ | Time of contact, min. | FeO found, g. |
|---|---|---|---|---|---|---|---|
| | Approx. temp., 25° | | | | Approx. temp., 25° | | |
| 1 | | | 0.0300 | 19 | 6 | 15 | 0.0323 |
| 2 | | | .0300 | 20 | 6 | 20 | .0328 |
| 3 | | | .0299 | 21[a] | 4 | | .0301 |
| 4 | | | .0301 | 22[a] | 8 | | .0301 |
| 5 | 4 | | .0299 | 23[a] | 12 | | .0300 |
| 6 | 4 | | .0300 | 24[a] | 8 | 5 | .0306 |
| 7 | 8 | | .0302 | | Approx. temp., 105° | | |
| 8 | 8 | | .0301 | 25 | 4 | 5 | .0296 |
| 9 | 12 | | .0301 | 26 | 4 | 5 | .0298 |
| 10 | 12 | | .0300 | 27 | 4 | 10 | .0292 |
| 11 | 16 | | .0302 | 28 | 4 | 10 | .0290 |
| 12 | 16 | | .0303 | 29 | 4 | 15 | .0288 |
| 13 | 4 | | .0302 | 30 | 4 | 15 | .0288 |
| 14 | 8 | | .0306 | 31 | 4 | 20 | .0286 |
| 15 | 8 | | .0307 | 32 | 4 | 20 | .0287 |
| 16 | 12 | | .0313 | 33 | 8 | 10 | .0288 |
| 17 | 6 | 1 | .0307 | 34 | 8 | 10 | .0290 |
| 18 | 6 | 6 | .0314 | 35 | 12 | 10 | .0280 |
| | | | | 36 | 12 | 10 | .0283 |

[a] Determinations marked thus were titrated in saturated boric acid solution.

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[6] Kehrmann and Micewicz, *Ber.*, **45**, 2641 (1912).

are saturated with boric acid (Expts. 21–24), the determinations can be carried out at ordinary temperatures with great accuracy. At elevated temperatures the dichromate slowly oxidizes the hydrofluoric acid at a rate which is dependent upon the temperature, the time and the relative concentrations of dichromate and fluoride (Expts. 25–36).

This destroyed the hope that it would be possible to decompose the silicate samples in the presence of an excess of potassium dichromate and eliminate entirely the danger of atmospheric oxidation during the decomposition. The results of some analyses by this method are shown in Table II, Method B, in comparison with values obtained by two other methods, and they are much too high. The conventional modified Pratt[7] procedure was used for Method A, substituting a 30cc. platinum crucible for the 100cc. crucible, which was not available; the inconvenience of this small crucible accounts largely for the rather considerable minus errors and lack of concordance and led to some improvements in the apparatus which was used in Method C, and which will now be described in detail.

A special cover of transparent bakelite was turned out on the lathe to fit exactly an ordinary platinum crucible and it was then provided with a bakelite tube for the introduction of carbon dioxide, and with a small bakelite funnel for the addition of the hydrofluoric acid and the escape of vapors and steam. This permitted closing the crucible tightly after weighing the sample, then displacing the air with carbon dioxide and adding the hydrofluoric acid through the funnel without raising the cover again.

TABLE II

FERROUS IRON IN A SILICATE ROCK

| Method A, % | Method B, % | Method C, % |
|---|---|---|
| 3.51 | 4.73 | 3.85 |
| 3.41 | 4.74 | 3.95 |
| 3.64 | 4.56 | 3.89 |
| 3.78 | 4.72 | 3.99 |

Since ferrous iron is oxidized with such extreme ease in the presence of fluorides, it is essential that the carbon dioxide be entirely free from air. The special Kipp generator first described by Henz,[8] and reproduced by Treadwell and Hall[9] in their textbook on analytical chemistry, was not available in this Laboratory, so an ordinary Kipp generator was modified to permit the complete expulsion of air by flushing with water. A two-hole rubber stopper at the outlet was fitted, in addition to the usual

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[7] Ref. 1, p. 203.

[8] Henz, *Chem.-Ztg.*, **26**, 386 (1902).

[9] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, **1924**, vol. 2, 6th ed., p. 210.

delivery tube, with another glass tube so bent as to reach the highest point in the gas chamber. The generator was placed in operation by charging with marble, filling completely with water, and then displacing the water with acid; the drainage tube was finally closed, the gas delivery tube opened, and the carbon dioxide allowed to escape through a wash bottle for several hours, before using for an analysis.

To test the efficacy of the apparatus, known amounts of ferrous iron were treated exactly as if they were silicate samples, and compared with results obtained in an ordinary crucible, as shown in Table III.

Table III

Efficacy of Special Apparatus in Preventing Oxidation

0.0266 g. of FeO present in each determination

| Detn. No. | Apparatus | Time for clearing air from crucible, min. | Time of contact with $H_2F_2$, min. | FeO found, g. |
|---|---|---|---|---|
| 1 | Ordinary | 5 | 15 | 0.0255 |
| 2 | Ordinary | 5 | 15 | .0253 |
| 3 | Special | 2 | 5 | .0259 |
| 4 | Special | 2 | 5 | .0259 |
| 5 | Special | 2 | 10 | .0256 |
| 6 | Special | 2 | 10 | .0256 |
| 7 | Special | 2 | 15 | .0256 |
| 8 | Special | 2 | 20 | .0256 |
| 9 | Special | 60 | 15 | .0264 |
| 10 | Special | 20 | 15 | .0267 |

Only by allowing the stream of carbon dioxide to pass through the crucible for 10 or 15 minutes could correct results be obtained, even with the new apparatus. Also there was always a little oxidation while pouring the mixture of ferrous iron and hydrofluoric acid from the crucible to the boric acid in the dish, so it was found desirable to add an excess of dichromate directly through the funnel, after cooling somewhat. The cover could then be removed, the sample safely transferred to a dish, and the excess of dichromate titrated with standard ferrous solution.

In a small crucible, a large concentration of mineral acid is desirable, in order to increase the solubility of the salts formed during the decomposition. Even concd. sulfuric acid seemed not to cause any oxidation of the iron, and 18 *N* acid is recommended. Hillebrand[10] explains the low results of some investigators as being caused by the oxidizing action of the concentrating sulfuric acid at high temperatures, yet in the Mitscherlich method rather concentrated sulfuric acid is used at a high temperature and under pressure. The possibility of oxidation of the iron by the sulfuric acid would undoubtedly be greater in the presence of hydrofluoric acid, but analyses have shown that the error from this source is

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[10] Ref. 1, p. 204.

not appreciable in practice. When potassium dichromate is to be used for the titration, hydrochloric acid may be used in the decomposition, if desired.

For the analysis of a silicate rock, 0.5g. samples of the coarse powder were weighed into the crucible, moistened with water and treated with 10 cc. of 12 *N* hydrochloric acid or 18 *N* sulfuric acid, a small coil of platinum wire was dropped in to prevent bumping, the cover fitted tightly, and carbon dioxide passed through for at least ten minutes while the mixture was being heated to boiling; as soon as steam began to escape, the gas stream was stopped. About 7 cc. of 48% hydrofluoric acid was then added through the funnel, and the mixture was gently boiled for 10 to 15 minutes, while being observed through the transparent cover. When the decomposition was complete, the gas stream was started and the crucible cooled until it could be held comfortably in the hand. An excess of dichromate was then added through the funnel, the cover removed and the contents poured onto solid boric acid in a ceresin-lined porcelain casserole; the mixture was titrated at once with standard ferrous solution, using diphenylamine as indicator. The analyses by Method C, Table II, were run in this way; they are somewhat higher than results obtained in an ordinary crucible, and show good concordance.

## Summary

Some peculiarities of diphenylamine as an indicator for the titration of ferrous iron by potassium dichromate have been discussed, and it has been shown that hydrofluoric acid is without effect upon it.

It has been shown that hydrofluoric acid does not reduce potassium dichromate at ordinary temperatures, but does so at higher temperatures, making impossible the analysis of silicates by decomposing them in the presence of an excess of dichromate.

New apparatus has been designed for the decomposition, and the conditions for its use have been determined.

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